Supporting Information

Synthesis of Benzoxazoles via the Copper-Catalyzed Hydroamination of Alkynones with 2-Aminophenols

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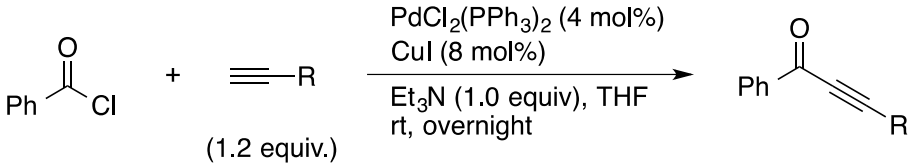
General experimental remarks

Commercially available chemicals were purchased from Aldrich, TCI, Kanto, and Wako and used without further purification unless otherwise noted. Trifluoromethyl group-containing alkyne **1** was prepared according to the reported procedures.[1] NMR spectra were recorded at 25 ˚C on a JEOL EX-270 spectrometer (270 MHz for ^{1}H, 67.8 MHz for ^{13}C) or a JEOL JNM ECP-500 spectrometer (126 MHz for ^{13}C, 471 MHz for ^{19}F). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane (0 ppm) for ^{1}H NMR. Chemical shifts of ^{13}C NMR are given relative to the solvent peak as an internal standard. ^{19}F NMR data are reported relative to external α,α,α-trifluorotoluene (–63.7 ppm). Multiplicities are indicated as br (broad), s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz). Melting points were measured on a Yanako MP-500P. Infrared (IR) spectra were recorded on JASCO FT/IR–4100. HRMS analyses were carried out using a JEOL AccuTOF LCplus for APCI-MS and ESI-MS and JEOL GCmate for EI-MS. Column chromatography and preparative thin-layer chromatography were conducted with silica gel 60N (KANTO CHEMICAL, spherical, neutral, 40-50 or 63-210 μm) and Wakogel® B-5F (45 μm), respectively. For thin-layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F254 0.25 mm) were used. Visualization was accomplished by UV light (254 nm), phosphomolybdic acid, and anisaldehyde.

General procedure for the preparation of alkynones

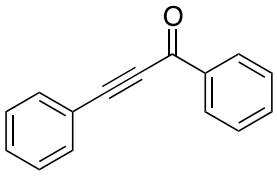
Scheme S1. Preparation of alkynones 4a, 4b, 4e, 4g, 4h, 4k, 4o, 4p, 4q:



Preparation of 1,3-Diphenylprop-2-yn-1-one (**4a**)[2]

$PdCl_2(PPh_3)_2$ (140 mg, 0.200 mmol) and CuI (76.2 mg, 0.400 mmol) were charged into a two-necked round flask and the flask was refilled with N_2. THF (17.0 mL) was added to the flask. Benzoyl chloride (703 mg, 5.00 mmol), phenyl acetylene (613 mg, 6.00 mmol), and triethylamine (506 mg, 5.00 mmol) were added to the mixture at room temperature. The reaction mixture was stirred at room temperature overnight.

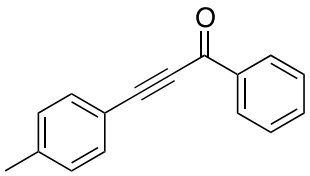
Saturated NH_4Cl solution was added to the mixture and the resulting aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 45/1) to give 1,3-diphenylprop-2-yn-1-one (**4a**) as a pale yellow solid (1.02 g, 4.95 mmol, 98% yield).



4a

^{1}H NMR (270 MHz, $CDCl_3$): δ 7.39–7.56 (m, 5H), 7.61–7.72 (m, 3H), 8.21–8.26 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 86.8, 93.1, 120.1, 128.6 (2C), 129.5, 130.8, 133.0, 134.1, 136.8, 178.0; GC-MS (EI): *m/z* 206 $[M]^+$.

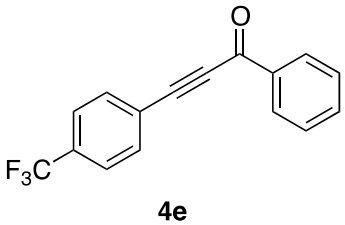
1-Phenyl-3-(*p*-tolyl)prop-2-yn-1-one (**4b**)[3]



4b

This compound was prepared according to the similar method to **4a** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 19/1). The resulting material was further purified by recrystallization from hot ethanol to give the desired product as a slightly brown solid (881 mg, 4.00 mmol, 79% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.22–7.26 (m, 2H), 7.49–7.67 (m, 5H), 8.21–8.25 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.7, 86.7, 93.8, 117.0, 128.6, 129.5 (2C), 133.1, 134.0, 136.9, 141.5, 178.0; GC-MS (EI): *m/z* 220 $[M]^+$.

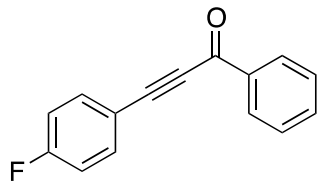
1-Phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (**4e**)[4]



4e

This compound was prepared according to the similar method to **4a** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 45/1). Pale yellow solid (1.10 g, 3.99 mmol, 78% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53–7.56 (m, 2H), 7.65–7.70 (m, 3H), 7.80 (d, J = 8.0 Hz, 2H), 8.22 (dd, J = 8.3, 1.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 88.1, 90.5, 123.6 (q, J_{CF} = 273 Hz), 124.0, 125.7 (q, J_{CF} = 4.0 Hz), 128.8, 129.7, 132.3 (q, J_{CF} = 33 Hz), 133.2, 134.5, 136.6, 177.7; ^{19}F NMR (471 MHz, $CDCl_3$): δ –64.1 (s); GC-MS (EI): *m/z* 274 $[M]^+$.

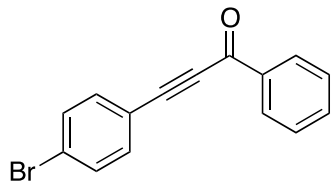
3-(4-Fluorophenyl)-1-phenylprop-2-yn-1-one (**4g**)[3]



4g

This compound was prepared according to the similar method to **4a** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 45/1). Slightly brown solid (311 mg, 1.39 mmol, 46% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10–7.15 (m, 2H), 7.51–7.54 (m, 2H), 7.62–7.71 (m, 3H), 8.20–8.22 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 86.8, 91.9, 116.2 (d, J_{CF} = 3.7 Hz), 116.2 (d, J_{CF} = 21.5 Hz), 128.6, 129.5, 134.2, 135.3 (d, J_{CF} = 8.4 Hz), 136.8, 164.0 (d, J_{CF} = 254 Hz), 177.8; ^{19}F NMR (471 MHz, $CDCl_3$): δ –106.97– –107.03 (m); GC-MS (EI): *m/z* 224 $[M]^+$.

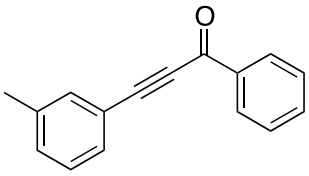
3-(4-Bromophenyl)-1-phenylprop-2-yn-1-one (**4h**)[5, 6]



4h

This compound was prepared according to the similar method to **4a** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 97/3). Pale yellow solid (628 mg, 2.20 mmol, 73% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.50–7.68 (m, 7H), 8.19–8.23 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 87.7, 91.6, 119.0, 125.6, 128.7, 129.6, 132.1, 134.3 (2C), 136.7, 177.8; GC-MS (EI): *m/z* 284 $[M]^+$.

1-Phenyl-3-(*m*-tolyl)prop-2-yn-1-one (**4k**)[7]

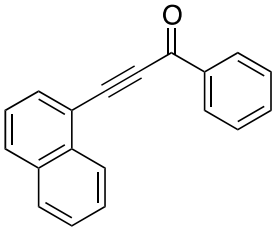


4k

This compound was prepared according to the similar method to **4a** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 97/3). Brown solid (575 mg, 2.61 mmol, 87% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.38 (s, 3H), 7.25–7.34 (m, 2H), 7.49–7.65 (m, 5H), 8.21–8.24 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.1, 86.6, 93.4, 119.8, 128.5 (2C), 129.5, 130.2, 131.7, 133.5 134.0, 136.9, 138.4, 178.0; GC-MS (EI): *m/z* 220 $[M]^+$.

3-(Naphthalen-1-yl)-1-phenylprop-2-yn-1-one (**4o**)[8]

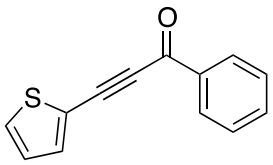
This compound was prepared according to the similar method to **4a** and the desired product was obtained after purification by silica gel column chromatography



4o

(Hexane/EtOAc = 97/3). Slightly brown solid (425 mg, 1.66 mmol, 55% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.47–7.68 (m, 6H), 7.88–7.98 (m, 3H), 8.29–8.33 (m, 2H), 8.42 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 91.4, 91.6, 117.7, 125.2, 125.8, 126.9, 127.7, 128.6, 128.7, 129.6, 131.5, 133.1, 133.2, 133.6, 134.1, 137.0, 178.0; GC-MS (EI): *m/z* 256 $[M]^+$.

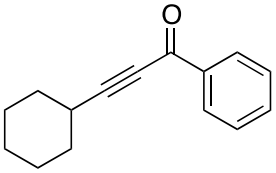
1-Phenyl-3-(thiophen-2-yl)prop-2-yn-1-one (**4p**)[9]



4p

This compound was prepared according to the similar method to **4a** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 19/1). Brown solid (403 mg, 1.90 mmol, 92% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.09–7.12 (m, 1H), 7.49–7.66 (m, 5H), 8.17–8.21 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 87.0, 91.6, 119.8, 127.7, 128.6, 129.4, 131.7, 134.1, 136.6, 136.7, 177.5; GC-MS (EI): *m/z* 212 $[M]^+$.

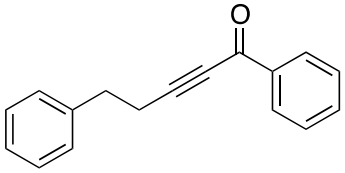
3-Cyclohexyl-1-phenylprop-2-yn-1-one (**4q**)[10]



4q

This compound was prepared according to the similar method to **4a** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 97/3). Brown oil (481 mg, 2.23 mmol, 75% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.33–1.44 (m, 3H), 1.50–1.67 (m, 3H), 1.70–1.79 (m, 2H), 1.87–1.92 (m, 2H), 2.67 (m, 1H), 7.42–7.48 (m, 2H), 7.54–7.60 (m, 1H), 8.12–8.16 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 24.4, 25.3, 29.0, 31.4, 79.3, 100.0, 128.2, 129.2, 133.5, 136.7, 177.9; GC-MS (EI): *m/z* 212 $[M]^+$.

1,5-Diphenylpent-2-yn-1-one (**4r**)

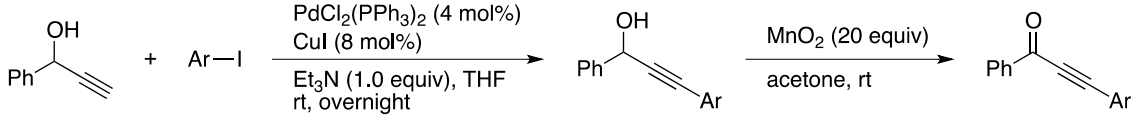


4r

This compound was prepared according to the similar method to **4a** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 97/3). Slightly brown oil (627 mg, 2.67 mmol, 89% yield); IR (neat) 3062, 3028, 2931, 2233, 2200, 1641, 1597, 1496, 1450, 849, 796, 748, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$):

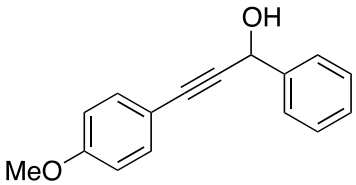
δ 2.80 (t, *J* = 7.1 Hz, 2H), 2.97 (t, *J* = 7.1 Hz, 2H), 7.23–7.27 (m, 3H), 7.31–7.34 (m, 2H), 7.40 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.54–7.57 (m, 1H), 7.97–7.99 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.1, 33.7, 80.1, 95.3, 126.5, 128.3 (2C), 128.4, 129.4, 133.7, 136.6, 139.5, 177.9; HRMS (APCI) $[M+H]^+$ Calcd for $C_{17}H_{15}O$ 235.1123; Found 235.1124.

Scheme S2. Preparation of alkynones 4d, 4c, 4f, 4i, 4j, 4l, 4m, 4n, 4r:



3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-ol (**4d'**)

$PdCl_2(PPh_3)_2$ (84.2 mg, 0.12 mmol) and CuI (45.7 mg, 0.24 mmol) were charged into a two-necked round flask and the flask was refilled with N_2. THF (10 mL) was added to the flask. 4-Iodoanisole (702 mg, 3.00 mmol), 1-Phenyl-2-propyn-1-ol (476 mg, 3.60 mmol), and triethylamine (304 mg, 3.00 mmol) were added to the mixture at room temperature. The reaction mixture was stirred at room temperature overnight. Saturated NH_4Cl solution was added to the mixture and the resulting aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 9/1) to give 3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ol (**4d'**) as a brown oil (406 mg, 1.70 mmol, 56% yield).

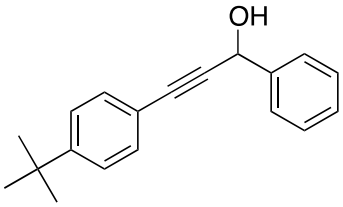


4d'

IR (neat) 3417, 3062, 3033, 2935, 2837, 2191, 1604, 1570, 1510, 1107, 833, 762, 700 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.31 (d, *J* = 6.2 Hz, 1H), 3.81 (s, 3H), 5.68 (d, *J* = 6.2 Hz, 1H), 6.82–6.87 (m, 2H), 7.31–7.44 (m, 5H), 7.59–7.64 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 55.3, 65.2, 86.6, 87.3, 113.9, 114.5, 126.7, 128.4, 128.6, 133.2, 140.8, 159.8; HRMS (EI) $[M]^+$ Calcd for $C_{16}H_{14}O_2$ 238.0994; Found 238.0992.

3-(4-(*tert*-Butyl)phenyl)-1-phenylprop-2-yn-1-ol (**4c'**)

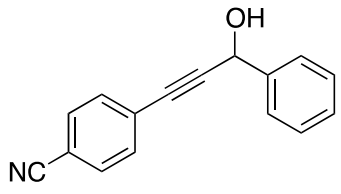
This compound was prepared according to the similar method to **4d'** and the desired product was obtained after purification by silica gel column chromatography



4c'

(Hexane/EtOAc = 9/1). Brown oil (429 mg, 1.62 mmol, 99% yield); IR (neat) 3438, 3062, 2868, 2197, 1643, 1504, 1363, 756, 698 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.31 (s, 9H), 2.28 (d, *J* = 5.8 Hz, 1H), 5.69 (d, *J* = 5.8 Hz, 1H), 7.26–7.44 (m, 7H), 7.61–7.64 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 31.1, 34.8, 65.2, 86.8, 88.0, 119.3, 125.3, 126.8, 128.4, 128.6, 131.5, 140.7, 151.9; HRMS (EI) $[M]^+$ Calcd for $C_{19}H_{20}O$ 264.1514; Found 264.1514.

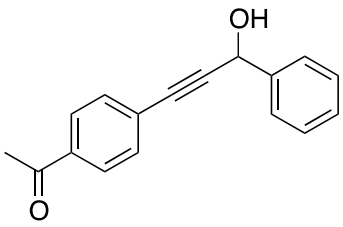
4-(3-Hydroxy-3-phenylprop-1-yn-1-yl)benzonitrile (**4f'**)



4f'

This compound was prepared according to the similar method to **4d'** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 9/1). Brown solid (485 mg, 2.08 mmol, 69% yield); M.p. 62–64 ˚C; IR (KBr) 3462, 3062, 2918, 2224, 1601, 1498, 835, 764, 694 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.39 (d, *J* = 6.1 Hz, 1H), 5.71 (d, *J* = 6.1 Hz, 1H), 7.34–7.46 (m, 3H), 7.53–7.63 (m, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 65.1, 84.8, 93.1, 112.0, 118.3, 126.6, 127.3, 128.7, 128.8, 132.0, 132.2, 140.0; HRMS (EI) $[M]^+$ Calcd for $C_{16}H_{11}NO$ 233.0841; Found 233.0839.

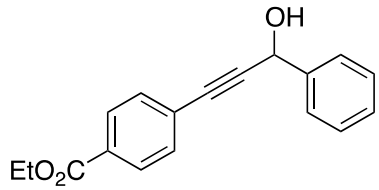
1-(4-(3-Hydroxy-3-phenylprop-1-yn-1-yl)phenyl)ethanone (**4i'**)



4i'

This compound was prepared according to the similar method to **4d'** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 9/1). Brown oil (680 mg, 2.72 mmol, 90% yield); IR (neat) 3460, 3032, 2866, 2202, 1682, 1601, 1554, 1493, 1360, 762, 698 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.56 (s, 3H), 2.96 (brs, 1H), 5.70 (s, 1H), 7.31–7.43 (m, 3H), 7.50 (dd, *J* = 6.7, 1.7 Hz, 2H), 7.58–7.61 (m, 2H), 7.86 (dd, *J* = 6.7, 1.7 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 26.5, 64.9, 85.5, 92.2, 126.6, 127.3, 128.1, 128.4, 128.6, 131.8 136.3, 140.3, 197.6; HRMS (EI) $[M]^+$ Calcd for $C_{17}H_{14}O_2$ 250.0994; Found 250.0994

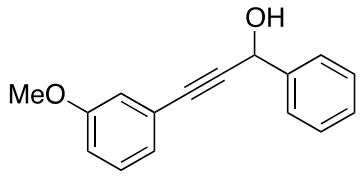
Ethyl 4-(3-hydroxy-3-phenylprop-1-yn-1-yl)benzoate (**4j'**)



4j'

This compound was prepared according to the similar method to **4d'** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 17/3). Slightly brown solid (857 mg, 3.06 mmol, 92% yield); M.p. 51–52 ˚C; IR (KBr) 3346, 3062, 2989, 2239, 1707, 1606, 1560, 1396, 816, 746 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.39 (t, *J* = 7.1 Hz, 3H), 2.43 (d, *J* = 6.1 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 5.71 (d, *J* = 6.1 Hz, 1H), 7.33–7.46 (m, 3H), 7.51–7.54 (m, 2H), 7.61 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.98–8.01 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 14.3, 61.2, 65.1, 85.8, 91.5, 126.7, 126.9, 128.6, 128.7, 129.4, 130.2, 131.6, 140.3, 166.0; HRMS (EI) $[M]^+$ Calcd for $C_{18}H_{16}O_3$ 280.1099; Found 280.1101.

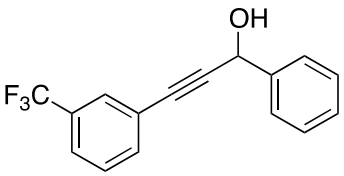
3-(3-Methoxyphenyl)-1-phenylprop-2-yn-1-ol (**4l'**)



4l'

This compound was prepared according to the similar method to **4d'** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 85/15). Brown oil (711 mg, 2.98 mmol, 99% yield); IR (neat) 3417, 3064, 2835, 2195, 1599, 783, 698 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.32 (brs, 1H), 3.79 (s, 3H), 5.69 (s, 1H), 6.87–6.91 (m, 1H), 7.00 (d, *J* = 1.4 Hz, 1H), 7.05–7.08 (m, 1H), 7.20–7.26 (m, 1H), 7.35–7.45 (m, 3H), 7.60–7.64 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 55.3, 65.1, 86.6, 88.5, 115.2, 116.5, 123.4, 124.3, 126.7, 128.4, 128.7, 129.4, 140.6, 159.3; HRMS (EI) $[M]^+$ Calcd for $C_{16}H_{14}O_2$ 238.0994; Found 238.0994.

1-Phenyl-3-(3-(trifluoromethyl)phenyl)prop-2-yn-1-ol (**4m'**)

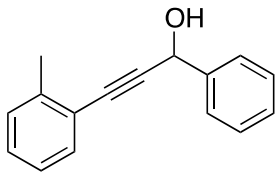


4m'

This compound was prepared according to the similar method to **4d'** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 9/1). Slightly brown oil (807 mg, 2.92 mmol, 98% yield); IR (neat) 3381, 3066, 2875, 2208, 1641, 1487, 1433, 1333, 802 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.30 (brs, 1H), 5.69 (s, 1H), 7.33–7.46 (m, 4H), 7.56–7.64 (m, 4H), 7.72 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$):

δ 65.1, 85.1, 90.3, 123.4, 123.7 (q, J_{CF} = 273 Hz), 125.2 (q, J_{CF} = 4.0 Hz), 126.7, 128.6 (q, J_{CF} = 4.0 Hz), 128.7, 128.8, 128.9, 131.0 (q, J_{CF} = 32.5 Hz), 134.9, 140.3; ^{19}F NMR (471 MHz, $CDCl_3$): δ –63.9 (s); HRMS (EI) $[M]^+$ Calcd for $C_{16}H_{11}OF_3$ 276.0762; Found 276.0767.

1-Phenyl-3-(*o*-tolyl)prop-2-yn-1-ol (**4n'**)

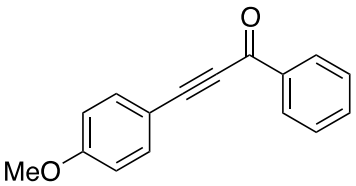


4n'

This compound was prepared according to the similar method to **4d'** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 85/15). Brown oil (551 mg, 2.48 mmol, 83% yield); IR (neat) 3363, 3062, 3030, 2920, 2225, 1601, 1487, 1379, 758 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.20 (brs, 1H), 2.44 (s, 3H), 5.73 (s, 1H), 7.11–7.25 (m, 3H), 7.31–7.46 (m, 4H), 7.62–7.65 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 20.7, 65.2, 85.6, 92.6, 122.1, 125.5, 126.7, 128.4, 128.6 (2C), 129.4, 132.1, 140.3, 140.8; HRMS (EI) $[M]^+$ Calcd for $C_{16}H_{14}O$ 222.1045; Found 222.1043.

Preparation of 3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one (**4d**)[3]

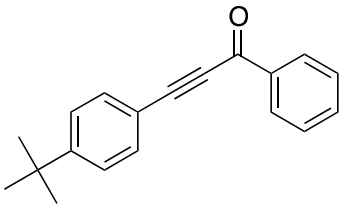
3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-ol (**4d'**) (233 mg, 0.980 mmol) was charged into a two-necked round flask and the flask was refilled with N_2. Acetone (6.6 mL) was added to the flask. MnO_2 (1.73 g, 19.9 mmol) was added to the mixture under N_2 and the resulting suspension was stirred at room temperature overnight. The suspension was filtrated with a pad of celite and the filtrate was concentrated *in vacuo*. The resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 9/1) to give 3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one (**4d**) as a pale yellow oil (200 mg, 0.846 mmol, 86% yield).



4d

^{1}H NMR (270 MHz, $CDCl_3$): δ 3.86 (s, 3H), 6.91–6.96 (m, 2H), 7.49–7.54 (m, 2H), 7.59–7.68 (m, 3H), 8.20–8.23 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 55.4, 86.9, 94.3, 111.9, 114.4, 128.5, 129.5, 133.9, 135.1, 137.0, 161.7, 178.0; GC-MS (EI): *m/z* 236 $[M]^+$.

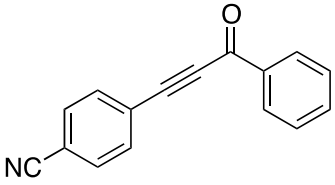
3-(4-(*tert*-Butyl)phenyl)-1-phenylprop-2-yn-1-one (**4c**)[3]



4c

This compound was prepared according to the similar method to **4d** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 9/1). Pale yellow oil (370 mg, 1.41 mmol, 87% yield) ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.34 (s, 9H), 7.43–7.55 (m, 4H), 7.60–7.66 (m, 3H), 8.21–8.25 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 31.0, 35.1, 86.7, 93.8, 117.0, 125.8, 128.6, 129.6, 133.0, 134.0, 137.0, 154.6, 178.1; GC-MS (EI): *m/z* 262 $[M]^+$.

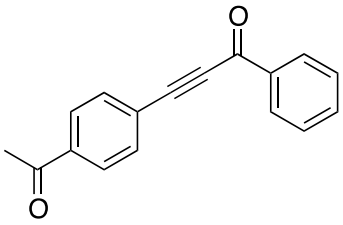
4-(3-Oxo-3-phenylprop-1-yn-1-yl)benzonitrile (**4f**)[11]



4f

This compound was prepared according to the similar method to **4d** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 9/1). Slightly brown solid (70.0 mg, 0.303 mmol, 30% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53–7.56 (m, 2H), 7.65–7.79 (m, 5H), 8.20 (dd, *J* = 8.8, 1.3 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 89.4, 89.6, 114.0, 117.8, 124.9, 128.8, 129.6, 132.3, 133.3, 134.6, 136.4, 177.4; GC-MS (EI): *m/z* 231 $[M]^+$.

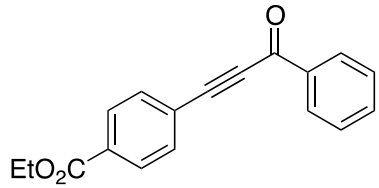
3-(4-Acetylphenyl)-1-phenylprop-2-yn-1-one (**4i**)[12]



4i

This compound was prepared according to the similar method to **4d** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 9/1). White solid (153 mg, 0.615 mmol, 41%); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.65 (s, 3H), 7.51–7.57 (m, 2H), 7.63–7.70 (m, 1H), 7.78 (dd, *J* = 6.7, 1.7 Hz, 2H), 8.01 (dd, *J* = 6.7, 1.7 Hz, 2H), 8.20–8.24 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 26.7, 88.7, 91.1, 124.7, 128.4, 128.7, 129.6, 133.1, 134.4, 136.6, 138.1, 177.7, 197.0; GC-MS (EI): *m/z* 248 $[M]^+$.

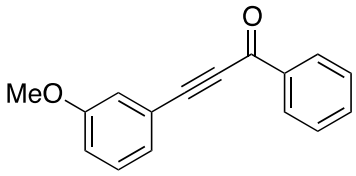
Ethyl 4-(3-oxo-3-phenylprop-1-yn-1-yl)benzoate (**4j**)[13]



4j

This compound was prepared according to the similar method to **4d** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 9/1). Slightly brown oil (390 mg, 1.40 mmol, 92%); ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.42 (t, *J* = 7.2 Hz, 3H), 4.41 (q, *J* = 7.2 Hz, 2H), 7.51–7.57 (m, 2H), 7.63–7.69 (m, 1H), 7.75 (dd, *J* = 6.6, 1.9 Hz, 2H), 8.10 (dd, *J* = 6.6, 1.9 Hz, 2H), 8.21–8.24 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 14.3, 61.4, 88.5, 91.3, 124.5, 128.7, 129.6, 129.7, 132.1, 132.8, 134.4, 136.6, 165.6, 177.7; GC-MS (EI): *m/z* 278 $[M]^+$.

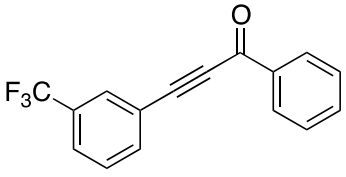
3-(3-Methoxyphenyl)-1-phenylprop-2-yn-1-one (**4l**)



4l

This compound was prepared according to the similar method to **4d** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 9/1). Pale yellow solid (162 mg, 0.687 mmol, 43% yield); M.p. 73–74 ˚C; IR (neat) 2964, 2195, 1639, 1597, 1579, 1238, 1043, 777, 700 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.83 (s, 3H), 7.00–7.05 (m, 1H), 7.18–7.19 (m, 1H), 7.25–7.35 (m, 2H), 7.48–7.55 (m, 2H), 7.59–7.66 (m, 1H), 8.20–8.24 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 55.3, 86.5, 92.9, 117.4, 117.5, 120.9, 125.5, 128.5, 129.5, 129.7, 134.1, 136.8, 159.4, 177.9; HRMS (APCI) $[M+H]^+$ Calcd for $C_{16}H_{13}O_2$ 237.0916; Found 237.0916.

1-Phenyl-3-(3-(trifluoromethyl)phenyl)prop-2-yn-1-one (**4m**)

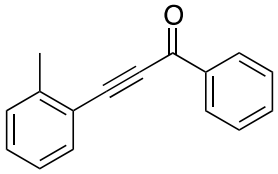


4m

This compound was prepared according to the similar method to **4d** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 9/1). Pale yellow solid (422 mg, 1.54 mmol, 94% yield); M.p. 74–75 ˚C; IR (neat) 3068, 2208, 1643, 1599, 1333, 1130, 903, 804, 694 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.50–7.75 (m, 5H), 7.84–7.86 (m, 1H), 7.92–7.93 (m, 1H), 8.20–8.24 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 87.6, 90.5, 121.2, 123.5 (q, J_{CF} = 273 Hz), 127.3 (q, J_{CF} = 3.6 Hz), 128.8, 129.4, 129.7, 129.7 (q, J_{CF} = 4.2 Hz), 131.5 (q, J_{CF} = 33.2 Hz), 134.5, 136.1,

136.6, 177.7; ^{19}F NMR (471 MHz, $CDCl_3$): δ –64.0 (s); HRMS (APCI) $[M+H]^+$ Calcd for $C_{16}H_{10}OF_3$ 275.0684; Found 275.0687.

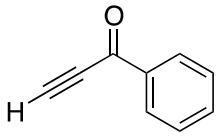
1-Phenyl-3-(*o*-tolyl)prop-2-yn-1-one (**4n**)[7]



4n

This compound was prepared according to the similar method to **4d** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 9/1). Pale yellow oil (319 mg, 1.45 mmol, 98% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.55 (s, 3H), 7.16–7.26 (m, 2H), 7.30–7.36 (m, 1H), 7.45–7.52 (m, 2H), 7.56–7.63 (m, 2H), 8.20–8.25 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 20.7, 90.6, 92.0, 119.7, 125.8, 128.4, 129.3, 129.7, 130.7, 133.5, 133.9, 136.8, 141.9, 177.7; GC-MS (EI): *m/z* 220 $[M]^+$.

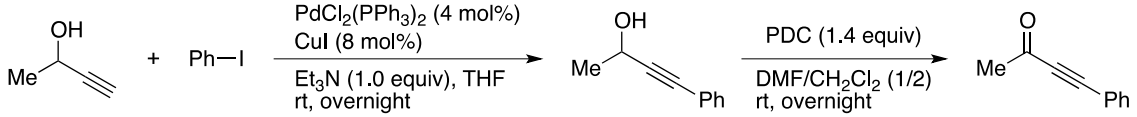
1-Phenylprop-2-yn-1-one (**4s**)



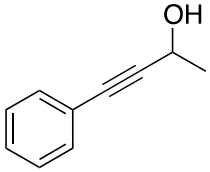
4s

This compound was prepared according to the similar method to **4d** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 9/1). Brown solid (140 mg, 1.08 mmol, 73% yield); M.p. 49–50 ˚C; IR (KBr) 3232, 3060, 2092, 1643, 1597, 1579, 1489, 700 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.45 (s, 1H), 7.47–7.53 (m, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 8.15–8.18 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 80.2, 80.8, 128.7, 129.7, 134.5, 136.1, 177.4; HRMS (EI) $[M]^+$ Calcd for C_9H_6O 130.0419; Found 130.0419.

Scheme S3. Preparation of alkynone 3:



Preparation of 4-phenylbut-3-yn-2-ol (**3'**)[14]: This compound was prepared according to the similar method to **4c'** (**Scheme S1**) and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 9/1).

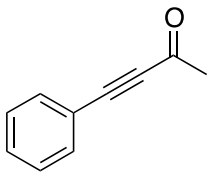


3'

Brown oil (2.14 g, 14.6 mmol, 96% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.56 (d, *J* = 6.6 Hz, 3H), 2.02 (brs, 1H), 4.76 (q, *J* = 6.6 Hz, 1H), 7.28–7.33 (m, 3H), 7.39–7.46 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 24.4, 58.8, 84.0, 90.9, 122.5, 128.3, 128.4, 131.6; GC-MS (EI): *m/z* 145 $[M–H]^+$.

Preparation of 4-phenylbut-3-yn-2-one (**3**)[2]:

Pyridinium dichromate (2.63g, 7.00 mmol) and DMF (3.3 mL) were charged into a round flask and then DCM (6.6 mL) and silica gel were added to the mixture. 4-Phenylbut-3-yn-2-ol (**3'**) (731 mg, 5.00 mmol) was added dropwise to the mixture at 0 ˚C. After treatment of the mixture with additional silica gel, the resulting mixture was stirred at room temperature overnight. The reaction mixture was filtrated with a pad of florisil using EtOAc and the filtrate was washed with water and brine. The resulting organic layer was dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 9/1) to give 4-phenylbut-3-yn-2-one (**3**) as a pale yellow oil (569 mg, 3.95 mmol, 80% yield).

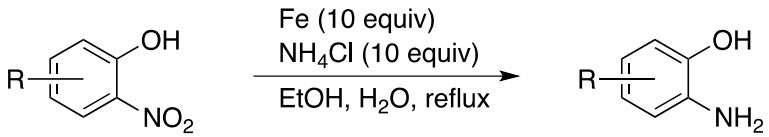


3

^{1}H NMR (270 MHz, $CDCl_3$): δ 2.44 (s, 3H), 7.33–7.48 (m, 3H), 7.54–7.59 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 32.6, 88.1, 90.1, 119.7, 128.5, 130.6, 132.9, 184.4; GC-MS (EI): *m/z* 144 $[M]^+$.

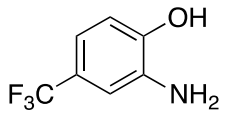
General procedure for the preparation of 2-aminophenol derivatives

Scheme S4. Preparation of 2-aminophenols 5f, 5h, 5j, 5k, 5l:



2-Nitro-4-(trifluoromethyl)phenol (622 mg, 3.00 mmol) and EtOH (43 mL) were charged into a round flask. Iron powder (1.68 g, 30.0 mmol) and a solution of NH_4Cl (1.60 g, 30.0 mmol) in H_2O (12 mL) were added to the mixture. The resulting mixture was refluxed for 1 h and then allowed to cool to room temperature. The resulting suspension was filtrated with a pad of celite and the filtrate was concentrated *in vacuo*. The resulting mixture was diluted with EtOAc and then H_2O was added. The aqueous

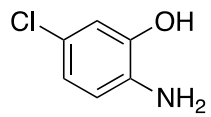
phase was extracted with EtOAc and the combined organic phase was washed with brine. After removal of the solvent, the crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 1/1) to give 2-amino-4-(trifluoromethyl)phenol (**5f**) as a white solid (363 mg, 2.05 mmol, 68% yield).



5f

M.p. 122–125 ˚C; IR (neat) 3383, 2972, 2708, 2630, 1618, 1329, 1113, 897, 822 cm^{-1}; ^{1}H NMR (270 MHz, DMSO–d_6): δ 4.95 (brs, 2H), 6.74 (d, J = 8.5 Hz, 1H), 6.80 (d, J = 8.5 Hz, 1H), 6.90 (s, 1H), 9.88 (brs, 1H); ^{13}C NMR (126 MHz, DMSO–d_6): δ 110.0 (q, J_{CF} = 3.6 Hz), 113.2 (q, J_{CF} = 4.0 Hz), 113.8, 120.2 (q, J_{CF} = 31.2 Hz), 125.1 (q, J_{CF} = 271 Hz), 137.4, 147.1; ^{19}F NMR (471 MHz, DMSO–d_6): δ –60.7 (s); HRMS (ESI) $[M+H]^+$ Calcd for $C_7H_7F_3NO$ 178.0480; Found 178.0486.

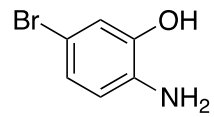
2-Amino-5-chlorophenol (**5h**)



5h

This compound was prepared according to the similar method to **5f** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 1/1). Brown solid (358 mg, 2.49 mmol, 81% yield); M.p. 153–154 ˚C; IR (neat) 3371, 3298, 2999, 2563, 1599, 1508, 1429, 1267, 1086, 887, 852 cm^{-1}; ^{1}H NMR (270 MHz, DMSO–d_6): δ 4.65 (brs, 2H), 6.569–6.574 (m, 2H), 6.66–6.67 (m, 1H), 9.48 (brs, 1H); ^{13}C NMR (67.8 MHz, DMSO–d_6): δ 114.0, 114.8, 118.9, 119.0, 135.9, 144.9; HRMS (ESI) $[M+H]^+$ Calcd for C_6H_7ClNO 144.0216; Found 144.0211.

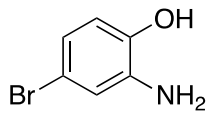
2-Amino-5-bromophenol (**5j**)



5j

This compound was prepared according to the similar method to **5f** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 1/1). Brown solid (820 mg, 4.36 mmol, 87% yield); M.p. 140–142 ˚C; IR (neat) 3369, 2991, 2540, 1585, 1500, 1425, 1078, 920, 852 cm^{-1}; ^{1}H NMR (270 MHz, DMSO–d_6): δ 4.67 (brs, 2H), 6.53 (dd, J = 8.5, 3.1 Hz, 1H), 6.66–6.71 (m, 1H), 6.77–6.79 (m, 1H), 9.45 (brs, 1H); ^{13}C NMR (67.8 MHz, DMSO–d_6): δ 106.1, 115.4, 116.7, 121.9, 136.3, 145.2; HRMS (ESI) $[M+H]^+$ Calcd for C_6H_7BrNO 187.9711; Found 187.9704.

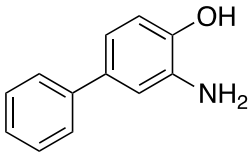
2-Amino-4-bromophenol (**5k**)



5k

This compound was prepared according to the similar method to **5f** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 1/1). Brown solid (493 mg, 2.62 mmol, 52% yield); M.p. 124–126 ˚C; IR (neat) 3379, 3307, 3068, 2688, 1589, 1500, 1200, 847, 804 cm^{-1}; ^{1}H NMR (270 MHz, DMSO–d_6): δ 4.80 (brs, 2H), 6.53 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.61 (d, *J* = 8.3 Hz, 1H), 6.76 (d, *J* = 2.4 Hz, 1H), 9.31 (brs, 1H); ^{13}C NMR (67.8 MHz, DMSO–d_6): δ 110.9, 115.8, 116.3, 118.4, 138.8, 143.4; HRMS (ESI) $[M+H]^+$ Calcd for C_6H_7BrNO 187.9711; Found 187.9706.

3-Amino-[1,1'-biphenyl]-4-ol (**5l**)



5l

This compound was prepared according to the similar method to **5f** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 1/1). Brown solid (493 mg, 2.62 mmol, 52% yield); M.p. decomp. (201 ˚C); IR (neat) 3383, 2974, 2708, 2630, 1618, 1527, 1331, 897, 822, 729 cm^{-1}; ^{1}H NMR (270 MHz, DMSO–d_6): δ 4.64 (brs, 2H), 6.70–6.78 (m, 2H), 6.94 (d, *J* = 2.2 Hz, 1H), 7.20–7.26 (m, 1H), 7.37 (dd, *J* = 7.9, 7.6 Hz, 2H), 7.50 (dd, *J* = 7.9, 0.95 Hz, 2H), 9.19 (brs, 1H); ^{13}C NMR (67.8 MHz, DMSO–d_6): δ 112.7, 114.7, 114.9, 125.9, 126.1, 128.7, 131.7, 136.9, 141.1, 144.0; HRMS (ESI) $[M+H]^+$ Calcd for $C_{12}H_{12}NO$ 186.0919; Found 186.0926.

General procedure for the synthesis of benzoxazoles via the copper-catalyzed hydroamination of alkynones with 2-aminophenols

Procedure A

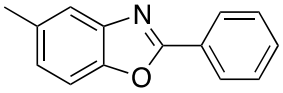
$Cu(OTf)_2$ (5.4 mg, 0.0150 mmol), alkynones **4** (0.300 mmol), and 2-aminophenol **5** (0.360 mmol) were charged into a screw vial and the vial was refilled with N_2. After the addition of *o*-xylene (0.6 mL), the resulting mixture was stirred at 120 ˚C for 19 h. The reaction was allowed to cool to room temperature and then quenched with water (1 mL). The aqueous phase was extracted with EtOAc (2 mL × 1). The organic phase was washed with brine (1 mL × 1) and dried over $MgSO_4$. After removal of the

solvent, the resulting crude mixture was purified by preparative thin-layer chromatography to give the benzoxazoles **6**.

Procedure B

$Cu(OTf)_2$ (5.4 mg, 0.0150 mmol), alkynones **4** (0.300 mmol), and 2-aminophenol **5** (0.360 mmol) were charged into a screw vial and the vial was refilled with N_2. After the addition of *o*-xylene (0.6 mL), the resulting mixture was stirred at 120 ˚C for 19 h. The reaction was allowed to cool to room temperature and then a solution of $NaBH_4$ (13.6 mg, 0.360 mmol) in MeOH (1.5 mL) was added. The resulting mixture was stirred for 15–30 min at room temperature and quenched with water (1 mL). The aqueous phase was extracted with EtOAc (2.5 mL × 1). The organic phase was washed with brine (1 mL × 1) and dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by preparative thin-layer chromatography to give the benzoxazoles **6**.

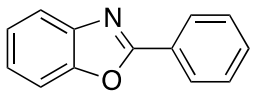
5-Methyl-2-phenylbenzo[*d*]oxazole (**6aa**)[15]



6aa

This compound was prepared according to the procedure A and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (57.4 mg, 0.274 mmol, 91% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.48 (s, 3H), 7.15 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.49–7.55 (m, 4H), 8.22–8.26 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 109.9, 119.9, 126.2, 127.3, 127.5, 128.8, 131.4, 134.4, 142.2, 149.0, 163.1; GC-MS (EI): *m/z* 209 $[M]^+$.

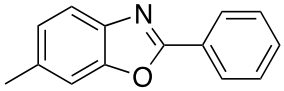
2-Phenylbenzo[*d*]oxazole (**6ab**)[15]



6ab

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (48.3 mg, 0.247 mmol, 82% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.32–7.38 (m, 2H), 7.50–7.60 (m, 4H), 7.76–7.81 (m, 1H), 8.24–8.29 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 110.6, 120.0, 124.6, 125.1, 127.1, 127.6, 128.9, 131.5, 142.0, 150.7, 163.0; GC-MS (EI): *m/z* 195 $[M]^+$.

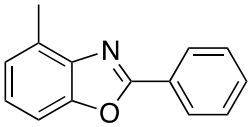
6-Methyl-2-phenylbenzo[*d*]oxazole (**6ac**)[15]



6ac

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (46.1 mg, 0.220 mmol, 73% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.51 (s, 3H), 7.15–7.18 (m, 1H), 7.38–7.39 (m, 1H), 7.49–7.54 (m, 3H), 7.64 (d, *J* = 7.8 Hz, 1H), 8.20–8.27 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.8, 110.8, 119.2, 125.9, 127.1, 127.5, 128.9, 131.4, 135.7, 139.6, 151.0, 162.5; GC-MS (EI): *m/z* 209 $[M]^+$.

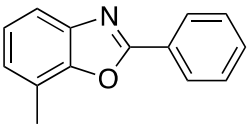
4-Methyl-2-phenylbenzo[*d*]oxazole (**6ad**)[15]



6ad

This compound was prepared according to the procedure A and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). Light brown solid (59.9 mg, 0.286 mmol, 95% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.67 (s, 3H), 7.11–7.14 (m, 1H), 7.19–7.25 (m, 1H), 7.37–7.40 (m, 1H), 7.48–7.52 (m, 3H), 8.22–8.29 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 16.5, 107.8, 124.7, 125.0, 127.4, 127.5, 128.8, 130.5, 131.2, 141.4, 150.5, 162.2; GC-MS (EI): *m/z* 209 $[M]^+$.

7-Methyl-2-phenylbenzo[*d*]oxazole (**6ae**)

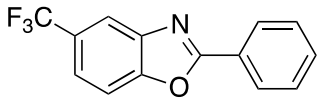


6ae

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (42.0 mg, 0.200 mmol, 67% yield); M.p. 61–63 ˚C; IR (neat) 3064, 2956, 1614, 1581, 1552, 1448, 1196, 1086, 1022, 777, 746, 704 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.59 (s, 3H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.22–7.27 (m, 1H), 7.51–7.55 (m, 3H), 7.60 (d, *J* = 8.1 Hz, 1H), 8.25–8.29 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 15.2, 117.3, 121.1, 124.5, 126.1, 127.3, 127.5, 128.8, 131.4, 141.6, 149.9, 162.7; HRMS (ESI) $[M+H]^+$ Calcd for $C_{14}H_{12}NO$ 210.0919; Found 210.0928.

2-Phenyl-5-(trifluoromethyl)benzo[*d*]oxazole (**6af**)

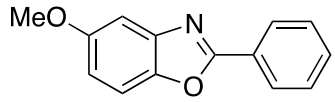
This compound was prepared according to the procedure A and the desired product was obtained after purification by preparative thin-layer chromatography (Pentane/Et_2O =



6af

9/1). White solid (67.4 mg, 0.256 mmol, 84% yield); M.p. 84–85 ˚C; IR (neat) 3072, 1630, 1558, 1489, 1340, 1109, 825, 706 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 7.48–7.66 (m, 5H), 8.03 (d, *J* = 0.54 Hz, 1H), 8.22–8.26 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 111.0, 117.7 (q, J_{CF} = 4.0 Hz), 122.3 (q, J_{CF} = 3.6 Hz), 124.2 (q, J_{CF} = 273 Hz), 126.5, 127.4 (q, J_{CF} = 32.8 Hz), 127.9, 129.1, 132.2, 142.3, 152.5, 164.8; ^{19}F NMR (471 MHz, $CDCl_3$): δ –62.1 (s); HRMS (ESI) $[M+H]^+$ Calcd for $C_{14}H_9F_3NO$ 264.0636; Found 264.0638.

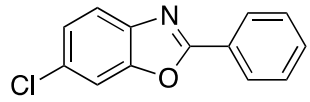
5-Methoxy-2-phenylbenzo[*d*]oxazole (**6ag**)[15]



6ag

This compound was prepared according to the procedure A and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (51.5 mg, 0.229 mmol, 76% yield); ^1H NMR (270 MHz, $CDCl_3$): δ 3.87 (s, 3H), 6.95 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.26 (d, *J* = 2.3 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.49–7.55 (m, 3H), 8.21–8.25 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 55.9, 102.8, 110.7, 113.7, 127.2, 127.5, 128.9, 131.4, 142.9, 145.4, 157.4, 163.8; GC-MS (EI): *m/z* 225 $[M]^+$.

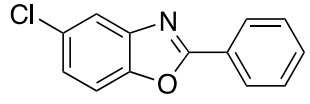
6-Chloro-2-phenylbenzo[*d*]oxazole (**6ah**)[15]



6ah

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (56.8 mg, 0.247 mmol, 82% yield); ^1H NMR (270 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.48–7.59 (m, 4H), 7.65–7.68 (m, 1H), 8.19–8.25 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 111.2, 120.4, 125.3, 126.7, 127.6, 129.0, 130.6, 131.8, 140.9, 150.9, 163.7; GC-MS (EI): *m/z* 229 $[M]^+$.

5-Chloro-2-phenylbenzo[*d*]oxazole (**6ai**)[16]

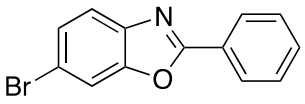


6ai

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (57.5 mg, 0.250 mmol, 83% yield); ^1H NMR (270 MHz, $CDCl_3$): δ 7.32 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.48–7.57 (m, 4H), 7.74–7.75 (m, 1H), 8.21–8.26 (m, 2H); ^{13}C

NMR (126 MHz, $CDCl_3$): δ 111.3, 120.0, 125.4, 126.7, 127.8, 129.0, 130.1, 131.9, 143.2, 149.3, 164.4; GC-MS (EI): *m/z* 229 $[M]^+$.

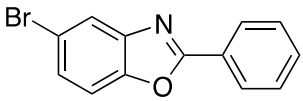
6-Bromo-2-phenylbenzo[*d*]oxazole (**6aj**)[15]



6aj

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (62.9 mg, 0.229 mmol, 76% yield as a 90:10 mixture of **6aj**:**6ab**); ^1H NMR (270 MHz, $CDCl_3$): δ 7.45–7.56 (m, 4H), 7.61–7.64 (m, 1H), 7.74 (d, *J* = 1.4 Hz, 1H), 8.18–8.24 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 114.1, 117.9, 120.9, 126.6, 127.6, 128.0, 128.9,.131.8, 141.3, 151.2, 163.5; GC-MS (EI): *m/z* 273 $[M]^+$.

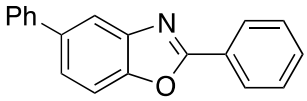
5-Bromo-2-phenylbenzo[*d*]oxazole (**6ak**)



6ak

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (61.5 mg, 0.224 mmol, 74% yield); M.p. 102–103 ˚C; IR (neat) 3059, 1608, 1550, 1487, 1281, 1057, 854, 808 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 7.45–7.57 (m, 5H), 7.89–7.90 (m, 1H), 8.21–8.25 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 111.8, 117.3, 123.0, 126.6, 127.7, 128.1, 129.0, 131.9, 143.7, 149.7, 164.1; HRMS (ESI) $[M+H]^+$ Calcd for $C_{13}H_9BrNO$ 273.9868; Found 273.9858.

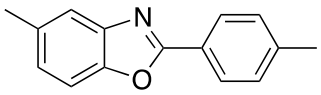
2,5-Diphenylbenzo[*d*]oxazole (**6al**)



6al

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (47.0 mg, 0.173 mmol, 57% yield); M.p. 123–125 ˚C; IR (neat) 3059, 1620, 1554, 818, 760, 696 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 7.33–7.39 (m, 1H), 7.43–7.65 (m, 9H), 7.96–7.97 (m, 1H), 8.23–8.30 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 110.5, 118.4, 124.7, 127.1, 127.2, 127.4, 127.6, 128.8, 128.9, 131.6, 138.4, 141.0, 142.7, 150.3, 163.6; HRMS (ESI) $[M+H]^+$ Calcd for $C_{19}H_{14}NO$ 272.1075; Found 272.1070.

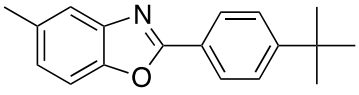
5-Methyl-2-(*p*-tolyl)benzo[*d*]oxazole (**6ba**)[17]



6ba

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (50.5 mg, 0.227 mmol, 76% yield as a 90:10 mixture of **6ba**:**6aa**); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.42 (s, 3H), 2.47 (s, 3H), 7.11–7.16 (m, 1H), 7.29–7.32 (m, 2H), 7.40–7.45 (m, 1H), 7.49–7.54 (m, 1H), 8.09–8.14 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 21.6, 109.8, 119.7, 124.5, 125.9, 127.5, 129.6, 134.2, 141.8, 142.3, 148.9, 163.3; GC-MS (EI): *m/z* 223 $[M]^+$.

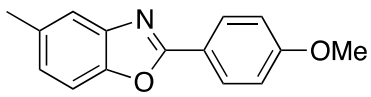
2-(4-(*tert*-Butyl)phenyl)-5-methylbenzo[*d*]oxazole (**6ca**)



6ca

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (44.5 mg, 0.168 mmol, 56% yield); M.p. 88–90 ˚C; IR (neat) 2962, 1618, 1576, 1554, 1363, 1109, 1057, 843, 827, 798 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.37 (s, 9H), 2.48 (s, 3H), 7.12–7.16 (m, 1H), 7.44 (d, *J* = 8.4 Hz, 1H) 7.51–7.56 (m, 3H), 8.14–8.19 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 31.1, 35.0, 109.8, 119.8, 124.5, 125.8, 125.9, 127.4, 134.2, 142.4, 148.9, 154.9, 163.3; HRMS (ESI) $[M+H]^+$ Calcd for $C_{18}H_{20}NO$ 266.1545; Found 266.1547.

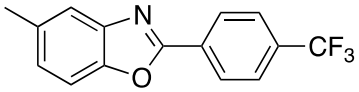
2-(4-Methoxyphenyl)-5-methylbenzo[*d*]oxazole (**6da**)



6da

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (47.2 mg, 0.197 mmol, 66% yield); m.p. 107–109 ˚C; IR (neat) 2974, 1606, 1558, 1500, 1174, 1020, 881, 841, 802 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.47 (s, 3H), 3.88 (s, 3H), 7.01 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.51 (s, 1H), 8.17 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 55.4, 109.7, 114.3, 119.5, 119.8, 125.7, 129.3, 134.2, 142.3, 148.8, 162.2, 163.2; HRMS (ESI) $[M+H]^+$ Calcd for $C_{15}H_{14}NO_2$ 240.1025; Found 240.1022.

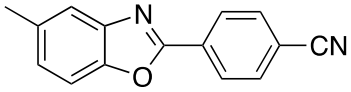
5-Methyl-2-(4-(trifluoromethyl)phenyl)benzo[*d*]oxazole (**6ea**)[18]



6ea

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Pentane/Et_2O = 9/1). White solid (42.3 mg, 0.153 mmol, 50% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.48 (s, 3H), 7.17–7.20 (m, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.55–7.56 (m, 1H), 7.74–7.77 (m, 2H), 8.31–8.34 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.5, 110.1, 120.2, 123.8 (q, J_{CF} = 273 Hz), 125.9 (q, J_{CF} = 4.0 Hz), 127.0, 127.8, 130.6, 132.8 (q, J_{CF} = 32.8 Hz), 134.8, 142.1, 149.1, 161.5; ^{19}F NMR (471 MHz, $CDCl_3$): δ –63.9 (s); GC-MS (EI): *m/z* 277 $[M]^+$.

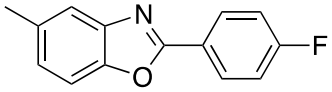
4-(5-methylbenzo[*d*]oxazol-2-yl)benzonitrile (**6fa**)



6fa

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (18.1 mg, 0.0773 mmol, 26% yield); M.p. 176–178 ˚C; IR (neat) 2929, 2225, 1570, 1547, 1493, 1281, 1059, 845, 796 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.50 (s, 3H), 7.21–7.25 (m, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.58–7.59 (m, 1H), 7.78–7.83 (m, 2H), 8.32–8.38 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 110.2, 114.5, 118.2, 120.3, 127.3, 127.8, 131.3, 132.6, 135.0, 142.0, 149.1, 161.0; HRMS (ESI) $[M+H]^+$ Calcd for $C_{15}H_{11}N_2O$ 235.0871; Found 235.0873.

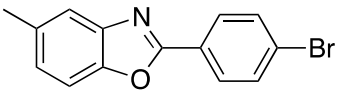
2-(4-Fluorophenyl)-5-methylbenzo[*d*]oxazole (**6ga**)[19]



6ga

This compound was prepared according to the procedure A and the desired product was obtained after purification by preparative thin-layer chromatography (Pentane/Et_2O = 9/1). White solid (50.6 mg, 0.22 mmol, 74% yield as a 74:26 mixture of **6ga**:**6aa** (determined by a GC-MS analysis)); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.48 (s, 3H), 7.13–7.24 (m, 3H), 7.41–7.46 (m, 1H), 7.50–7.53 (m, 1H), 8.19–8.26 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 109.9, 116.1 (d, J_{CF} = 22.3 Hz), 119.9, 123.6 (d, J_{CF} = 3.4 Hz), 126.2, 129.7 (d, J_{CF} = 8.9 Hz), 134.5, 142.2, 149.0, 162.2, 164.7 (d, J_{CF} = 252 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ –108.71– –108.70 (m); GC-MS (EI): *m/z* 227 $[M]^+$.

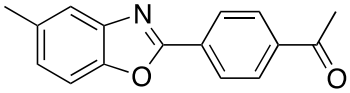
2-(4-Bromophenyl)-5-methylbenzo[*d*]oxazole (**6ha**)[20]



6ha

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Pentane/Et_2O = 9/1). White solid (60 mg, 0.208 mmol, 69% yield as a 87:13 mixture of **6ha**:**6aa**); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.49 (s, 3H), 7.15–7.19 (m, 1H), 7.43–7.47 (m, 1H), 7.51–7.56 (m, 1H), 7.63–7.68 (m, 2H), 8.07–8.12 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 110.0, 120.0, 126.0, 126.2, 126.5, 128.9, 132.1, 134.6, 142.2, 149.0, 162.2; GC-MS (EI): *m/z* 287 $[M]^+$.

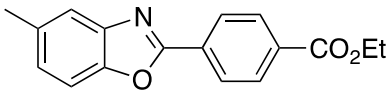
1-(4-(5-Methylbenzo[*d*]oxazol-2-yl)phenyl)ethanone (**6ia**)



6ia

This compound was prepared according to the procedure A and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (17.7 mg, 0.0704 mmol, 23% yield); M.p. 157–158 ˚C; IR (neat) 2931, 1670, 1408, 1354, 841, 804, 756 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.50 (s, 3H), 2.67 (s, 3H), 7.19–7.22 (m, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 0.54 Hz, 1H), 8.08–8.11 (m, 2H), 8.34 (dd, *J* = 6.8, 1.5 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 26.8, 110.1, 120.2, 127.0, 127.6, 128.8, 131.2, 134.8, 138.8, 142.1, 149.1, 161.9, 197.4; HRMS (ESI) $[M+H]^+$ Calcd for $C_{16}H_{14}NO_2$ 252.1025; Found 252.1032.

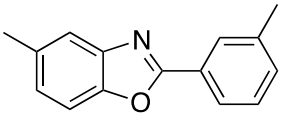
Ethyl 4-(5-methylbenzo[*d*]oxazol-2-yl)benzoate (**6ja**)[21]



6ja

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (16.1 mg, 0.0572 mmol, 19% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.43 (t, *J* = 7.1 Hz, 3H), 2.49 (s, 3H), 4.42 (q, *J* = 7.1 Hz, 2H), 7.19 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.57–7.58 (m, 1H), 8.16–8.20 (m, 2H), 8.30 (dd, *J* = 6.6, 1.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.3, 21.5, 61.3, 110.1, 120.2, 126.9, 127.3, 130.0, 131.1, 132.7, 134.7, 142.2, 149.1, 162.0, 165.9; GC-MS (EI): *m/z* 281 $[M]^+$.

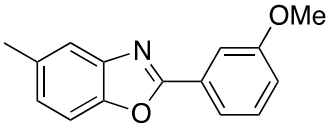
5-Methyl-2-(*m*-tolyl)benzo[*d*]oxazole (**6ka**)[22]



6ka

This compound was prepared according to the procedure A and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (55.2 mg, 0.248 mmol, 82% yield as a 95:5 mixture of **6ka**:**6aa**); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.46 (s, 3H), 2.49 (s, 3H), 7.14–7.18 (m, 1H), 7.33–7.47 (m, 3H), 7.51–7.55 (m, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 8.08–8.09 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.3, 21.4, 109.8, 119.8, 124.6, 126.1, 127.1, 128.0, 128.7, 132.1, 134.2, 138.6, 142.2, 148.9, 163.2; GC-MS (EI): *m/z* 223 $[M]^+$.

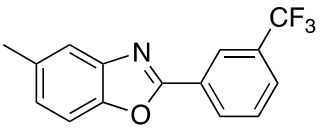
2-(3-Methoxyphenyl)-5-methylbenzo[*d*]oxazole (**6la**)[17]



6la

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (48.9 mg, 0.203 mmol, 68% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.48 (s, 3H), 3.91 (s, 3H), 7.05–7.09 (m, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.39–7.46 (m, 2H), 7.55 (s, 1H), 7.76–7.77 (m, 1H), 7.83 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 55.5, 109.9, 111.8, 118.2, 119.8, 120.0, 126.3, 128.4, 129.9, 134.4, 142.1, 148.9, 159.9, 163.0; GC-MS (EI): *m/z* 239 $[M]^+$.

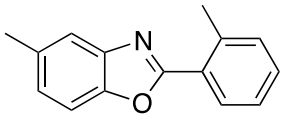
5-Methyl-2-(3-(trifluoromethyl)phenyl)benzo[*d*]oxazole (**6ma**)



6ma

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Pentane/Et_2O = 9/1). White solid (54.0 mg, 0.195 mmol, 65% yield as a 92:8 mixture of **6ma**:**6aa**); M.p. 84–93 ˚C; IR (neat) 3059, 1624, 1556, 1344, 1115, 1057, 804, 773 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.49 (s, 3H), 7.18–7.21 (m, 1H), 7.43–7.57 (m, 2H), 7.65 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 8.41 (d, *J* = 7.6 Hz, 1H), 8.51 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.5, 110.1, 120.2, 123.7 (q, J_{CF} = 273 Hz), 124.4 (q, J_{CF} = 3.6 Hz), 126.9, 127.8 (q, J_{CF} = 4.0 Hz), 128.2, 129.5, 130.5, 131.6 (q, J_{CF} = 33.2 Hz), 134.8, 142.1 149.1, 161.6; ^{19}F NMR (471 MHz, $CDCl_3$): δ –63.8 (s); HRMS (ESI) $[M+H]^+$ Calcd for $C_{15}H_{11}F_3NO$ 278.0793; Found 278.0796.

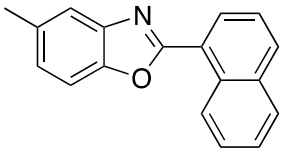
5-Methyl-2-(*o*-tolyl)benzo[*d*]oxazole (**6na**)[22]



6na

This compound was prepared according to the procedure A and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). White solid (47.1 mg, 0.212 mmol, 70% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.49 (s, 3H), 2.80 (s, 3H), 7.15–7.19 (m, 1H), 7.30–7.47 (m, 4H), 7.58–7.59 (m, 1H), 8.14–8.18 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 22.2, 109.8, 120.0, 126.0, 126.1, 126.4, 129.9, 130.8, 131.7, 134.1, 138.7, 142.3, 148.5, 163.5; GC-MS (EI): *m/z* 223 $[M]^+$.

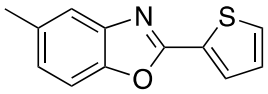
5-Methyl-2-(naphthalen-1-yl)benzo[*d*]oxazole (**6oa**)[19]



6oa

This compound was prepared according to the procedure A and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). Yellow solid (11.8 mg, 0.0455 mmol, 15% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.52 (s, 3H), 7.19–7.23 (m, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.56–7.63 (m, 2H), 7.66–7.74 (m, 2H), 7.94 (dd, *J* = 8.1, 0.81 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 8.41 (dd, *J* = 8.0, 1.2 Hz, 1H), 9.45 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 109.9, 120.2, 123.8, 124.9, 126.3, 126.4 (2C), 127.8, 128.6, 129.2, 130.7, 132.1 134.0, 134.3, 142.5, 148.4, 162.9; GC-MS (EI): *m/z* 259 $[M]^+$.

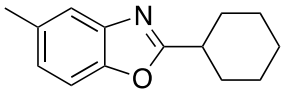
5-Methyl-2-(thiophen-2-yl)benzo[*d*]oxazole (**6pa**)[19]



6pa

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). Pale yellow solid (19.1 mg, 0.0887 mmol, 30% yield as a 99:1 mixture of **6pa**:**6aa**); ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.47 (s, 3H), 7.12–7.20 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.51–7.55 (m, 2H), 7.88–7.90 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 109.7, 119.7, 126.1, 128.2, 129.7, 129.8, 130.0, 134.5, 142.1, 148.6, 159.1; GC-MS (EI): *m/z* 215 $[M]^+$.

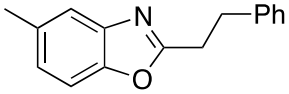
2-Cyclohexyl-5-methylbenzo[*d*]oxazole (**6qa**)[23]



6qa

This compound was prepared according to the procedure B and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). Yellow oil (53.8 mg, 0.250 mmol, 82% yield as a 93:7 mixture of **6qa**:**6aa**); ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.25–1.50 (m, 3H), 1.62–1.76 (m, 3H), 1.84–1.90 (m, 2H), 2.13–2.18 (m, 2H), 2.45 (s, 3H), 2.87–2.98 (m, 1H), 7.07–7.10 (m, 1H), 7.31–7.35 (m, 1H), 7.45–7.47 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.4, 25.6, 25.7, 30.5, 37.9, 109.6, 119.5, 125.3, 133.7, 141.4, 148.8, 170.5; GC-MS (EI): *m/z* 215 $[M]^+$.

5-Methyl-2-phenethylbenzo[*d*]oxazole (**6ra**)



6ra

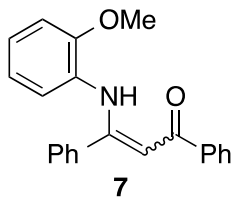
This compound was prepared according to the procedure A and the desired product was obtained after purification by preparative thin-layer chromatography (Pentane/Et_2O = 9/1). Brown oil (44.5 mg, 0.188 mmol, 62% yield); IR (neat) 3028, 2925, 2864, 1574, 1481, 1454, 1261, 800, 750, 698 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.45 (s, 3H), 3.21 (s, 4H), 7.07–7.11 (m, 1H), 7.17–7.36 (m, 6H), 7.45–7.46 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.4, 30.5, 32.8, 109.6, 119.5, 125.5, 126.4, 128.2, 128.6, 133.9, 140.1, 141.4, 149.0, 166.3; HRMS (ESI) $[M+H]^+$ Calcd for $C_{16}H_{16}NO$ 238.1232; Found 238.1237.

Preliminary mechanistic experiments

Cu-Catalyzed hydroamination of alkynone 4a with *o*-anisidine

$Cu(OTf)_2$ (5.4 mg, 0.0150 mmol), alkynone **4a** (61.9 mg, 0.300 mmol), and *o*-anisidine (37.3 mg, 0.300 mmol) were charged into a screw vial and the vial was refilled with N_2. After the addition of *o*-xylene (0.6 mL), the resulting mixture was stirred at 120 ˚C for 19 h. The reaction was allowed to cool to room temperature and then quenched with water (1 mL). The aqueous phase was extracted with EtOAc (2 mL × 1). The organic phase was washed with brine (1 mL × 1) and dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by preparative thin-layer chromatography (Pentane/EtOAc = 1/1) to give the hydroamination product **7**.

3-((2-Methoxyphenyl)amino)-1,3-diphenylprop-2-en-1-one (**7**)



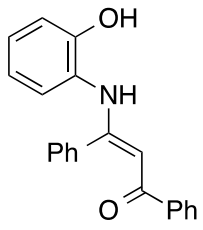
7

Slightly brown solid (65.7 mg, 0.199 mmol, 66% yield); M.p. 104–105 ˚C; IR (neat) 3060, 2837, 1597, 1568, 1516, 1493, 1464, 1254, 1024, 746, 698 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.91 (s, 3H), 6.09 (s, 1H), 6.39 (d, *J* = 7.9 Hz, 1H), 6.56 (dd, *J* = 7.9, 7.6 Hz, 1H), 6.84–6.87 (m, 1H), 6.92–6.98 (m, 1H), 7.30–7.47 (m, 8H), 7.95–8.00 (dd, *J* = 7.6, 2.2 Hz, 2H), 12.7 (brs, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 55.7, 97.4, 110.8, 119.9, 123.3, 124.5, 127.3, 128.0, 128.2, 128.4, 128.6, 129.5, 131.1, 136.3, 140.0, 151.2, 160.8, 189.4; HRMS (ESI) $[M+H]^+$ Calcd for $C_{22}H_{20}NO_2$ 330.1494; Found 330.1494.

Synthesis of possible intermediate 8

This compound was prepared according to the literature procedure[24] and the NMR data were consistent with the reported values.

(*E*)-3-((2-Hydroxyphenyl)amino)-1,3-diphenylprop-2-en-1-one (**8**)[24]



8

^{1}H NMR (270 MHz, DMSO–d_6): δ 6.11 (s, 1H), 6.27 (d, *J* = 8.4 Hz, 1H), 6.40–6.46 (m, 1H), 6.80–6.90 (m, 2H), 7.39–7.53 (m, 8H), 7.98 (d, *J* = 8.4 Hz, 2H), 10.1 (s, 1H), 12.6 (s, 1H); ^{13}C NMR (67.8 MHz, DMSO–d_6): δ 96.3, 115.6, 118.6, 123.5, 124.9, 126.9, 127.1, 128.0, 128.5, 128.6, 129.8, 131.4, 135.6, 139.4, 149.3, 160.8, 187.9; ESI-MS : *m/z* 338 $[M+Na]^+$.

Cu-Catalyzed transformation of possible intermediate 8 to benzoxazole 6ab

$Cu(OTf)_2$ (2.7 mg, 0.0075 mmol) and **8** (47.5 mg, 0.150 mmol) were charged into a screw vial and the vial was refilled with N_2. After the addition of *o*-xylene (0.3 mL), the resulting mixture was stirred at 120 ˚C for 23 h. The reaction was allowed to cool to room temperature and then quenched with water (0.5 mL). The aqueous phase was extracted with EtOAc (1 mL × 1). The organic phase was washed with brine (0.5 mL × 1) and dried over $MgSO_4$. After removal of the solvent, the yield of benzoxazole **6ab** was determined by ^{1}H NMR analysis as of the resulting crude mixture using dibromomethane as an internal standard.

6. References

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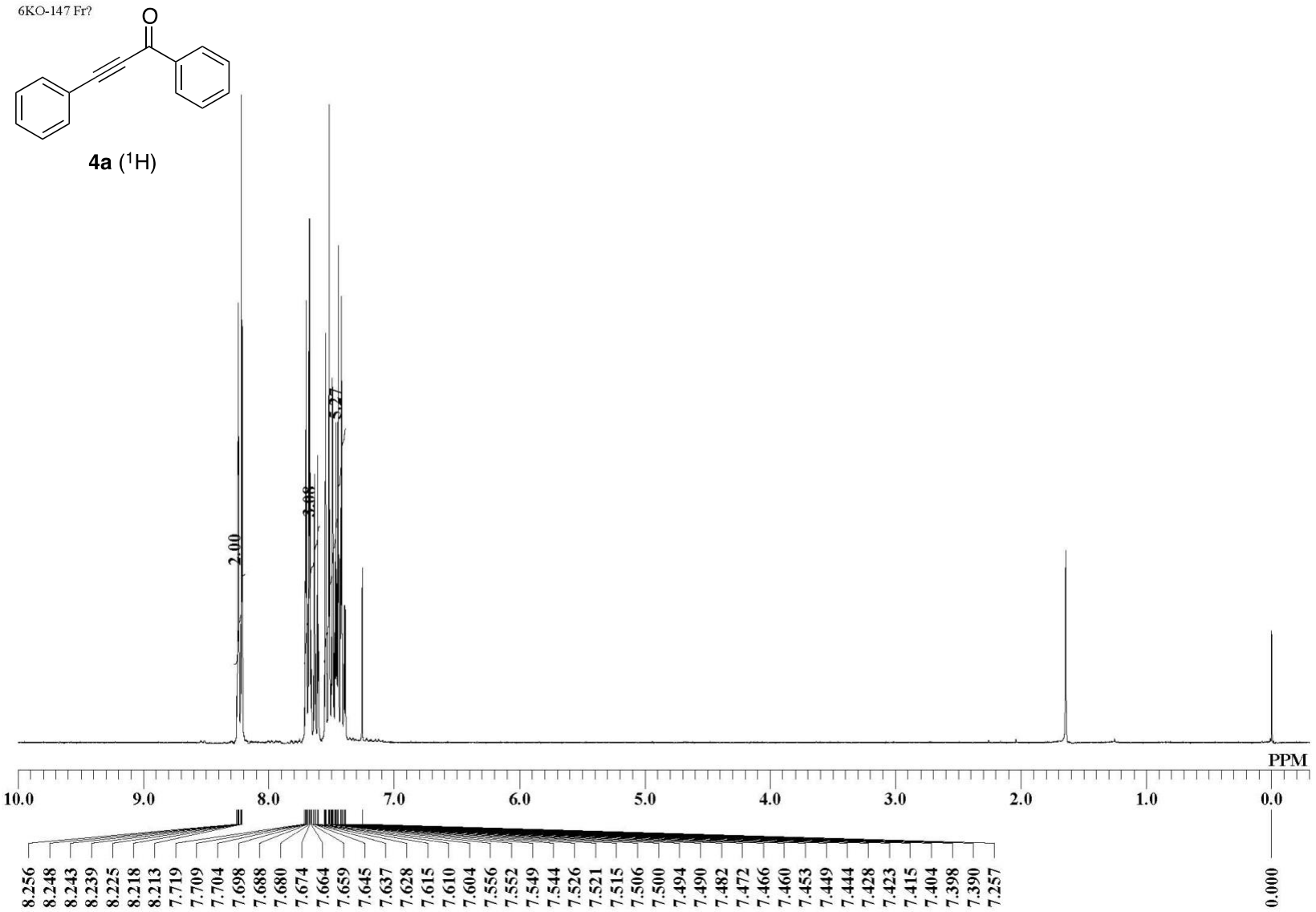
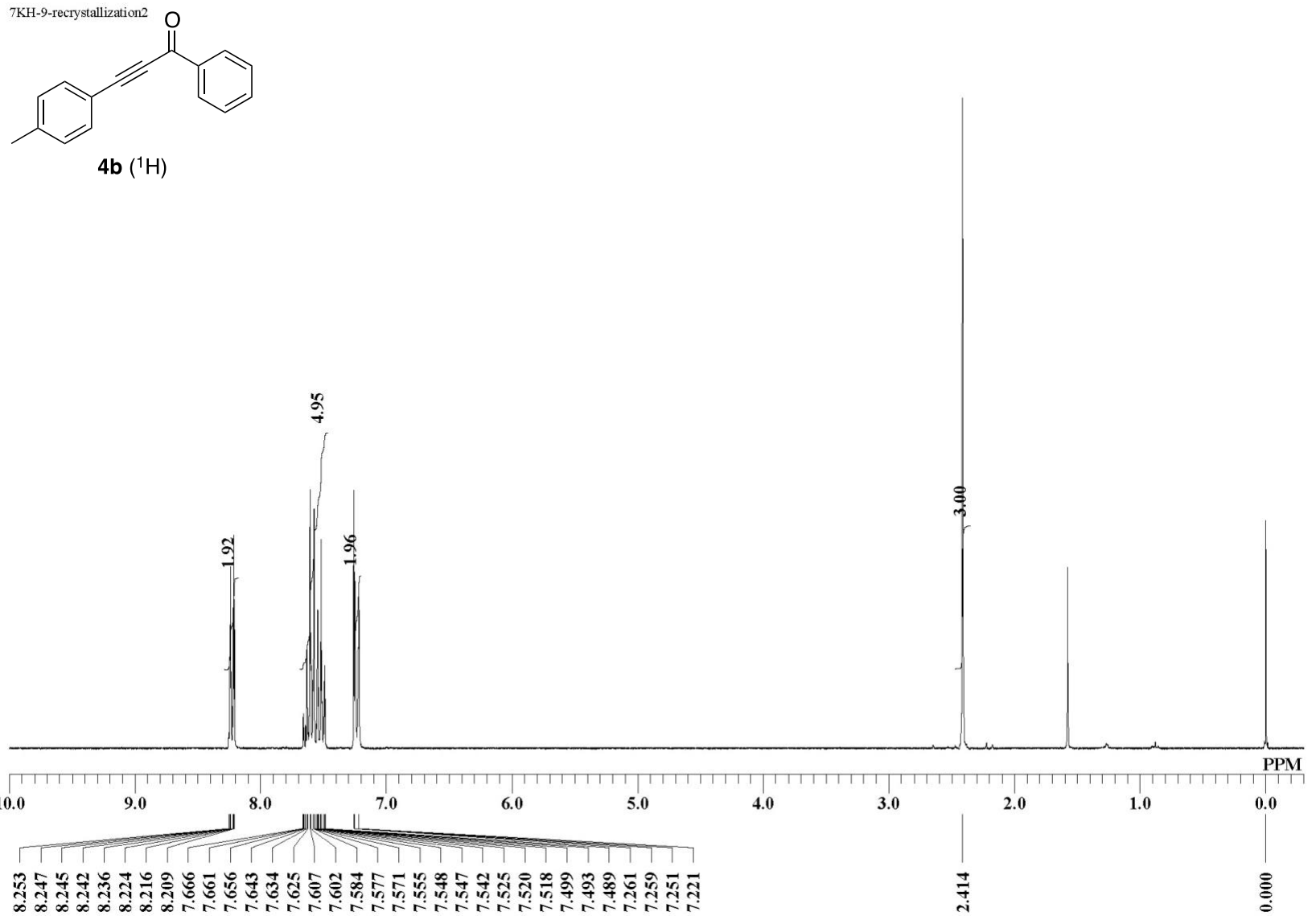
Copies of NMR spectra (^{1}H, ^{13}C, and ^{19}F)

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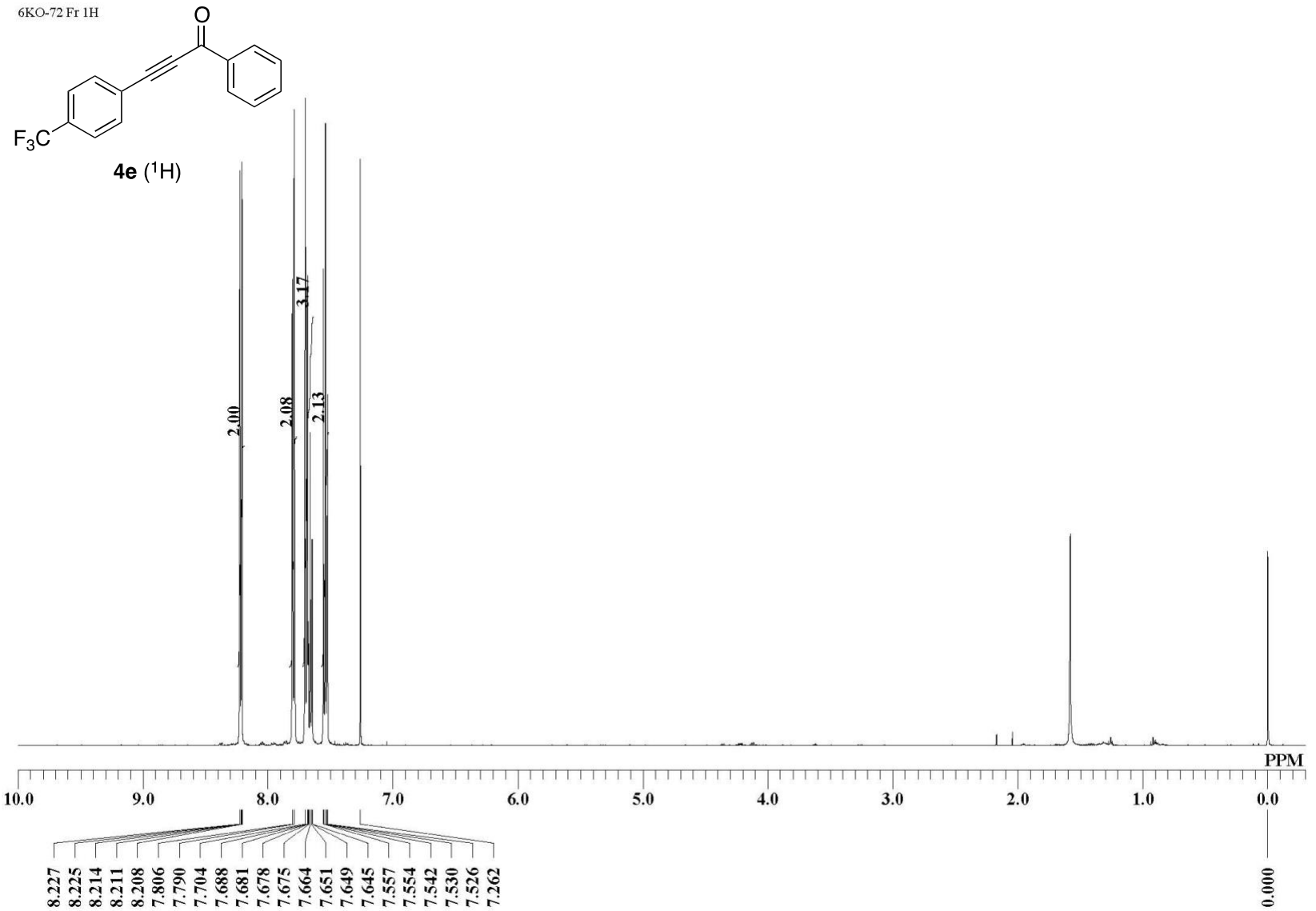
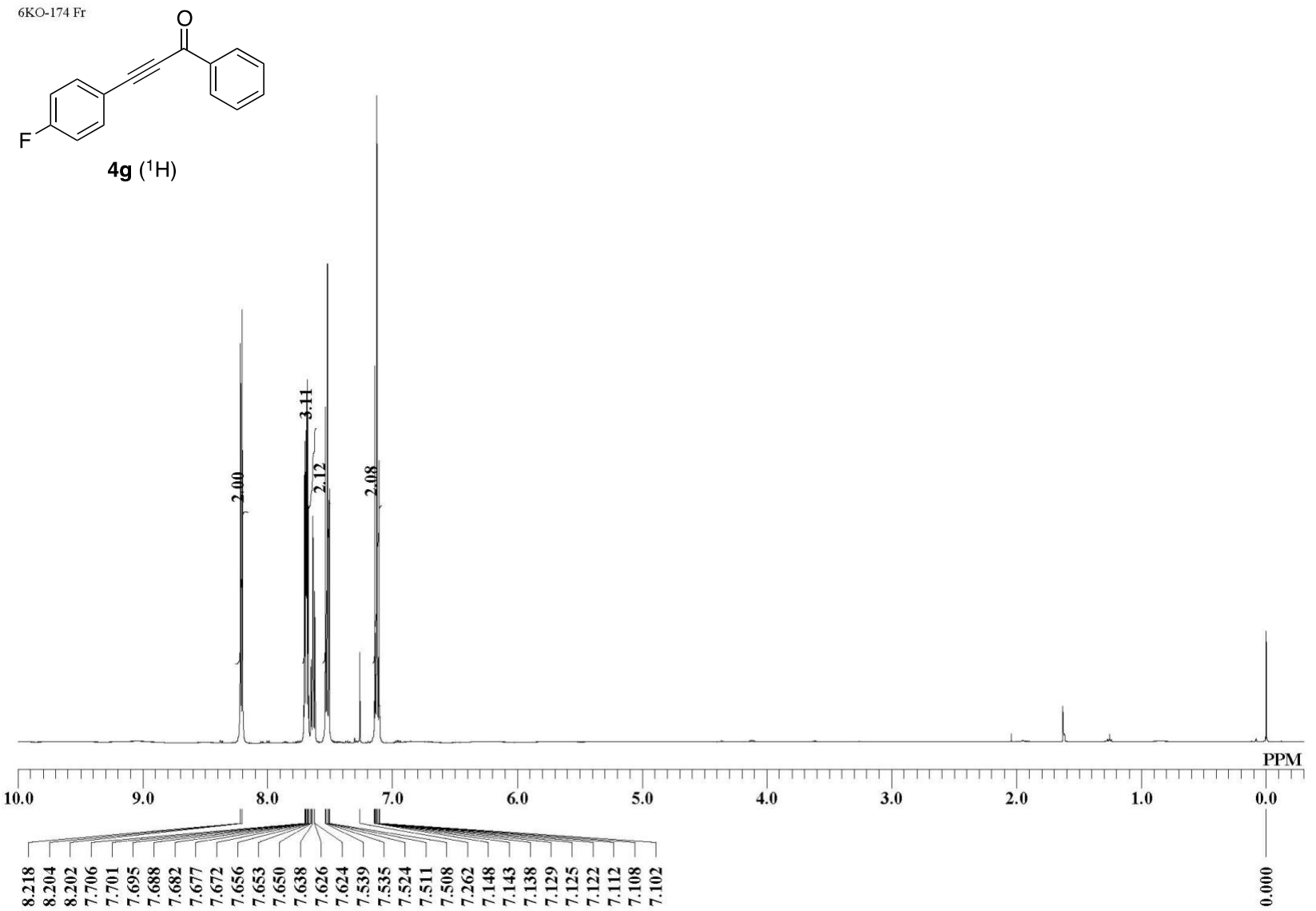
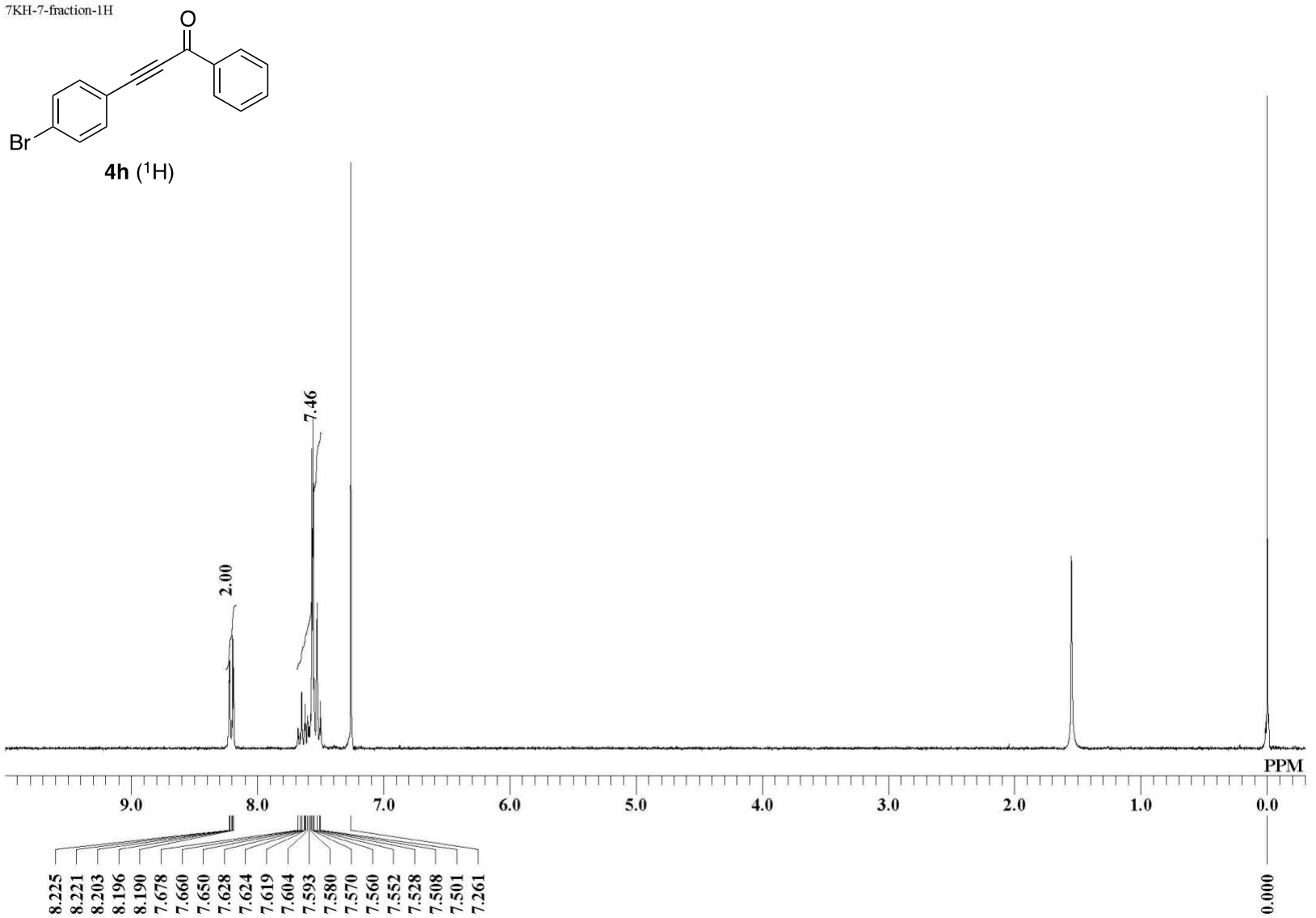
O
4b (1H)
4.95
1.92
1.96
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.253
8.247
8.245
8.242
8.236
8.224
8.216
8.209
7.666
7.661
7.656
7.643
7.634
7.625
7.607
7.602
7.584
7.577
7.571
7.555
7.548
7.547
7.542
7.525
7.520
7.518
7.499
7.493
7.489
7.261
7.259
7.251
7.221
2.414
0.000


6KO-72 Fr 1H
O
F3C
4e (1H)
2.00
2.08
3.17
2.13
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.227
8.225
8.214
8.211
8.208
7.806
7.790
7.704
7.688
7.681
7.678
7.675
7.664
7.651
7.649
7.645
7.557
7.554
7.542
7.530
7.526
7.262
0.000


6KO-174 Fr
O
F
4g (1H)
2.00
3.11
2.12
2.08
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.218
8.204
8.202
7.706
7.701
7.695
7.688
7.682
7.677
7.672
7.656
7.653
7.650
7.638
7.626
7.624
7.539
7.535
7.524
7.511
7.508
7.262
7.148
7.143
7.138
7.129
7.125
7.122
7.112
7.108
7.102
0.000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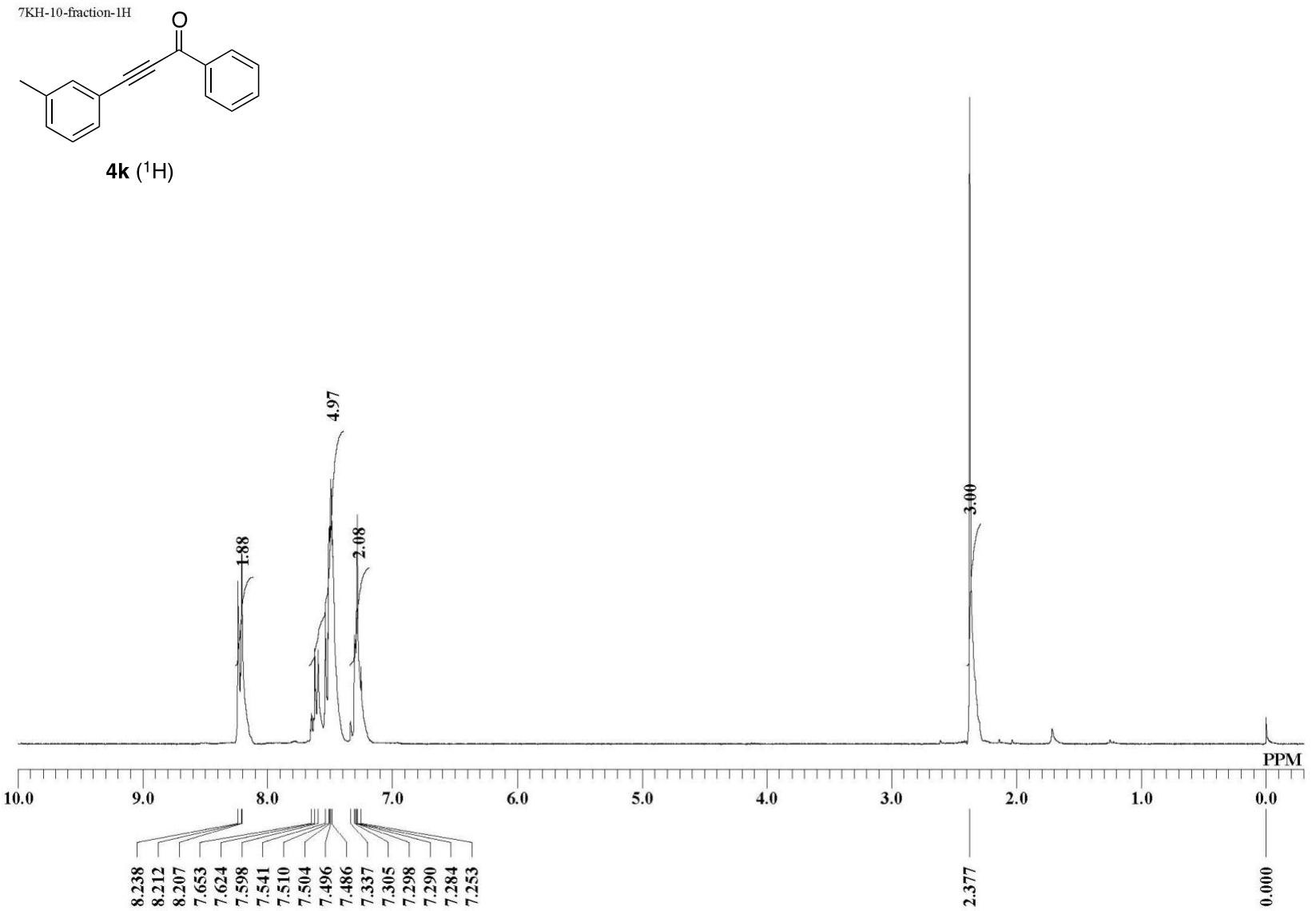
O
Br
4h (1H)
2.00
7.46
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.225
8.221
8.203
8.196
8.190
7.678
7.660
7.650
7.628
7.624
7.619
7.604
7.593
7.580
7.570
7.560
7.552
7.528
7.508
7.501
7.261
0.000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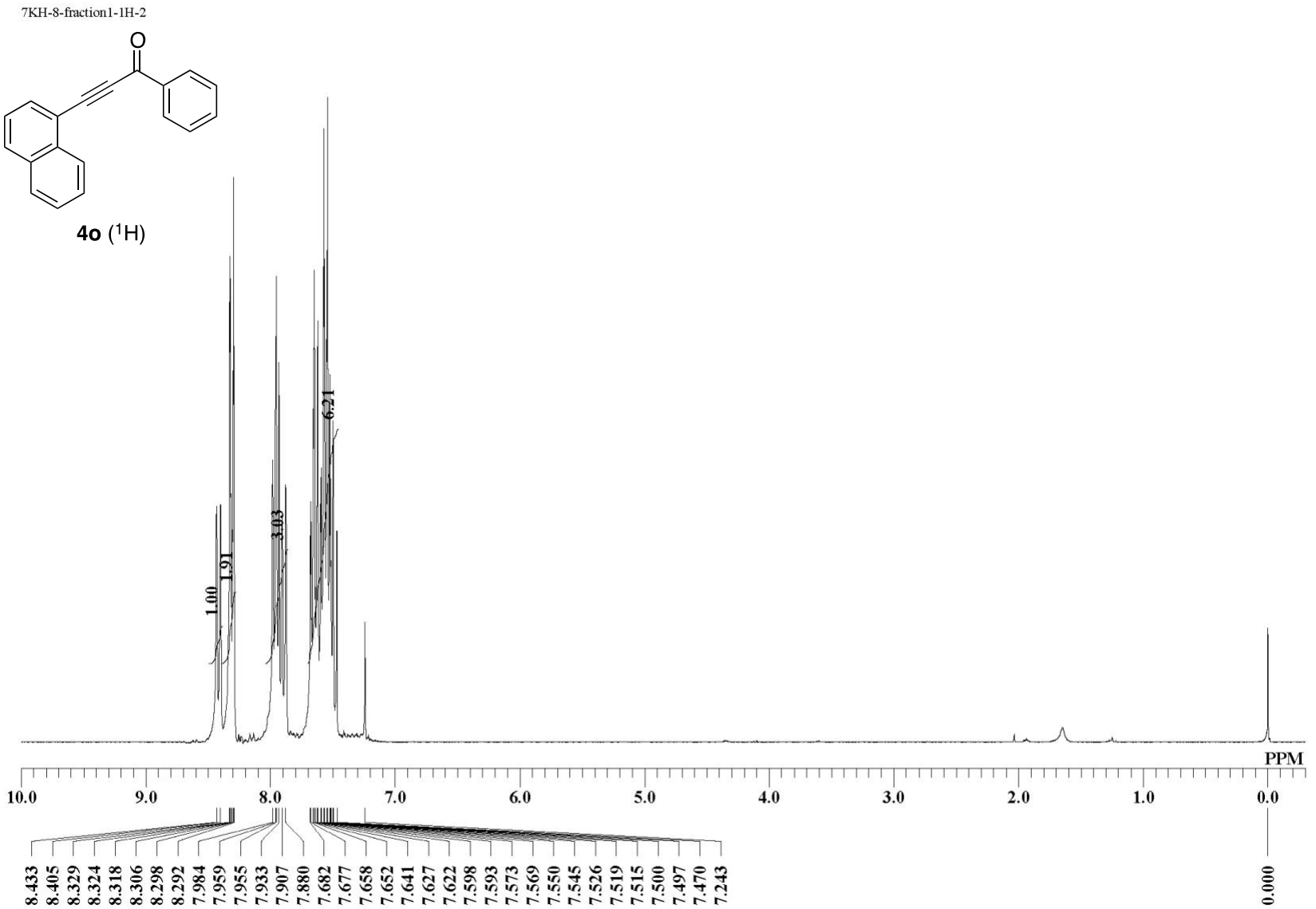
O
4k (1H)
4.97
1.88
2.08
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.238
8.212
8.207
7.653
7.624
7.598
7.541
7.510
7.504
7.496
7.486
7.337
7.305
7.298
7.290
7.284
7.253
2.377
0.000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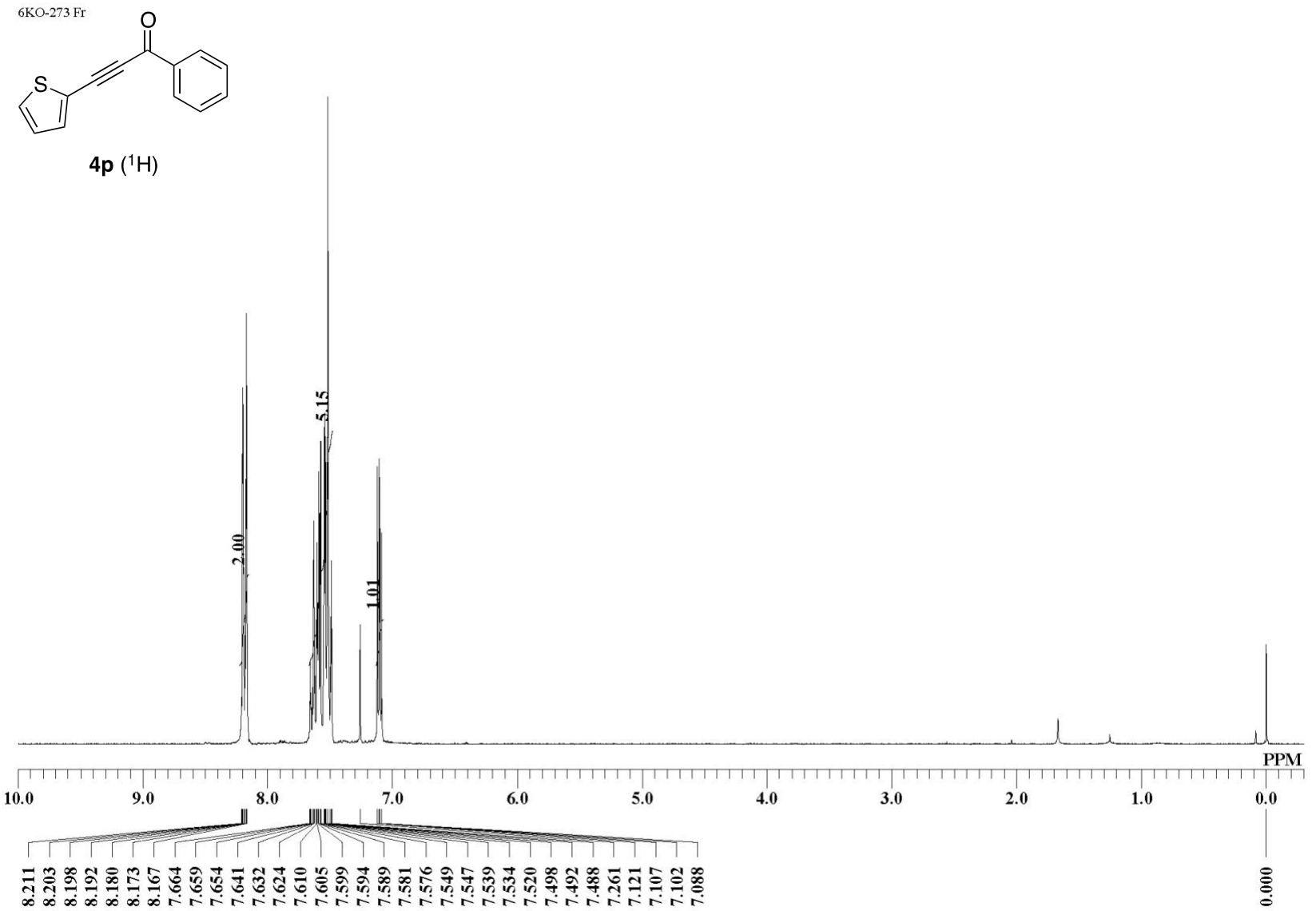
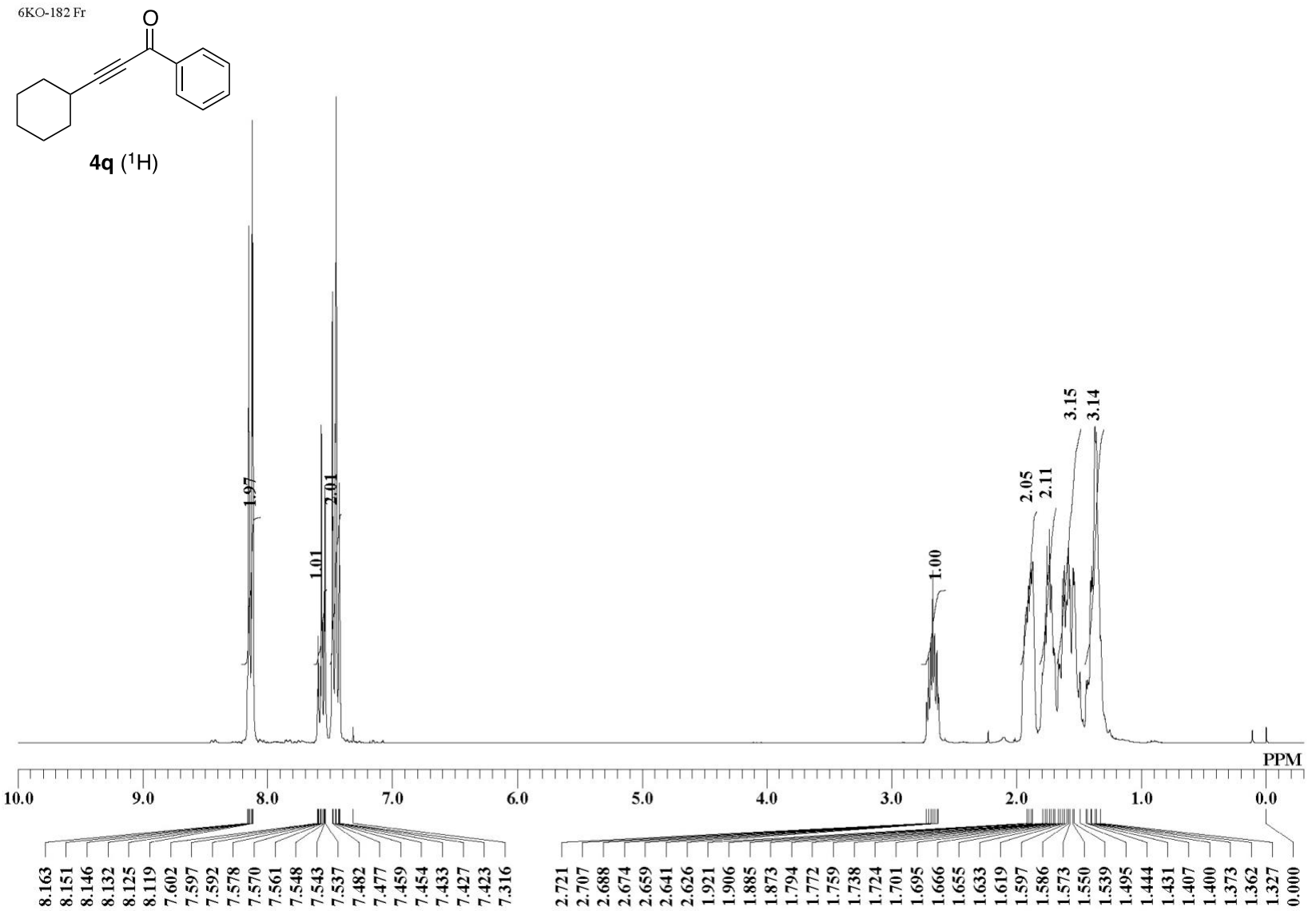
O
4o (1H)
1.00
1.91
3.03
6.21
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.433
8.405
8.329
8.324
8.318
8.306
8.298
8.292
7.984
7.959
7.955
7.933
7.907
7.880
7.682
7.677
7.658
7.652
7.641
7.627
7.622
7.598
7.593
7.573
7.569
7.550
7.545
7.526
7.519
7.515
7.500
7.497
7.470
7.243
0.000


6KO-273 Fr
O
S
4p (1H)
2.00
5.15
1.01
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.211
8.203
8.198
8.192
8.180
8.173
8.167
7.664
7.659
7.654
7.641
7.632
7.624
7.610
7.605
7.599
7.594
7.589
7.581
7.576
7.549
7.547
7.539
7.534
7.520
7.498
7.492
7.488
7.261
7.121
7.107
7.102
7.088
0.000


6KO-182 Fr
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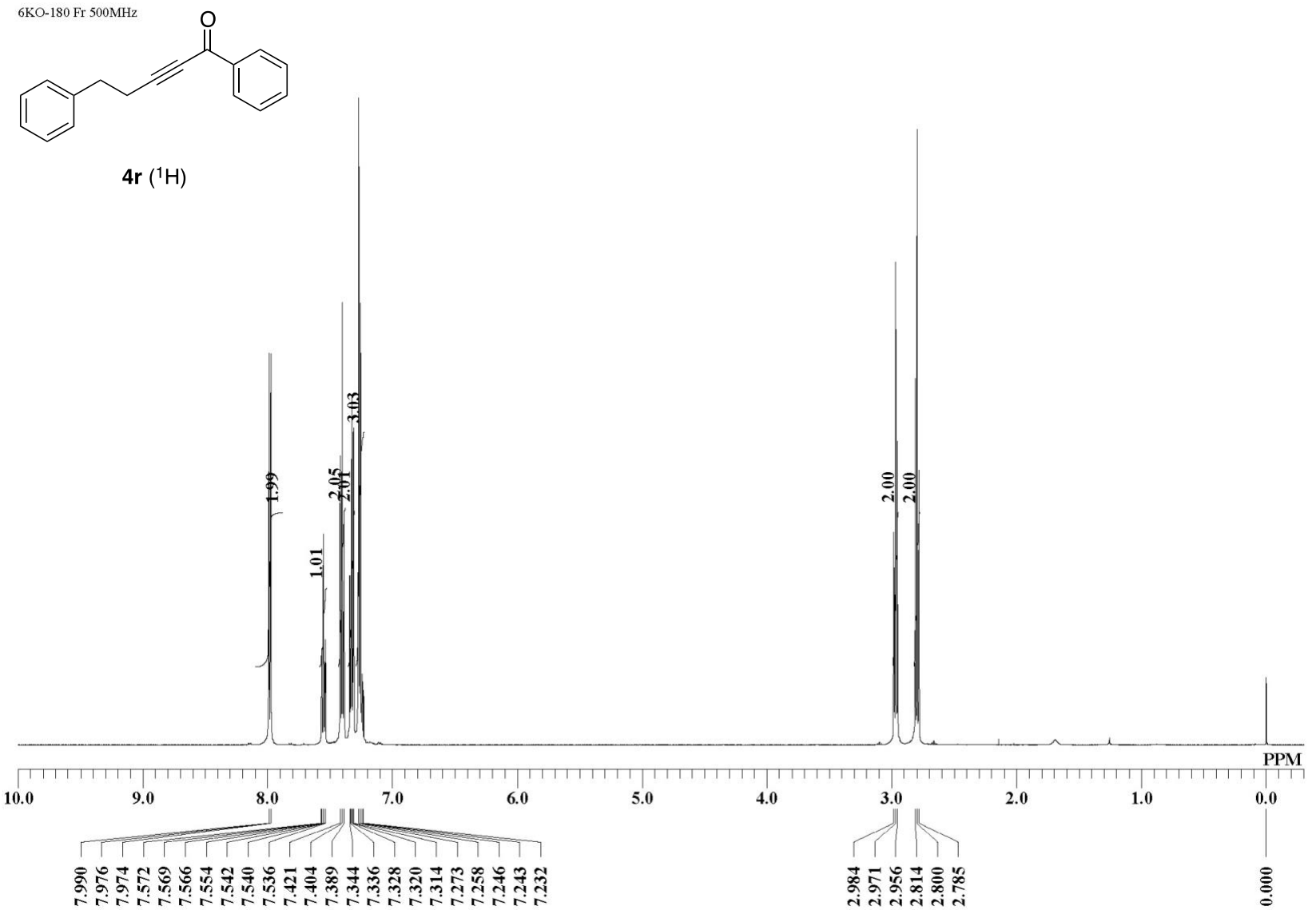
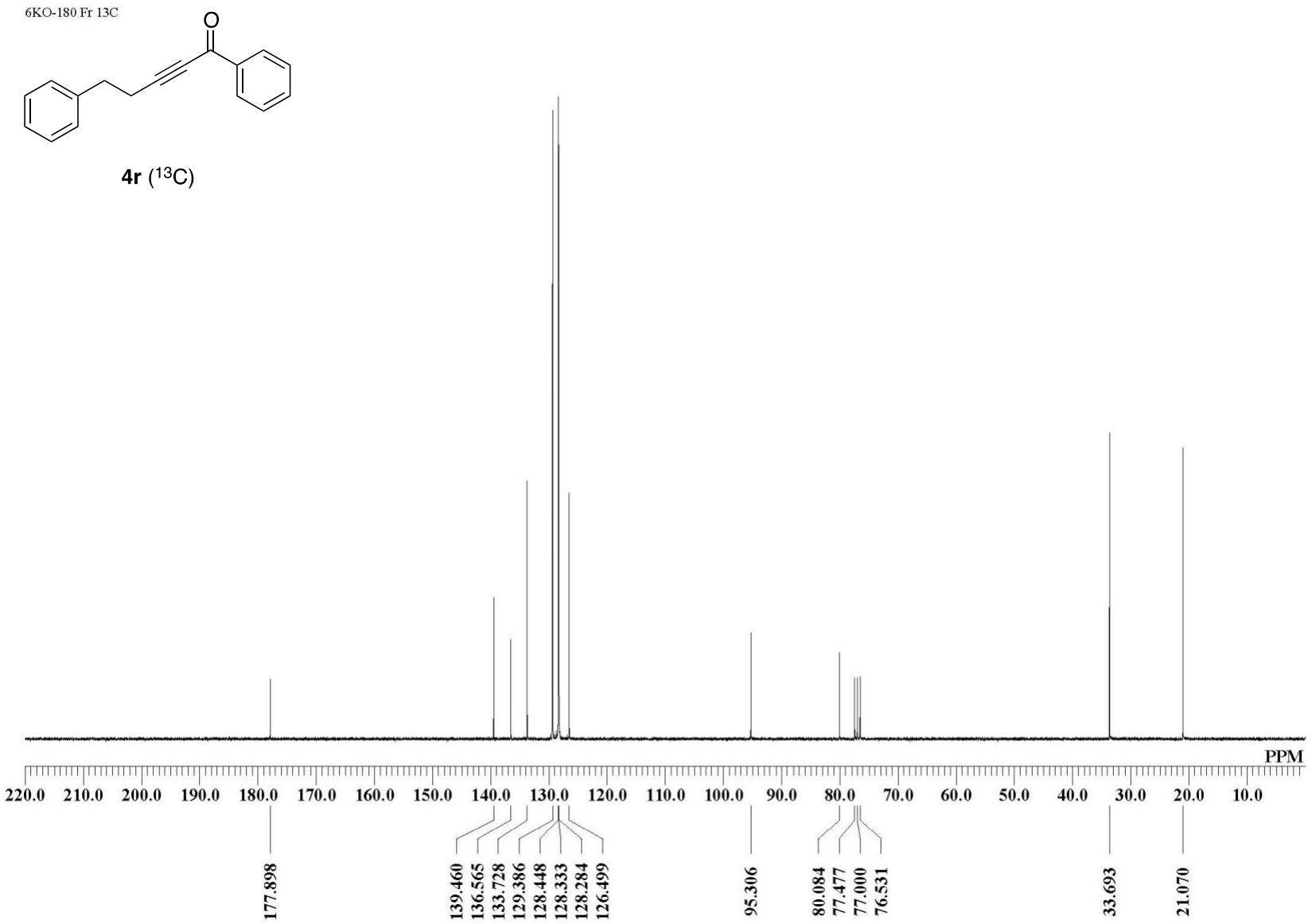
4q (1H)
1.97
1.01
2.01
1.00
2.05
2.11
3.15
3.14
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.163
8.151
8.146
8.132
8.125
8.119
7.602
7.597
7.592
7.578
7.570
7.561
7.548
7.543
7.537
7.482
7.477
7.459
7.454
7.433
7.427
7.423
7.316
2.721
2.707
2.688
2.674
2.659
2.641
2.626
1.921
1.906
1.885
1.873
1.794
1.772
1.759
1.738
1.724
1.701
1.695
1.666
1.655
1.633
1.619
1.597
1.586
1.573
1.550
1.539
1.495
1.444
1.431
1.407
1.400
1.373
1.362
1.327
0.000


6KO-180 Fr 500MHz
O
4r (1H)
1.99
1.01
2.05
2.01
3.03
2.00
2.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.990
7.976
7.974
7.572
7.569
7.566
7.554
7.542
7.540
7.536
7.421
7.404
7.389
7.344
7.336
7.328
7.320
7.314
7.273
7.258
7.246
7.243
7.232
2.984
2.971
2.956
2.814
2.800
2.785
0.000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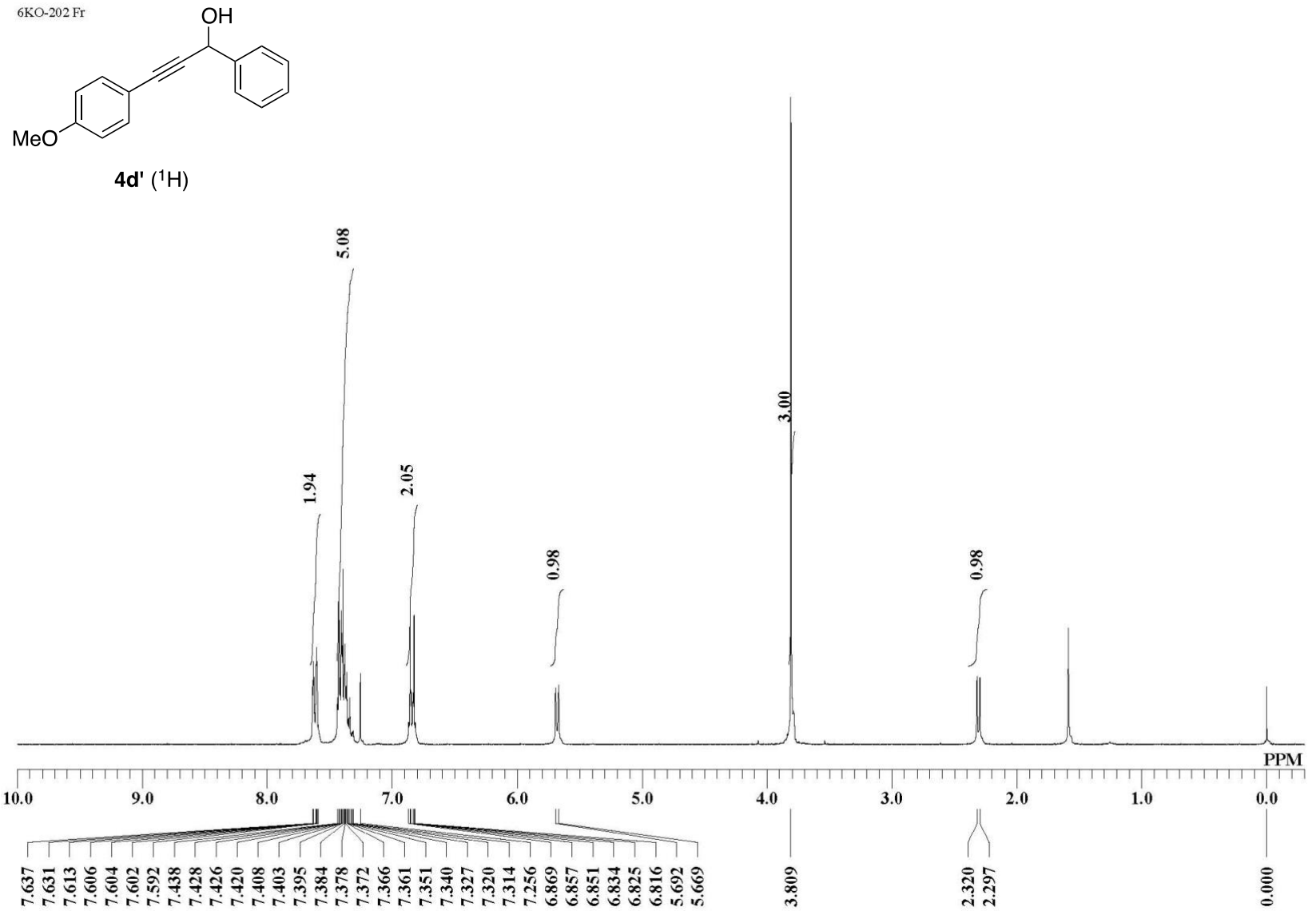
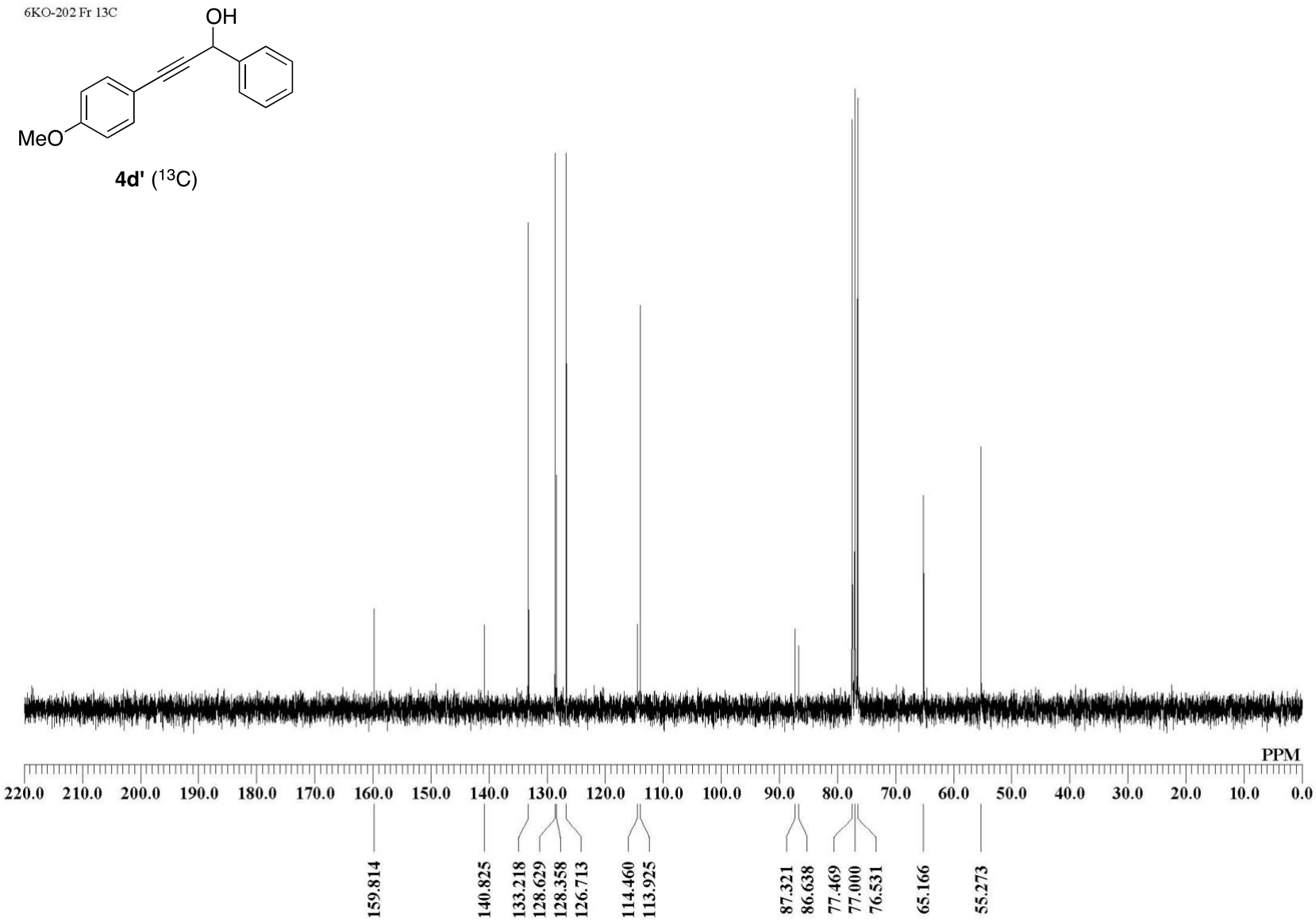
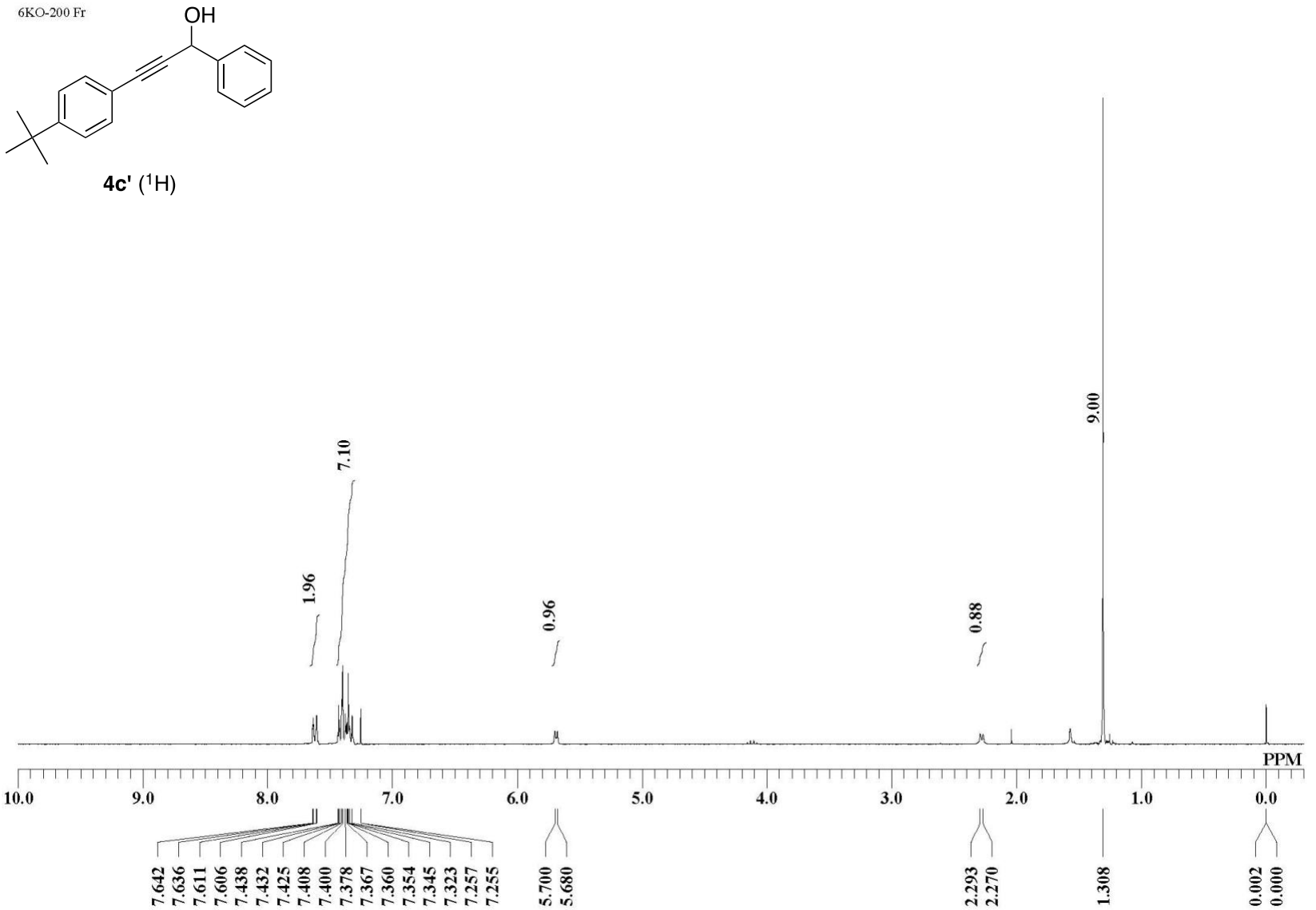
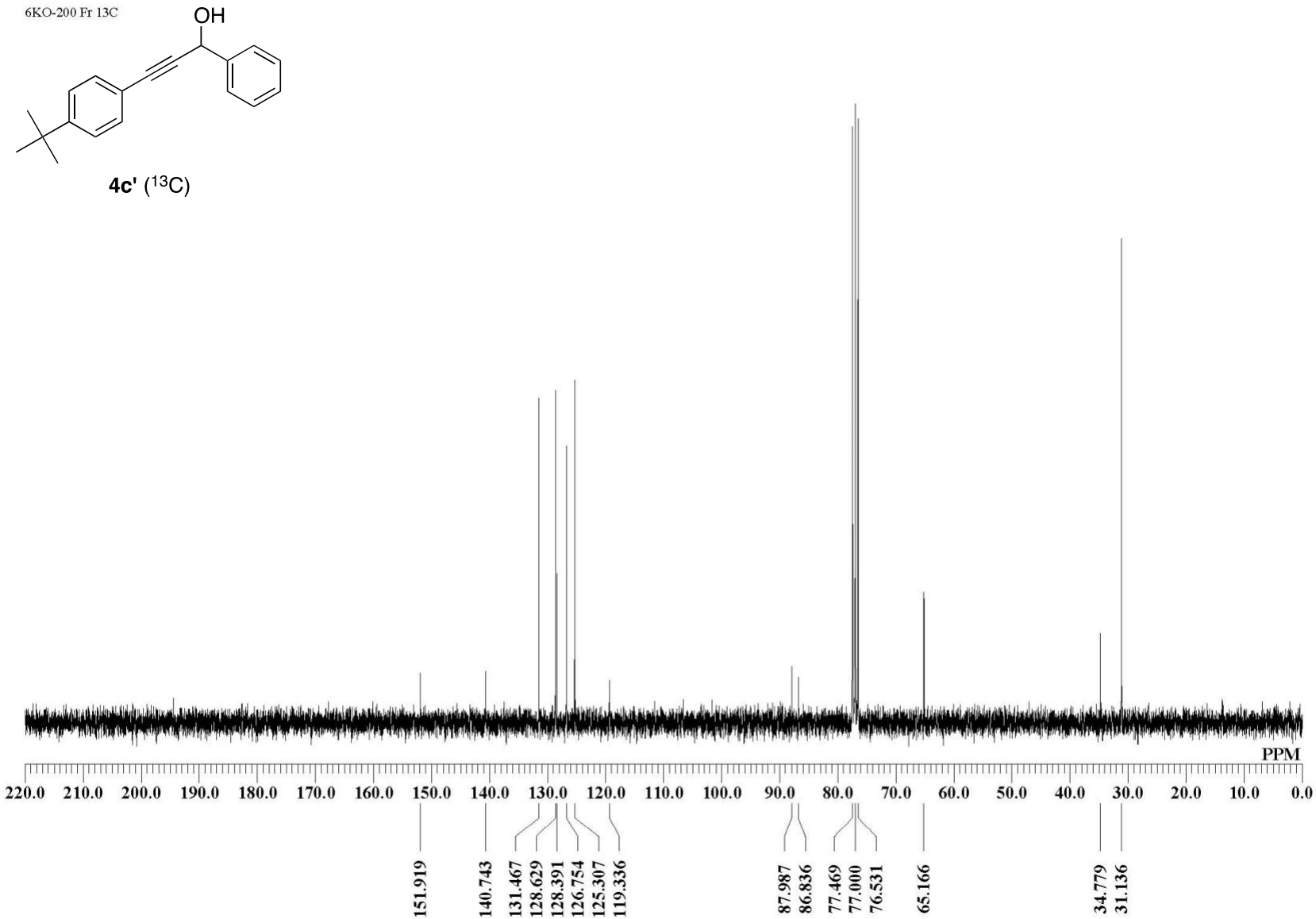
O
4r (13C)
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
177.898
139.460
136.565
133.728
129.386
128.448
128.333
128.284
126.499
95.306
80.084
77.477
77.000
76.531
33.693
21.070


6KO-202 Fr
OH
MeO
4d' (1H)
5.08
1.94
2.05
0.98
3.00
0.98
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.637
7.631
7.613
7.606
7.604
7.602
7.592
7.438
7.428
7.426
7.420
7.408
7.403
7.395
7.384
7.378
7.372
7.366
7.361
7.351
7.340
7.327
7.320
7.314
7.256
6.869
6.857
6.851
6.834
6.825
6.816
5.692
5.669
3.809
2.320
2.297
0.000


6KO-202 Fr 13C
OH
MeO
4d' (13C)
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
159.814
140.825
133.218
128.629
128.358
126.713
114.460
113.925
87.321
86.638
77.469
77.000
76.531
65.166
55.273


6KO-200 Fr
OH
4c' (1H)
1.96
7.10
0.96
0.88
9.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.642
7.636
7.611
7.606
7.438
7.432
7.425
7.408
7.400
7.378
7.367
7.360
7.354
7.345
7.323
7.257
7.255
5.700
5.680
2.293
2.270
1.308
0.002
0.000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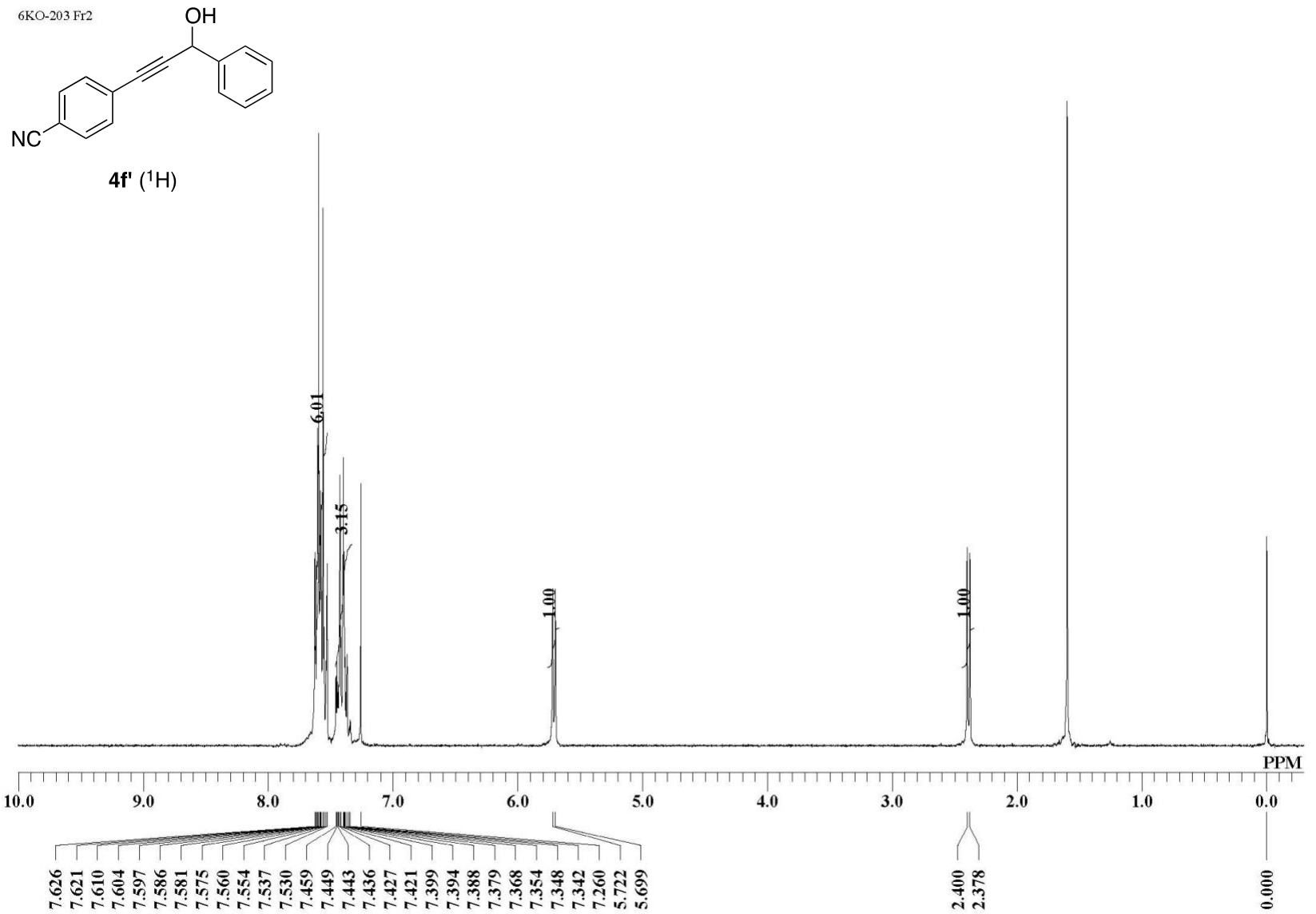
OH
4c' (13C)
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
151.919
140.743
131.467
128.629
128.391
126.754
125.307
119.336
87.987
86.836
77.469
77.000
76.531
65.166
34.779
31.136


6KO-203 Fr2
OH
NC
4f' (1H)
6.01
3.15
1.00
1.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.626
7.621
7.610
7.604
7.597
7.586
7.581
7.575
7.560
7.554
7.537
7.530
7.459
7.449
7.443
7.436
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7.394
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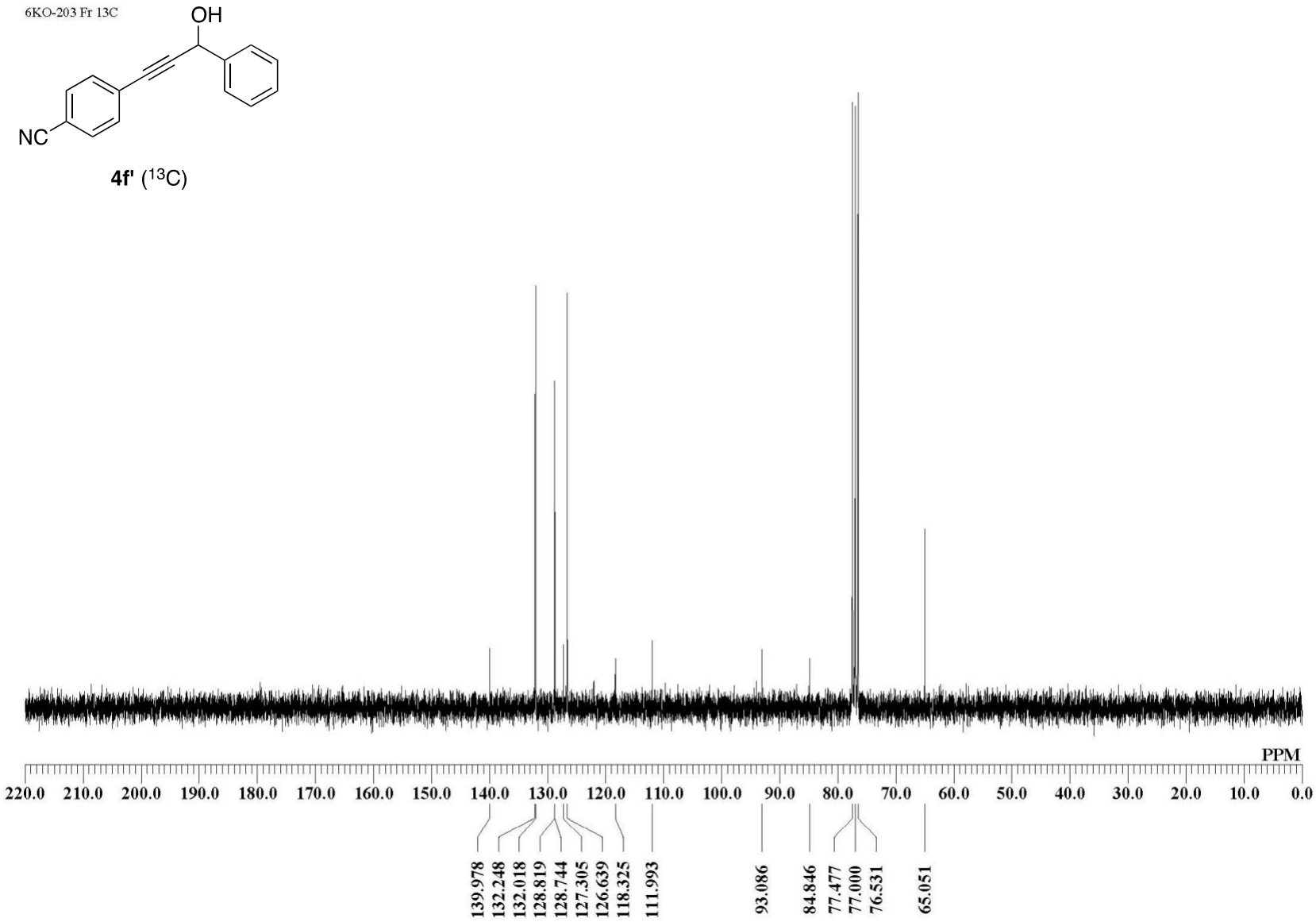
2.378
0.000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OH
NC
4f' (13C)
PPM
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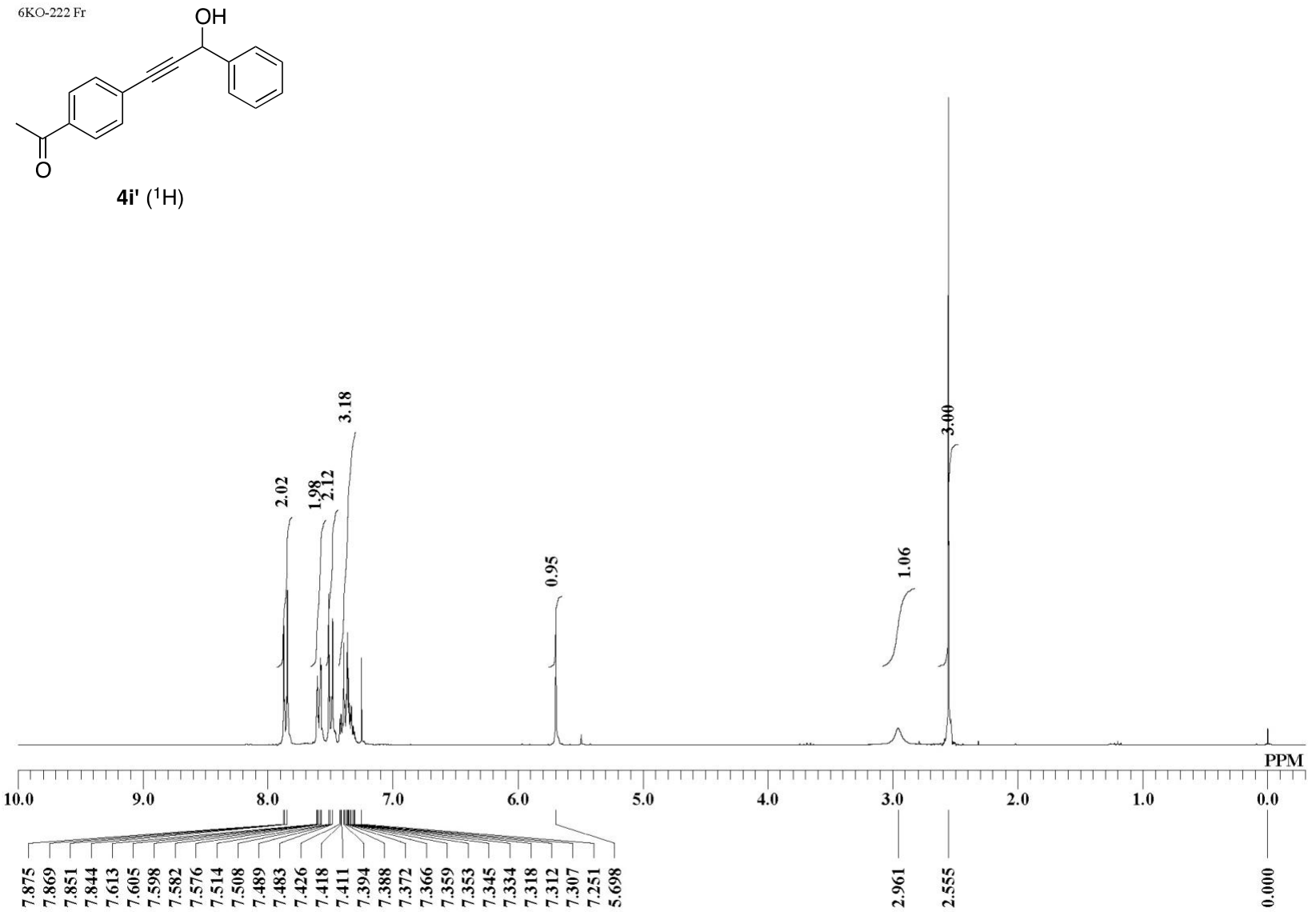
139.978
132.248
132.018
128.819
128.744
127.305
126.639
118.325
111.993
93.086
84.846
77.477
77.000
76.531
65.051


6KO-222 Fr
OH
O
4i' (1H)
2.02
1.98
2.12
3.18
0.95
1.06
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.875
7.869
7.851
7.844
7.613
7.605
7.598
7.582
7.576
7.514
7.508
7.489
7.483
7.426
7.418
7.411
7.394
7.388
7.372
7.366
7.359
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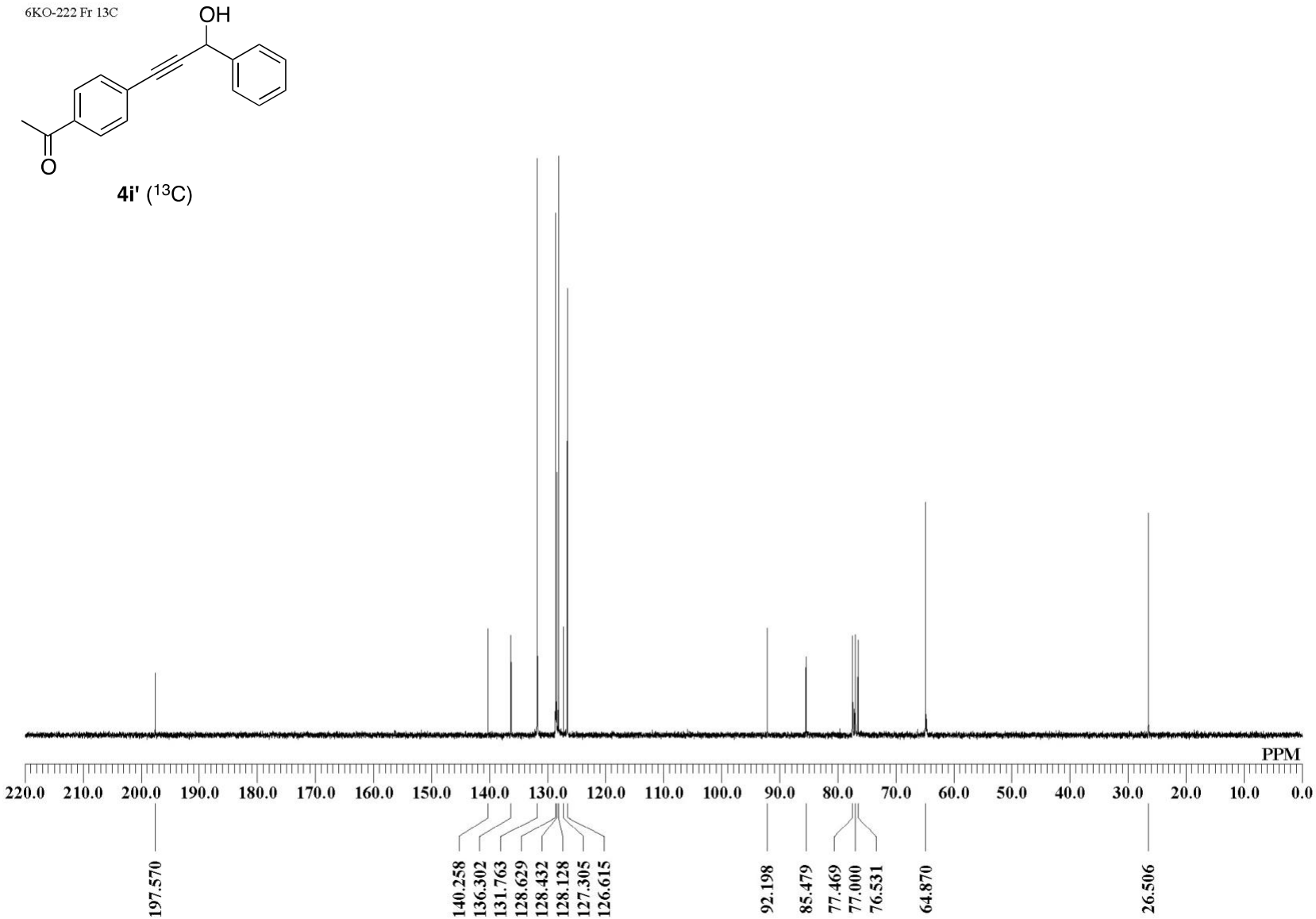
7.307
7.251
5.698
2.961
2.555
0.000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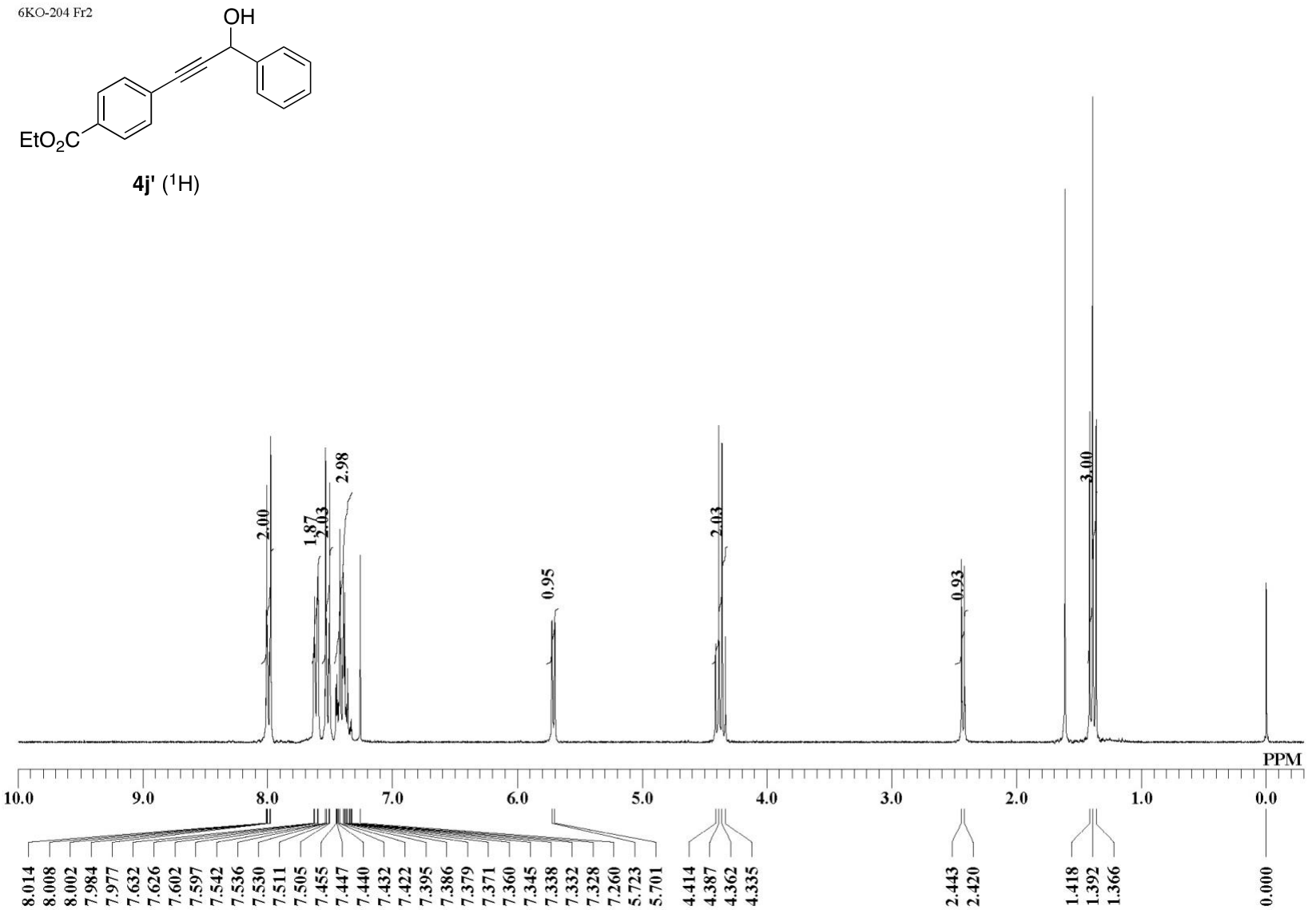
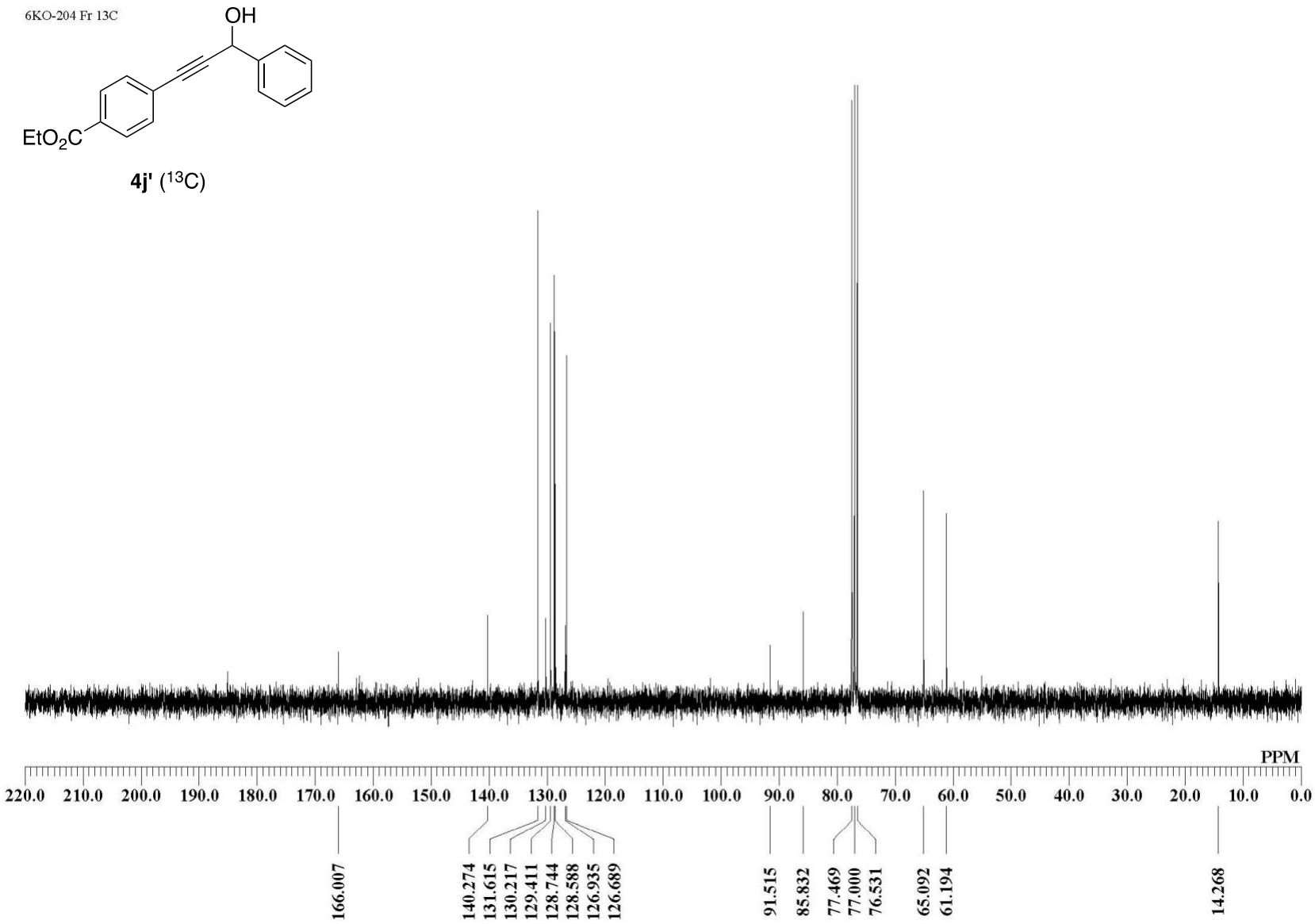
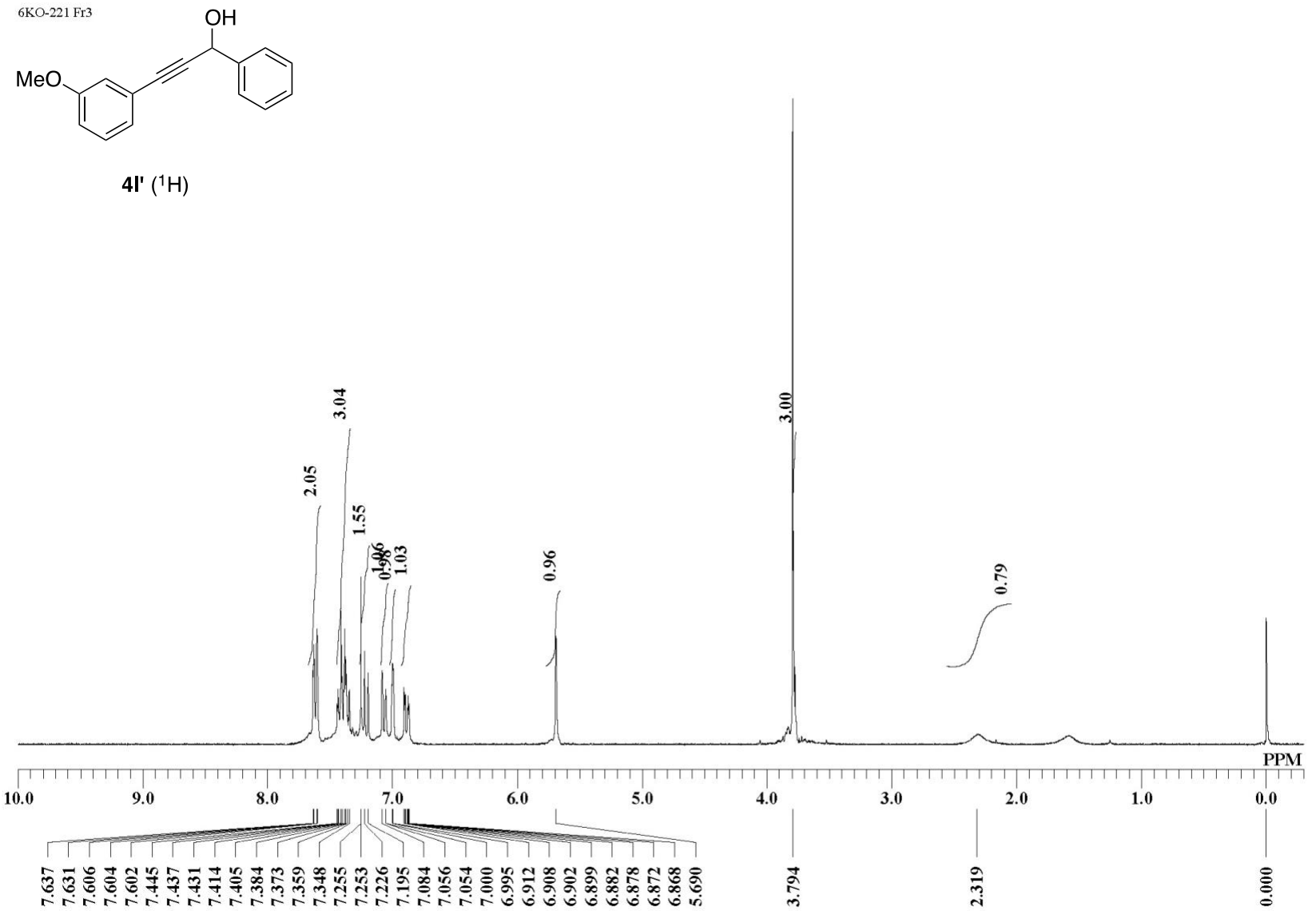
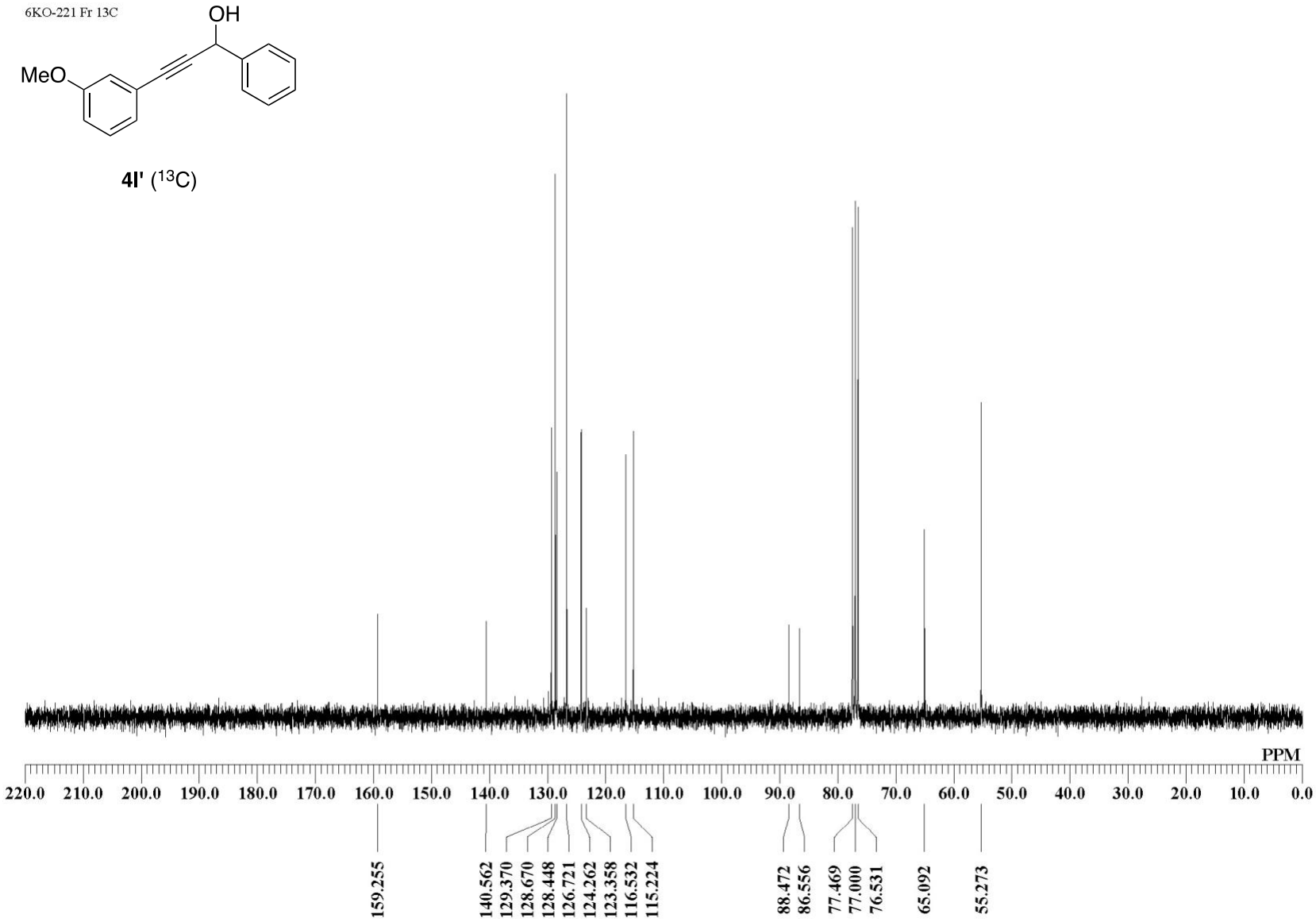
OH
O
4i' (13C)
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
197.570
140.258
136.302
131.763
128.629
128.432
128.128
127.305
126.615
92.198
85.479
77.469
77.000
76.531
64.870
26.506

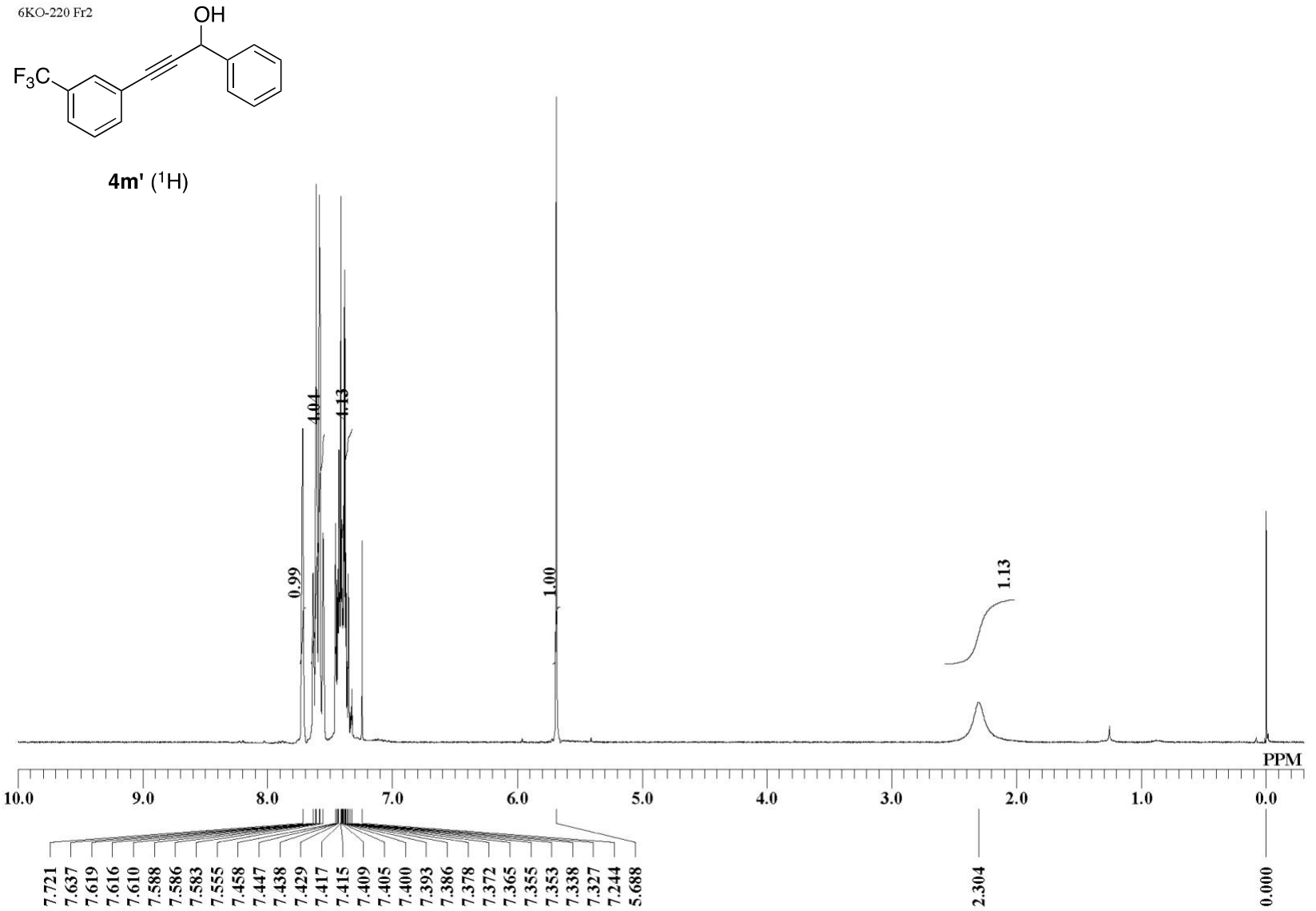

6KO-204 Fr2
OH
EtO2C
4j' (1H)
2.00
1.87
2.03
2.98
0.95
2.03
0.93
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.014
8.008
8.002
7.984
7.977
7.632
7.626
7.602
7.597
7.542
7.536
7.530
7.511
7.505
7.455
7.447
7.440
7.432
7.422
7.395
7.386
7.379
7.371
7.360
7.345
7.338
7.332
7.328
7.260
5.723
5.701
4.414
4.387
4.362
4.335
2.443
2.420
1.418
1.392
1.366
0.000

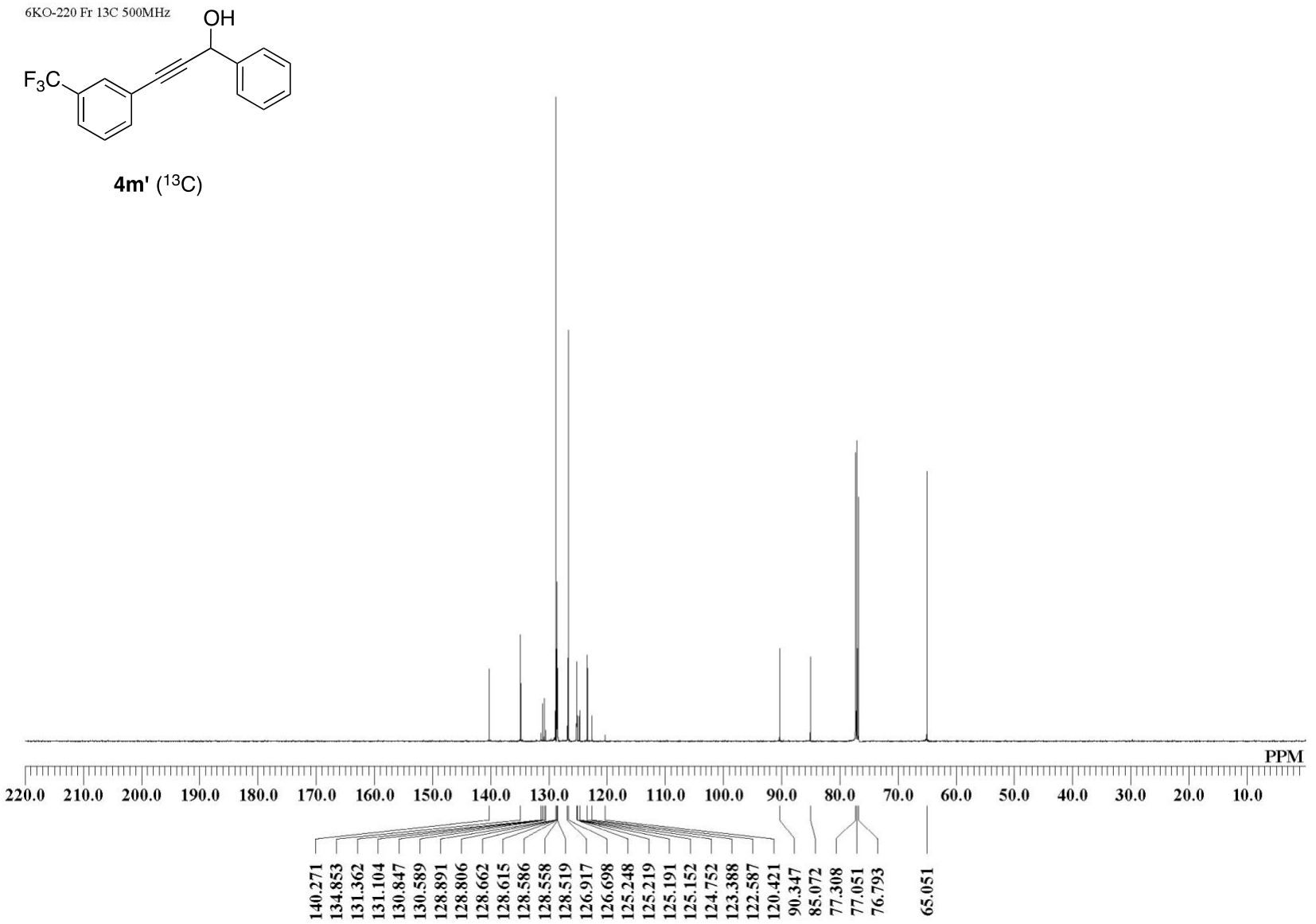

6KO-204 Fr 13C
OH
EtO2C
4j' (13C)
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
166.007
140.274
131.615
130.217
129.411
128.744
128.588
126.935
126.689
91.515
85.832
77.469
77.000
76.531
65.092
61.194
14.268


6KO-221 Fr3
OH
MeO
4l' (1H)
2.05
3.04
1.55
1.06
0.98
1.03
0.96
3.00
0.79
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.637
7.631
7.606
7.604
7.602
7.445
7.437
7.431
7.414
7.405
7.384
7.373
7.359
7.348
7.255
7.253
7.226
7.195
7.084
7.056
7.054
7.000
6.995
6.912
6.908
6.902
6.899
6.882
6.878
6.872
6.868
5.690
3.794
2.319
0.000

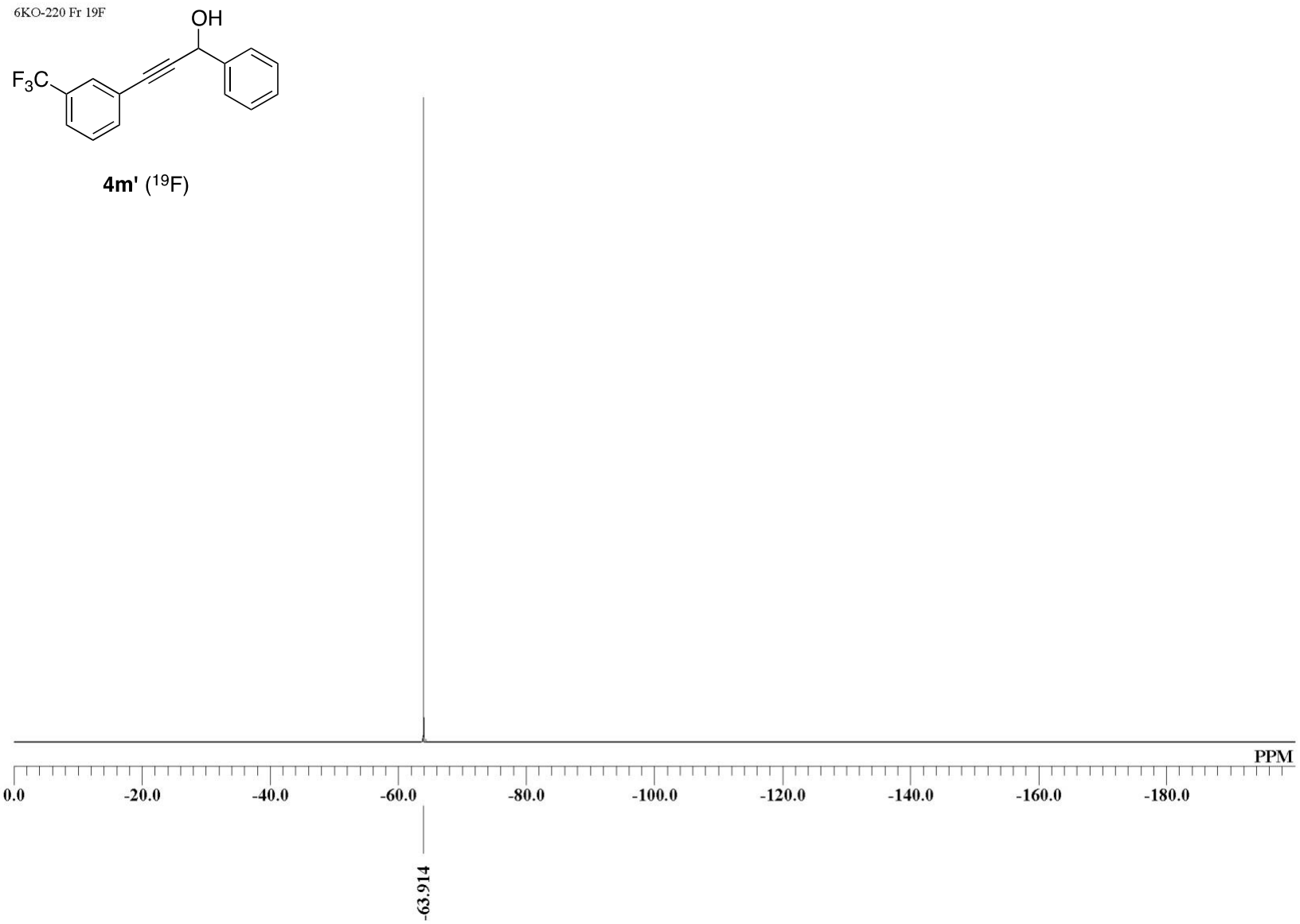

6KO-221 Fr 13C
OH
MeO
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
159.255
140.562
129.370
128.670
128.448
126.721
124.262
123.358
116.532
115.224
88.472
86.556
77.469
77.000
76.531
65.092
55.273

4l' (^{13}C)

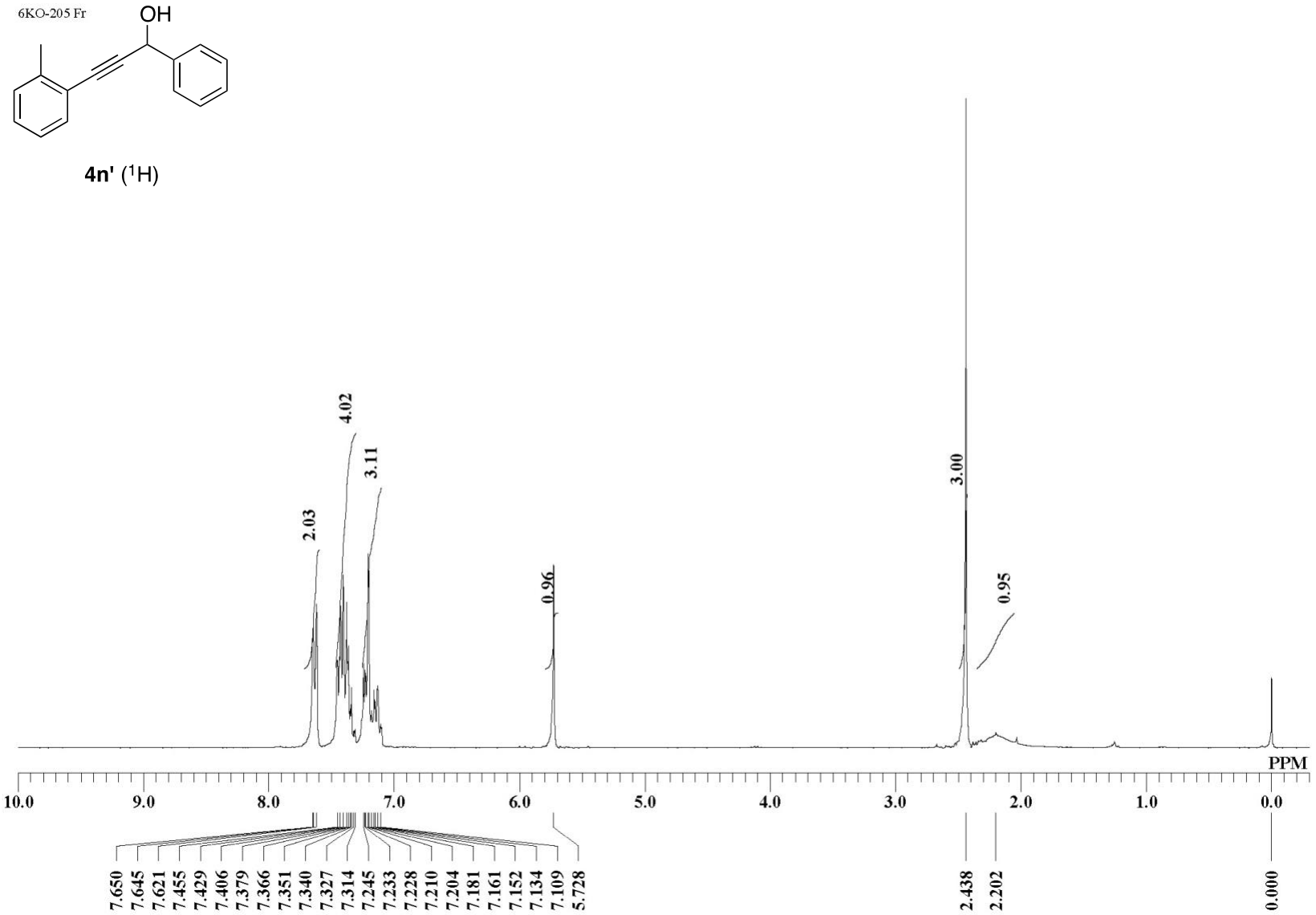

6KO-220 Fr2
OH
F3C
4m' (1H)
0.99
4.04
4.13
1.00
1.13
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.721
7.637
7.619
7.616
7.610
7.588
7.586
7.583
7.555
7.458
7.447
7.438
7.429
7.417
7.415
7.409
7.405
7.400
7.393
7.386
7.378
7.372
7.365
7.355
7.353
7.338
7.327
7.244
5.688
2.304
0.000

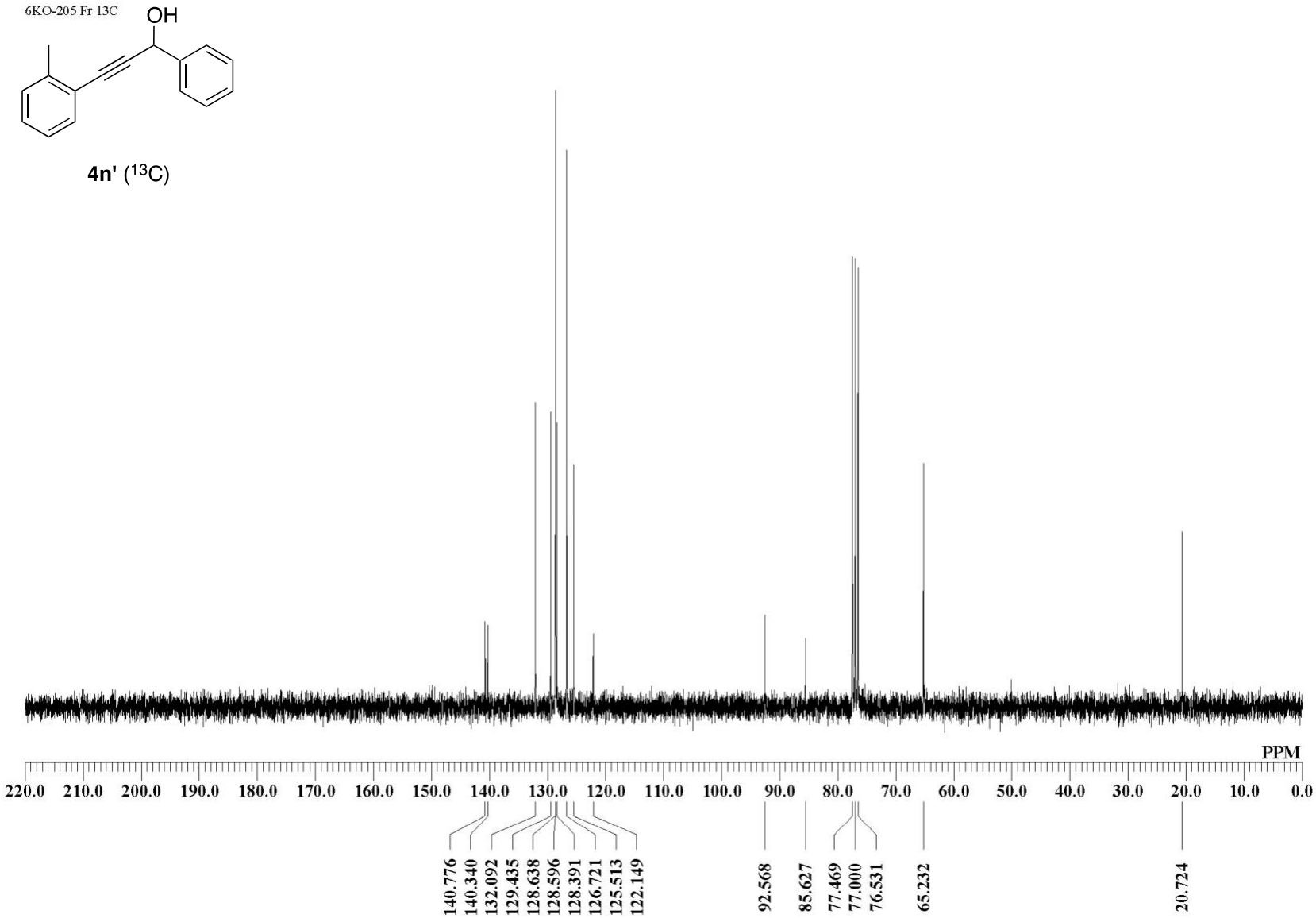

6KO-220 Fr 13C 500MHz
OH
F3C
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
140.271
134.853
131.362
131.104
130.847
130.589
128.891
128.806
128.662
128.615
128.586
128.558
128.519
126.917
126.698
125.248
125.219
125.191
125.152
124.752
123.388
122.587
120.421
90.347
85.072
77.308
77.051
76.793
65.051

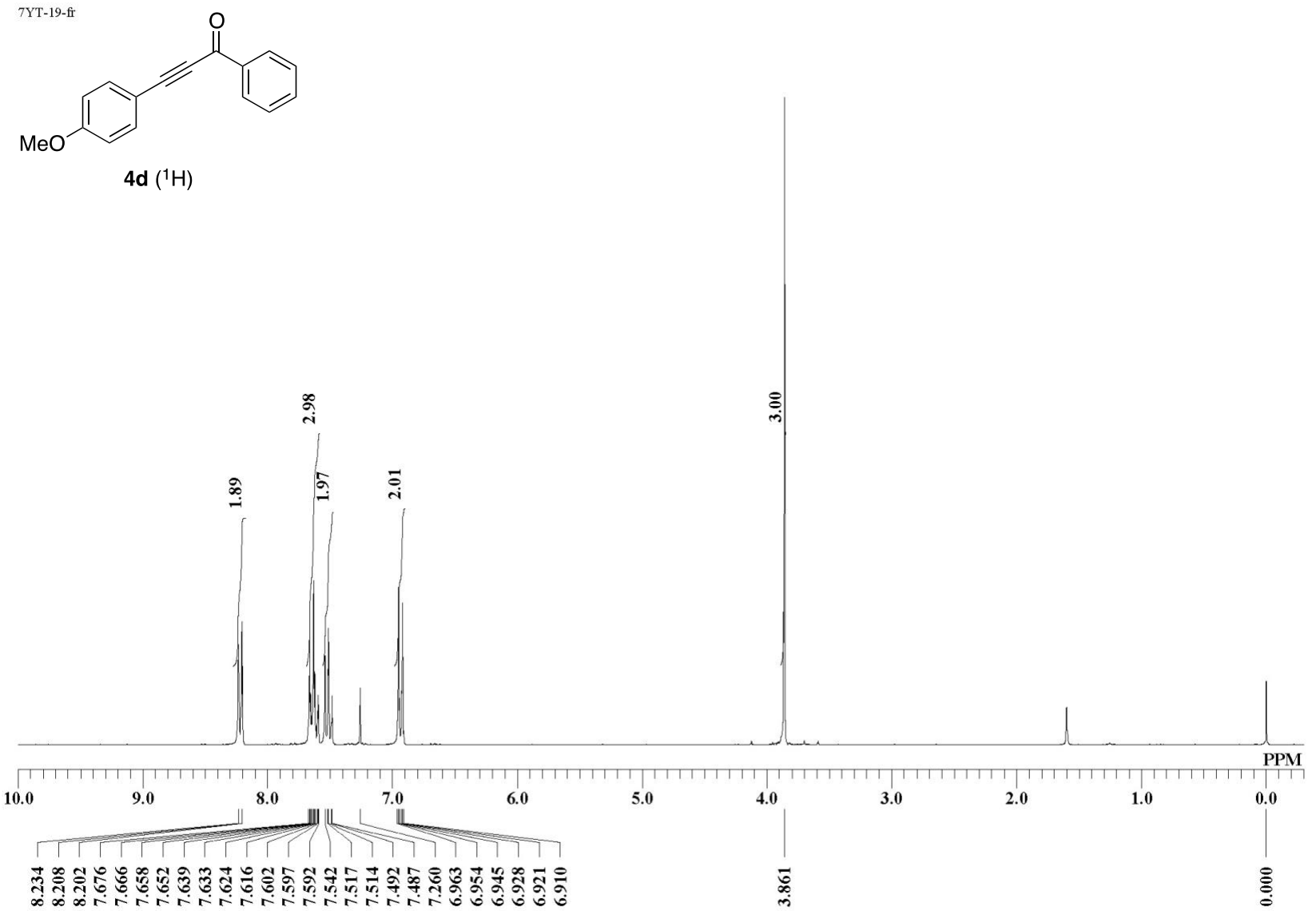
4m' (^{13}C)

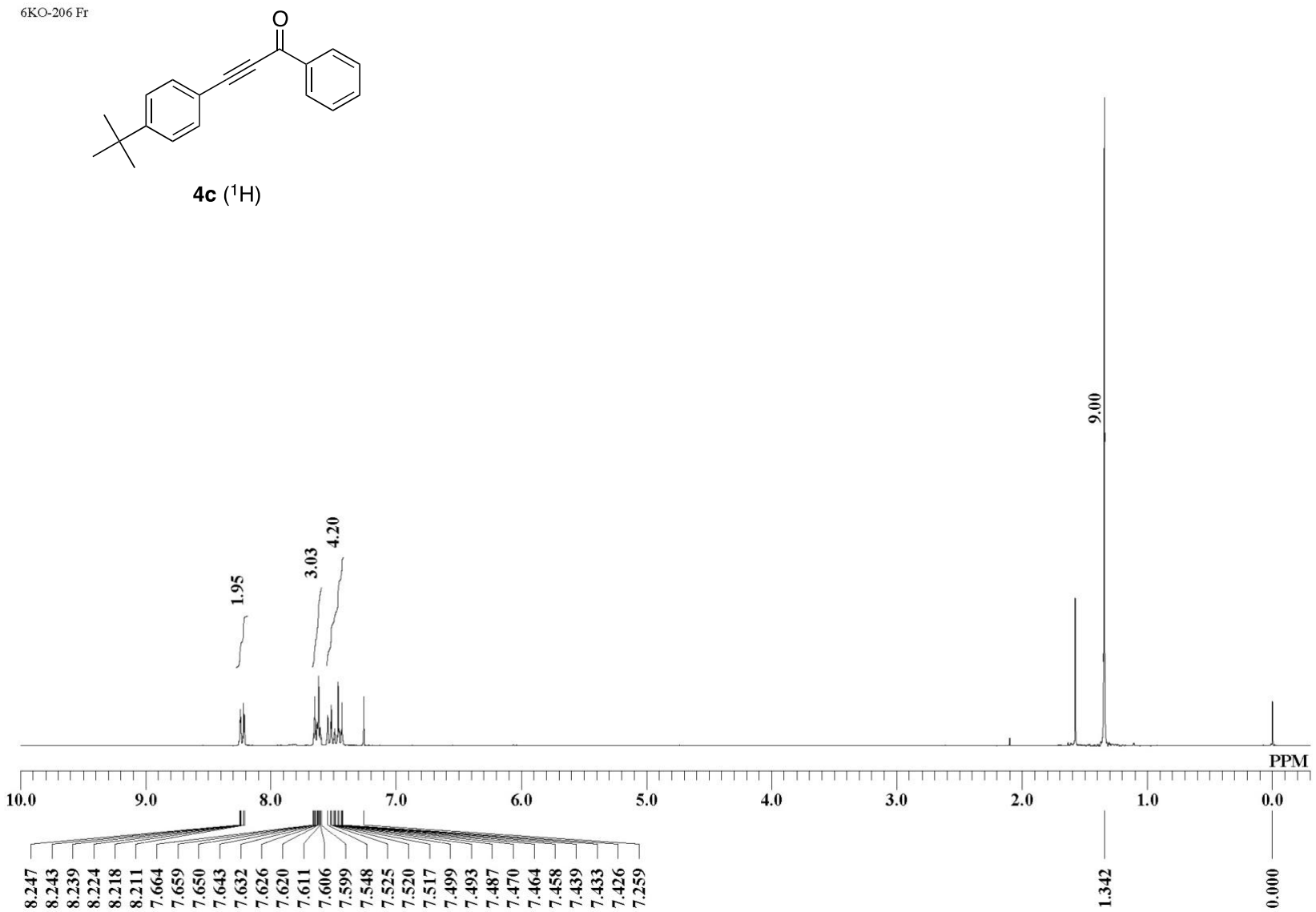

6KO-220 Fr 19F
OH
F3C
PPM
0.0
-20.0
-40.0
-60.0
-80.0
-100.0
-120.0
-140.0
-160.0
-180.0
-63.914

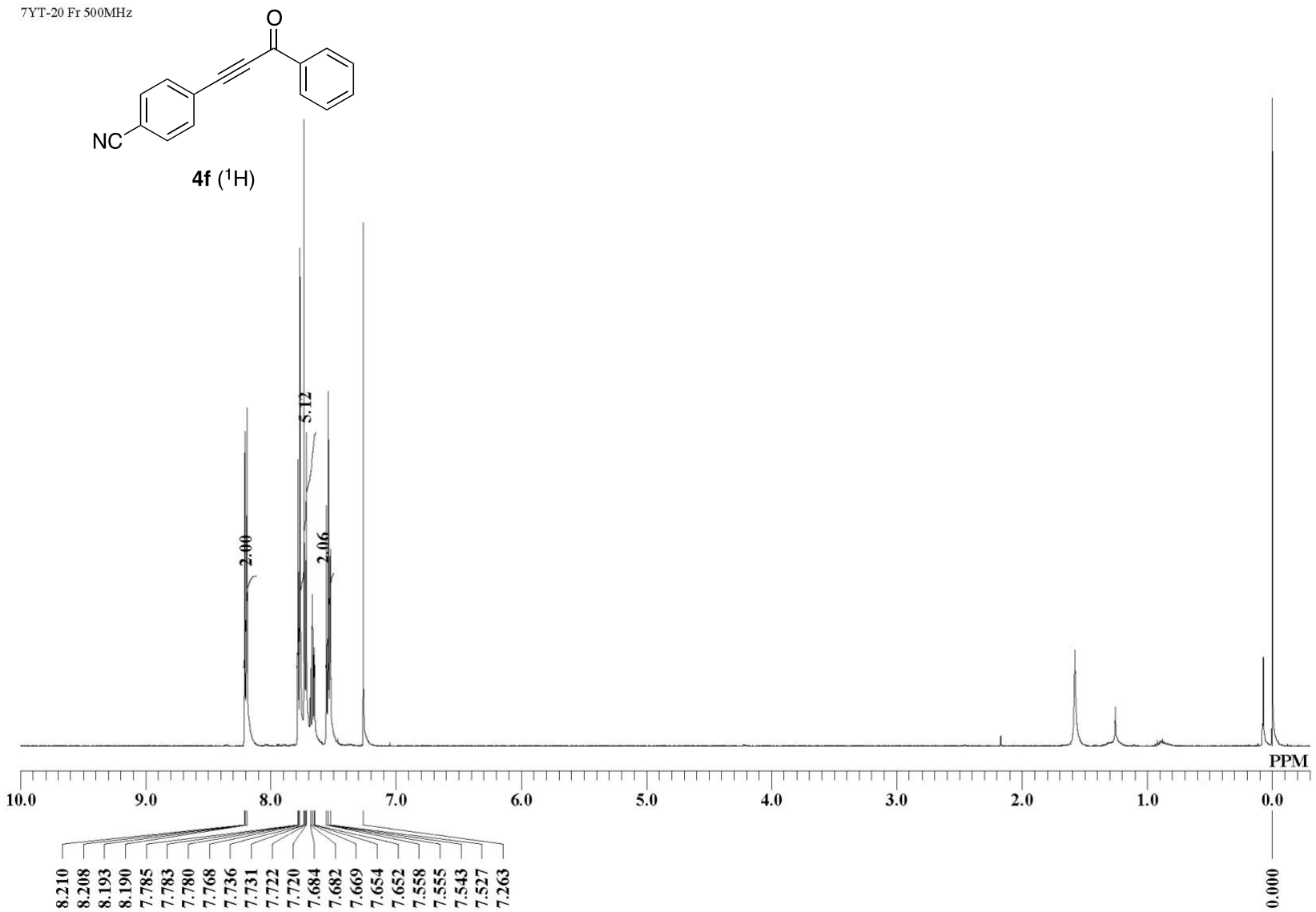
4m' (^{19}F)

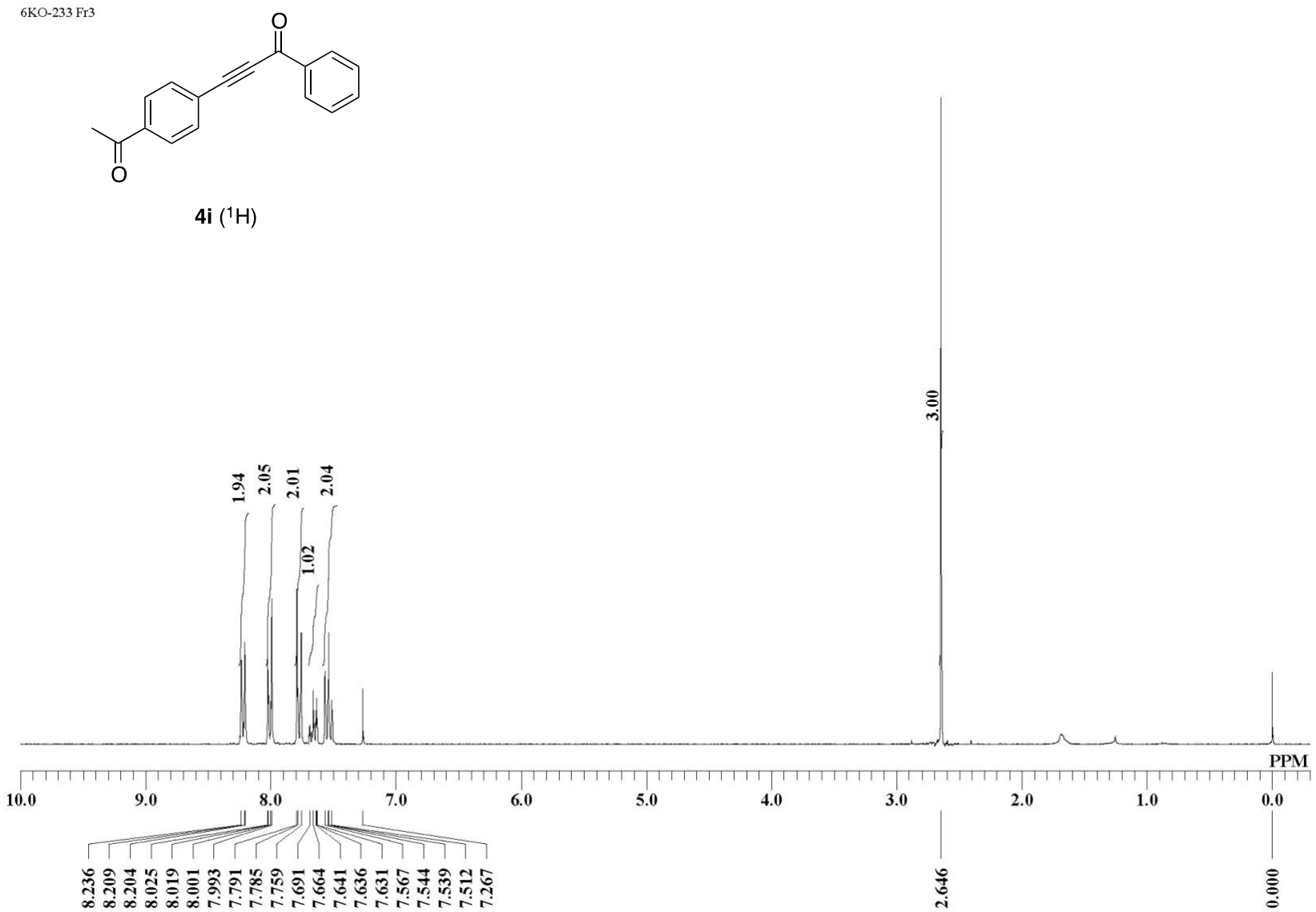

6KO-205 Fr
OH
4n' (1H)
2.03
4.02
3.11
0.96
3.00
0.95
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.650
7.645
7.621
7.455
7.429
7.406
7.379
7.366
7.351
7.340
7.327
7.314
7.245
7.233
7.228
7.210
7.204
7.181
7.161
7.152
7.134
7.109
5.728
2.438
2.202
0.000

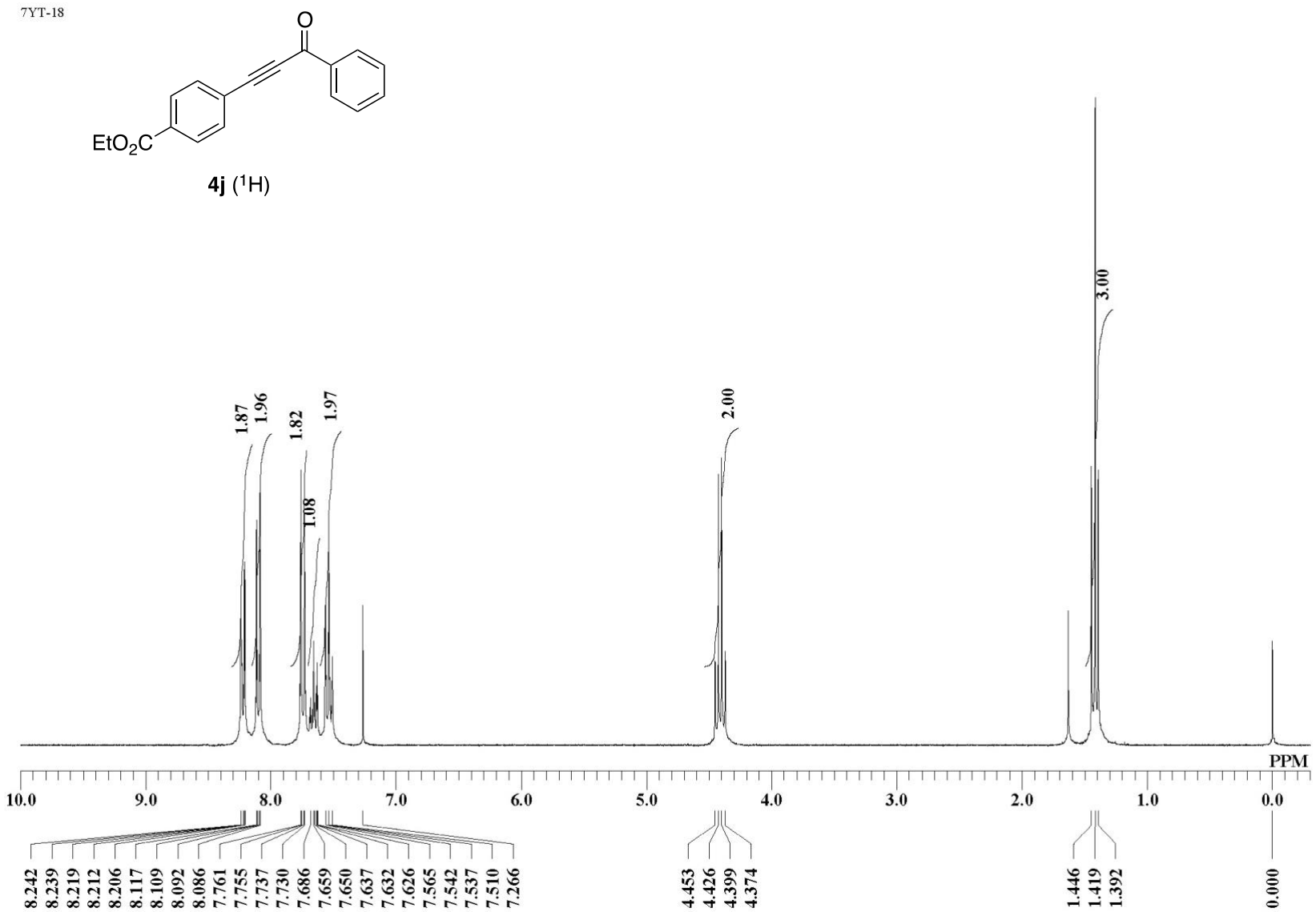

6KO-205 Fr 13C
OH
4n' (13C)
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
140.776
140.340
132.092
129.435
128.638
128.596
128.391
126.721
125.513
122.149
92.568
85.627
77.469
77.000
76.531
65.232
20.724


7YT-19-fr
O
MeO
4d (1H)
1.89
2.98
1.97
2.01
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.234
8.208
8.202
7.676
7.666
7.658
7.652
7.639
7.633
7.624
7.616
7.602
7.597
7.592
7.542
7.517
7.514
7.492
7.487
7.260
6.963
6.954
6.945
6.928
6.921
6.910
3.861
0.000

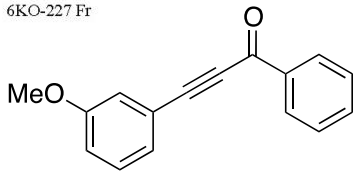

6KO-206 Fr
O
4c (1H)
9.00
4.20
3.03
1.95
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.247
8.243
8.239
8.224
8.218
8.211
7.664
7.659
7.650
7.643
7.632
7.626
7.620
7.611
7.606
7.599
7.548
7.525
7.520
7.517
7.499
7.493
7.487
7.470
7.464
7.458
7.439
7.433
7.426
7.259
1.342
0.000


7YT-20 Fr 500MHz
O
NC
4f (1H)
5.12
2.00
2.06
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.210
8.208
8.193
8.190
7.785
7.783
7.780
7.768
7.736
7.731
7.722
7.720
7.684
7.682
7.669
7.654
7.652
7.558
7.555
7.543
7.527
7.263
0.000

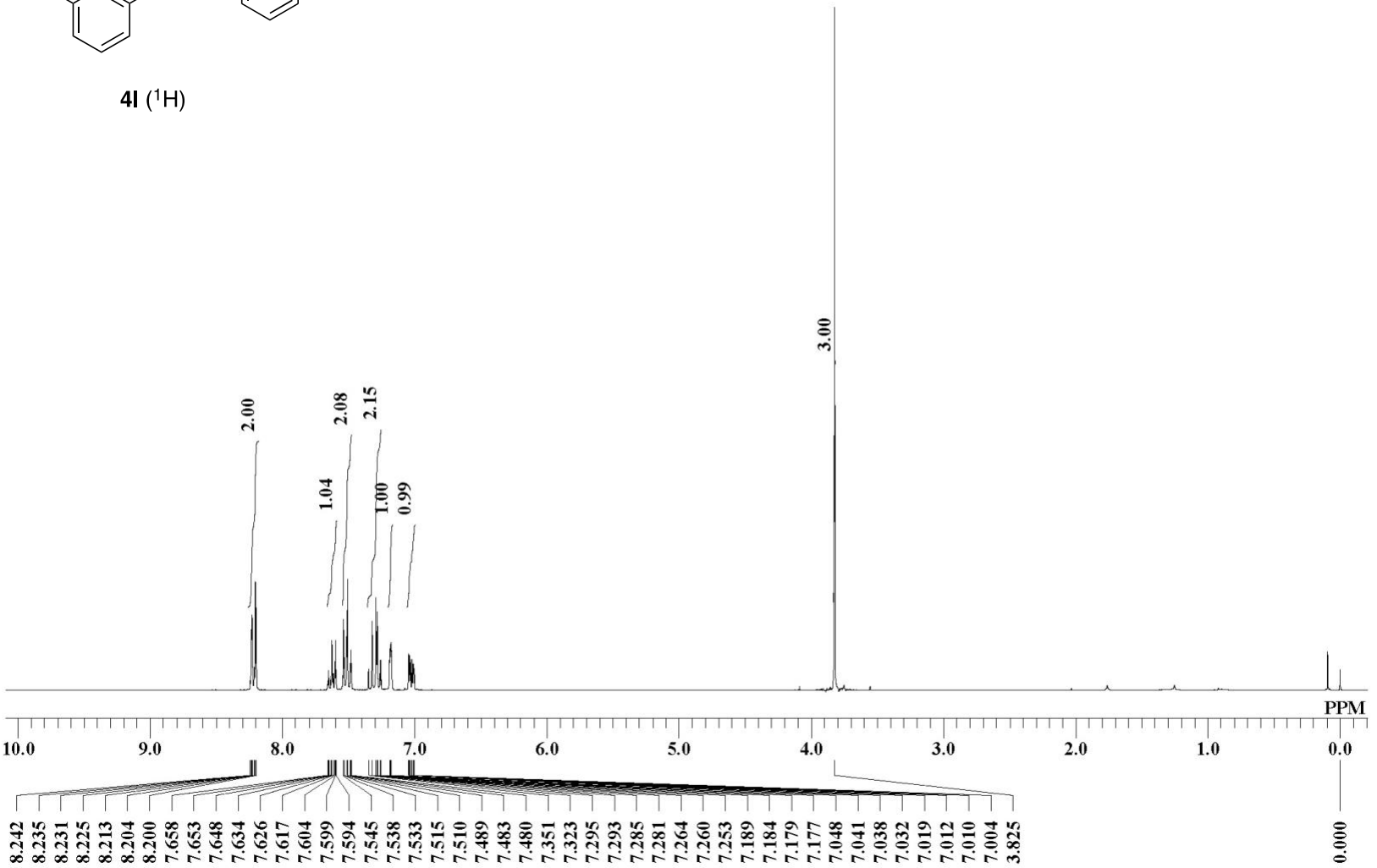

6KO-233 Fr3
O
O
4i (1H)
3.00
1.94
2.05
2.01
1.02
2.04
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.236
8.209
8.204
8.025
8.019
8.001
7.993
7.791
7.785
7.759
7.691
7.664
7.641
7.636
7.631
7.567
7.544
7.539
7.512
7.267
2.646
0.000

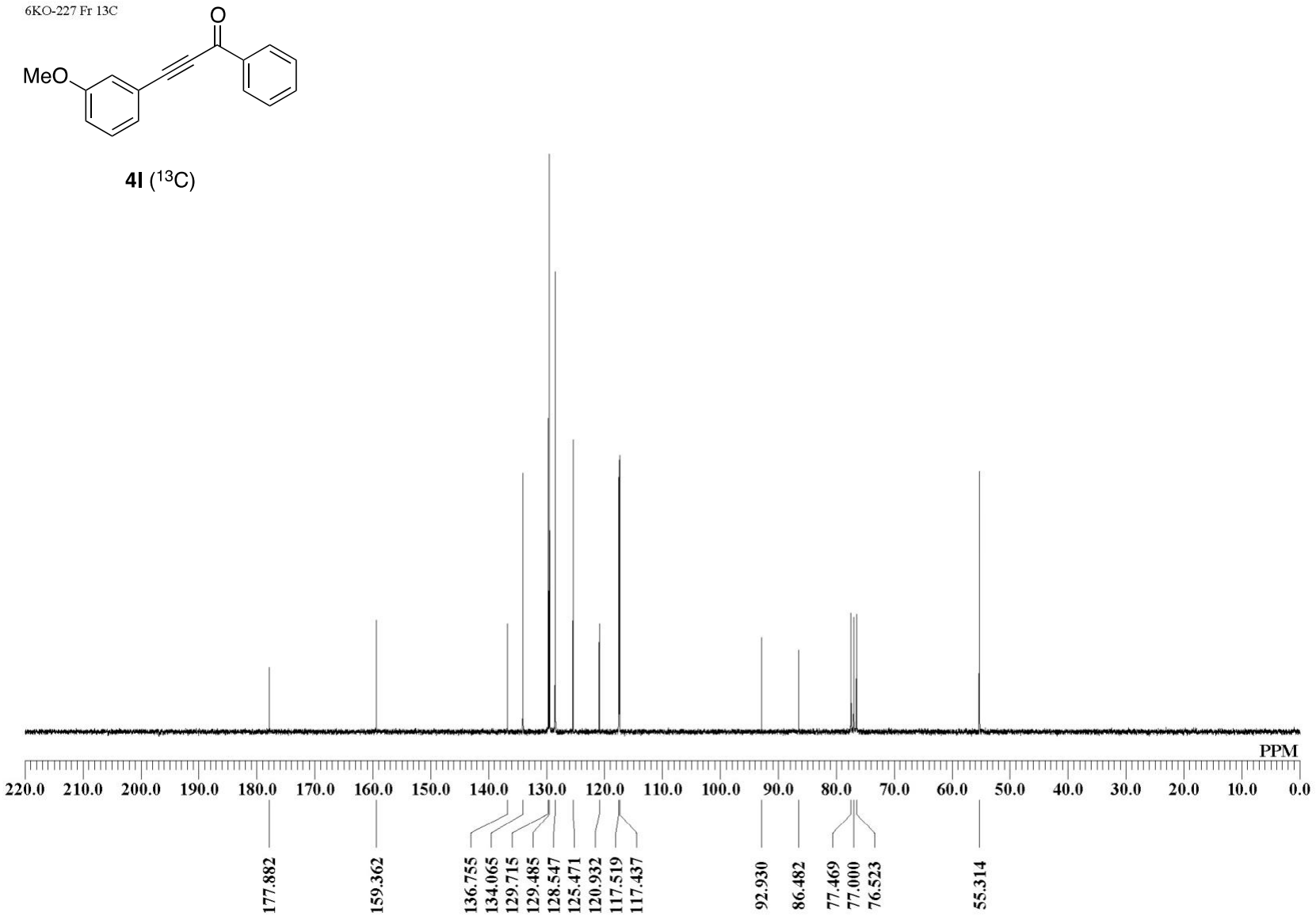

7YT-18
O
EtO2C
4j (1H)
1.87
1.96
1.82
1.08
1.97
2.00
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.242
8.239
8.219
8.212
8.206
8.117
8.109
8.092
8.086
7.761
7.755
7.737
7.730
7.686
7.659
7.650
7.637
7.632
7.626
7.565
7.542
7.537
7.510
7.266
4.453
4.426
4.399
4.374
1.446
1.419
1.392
0.000

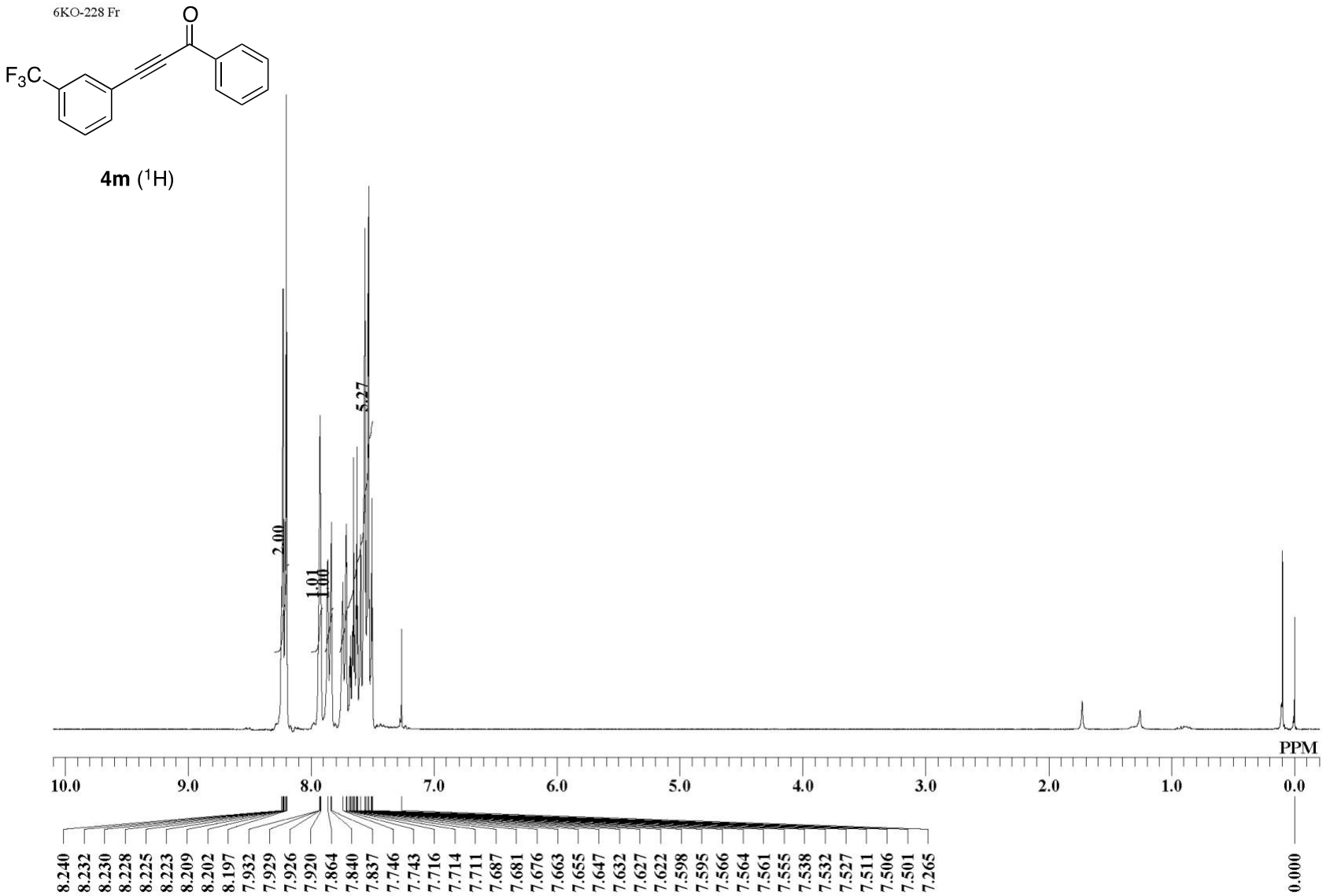
6KO-227 Fr

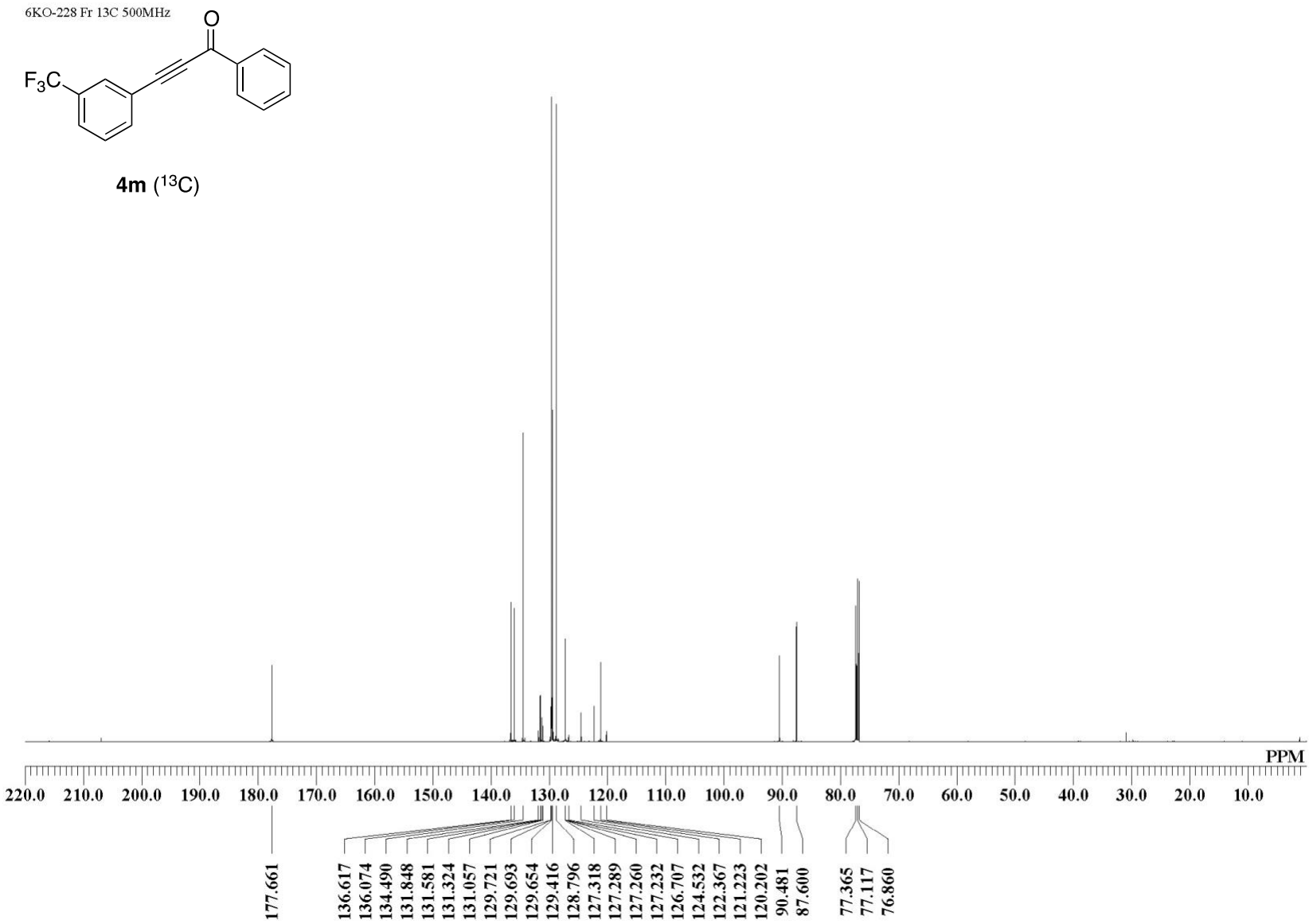


4l (^{1}H)

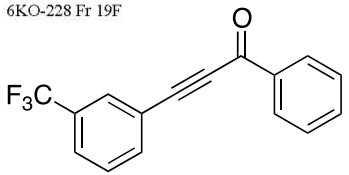



6KO-227 Fr 13C
O
MeO
4l (^{13}C)
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
177.882
159.362
136.755
134.065
129.715
129.485
128.547
125.471
120.932
117.519
117.437
92.930
86.482
77.469
77.000
76.523
55.314

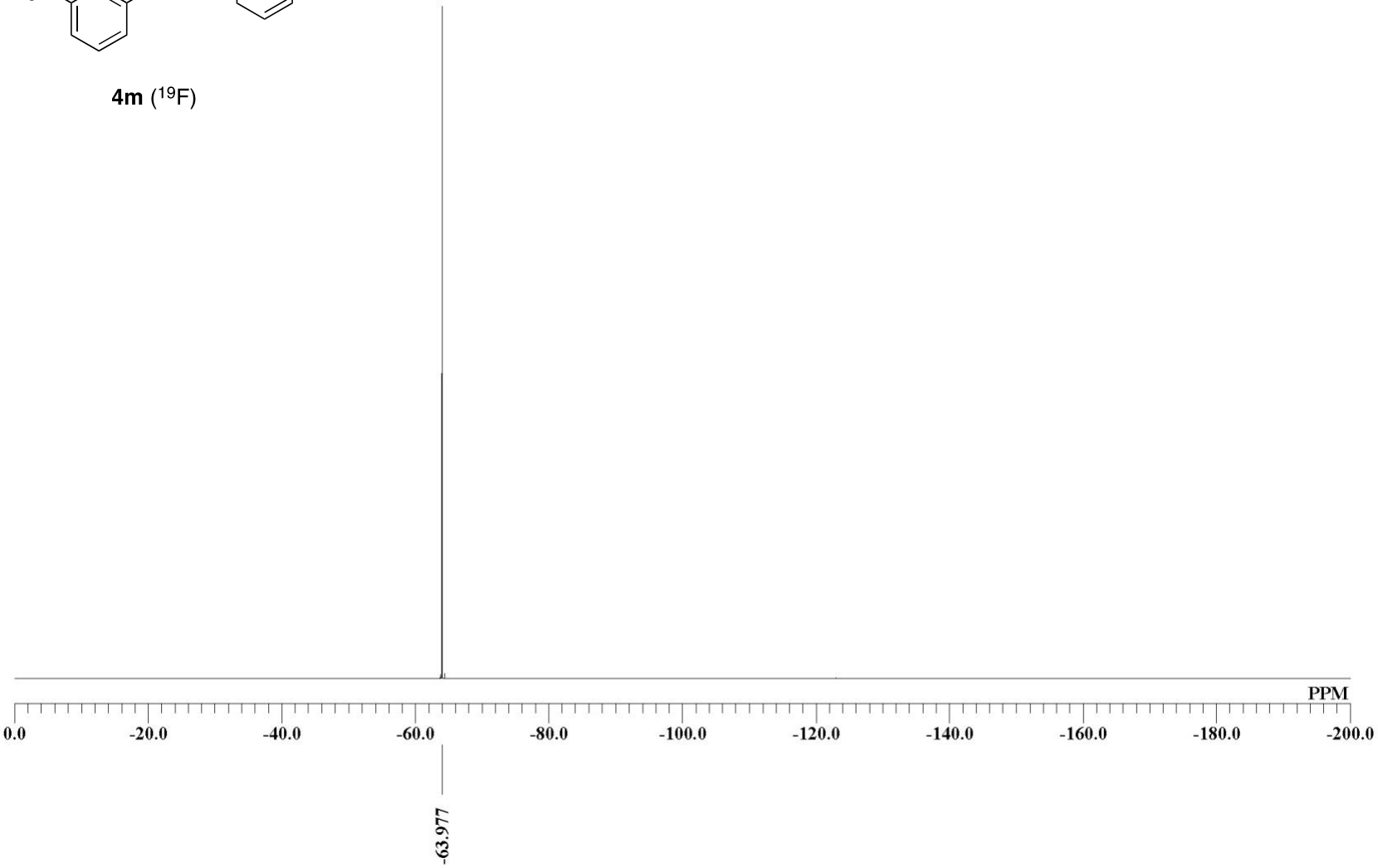

6KO-228 Fr
O
F3C
4m (1H)
2.00
1.01
1.00
5.27
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.240
8.232
8.230
8.228
8.225
8.223
8.209
8.202
8.197
7.932
7.929
7.926
7.920
7.864
7.840
7.837
7.746
7.743
7.716
7.714
7.711
7.687
7.681
7.676
7.663
7.655
7.647
7.632
7.627
7.622
7.598
7.595
7.566
7.564
7.561
7.555
7.538
7.532
7.527
7.511
7.506
7.501
7.265
0.000

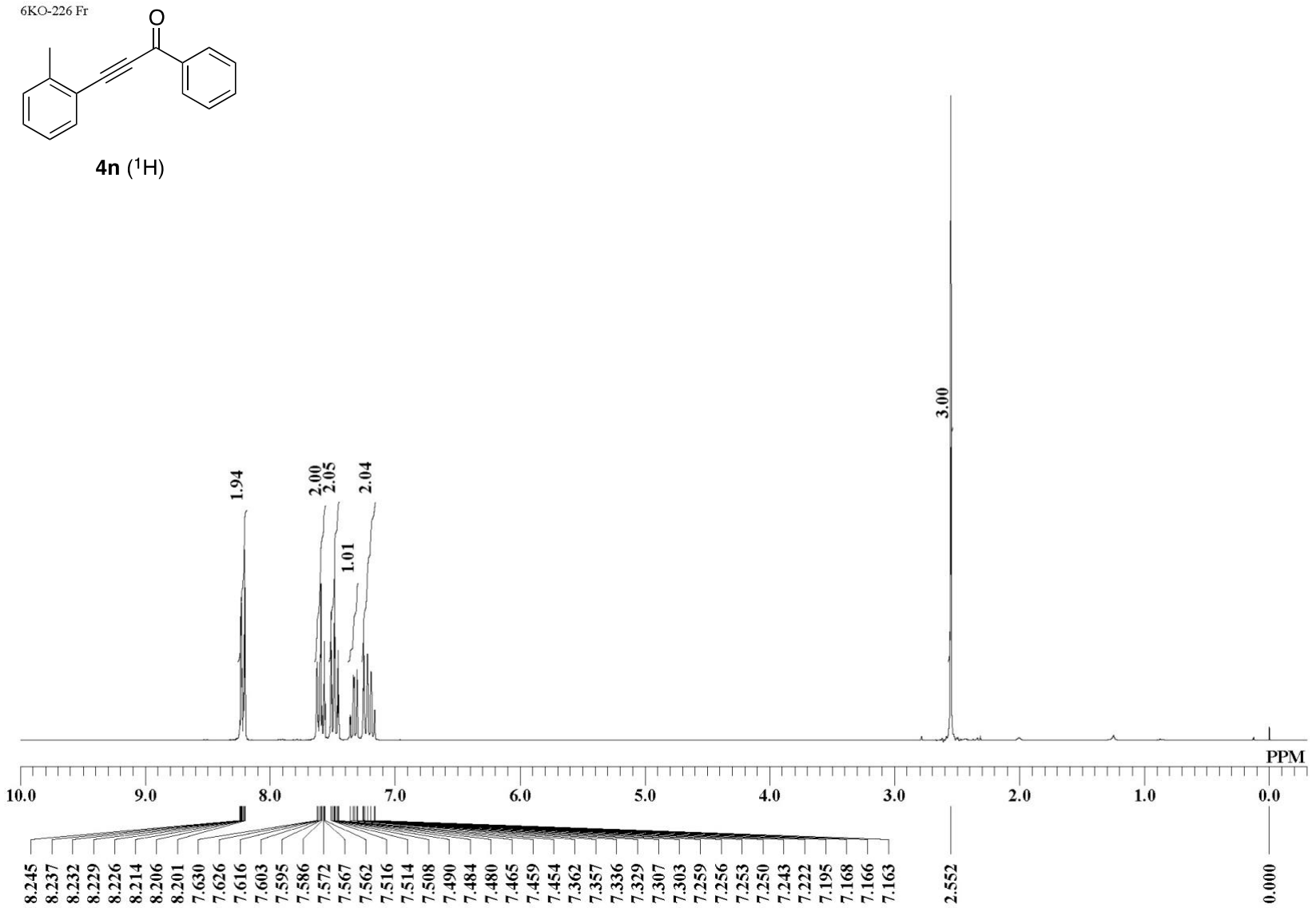

6KO-228 Fr 13C 500MHz
O
F3C
4m (13C)
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
177.661
136.617
136.074
134.490
131.848
131.581
131.324
131.057
129.721
129.693
129.654
129.416
128.796
127.318
127.289
127.260
127.232
126.707
124.532
122.367
121.223
120.202
90.481
87.600
77.365
77.117
76.860

6KO-228 Fr 19F

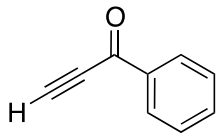


4m (^{19}F)

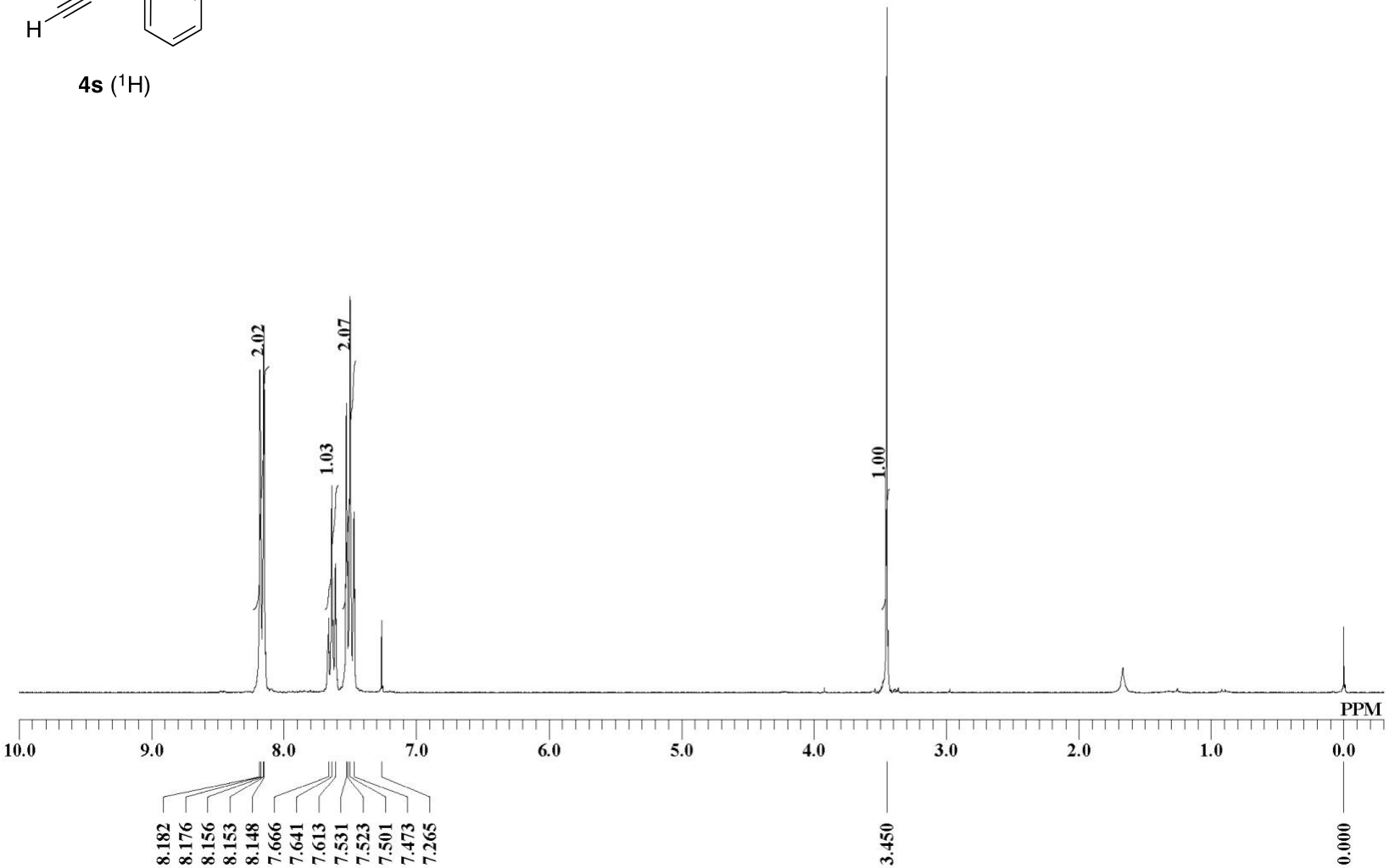



6KO-226 Fr
O
4n (1H)
1.94
2.00
2.05
1.01
2.04
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.245
8.237
8.232
8.229
8.226
8.214
8.206
8.201
7.630
7.626
7.616
7.603
7.595
7.586
7.572
7.567
7.562
7.516
7.514
7.508
7.490
7.484
7.480
7.465
7.459
7.454
7.362
7.357
7.336
7.329
7.307
7.303
7.259
7.256
7.253
7.250
7.243
7.222
7.195
7.168
7.166
7.163
2.552
0.000

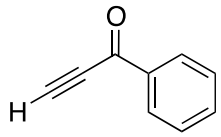
7YT-21-fr



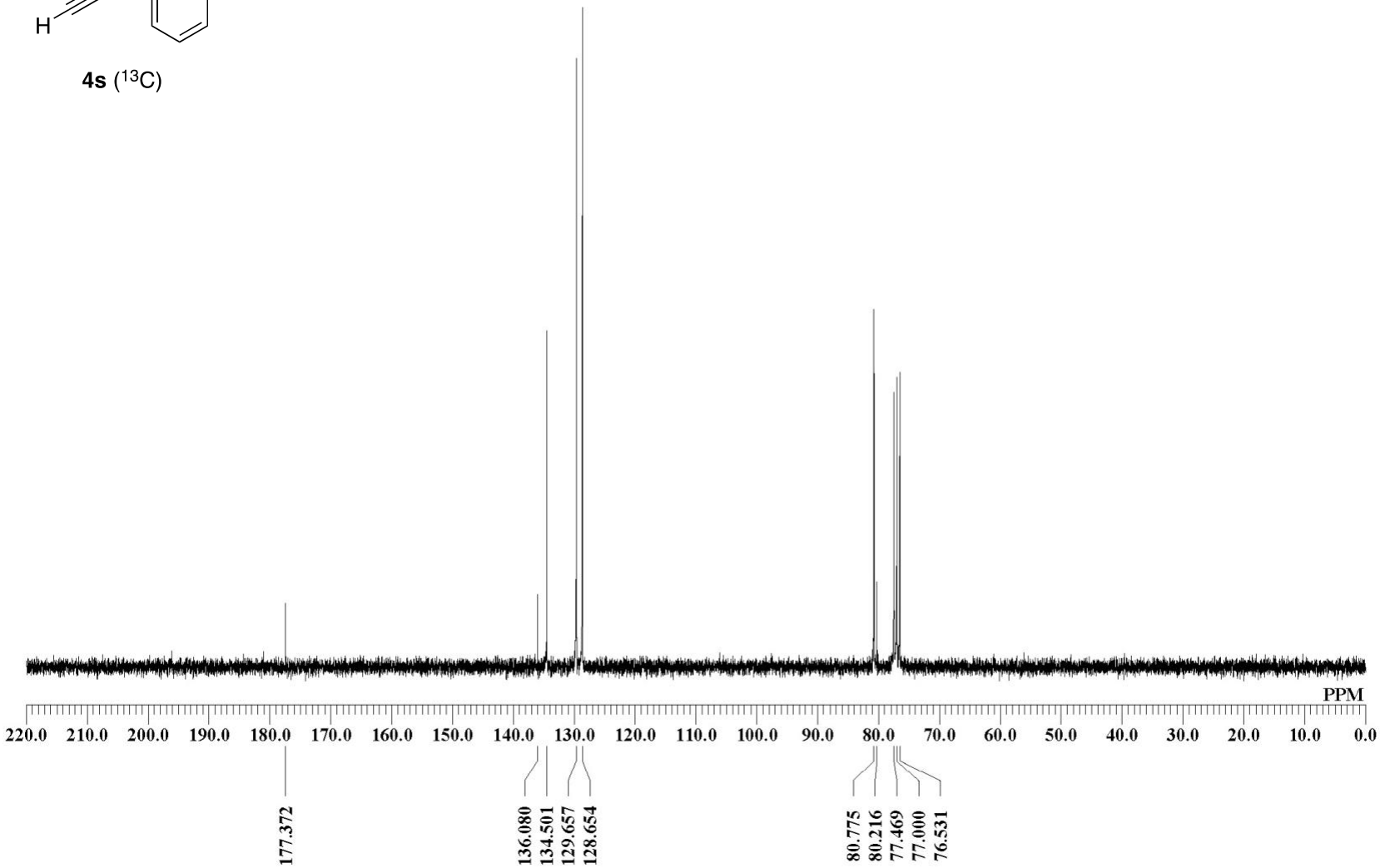
4s (^{1}H)



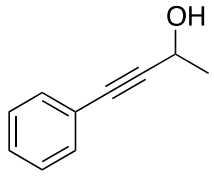
7YT-21 fr 13C



4s (^{13}C)

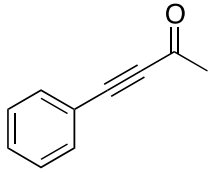


4-Phenyl-3-butyn-2-ol



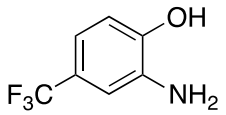
3' (^{1}H)

6KO-104-fr

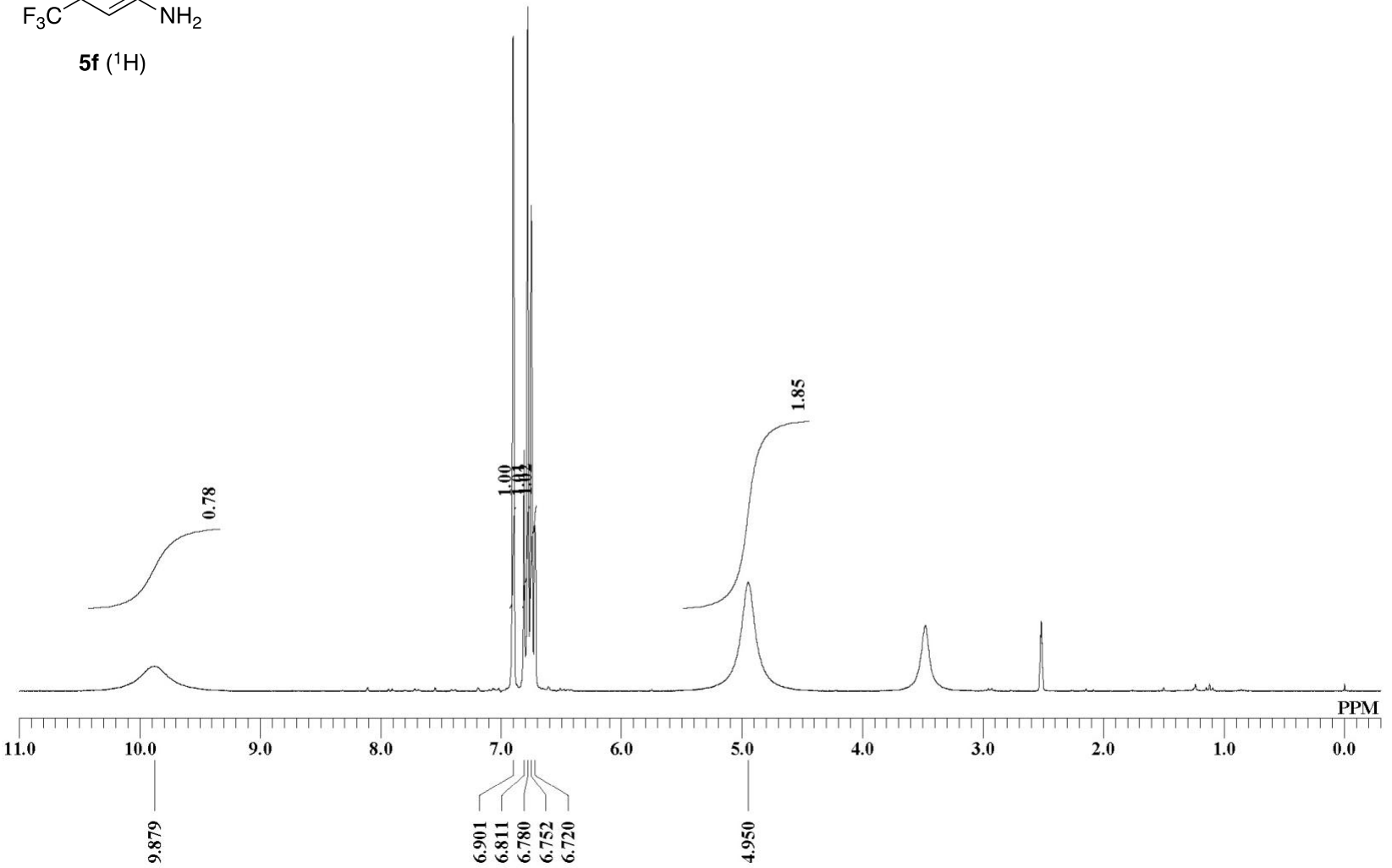


3 (^{1}H)

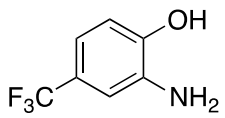
6KO-219 Fr3



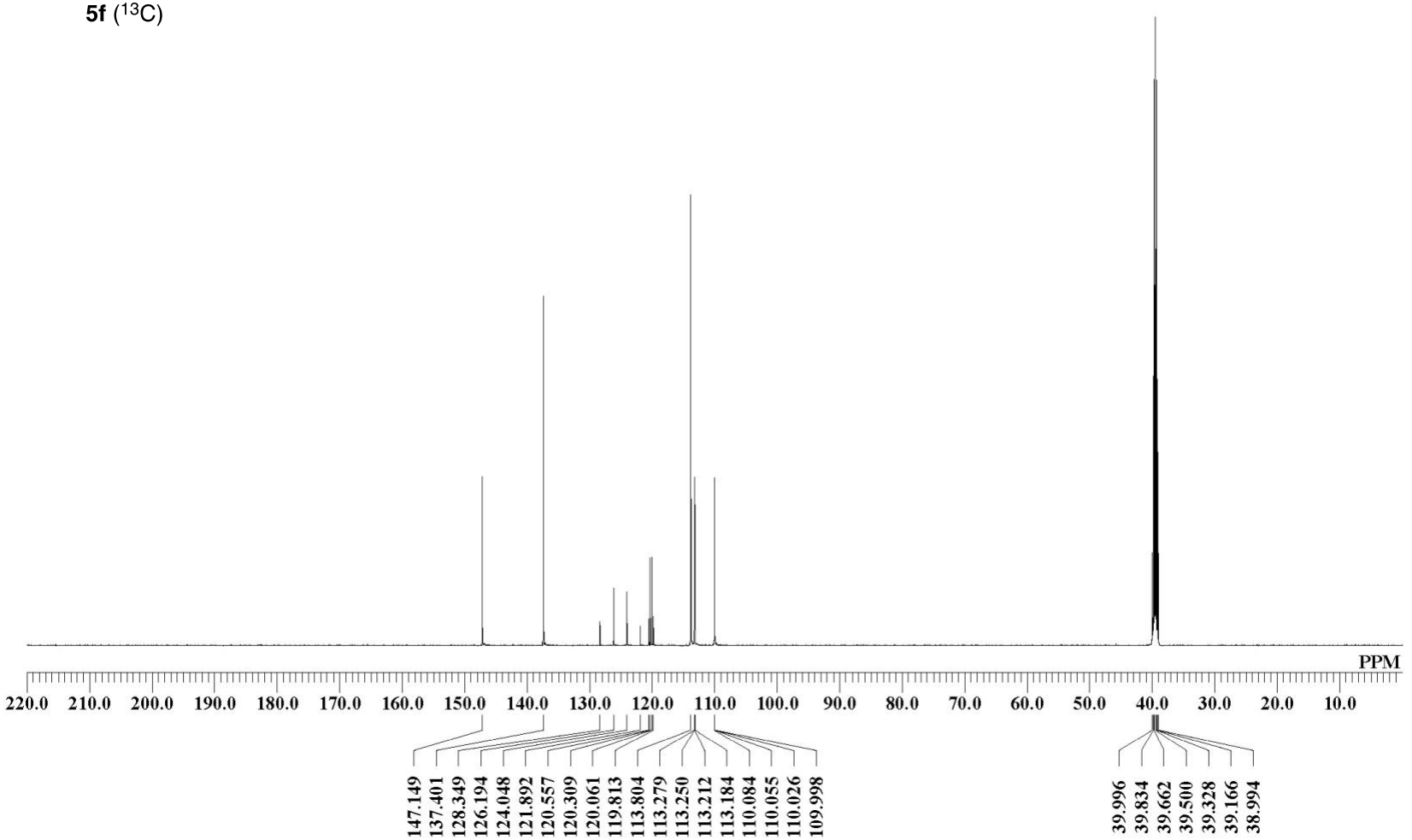
5f (^{1}H)



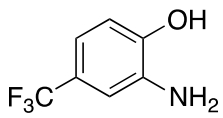
6KO-219 Fr 13C 500MHz



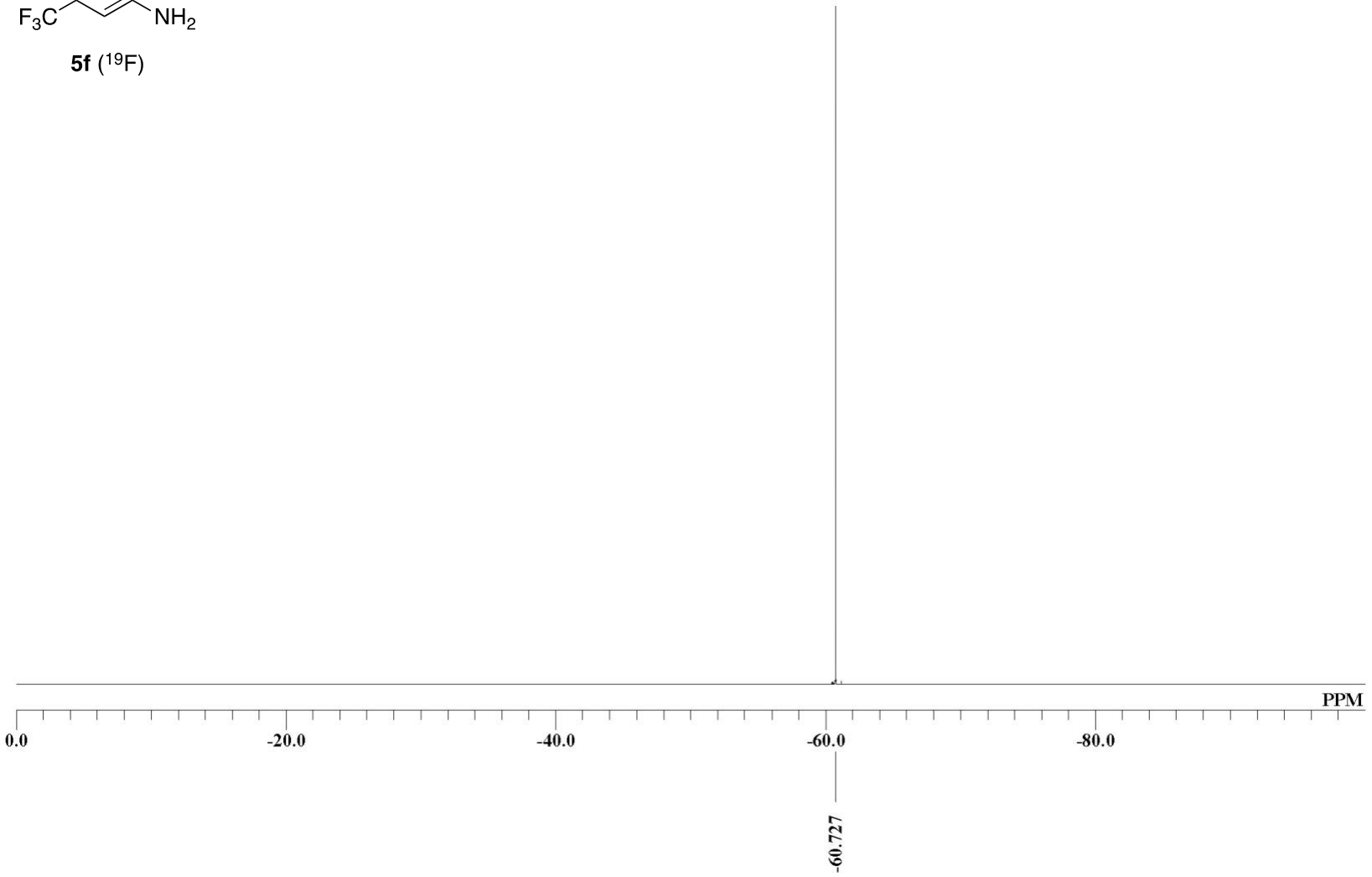
5f (^{13}C)



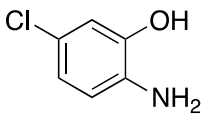
6KO-219 Fr 19F2



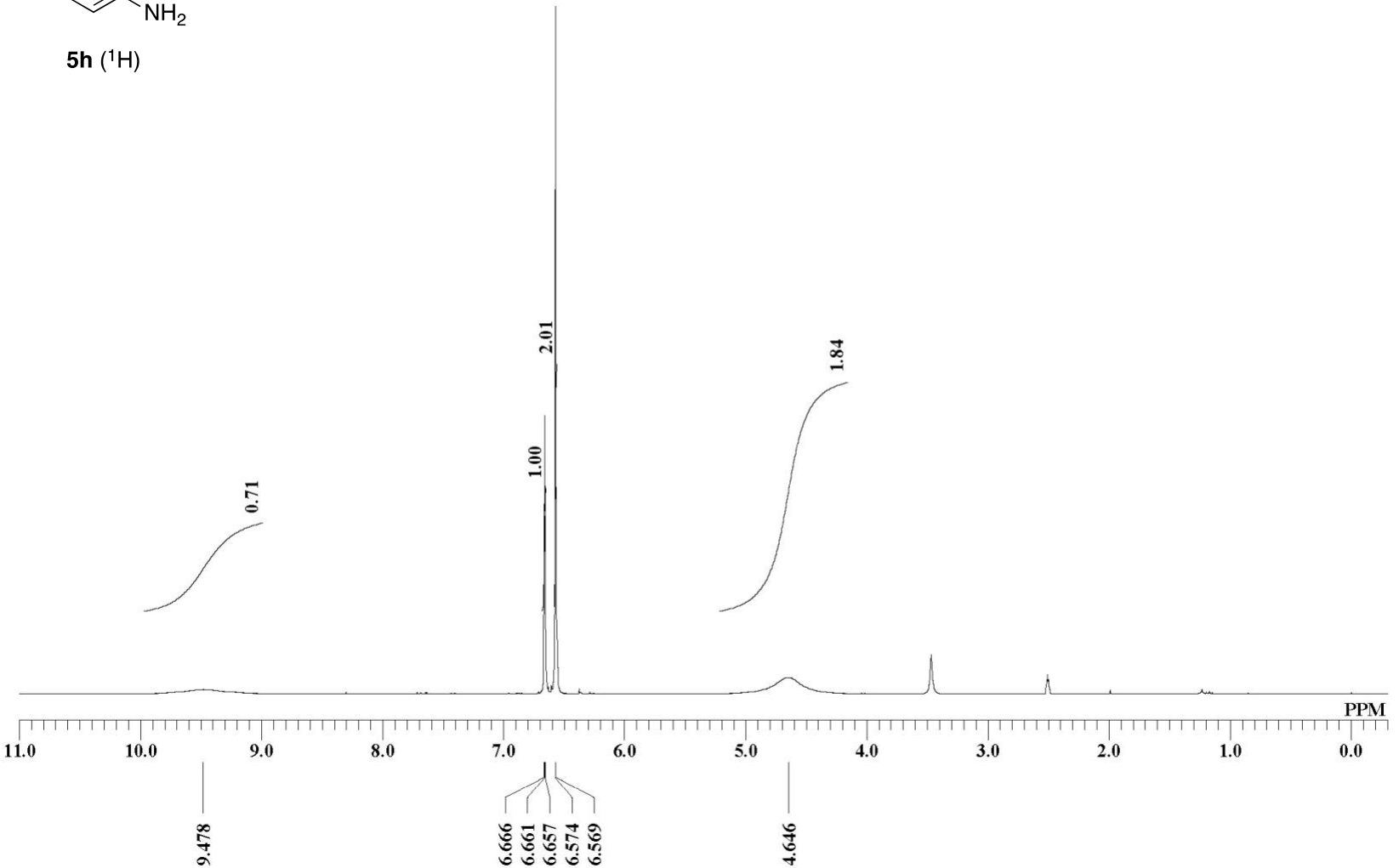
5f (^{19}F)

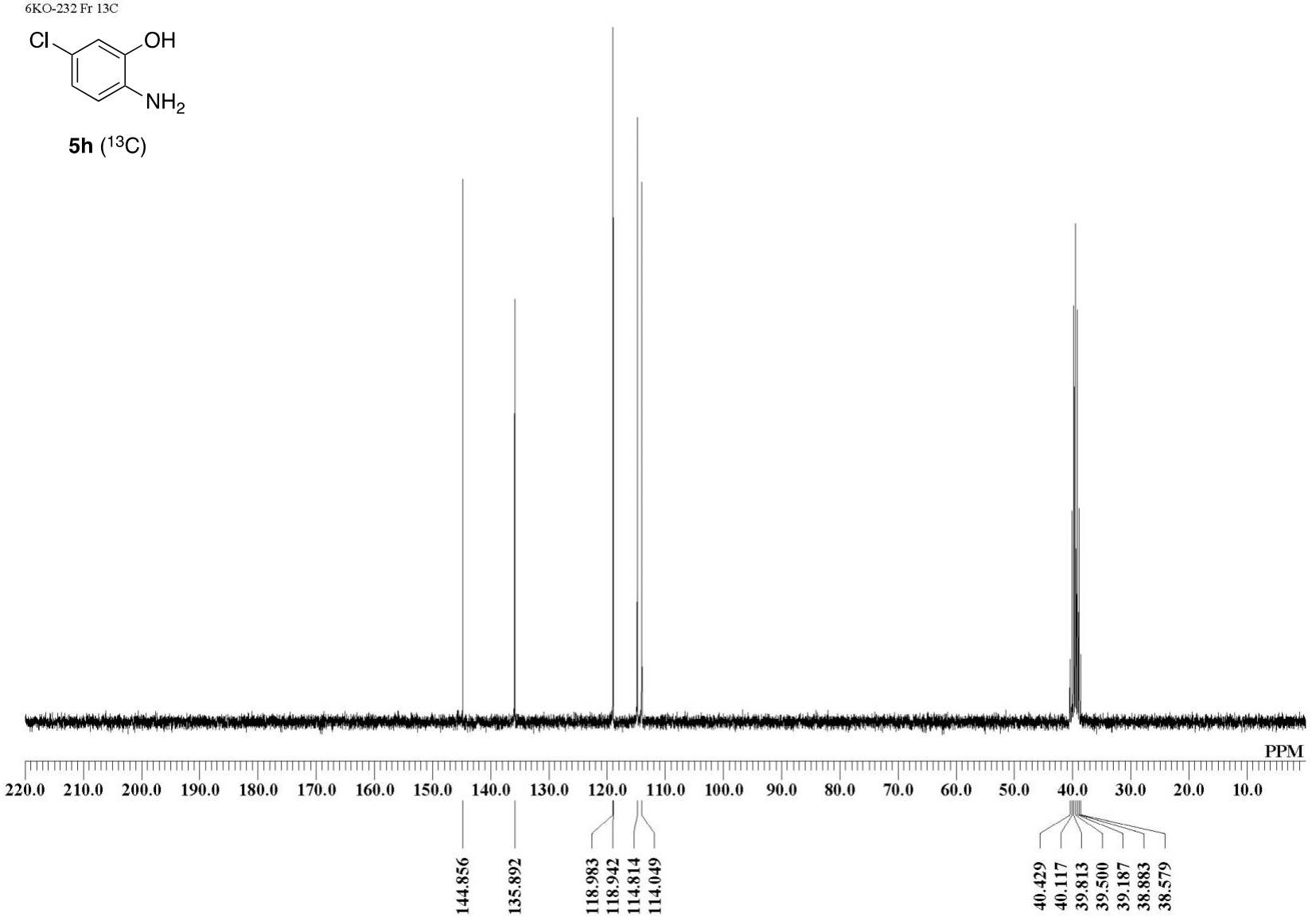


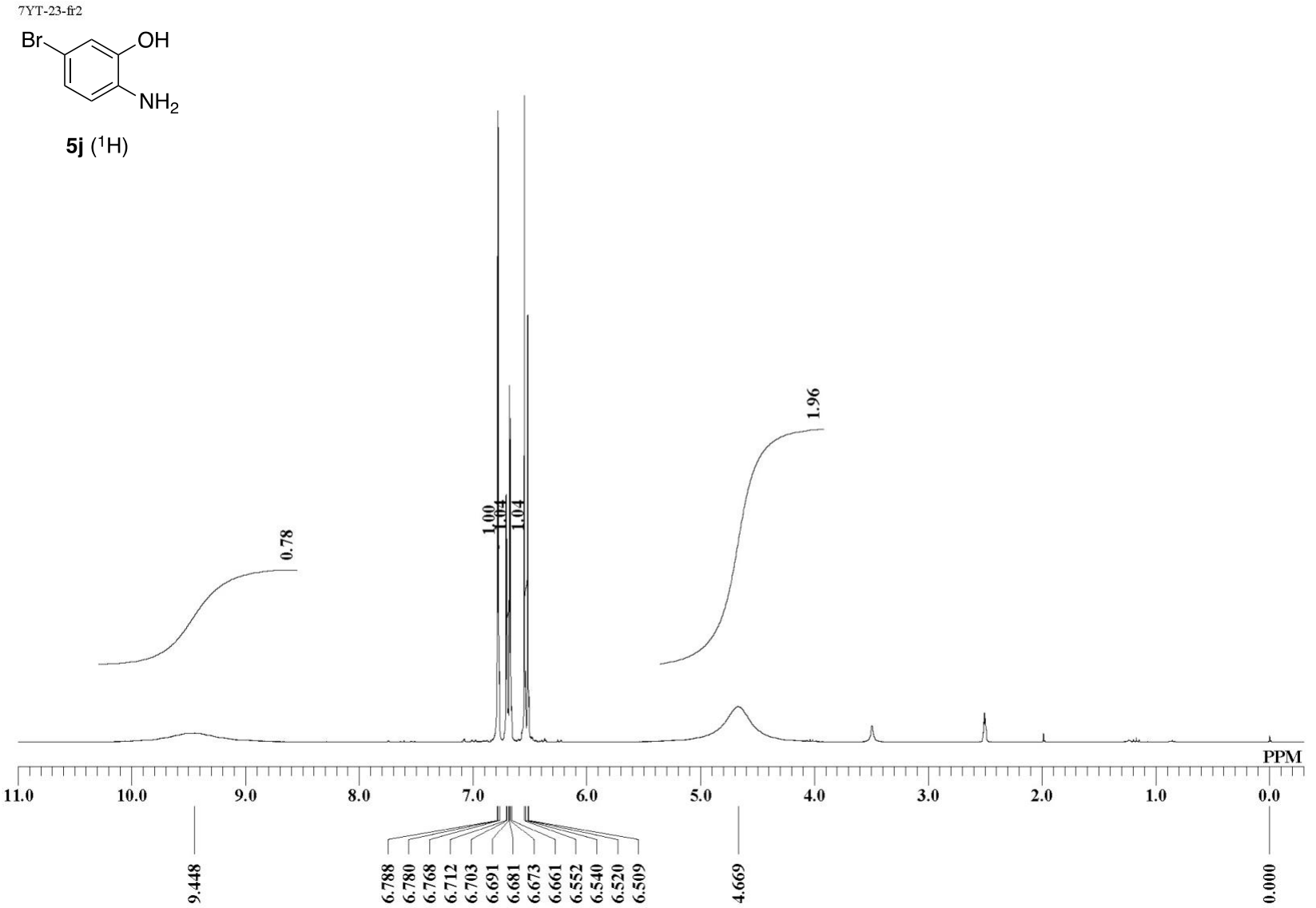
6KO-232 Fr



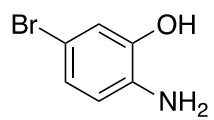
5h (^{1}H)



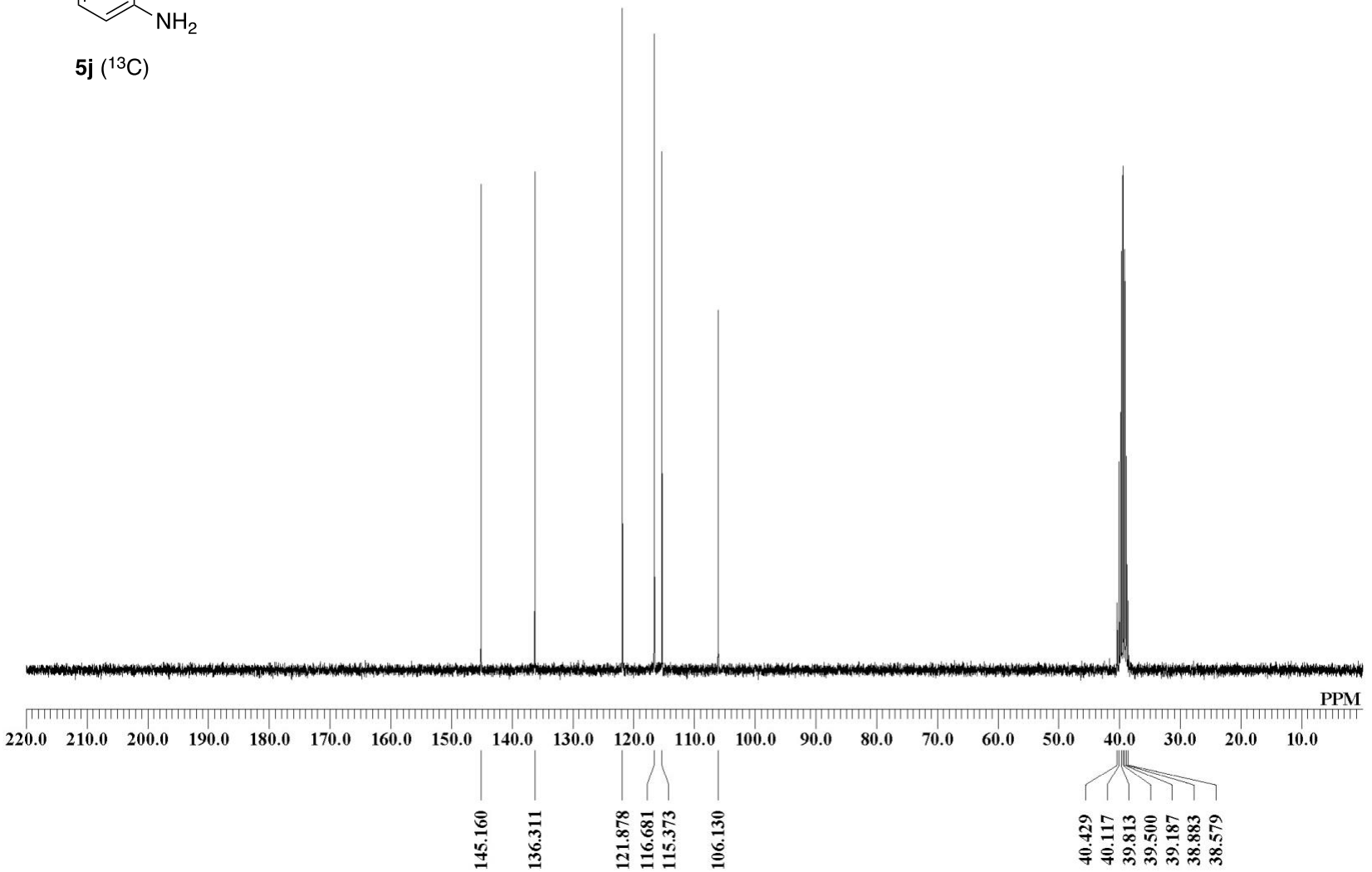

6KO-232 Fr 13C
Cl
OH
NH2
5h (13C)
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
144.856
135.892
118.983
118.942
114.814
114.049
40.429
40.117
39.813
39.500
39.187
38.883
38.579

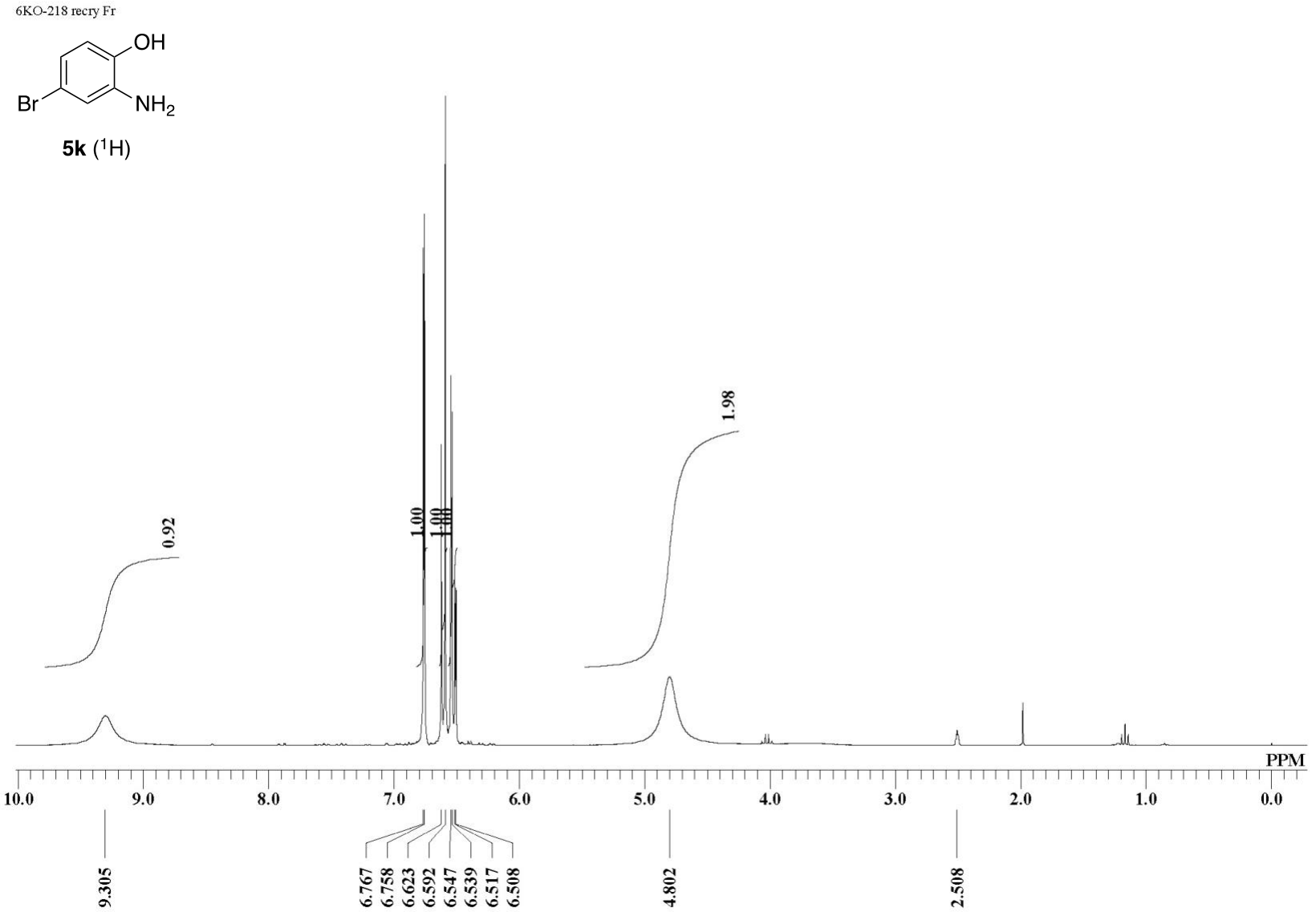

7YT-23-fr2
Br
OH
NH2
5j (1H)
0.78
1.00
1.04
1.04
1.96
PPM
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
9.448
6.788
6.780
6.768
6.712
6.703
6.691
6.681
6.673
6.661
6.552
6.540
6.520
6.509
4.669
0.000

7YT-23 fr 13C DMSO

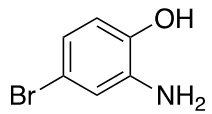


5j (^{13}C)

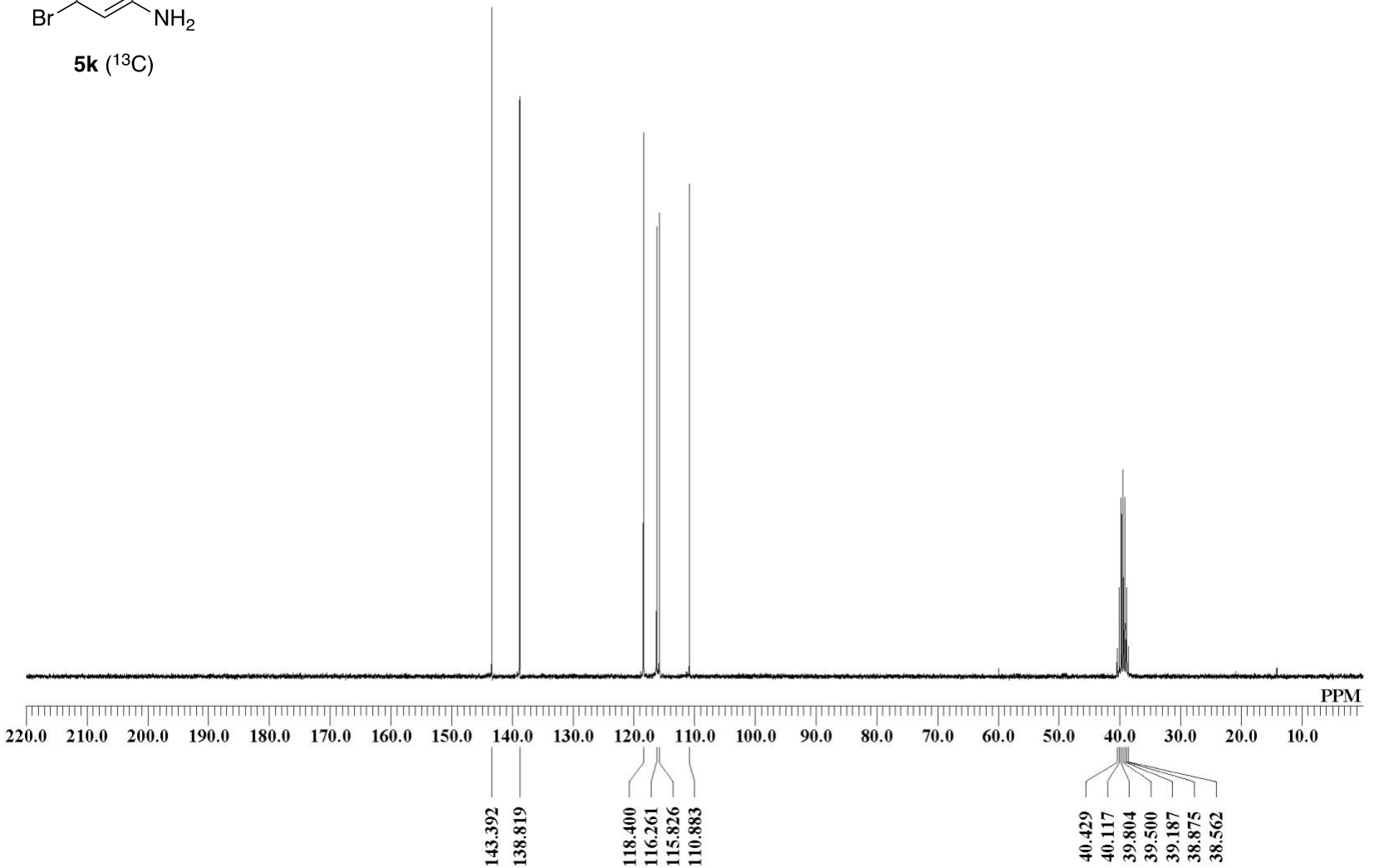


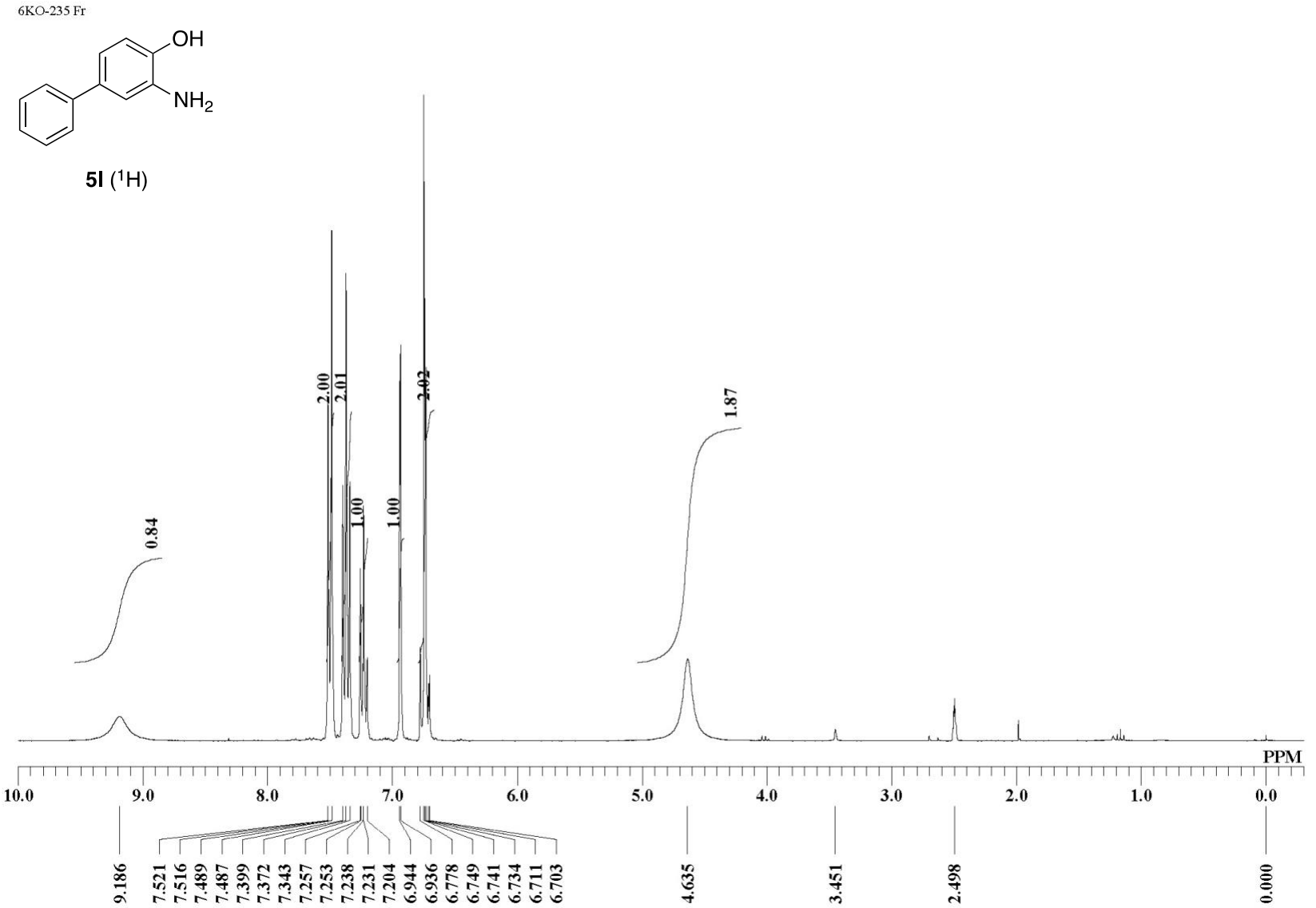

6KO-218 recry Fr
OH
Br
NH2
5k (1H)
0.92
1.00
1.98
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
9.305
6.767
6.758
6.623
6.592
6.547
6.539
6.517
6.508
4.802
2.508

6KO-218 recry Fr 13C

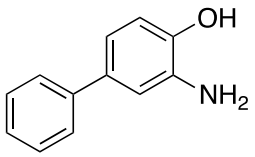


5k (^{13}C)

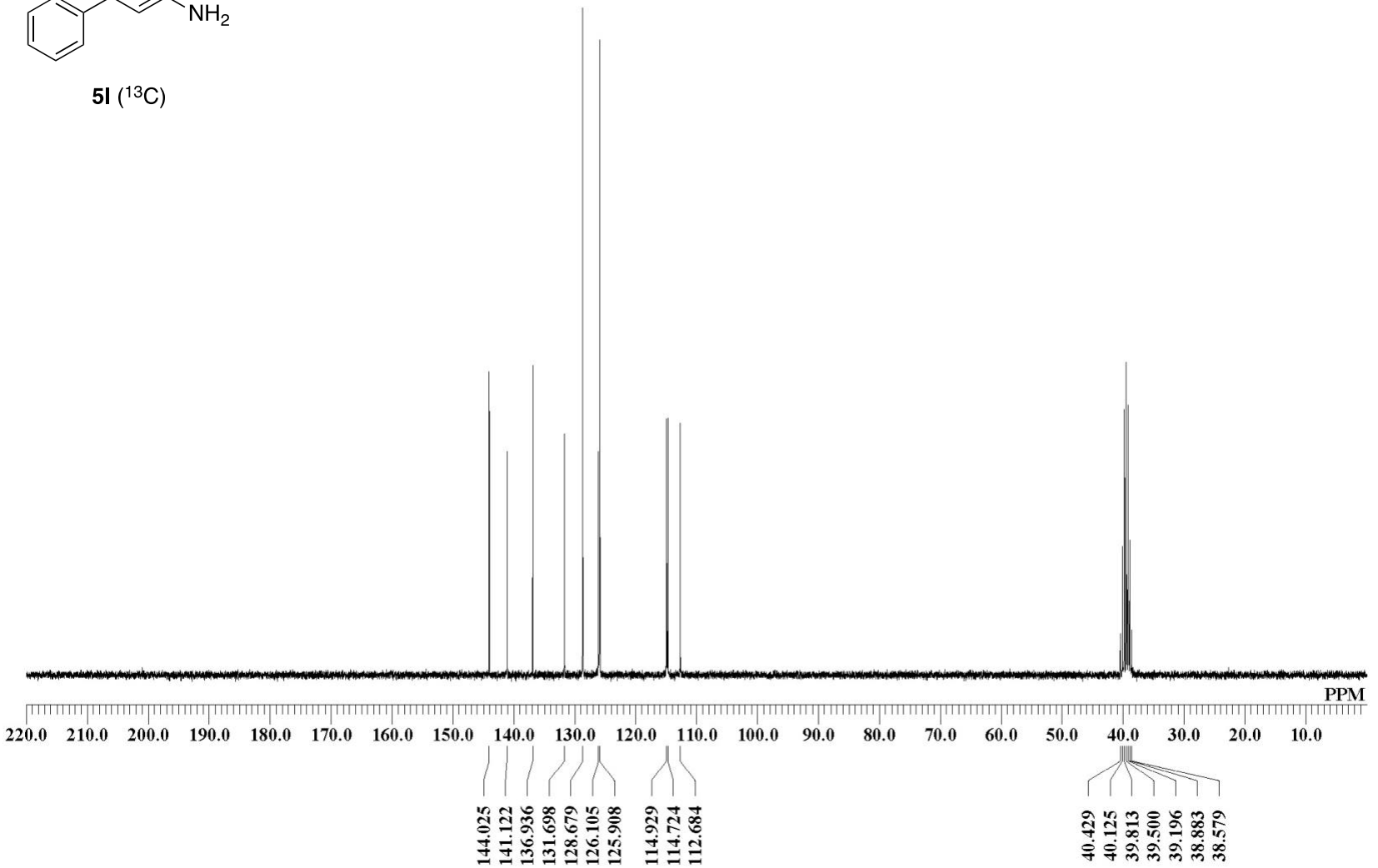



6KO-235 Fr
OH
NH2
5l (1H)
0.84
2.00
2.01
1.00
1.00
2.02
1.87
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
9.186
7.521
7.516
7.489
7.487
7.399
7.372
7.343
7.257
7.253
7.238
7.231
7.204
6.944
6.936
6.778
6.749
6.741
6.734
6.711
6.703
4.635
3.451
2.498
0.000

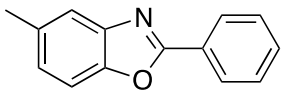
6KO-235 Fr 13C



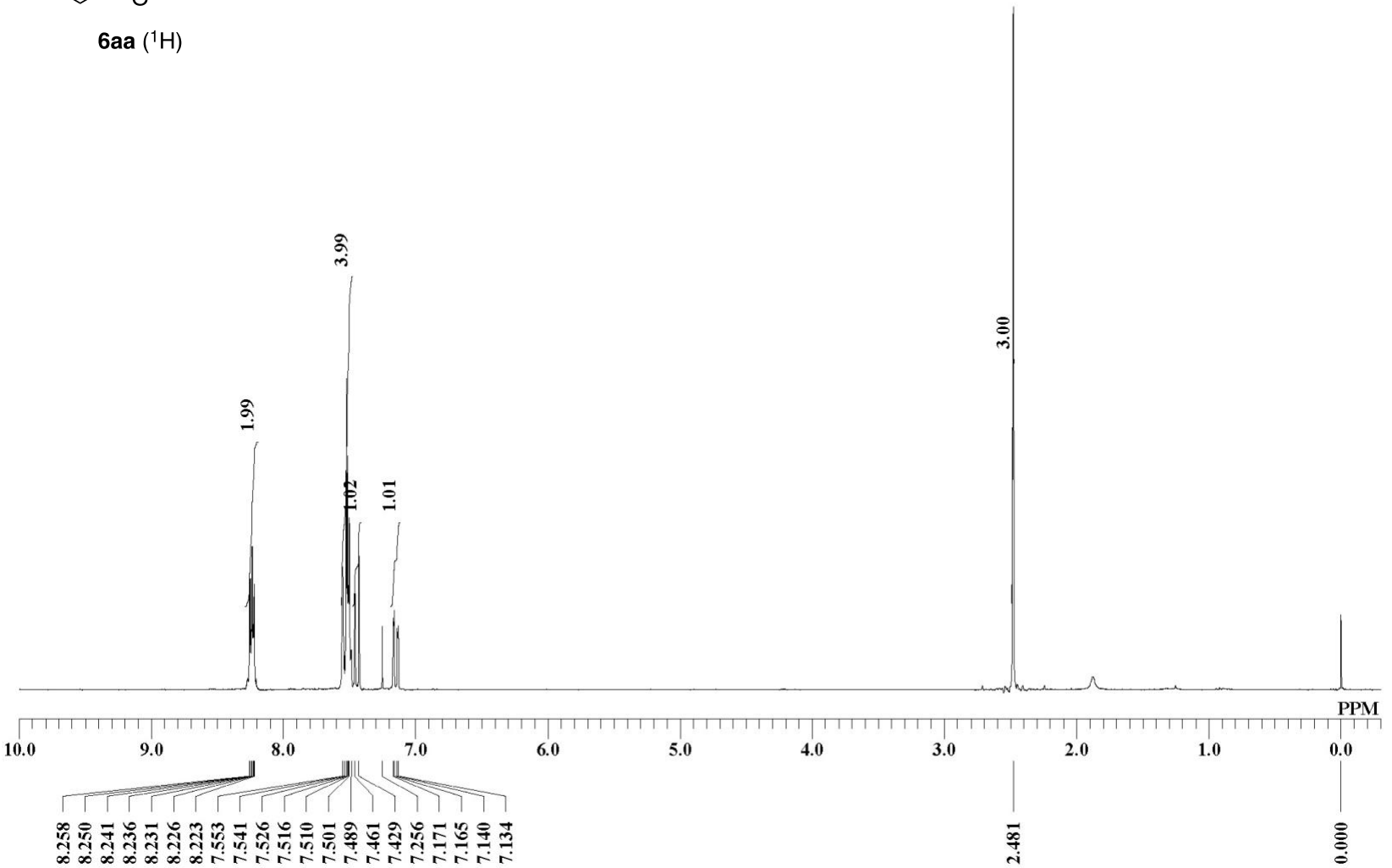
5l (^{13}C)



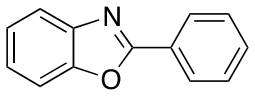
6KO-229 Fr



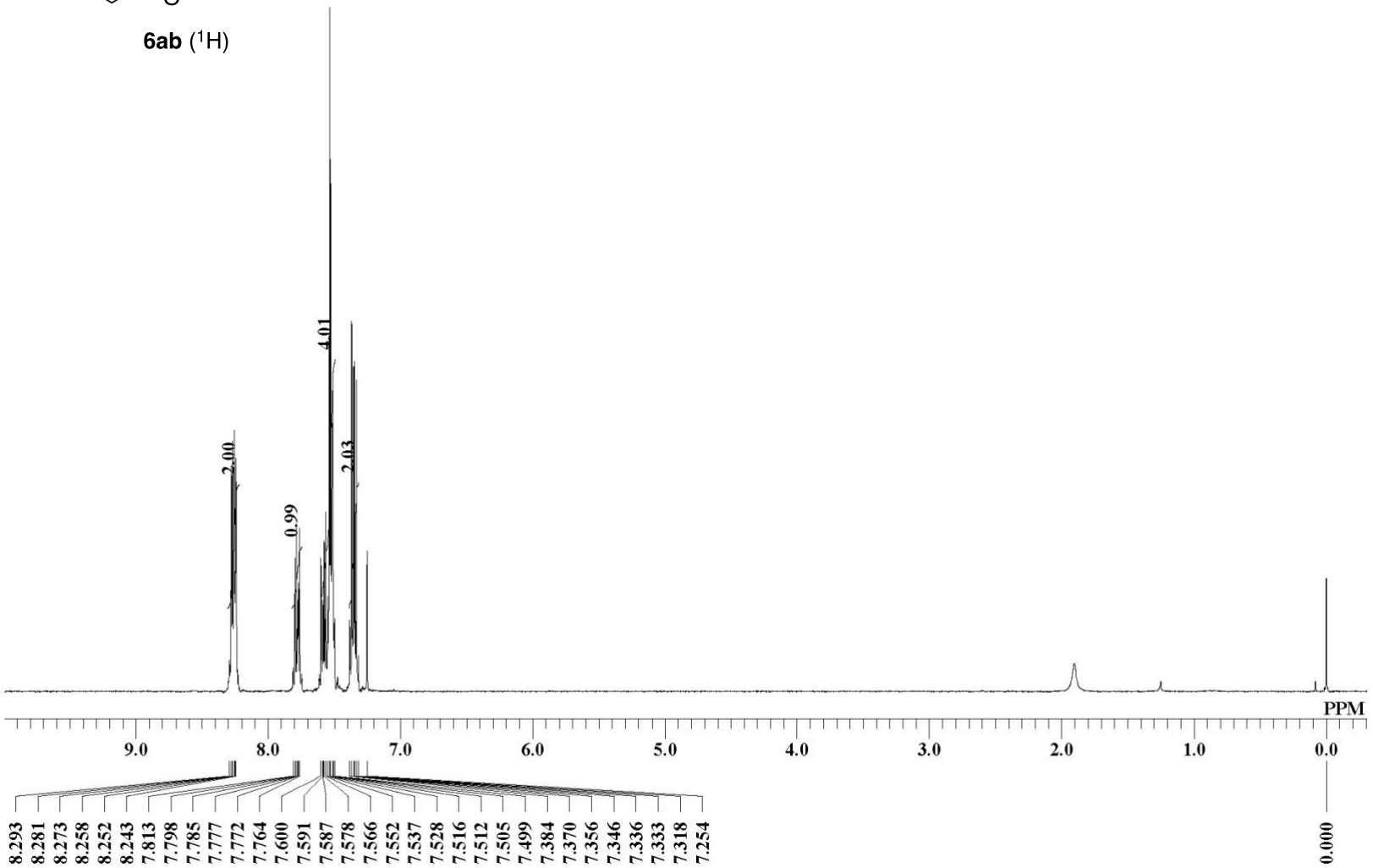
6aa (^{1}H)



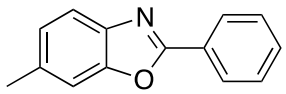
6KO-217 Fr3



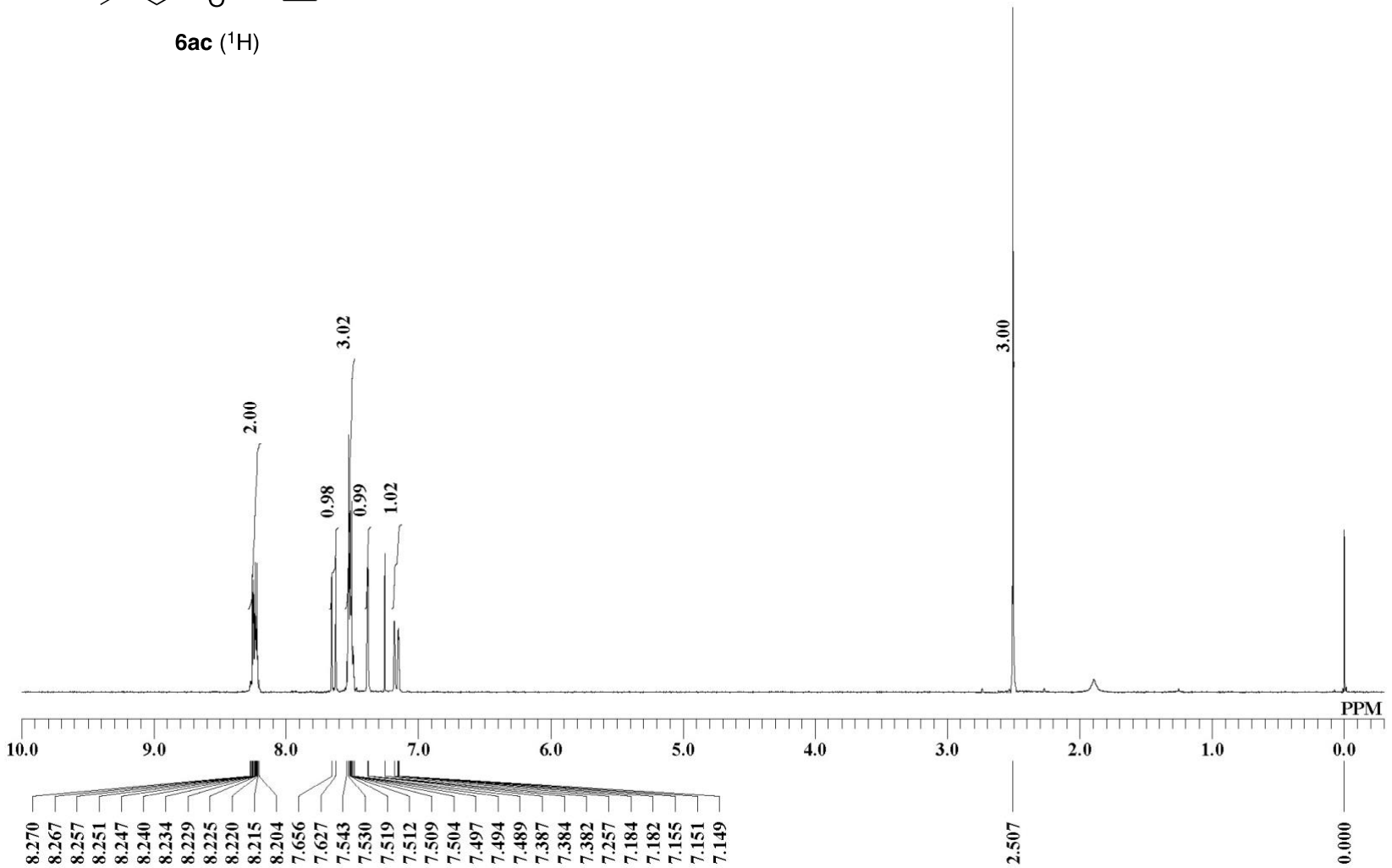
6ab (^{1}H)



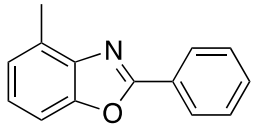
6KO-225 Fr2



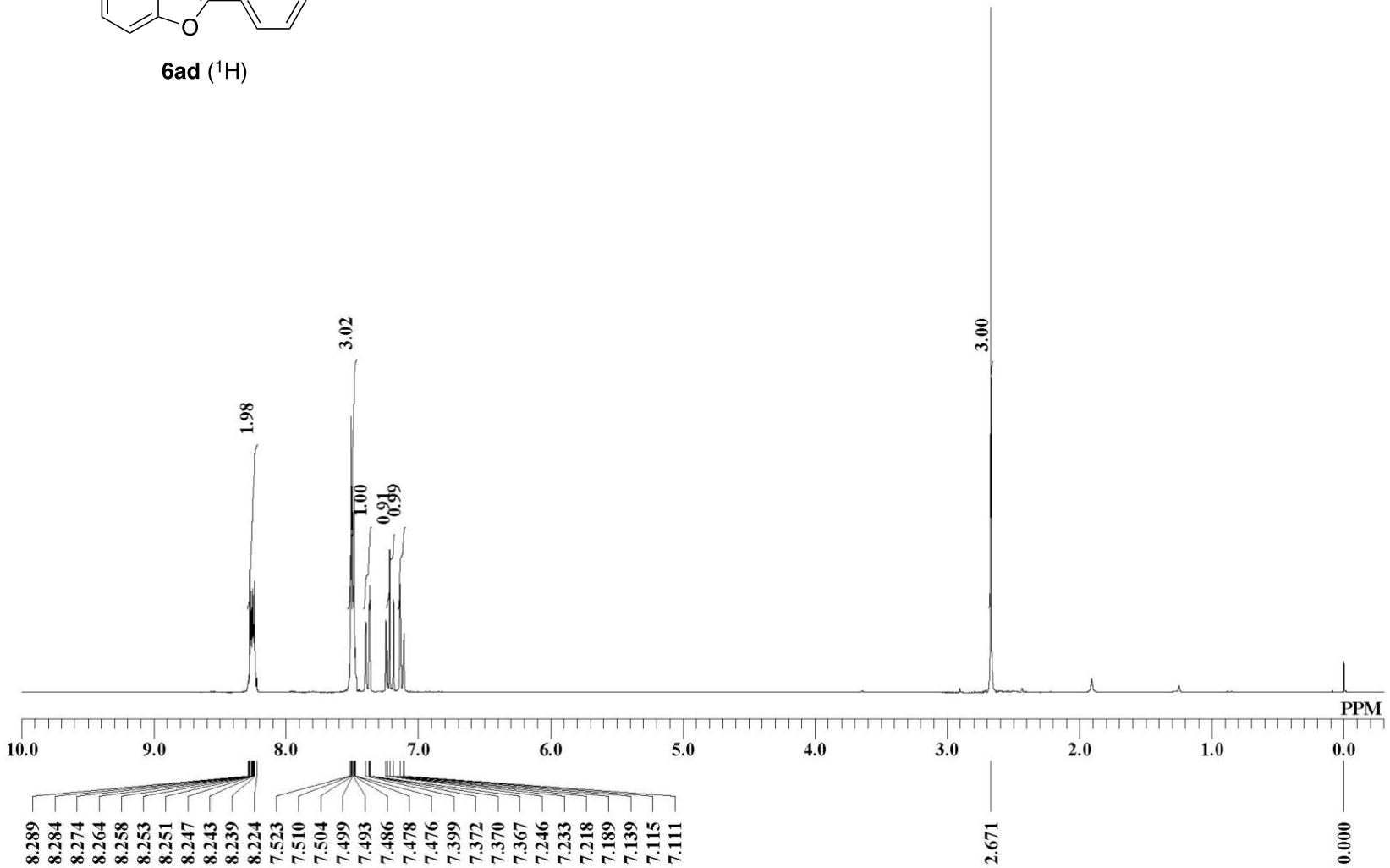
6ac (^{1}H)



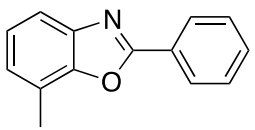
6KO-254 Fr



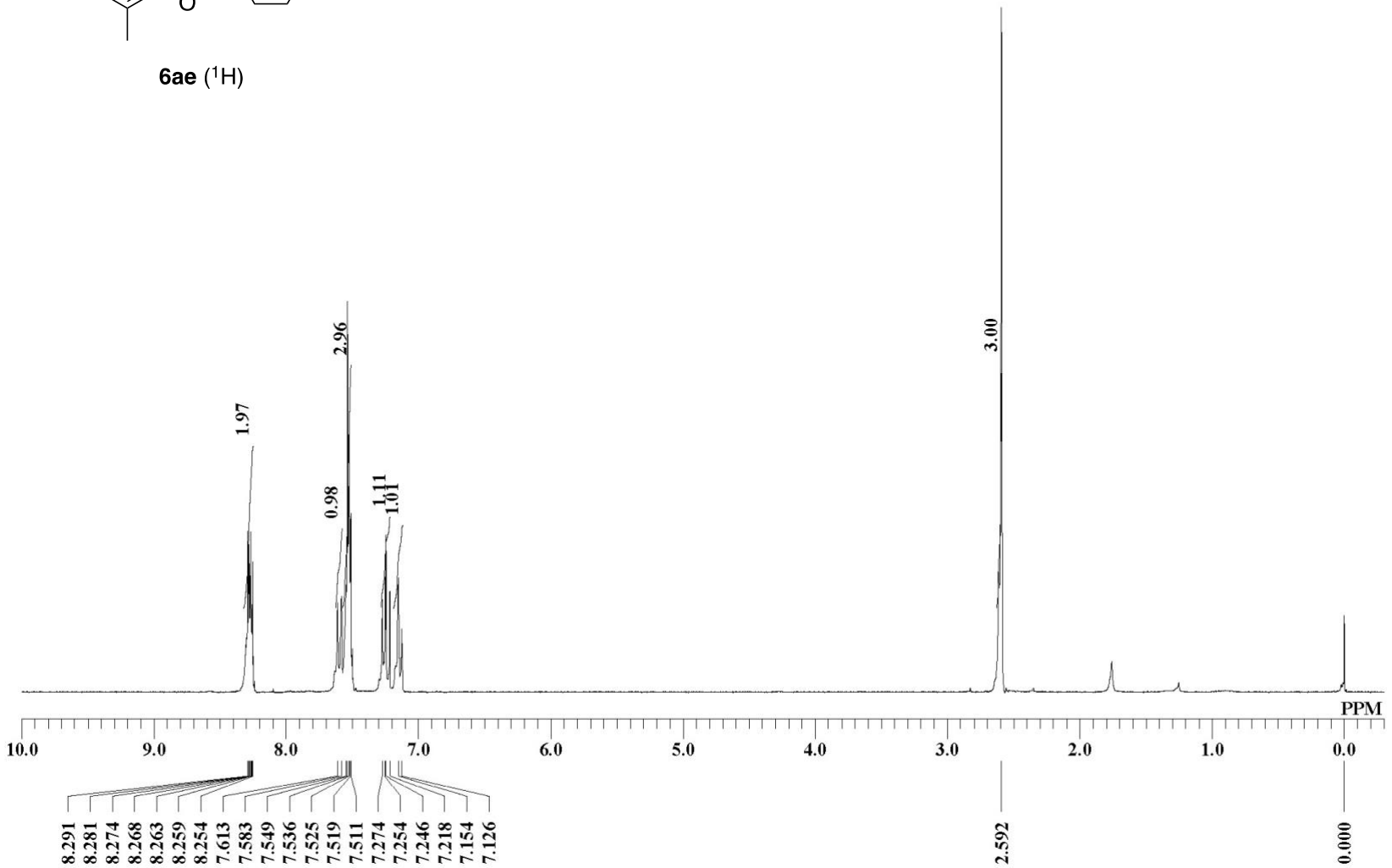
6ad (^{1}H)



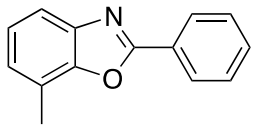
6KO-255 Fr2



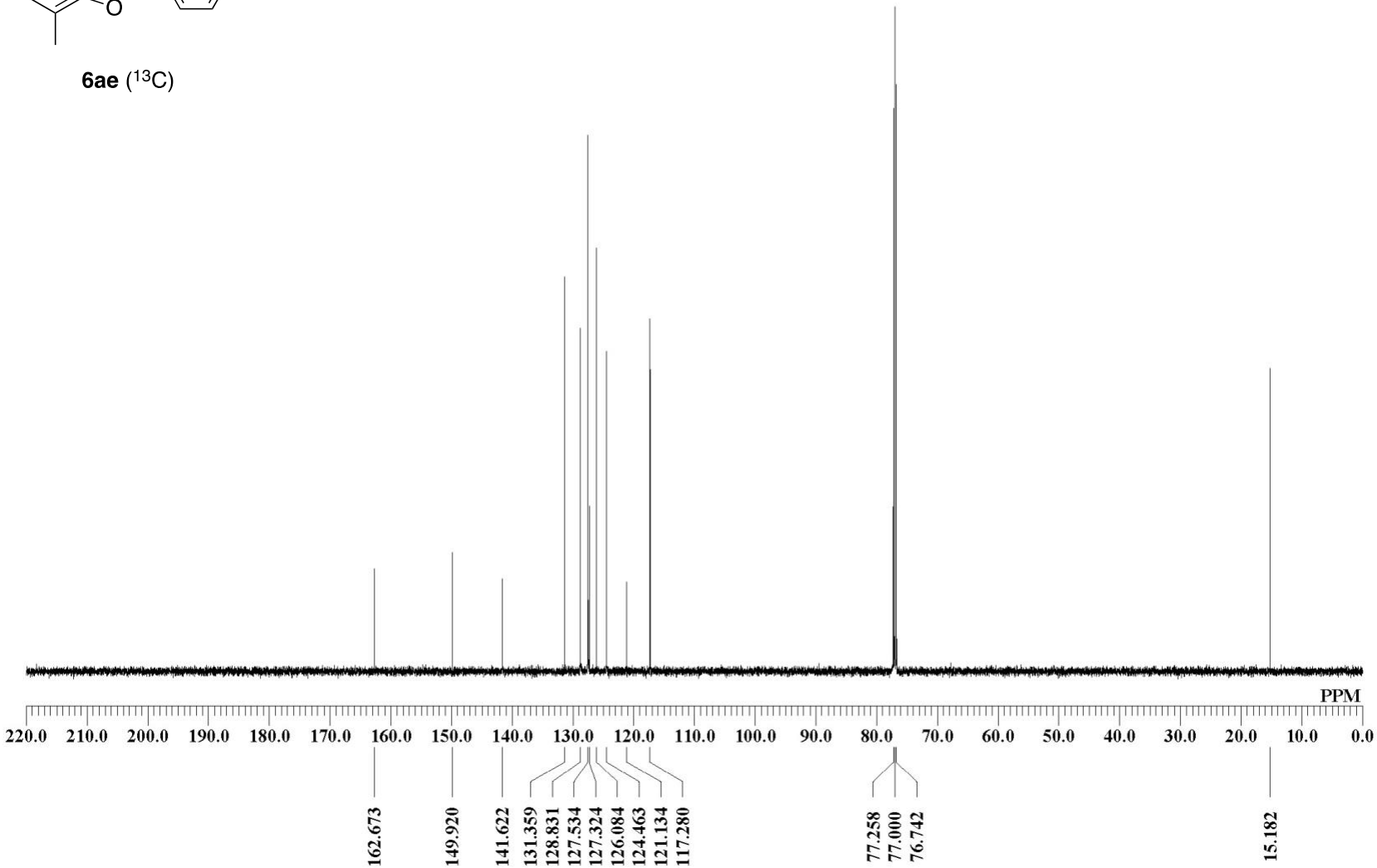
6ae (^{1}H)

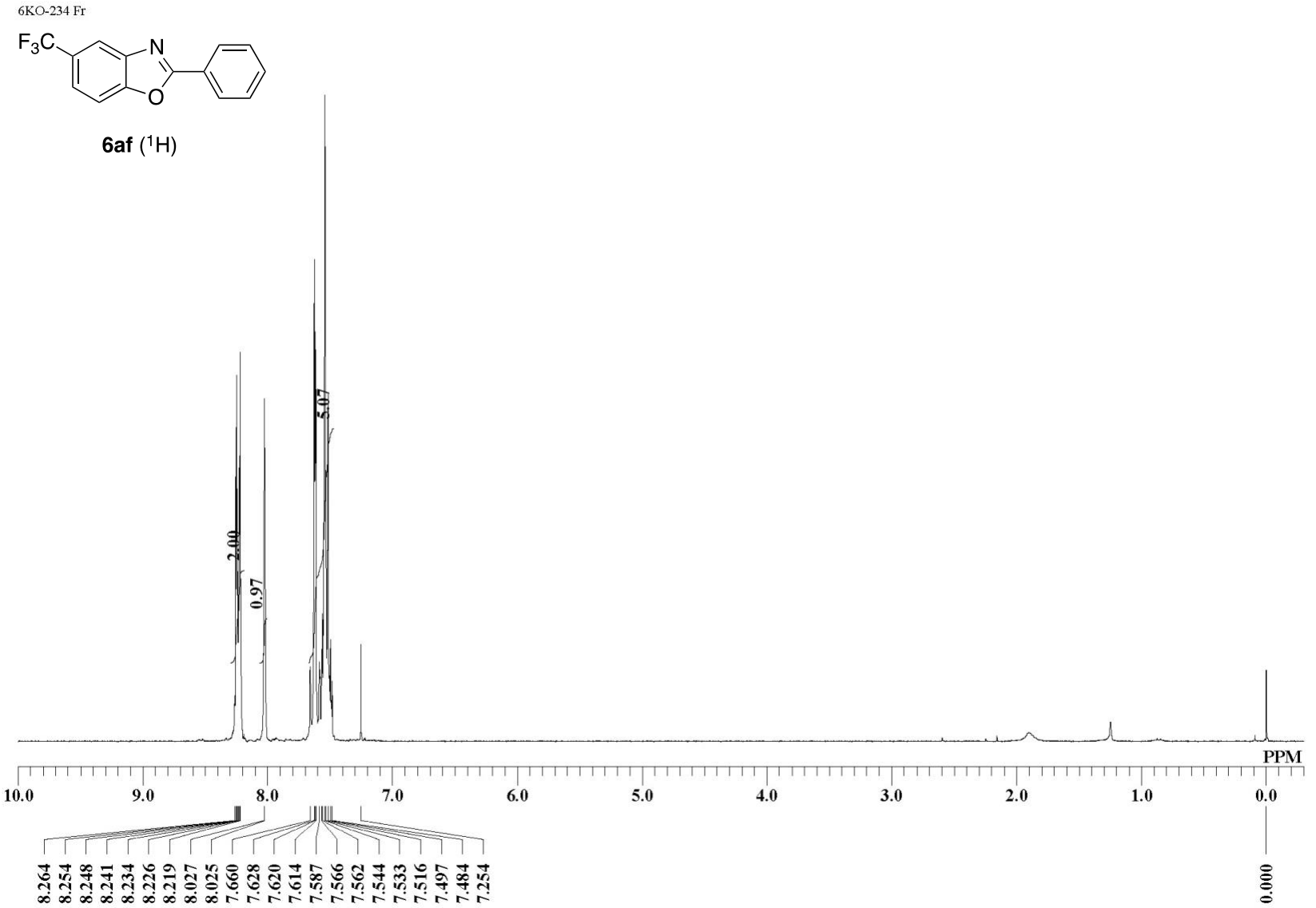


6KO-255 Fr 13C 500MHz

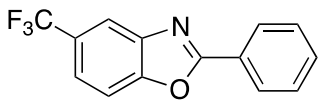


6ae (^{13}C)

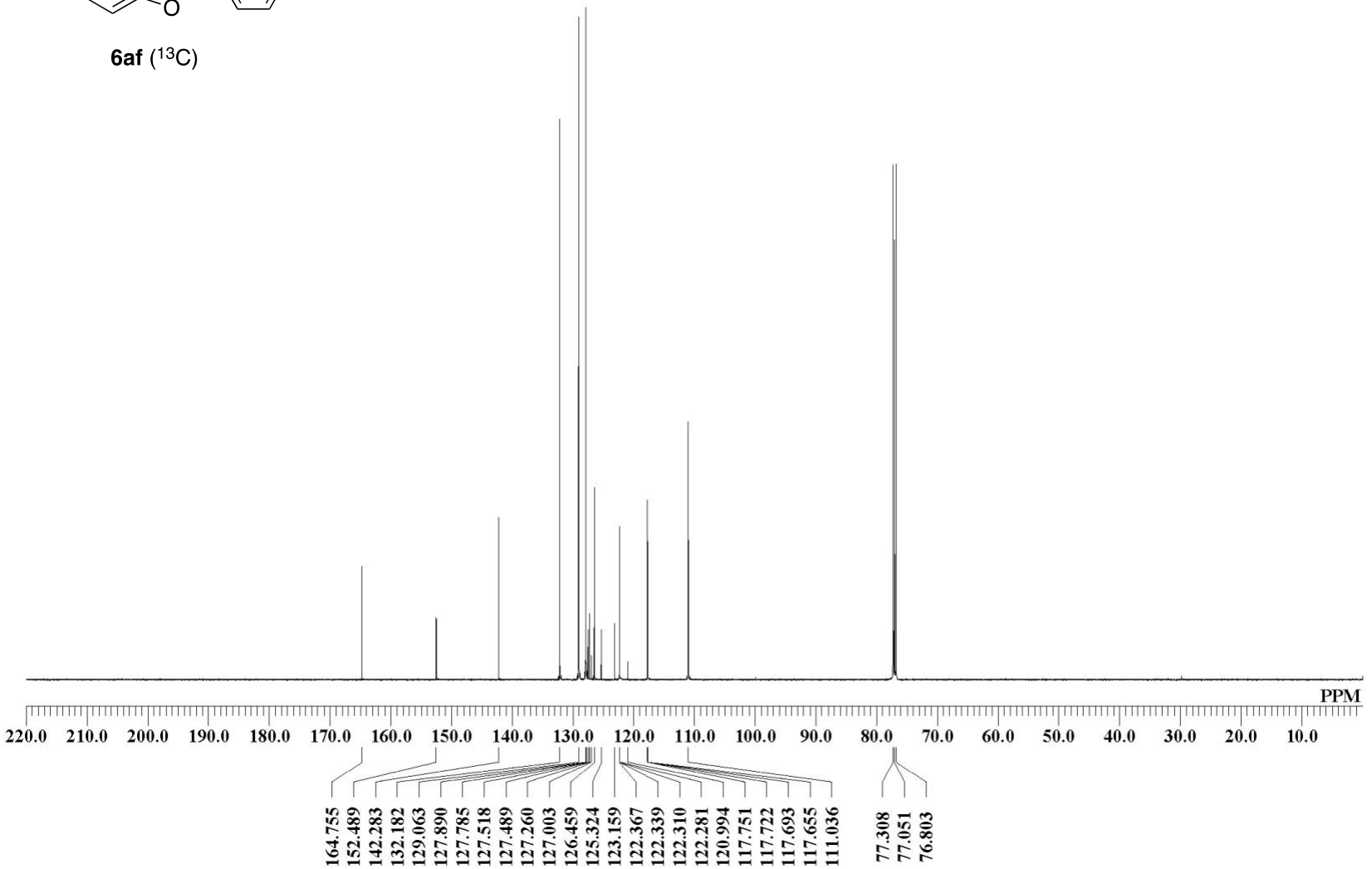



6KO-234 Fr
F3C
N
O
6af (1H)
2.00
0.97
5.07
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.264
8.254
8.248
8.241
8.234
8.226
8.219
8.027
8.025
7.660
7.628
7.620
7.614
7.587
7.566
7.562
7.544
7.533
7.516
7.497
7.484
7.254
0.000

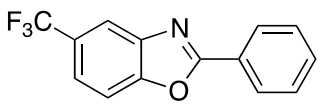
6KO-234 Fr 13C 500MHz 2



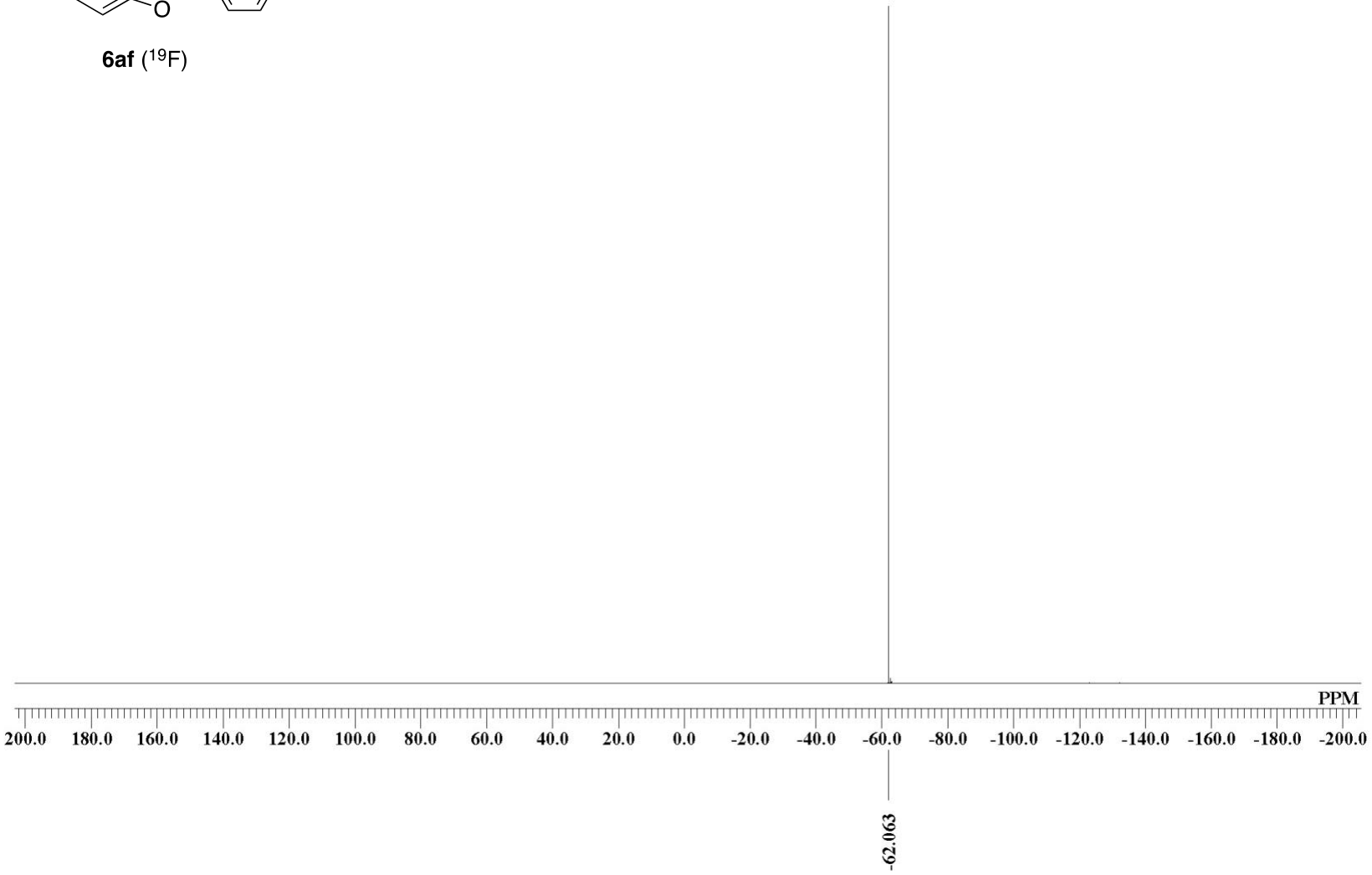
6af (^{13}C)



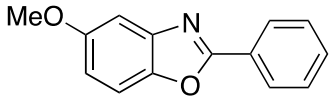
6KO-234 Fr 19F



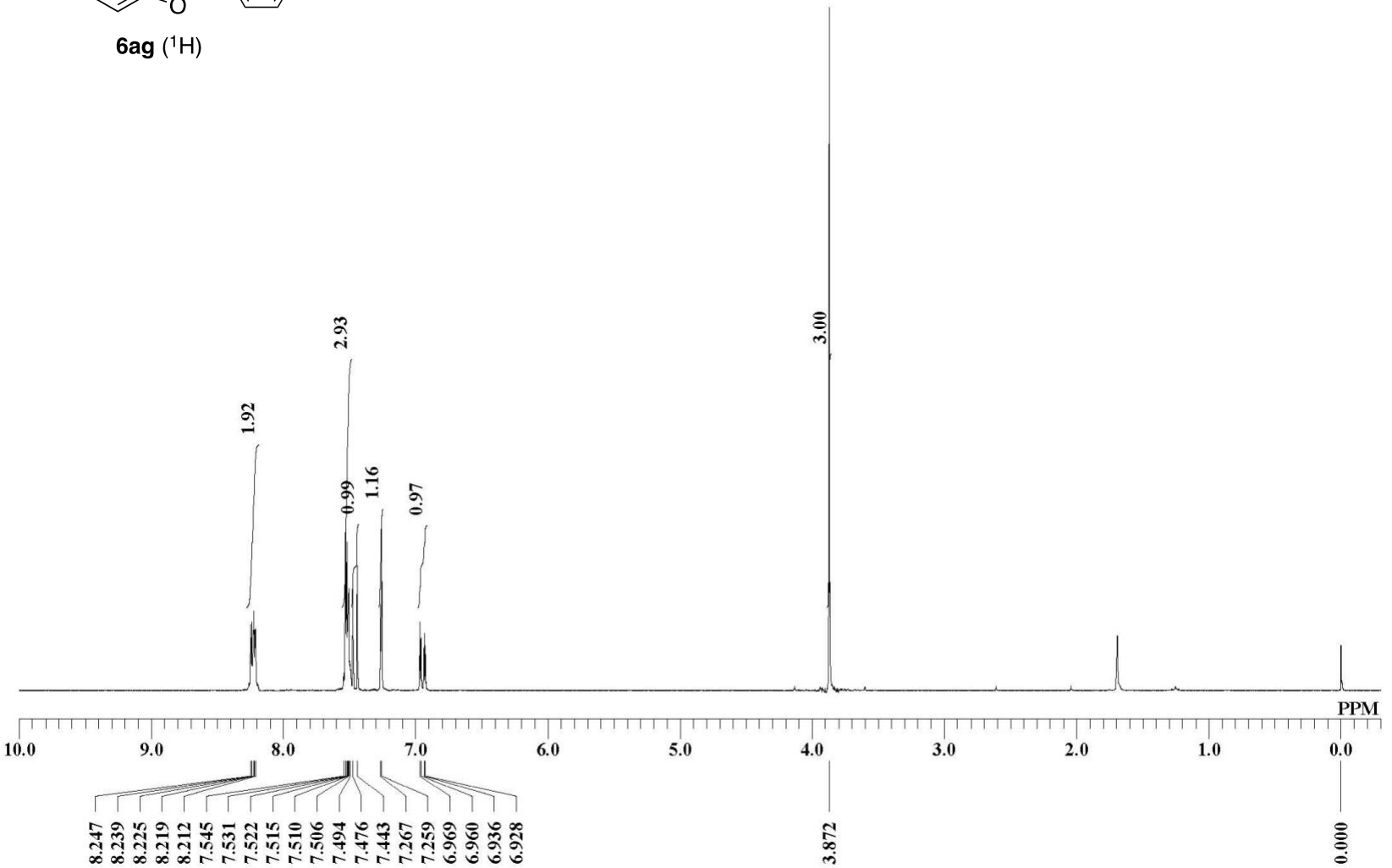
6af (^{19}F)

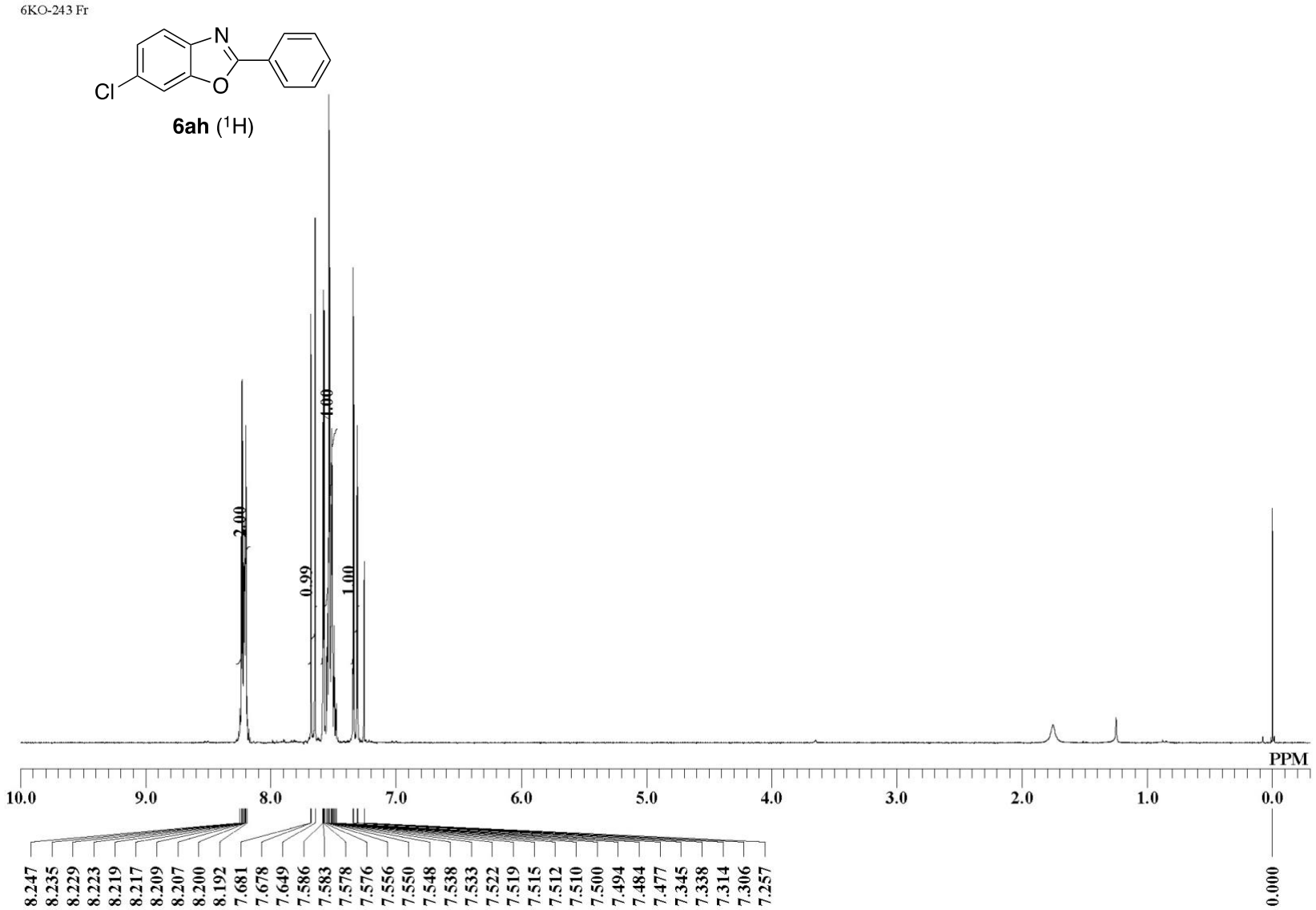


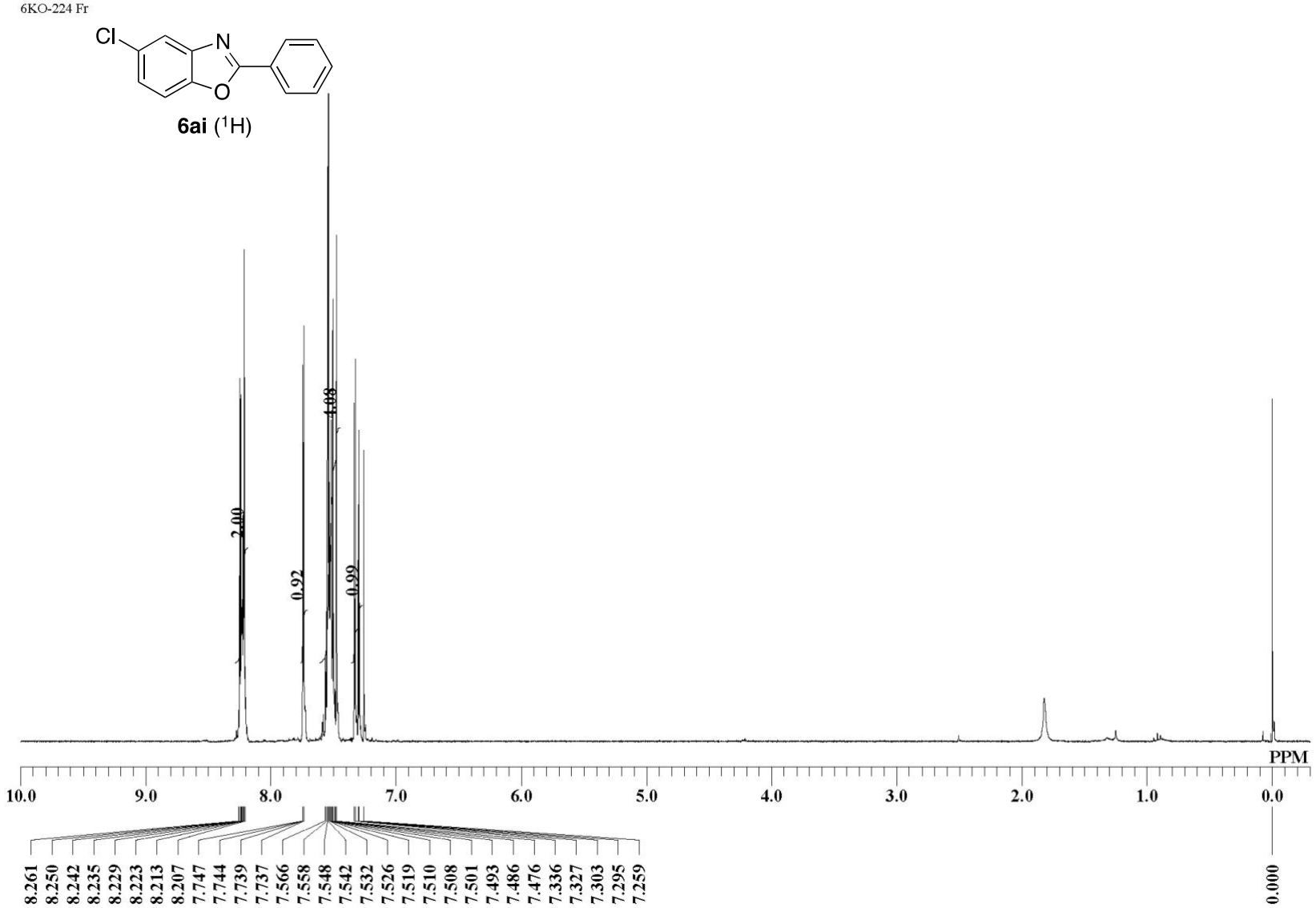
6KO-194 Fr

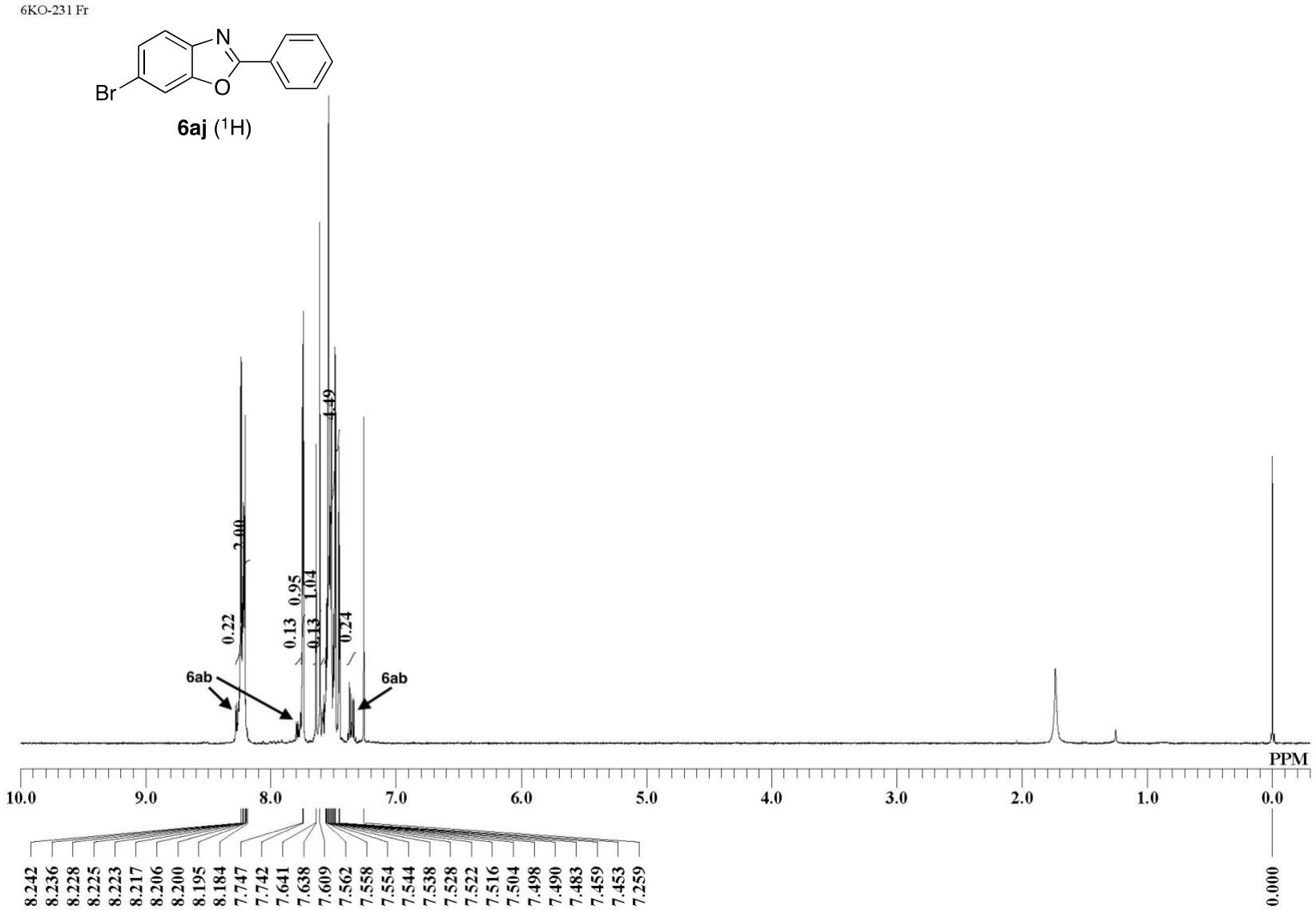


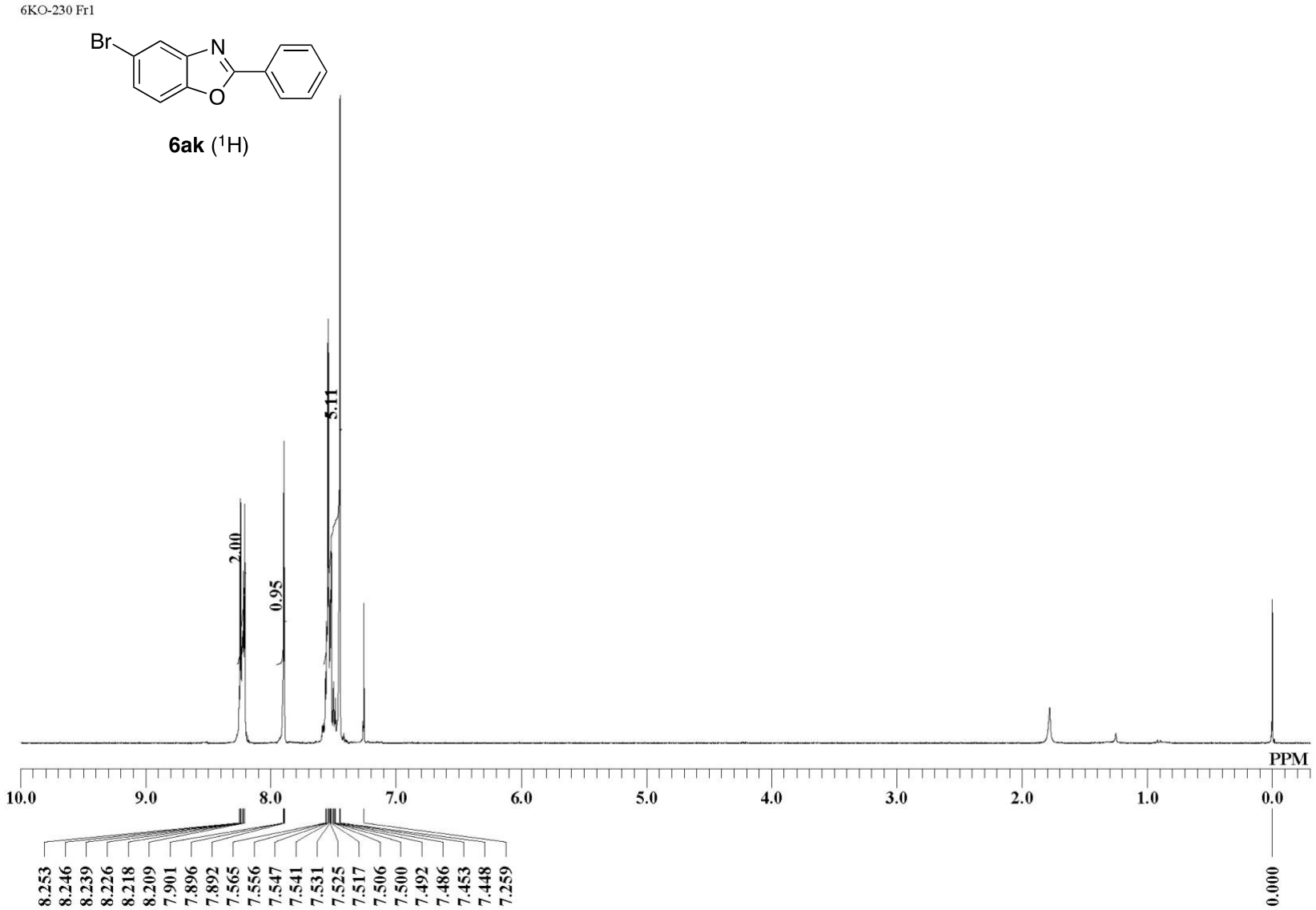
6ag (^{1}H)



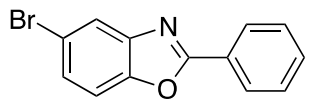

6KO-243 Fr
N
O
Cl
6ah (1H)
2.00
0.99
1.00
1.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.247
8.235
8.229
8.223
8.219
8.217
8.209
8.207
8.200
8.192
7.681
7.678
7.649
7.586
7.583
7.578
7.576
7.556
7.550
7.548
7.538
7.533
7.522
7.519
7.515
7.512
7.510
7.500
7.494
7.484
7.477
7.345
7.338
7.314
7.306
7.257
0.000


6KO-224 Fr
Cl
N
O
6ai (1H)
2.00
0.92
4.08
0.99
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.261
8.250
8.242
8.235
8.229
8.223
8.213
8.207
7.747
7.744
7.739
7.737
7.566
7.558
7.548
7.542
7.532
7.526
7.519
7.510
7.508
7.501
7.493
7.486
7.476
7.336
7.327
7.303
7.295
7.259
0.000

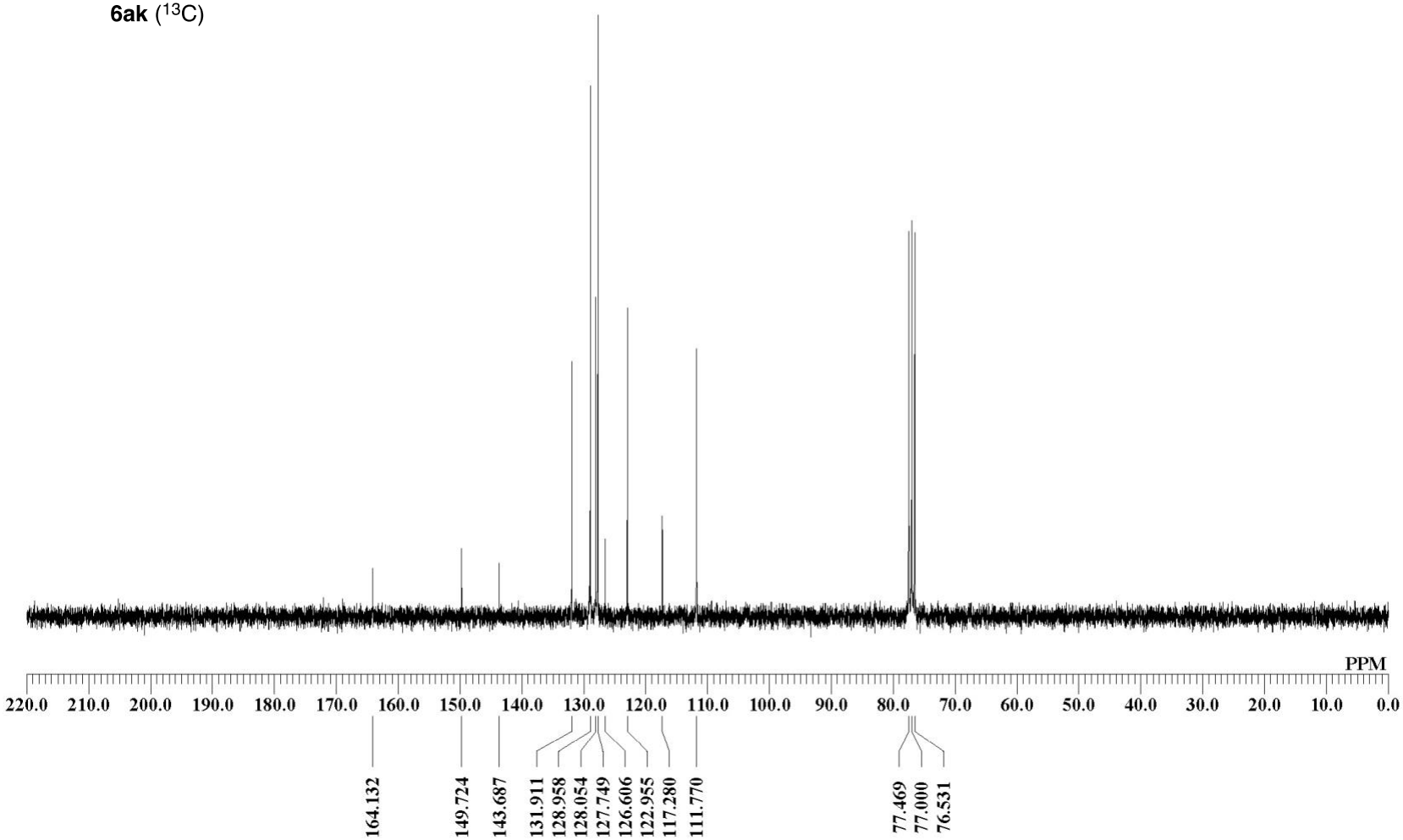

6KO-231 Fr
N
O
Br
6aj (1H)
2.00
0.22
0.95
1.04
0.13
0.13
4.49
0.24
6ab
6ab
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.242
8.236
8.228
8.225
8.223
8.217
8.206
8.200
8.195
8.184
7.747
7.742
7.641
7.638
7.609
7.562
7.558
7.554
7.544
7.538
7.528
7.522
7.516
7.504
7.498
7.490
7.483
7.459
7.453
7.259
0.000

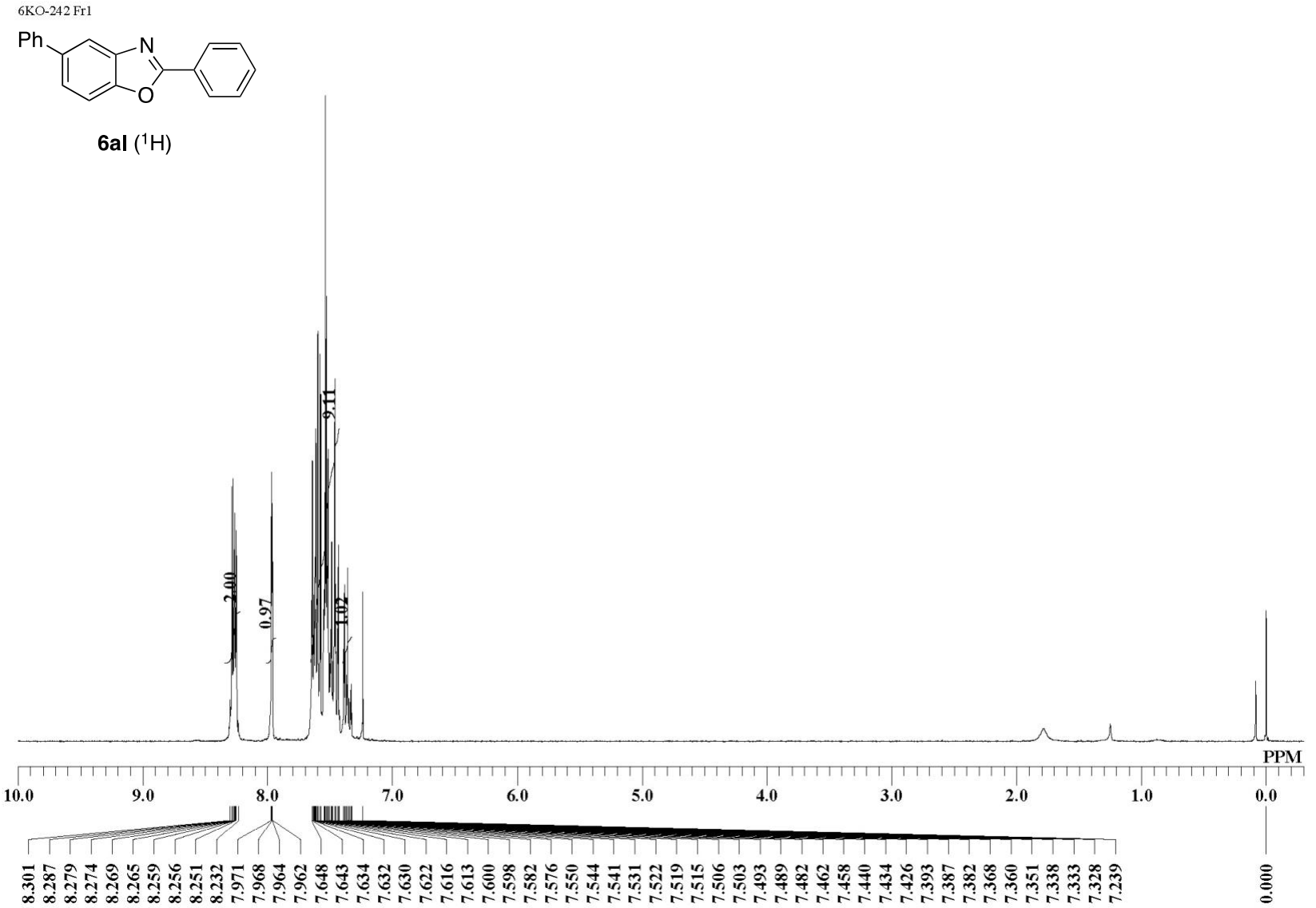

6KO-230 Fr1
Br
N
O
6ak (1H)
2.00
0.95
5.11
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.253
8.246
8.239
8.226
8.218
8.209
7.901
7.896
7.892
7.565
7.556
7.547
7.541
7.531
7.525
7.517
7.506
7.500
7.492
7.486
7.453
7.448
7.259
0.000

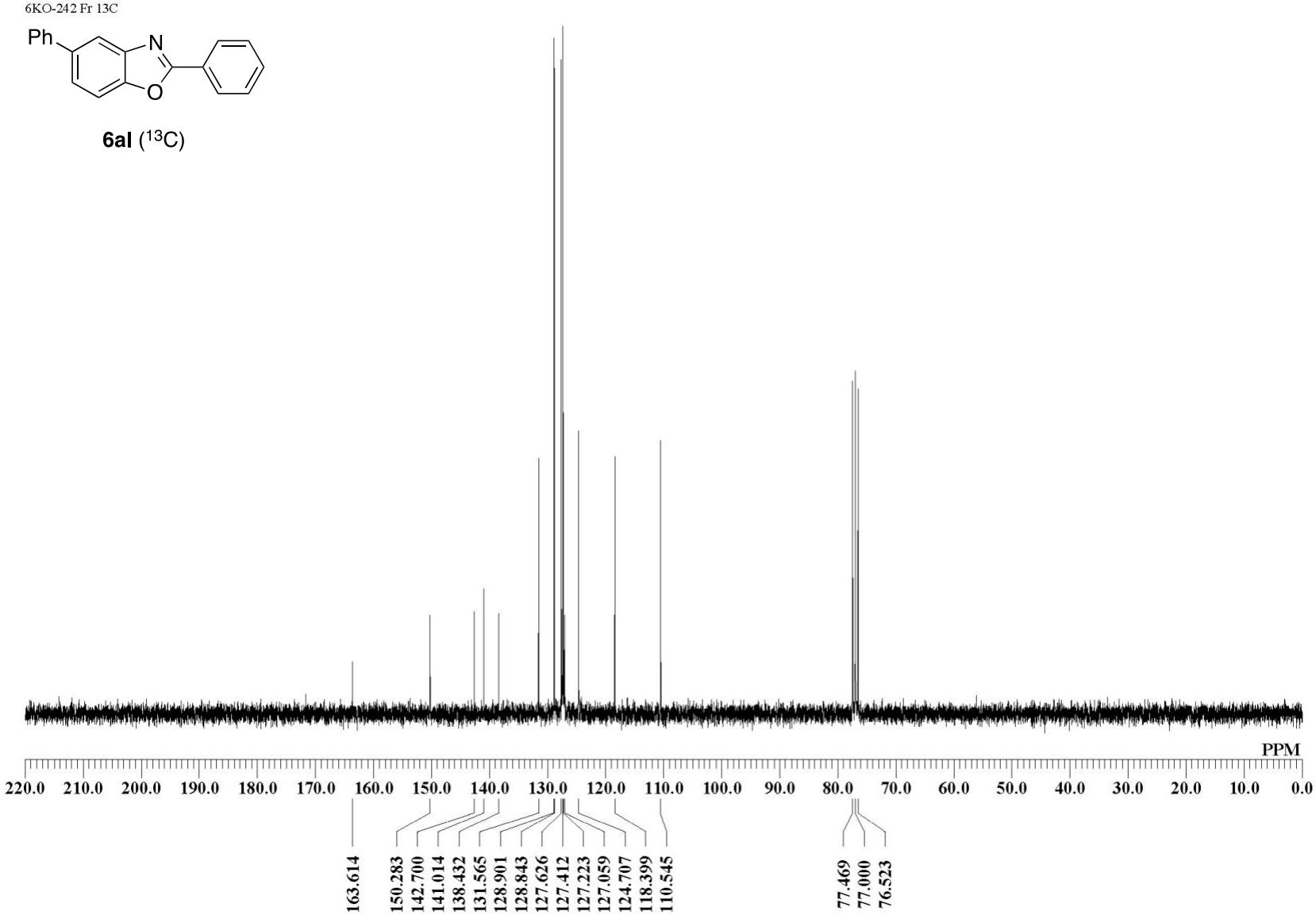
6KO-230 Fr 13C

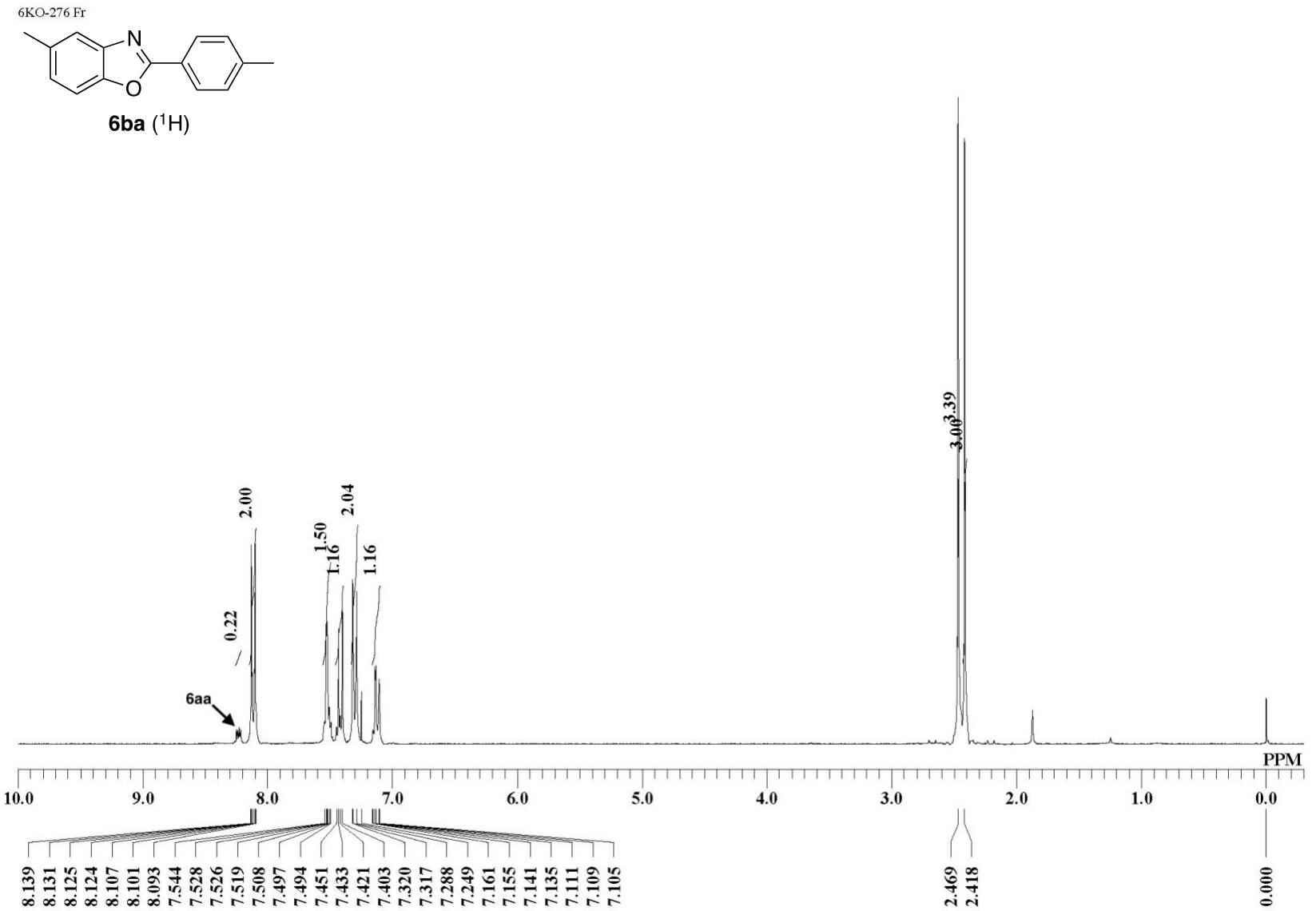


6ak (^{13}C)

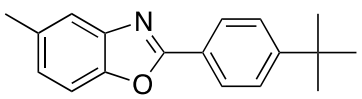



6KO-242 Fr1
Ph
N
O
6aI (1H)
2.00
0.97
9.11
1.02
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.301
8.287
8.279
8.274
8.269
8.265
8.259
8.256
8.251
8.232
7.971
7.968
7.964
7.962
7.648
7.643
7.634
7.632
7.630
7.622
7.616
7.613
7.600
7.598
7.582
7.576
7.550
7.544
7.541
7.531
7.522
7.519
7.515
7.506
7.503
7.493
7.489
7.482
7.462
7.458
7.440
7.434
7.426
7.393
7.387
7.382
7.368
7.360
7.351
7.338
7.333
7.328
7.239
0.000

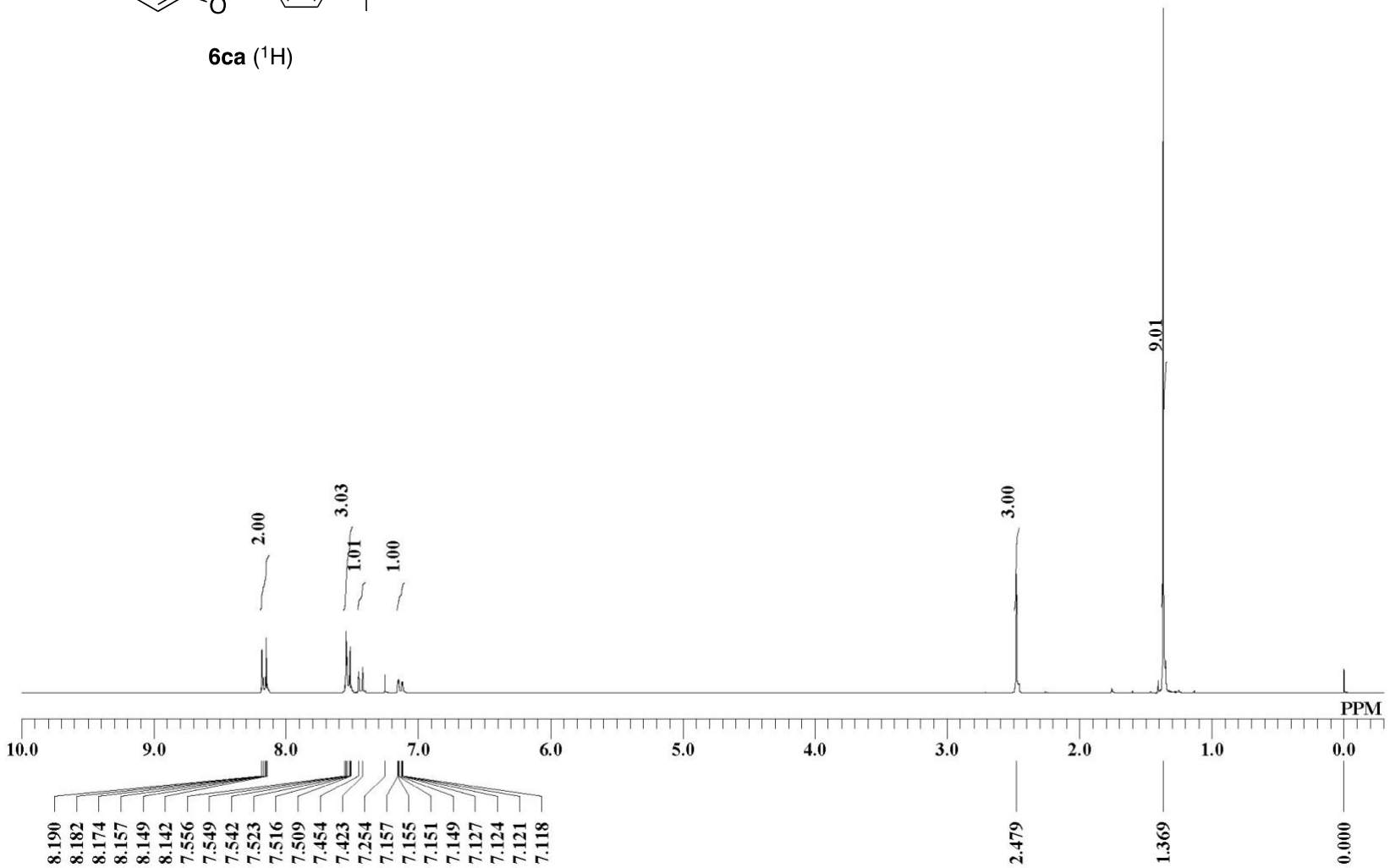

6KO-242 Fr 13C
Ph
N
O
6aI (^{13}C)
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
163.614
150.283
142.700
141.014
138.432
131.565
128.901
128.843
127.626
127.412
127.223
127.059
124.707
118.399
110.545
77.469
77.000
76.523


6KO-276 Fr
6ba (1H)
6aa
0.22
2.00
1.50
1.16
2.04
1.16
3.39
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.139
8.131
8.125
8.124
8.107
8.101
8.093
7.544
7.528
7.526
7.519
7.508
7.497
7.494
7.451
7.433
7.421
7.403
7.320
7.317
7.288
7.249
7.161
7.155
7.141
7.135
7.111
7.109
7.105
2.469
2.418
0.000

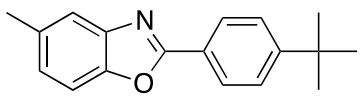
6KO-272 Fr



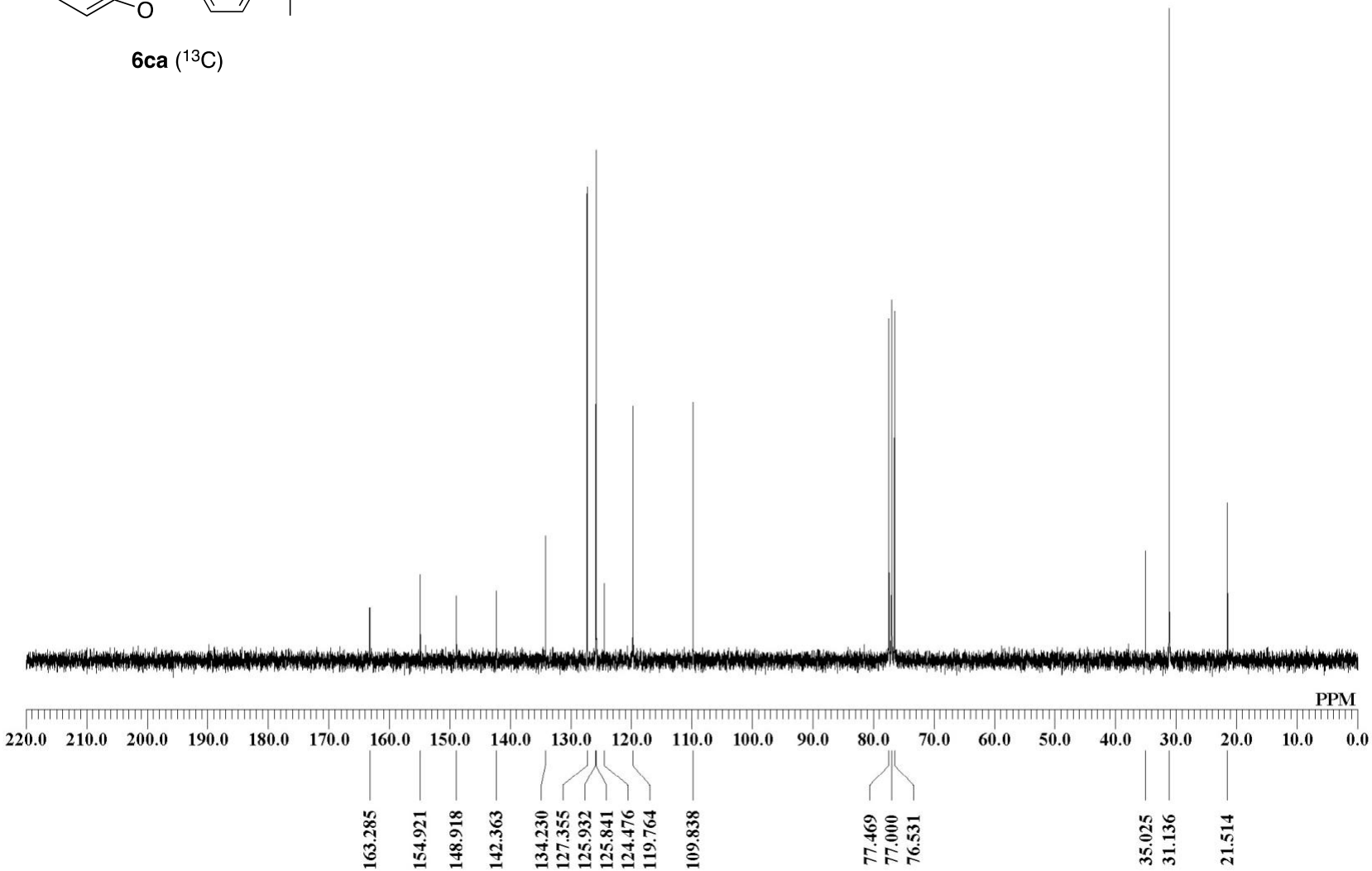
6ca (^{1}H)



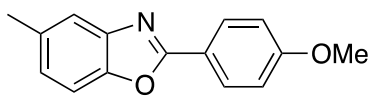
6KO-272 Fr 13C



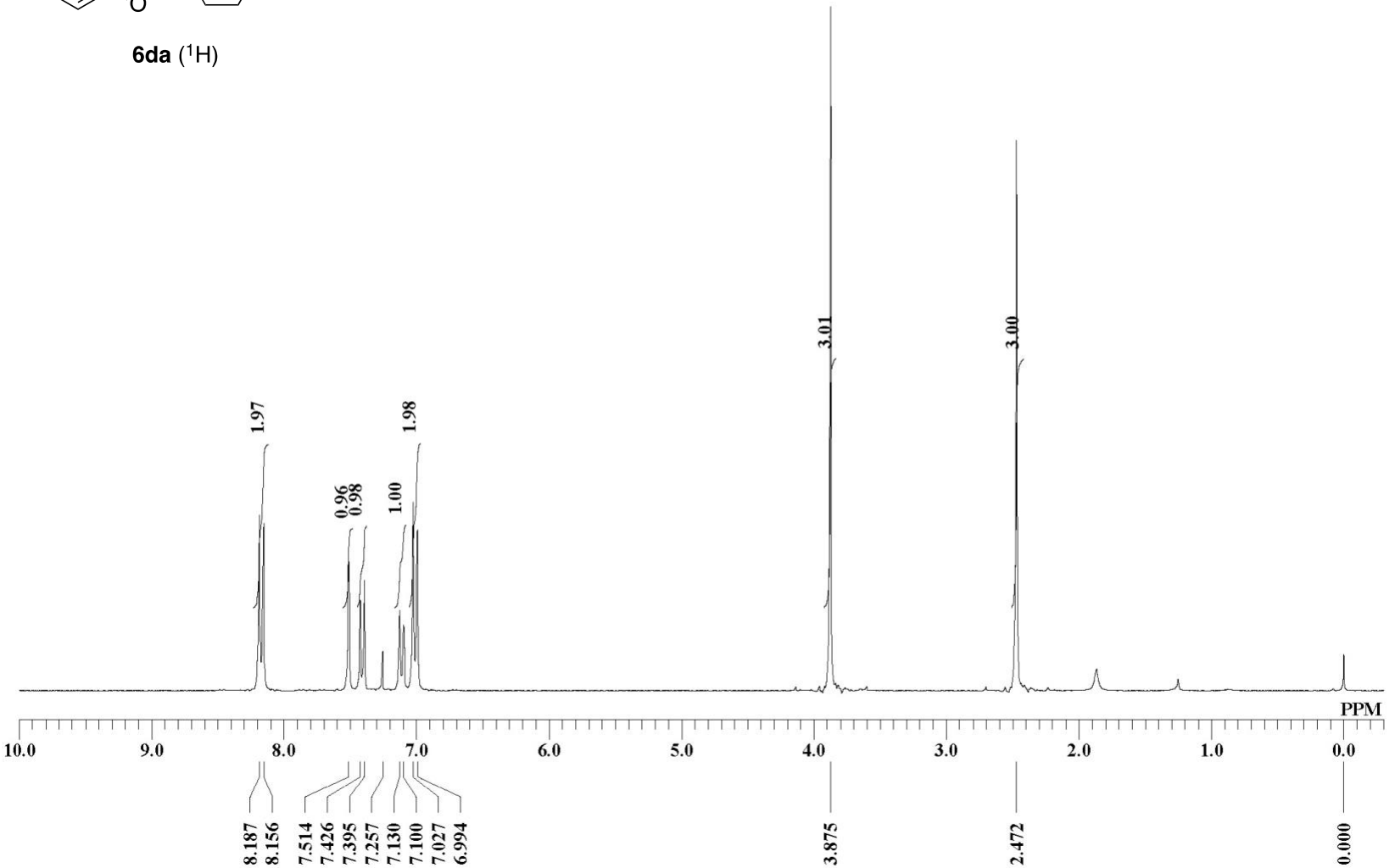
6ca (^{13}C)



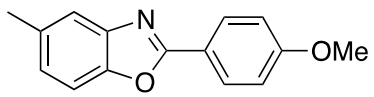
6KO-256 Fr



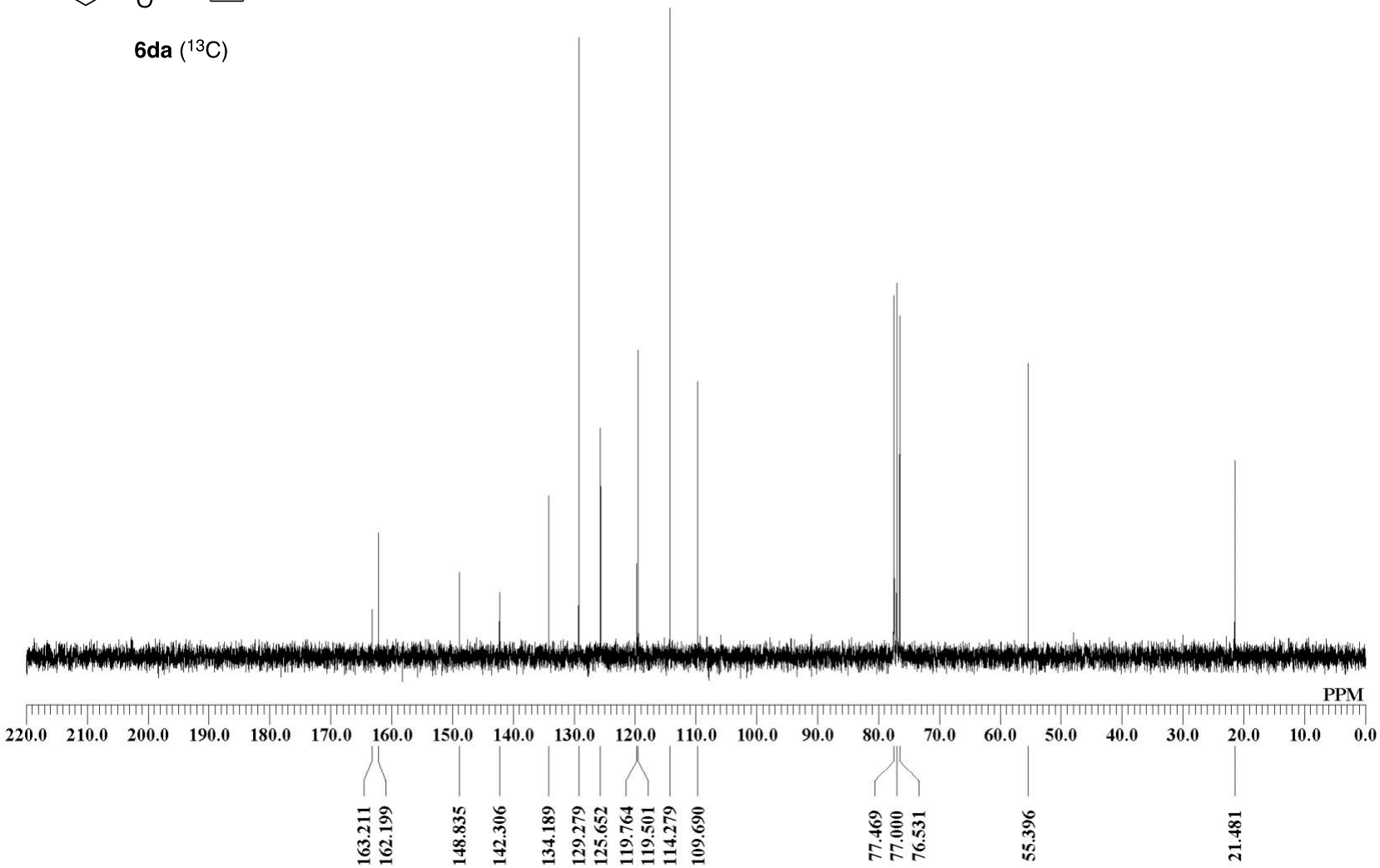
6da (^{1}H)

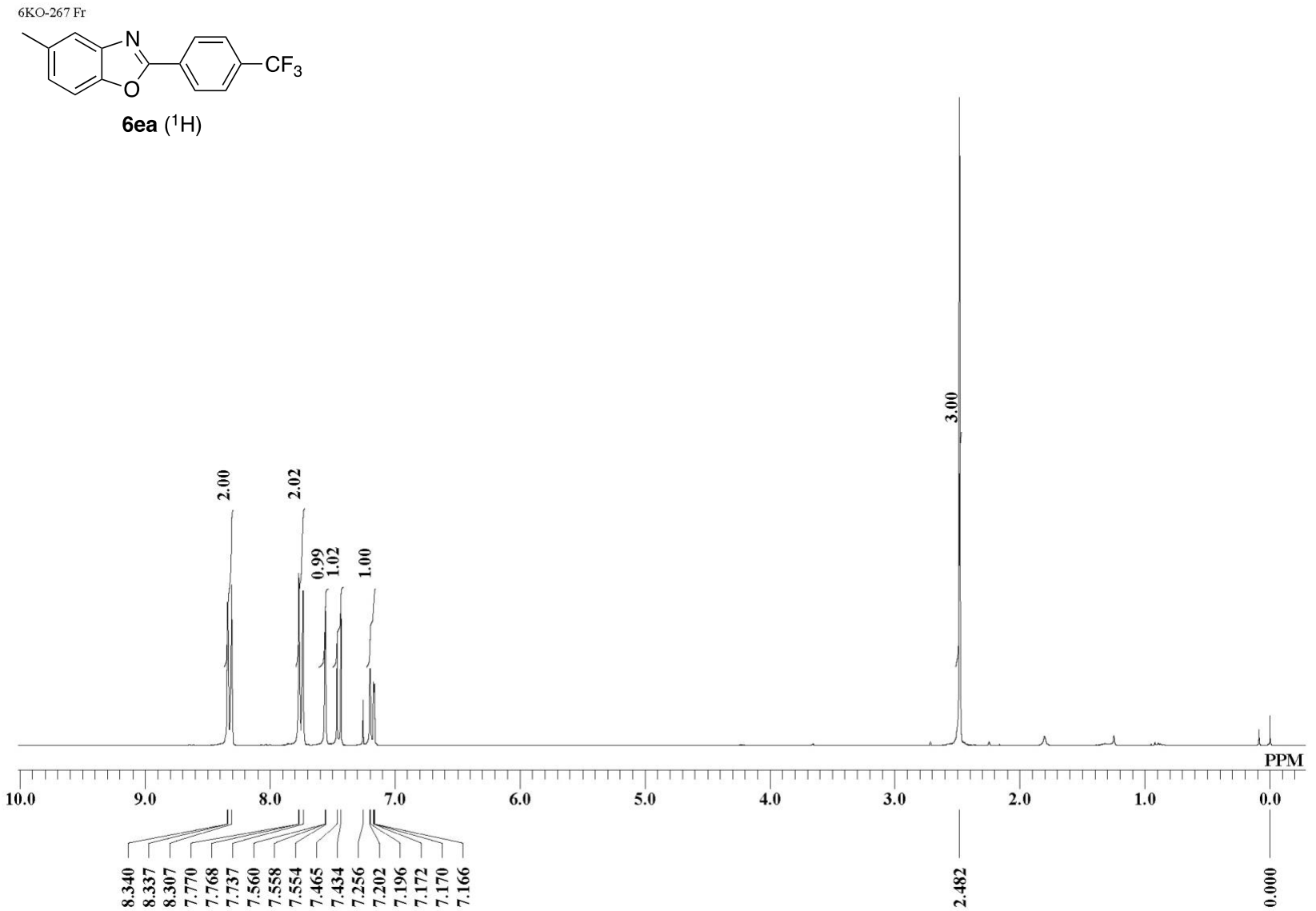


6KO-256 Fr 13C3

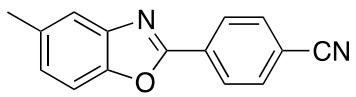


6da (^{13}C)

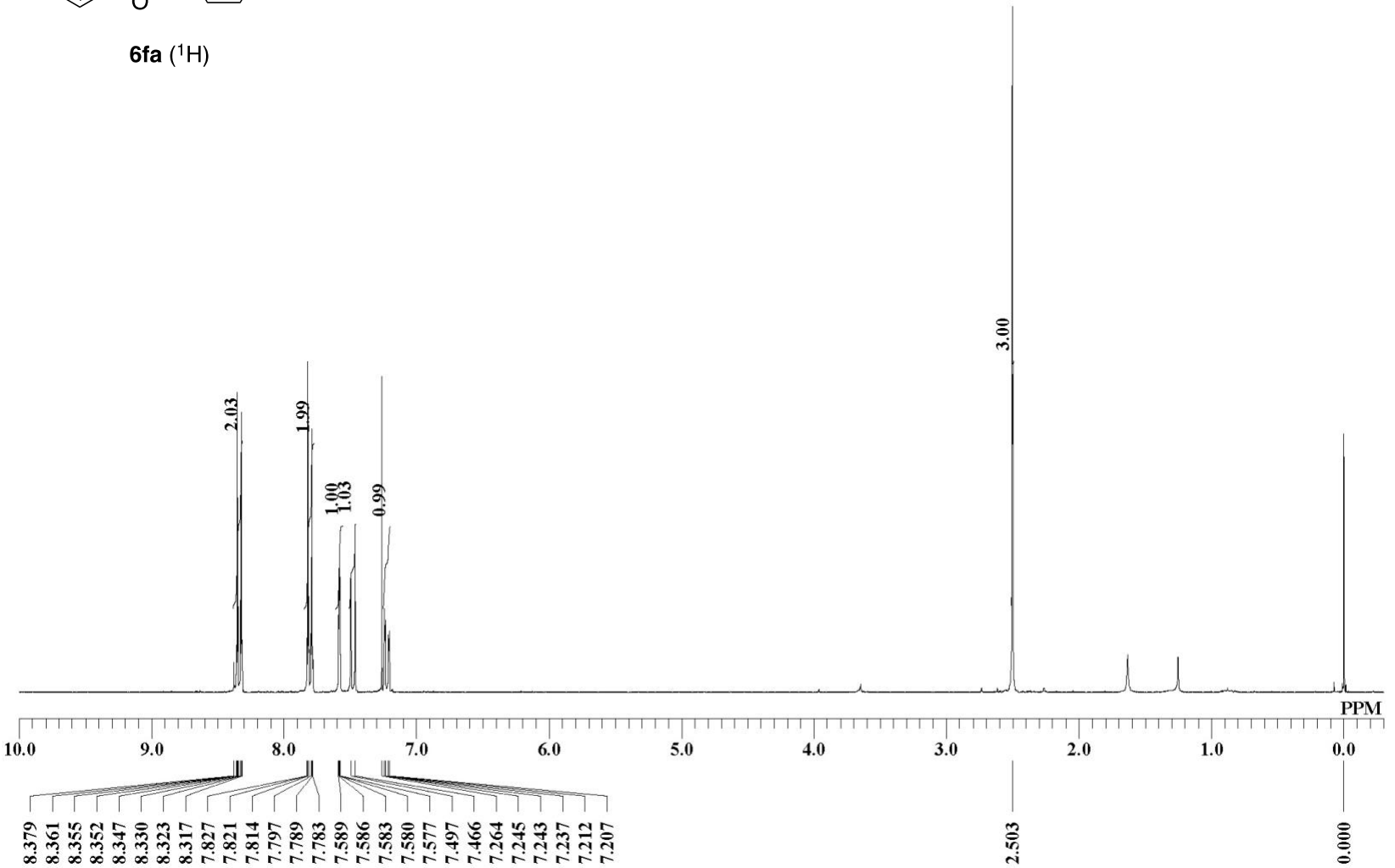



6KO-267 Fr
N
O
CF3
6ea (1H)
2.00
2.02
0.99
1.02
1.00
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.340
8.337
8.307
7.770
7.768
7.737
7.560
7.558
7.554
7.465
7.434
7.256
7.202
7.196
7.172
7.170
7.166
2.482
0.000

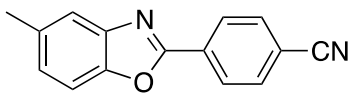
6KO-270 Fr



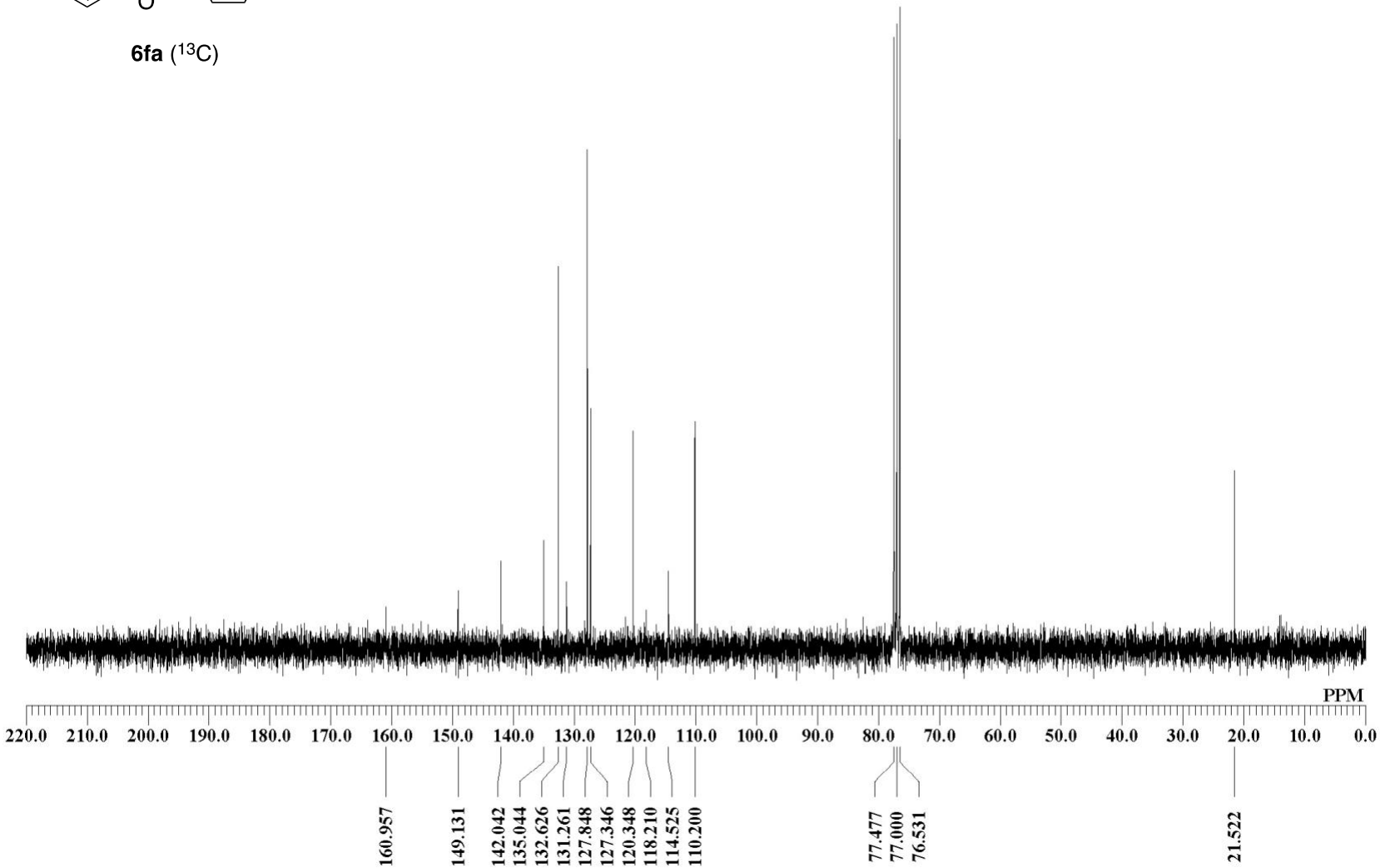
6fa (^{1}H)



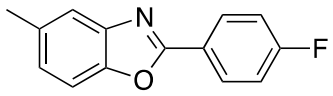
6KO-270 Fr 13C



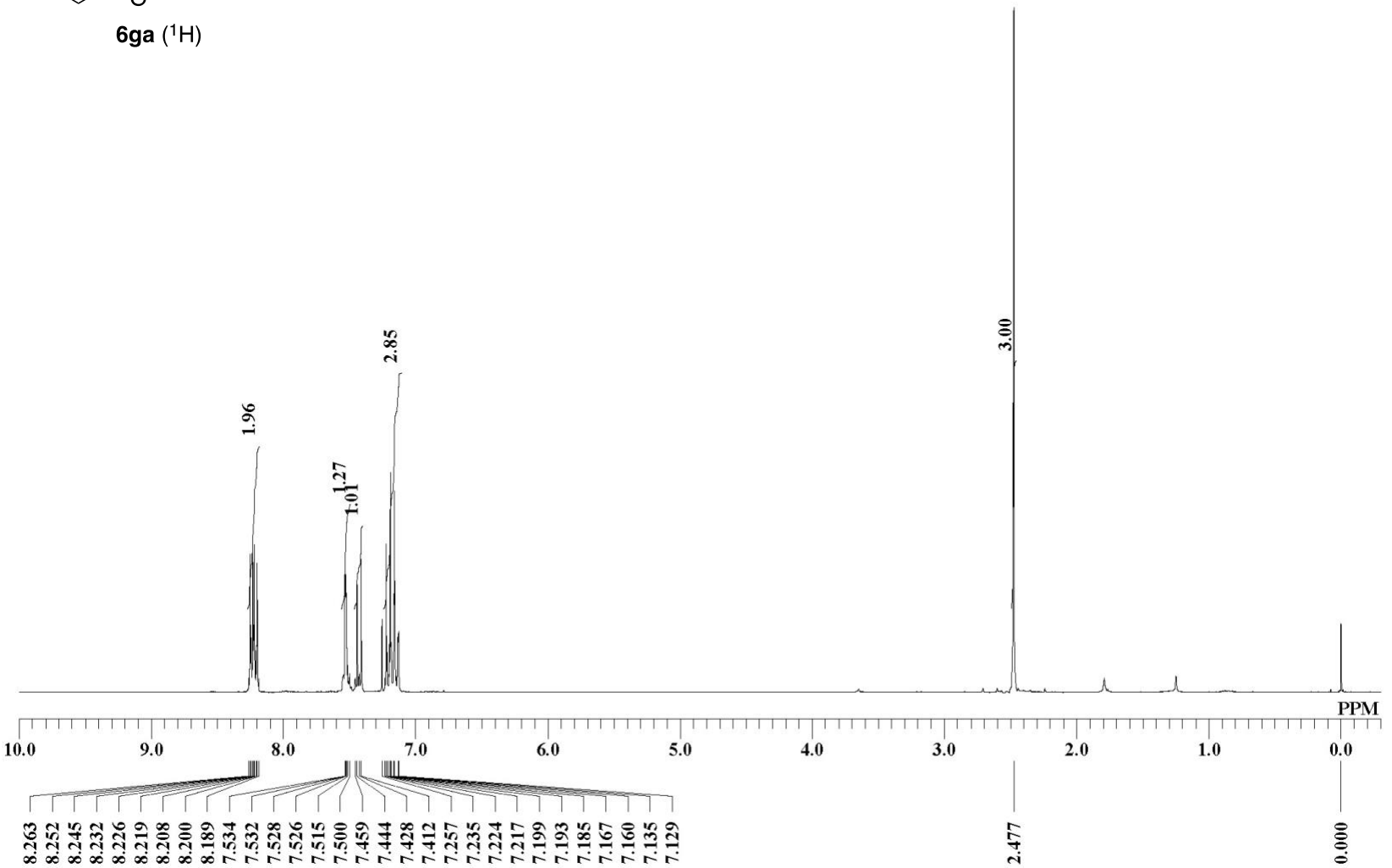
6fa (^{13}C)

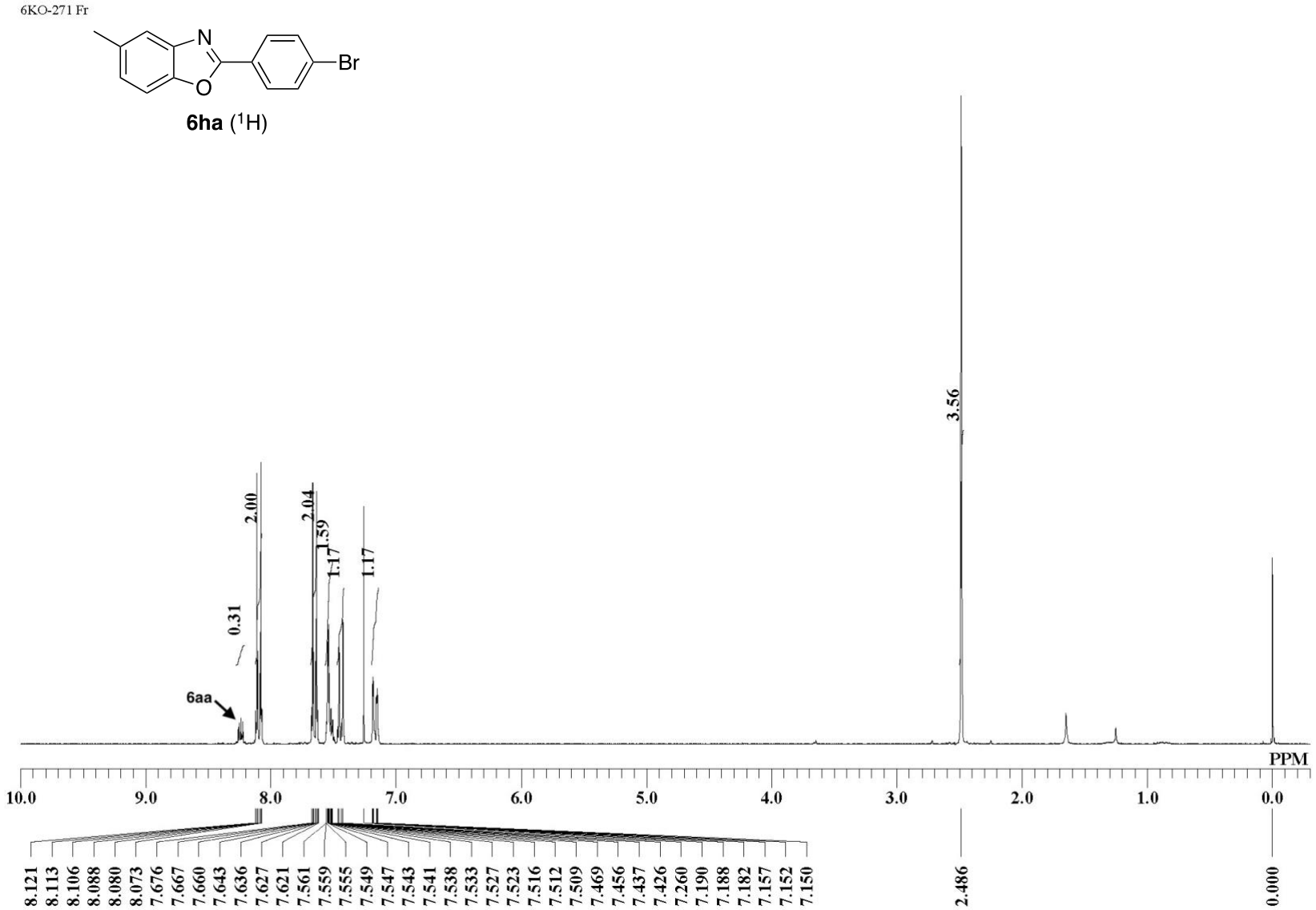


6KO-269 Fr

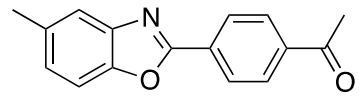


6ga (^{1}H)

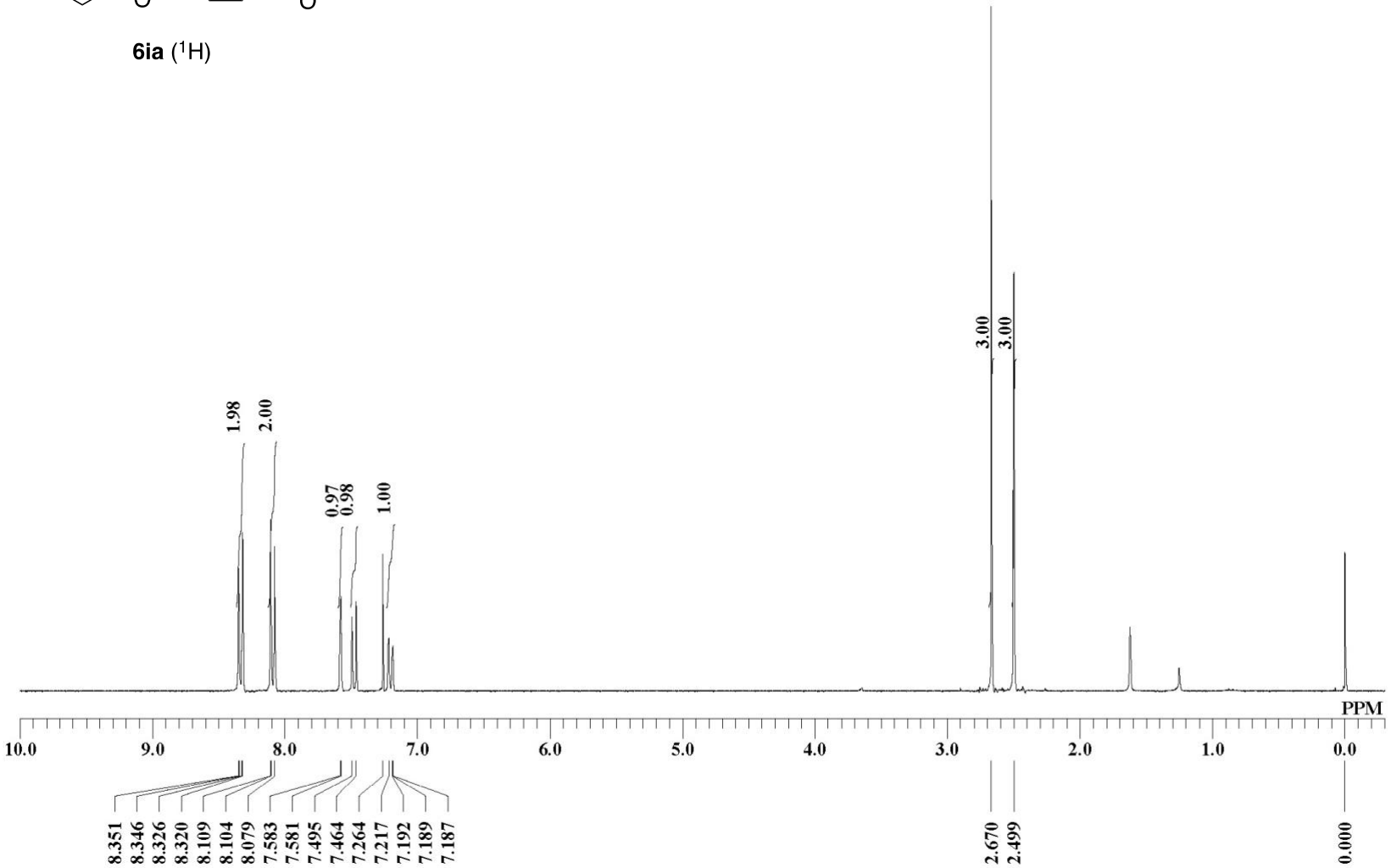



6KO-271 Fr
N
O
Br
6ha (1H)
3.56
2.00
2.04
1.59
1.17
1.17
0.31
6aa
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.121
8.113
8.106
8.088
8.080
8.073
7.676
7.667
7.660
7.643
7.636
7.627
7.621
7.561
7.559
7.555
7.549
7.547
7.543
7.541
7.538
7.533
7.527
7.523
7.516
7.512
7.509
7.469
7.456
7.437
7.426
7.260
7.190
7.188
7.182
7.157
7.152
7.150
2.486
0.000

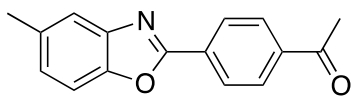
6KO-259 Fr3



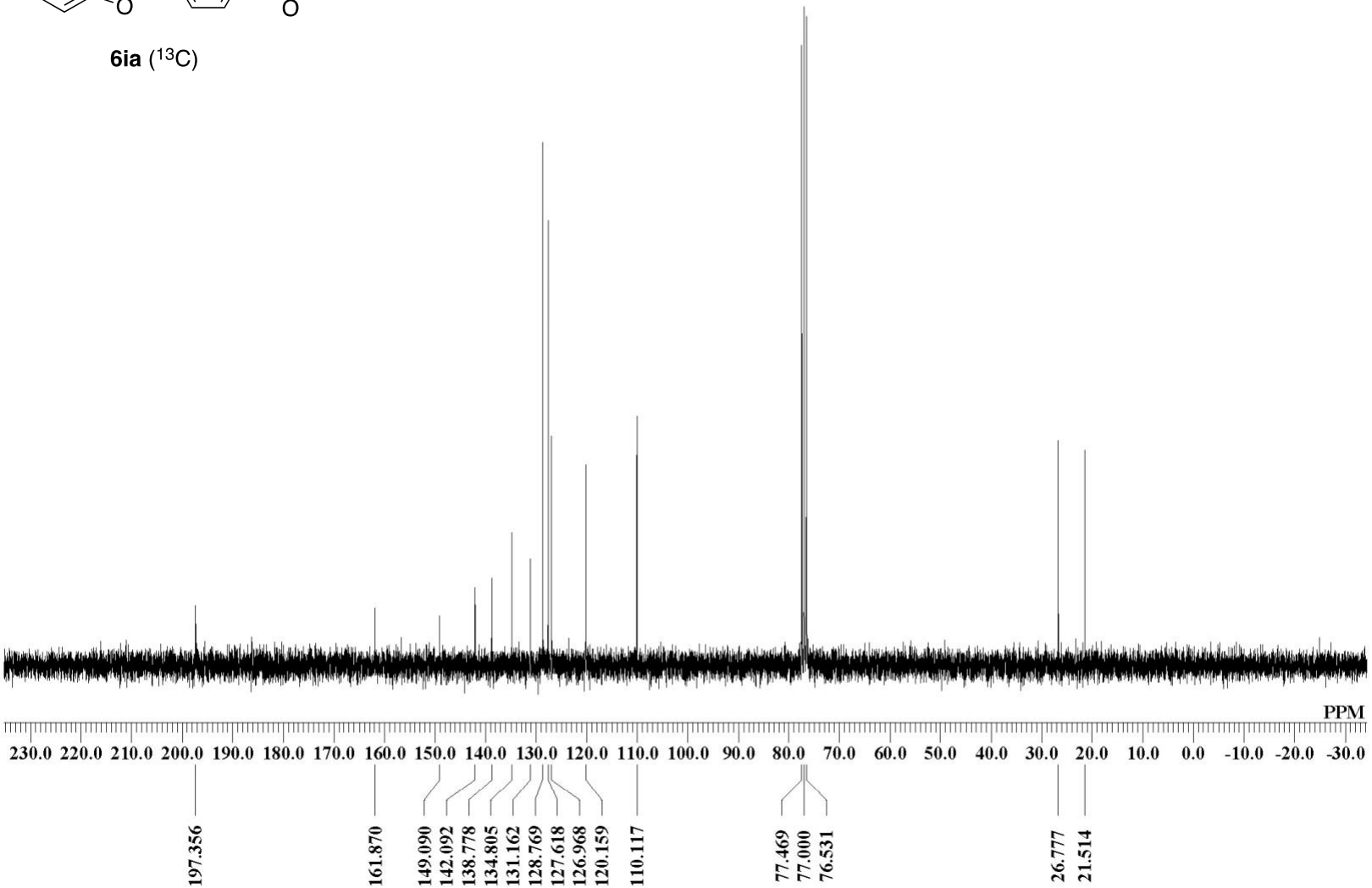
6ia (^{1}H)

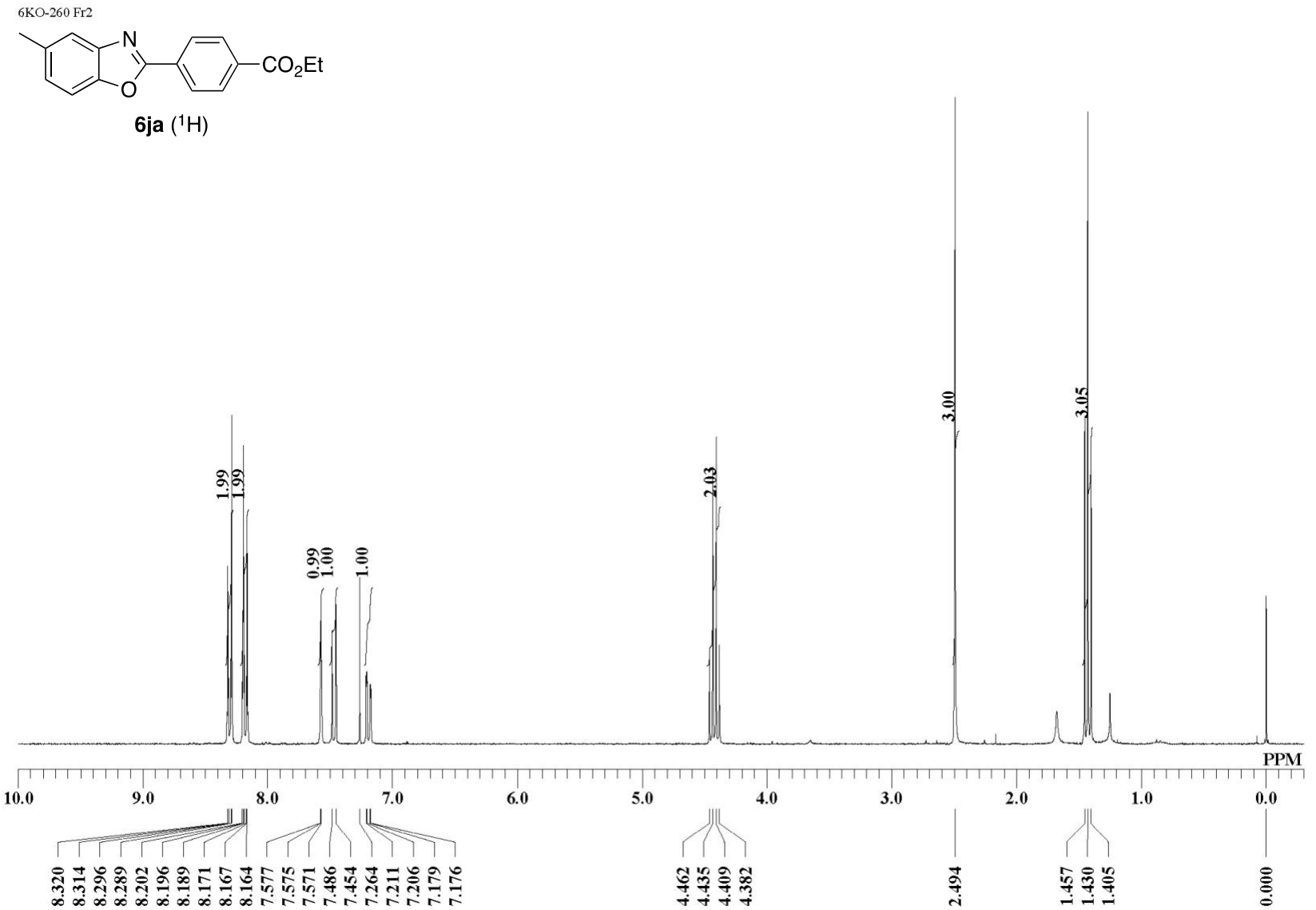


6KO-259 Fr 13C

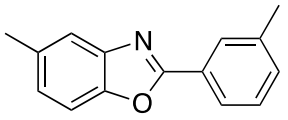


6ia (^{13}C)

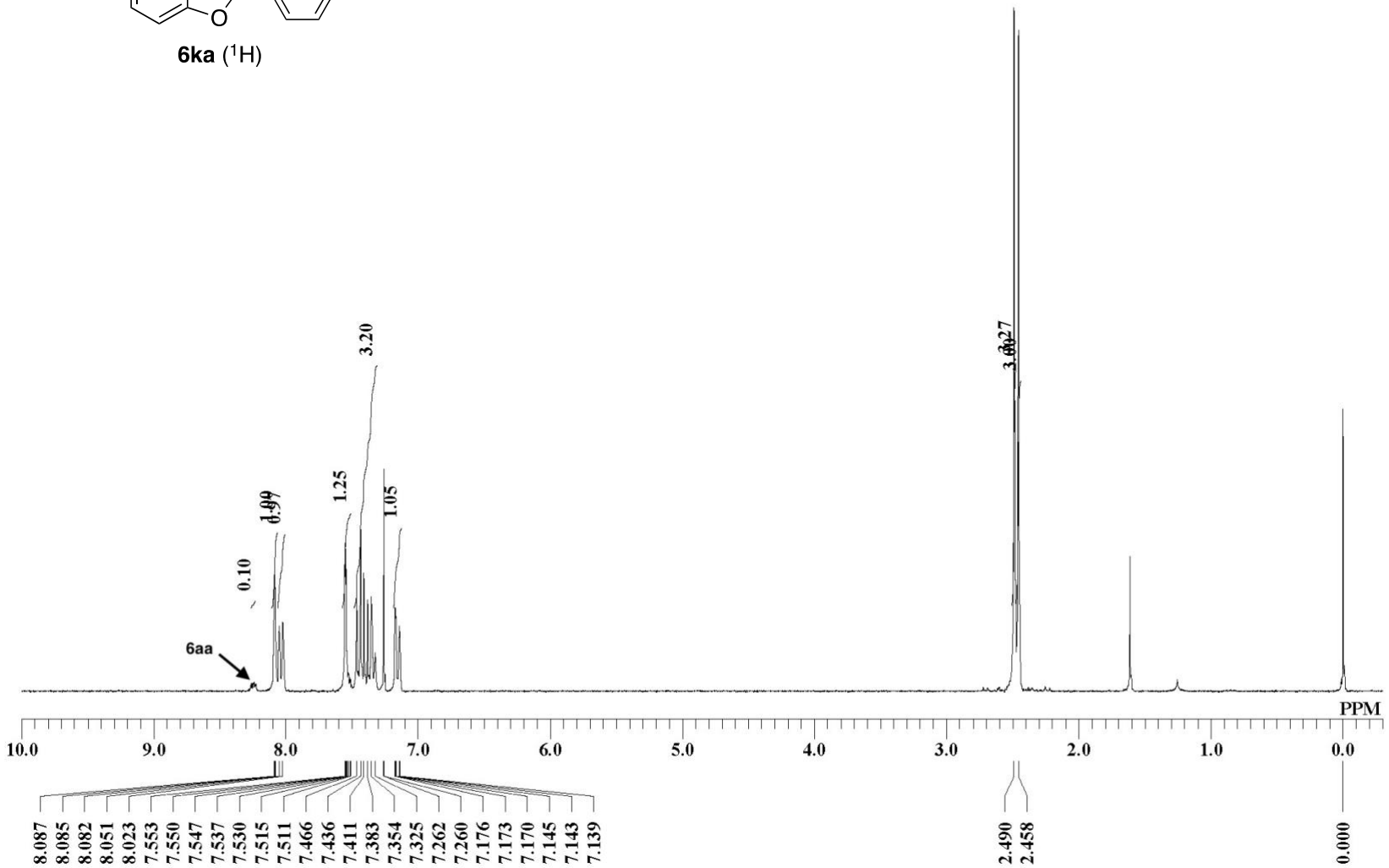



6KO-260 Fr2
N
O
CO2Et
6ja (1H)
1.99
1.99
0.99
1.00
1.00
2.03
3.00
3.05
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.320
8.314
8.296
8.289
8.202
8.196
8.189
8.171
8.167
8.164
7.577
7.575
7.571
7.486
7.454
7.264
7.211
7.206
7.179
7.176
4.462
4.435
4.409
4.382
2.494
1.457
1.430
1.405
0.000

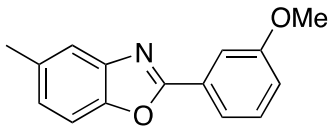
6KO-277 Fr



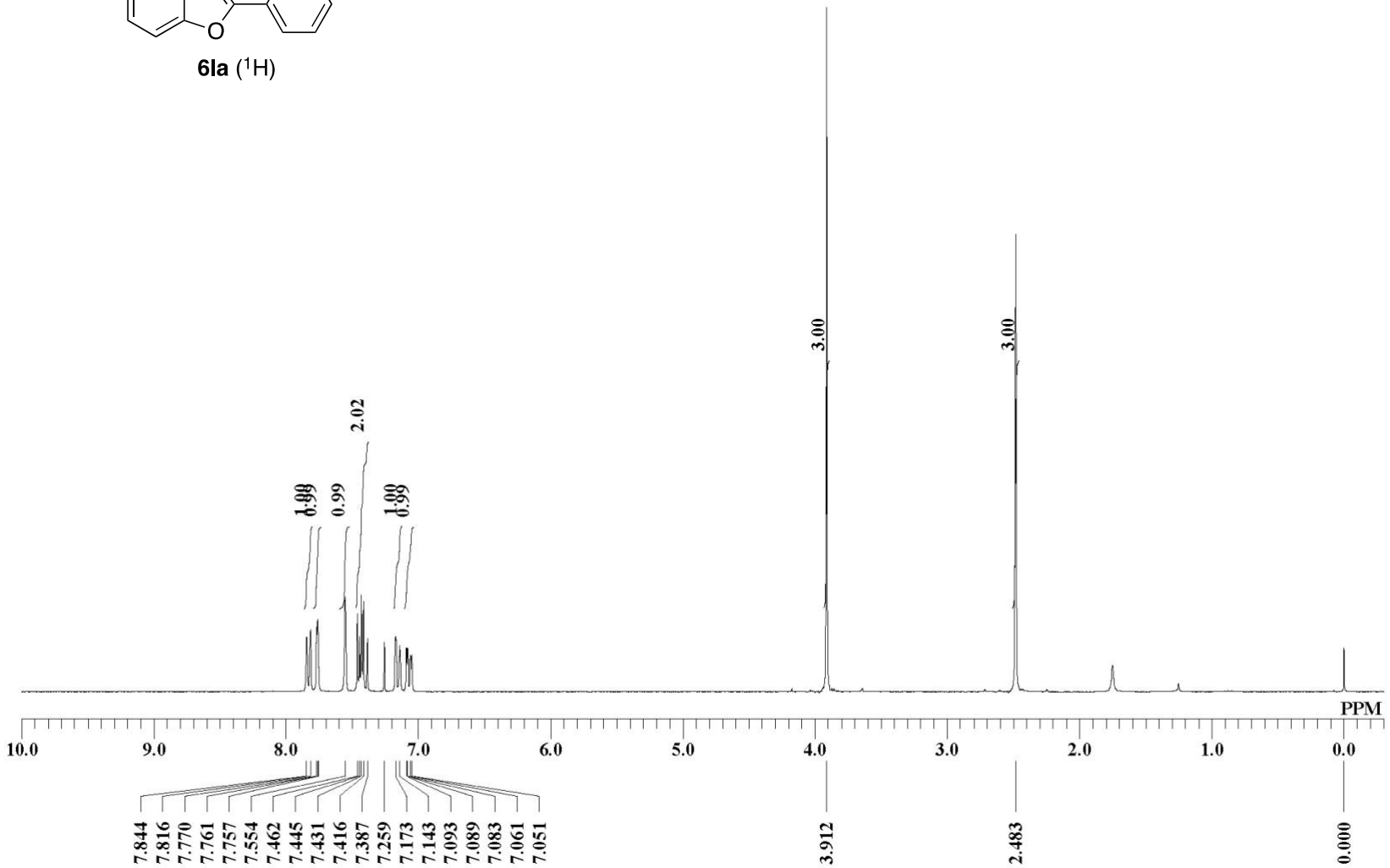
6ka (^{1}H)



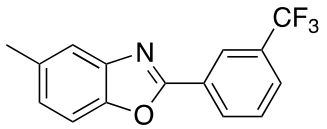
6KO-257 Fr



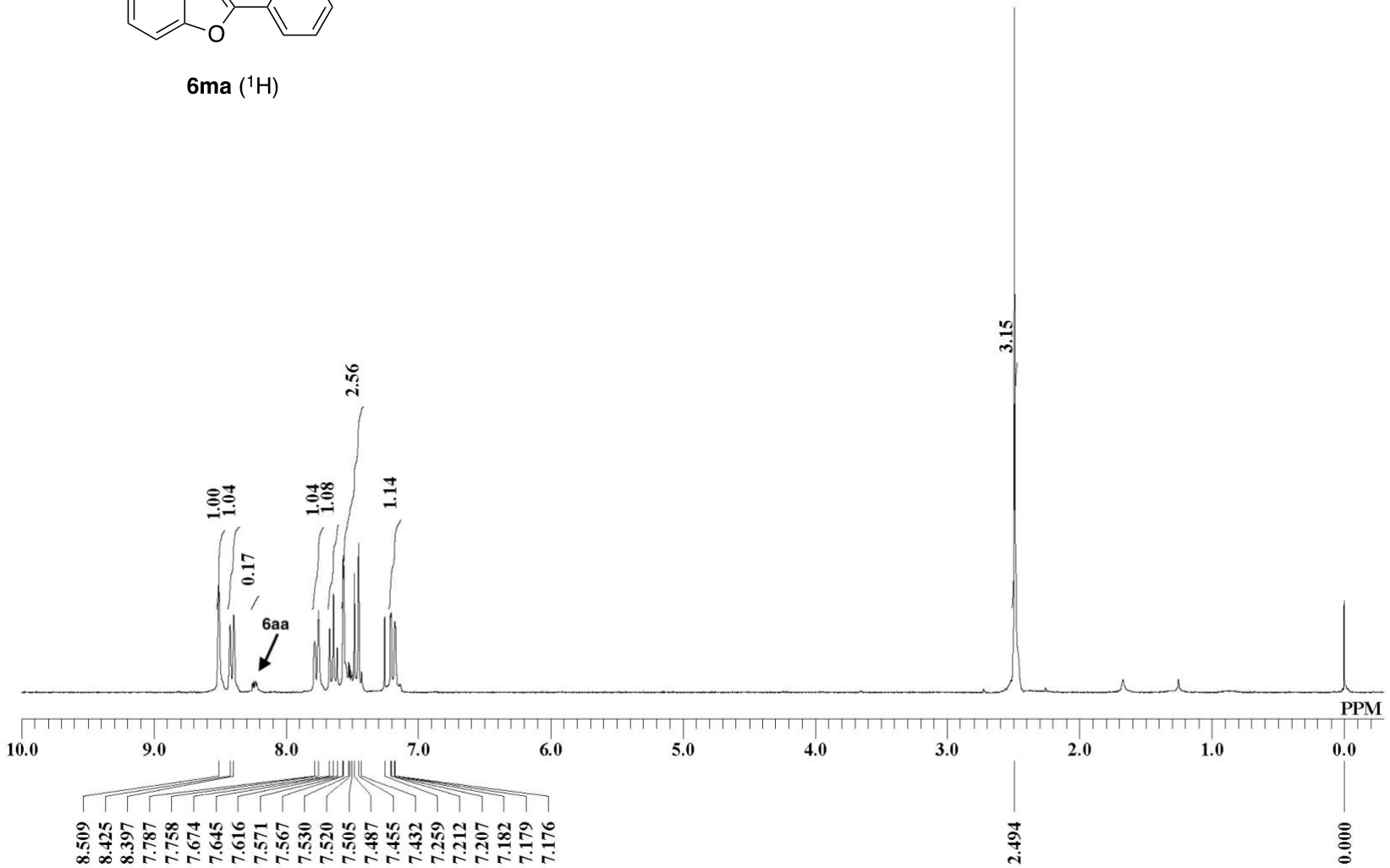
6la (^{1}H)



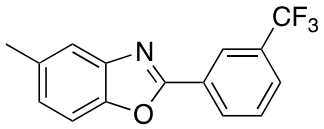
6KO-268 Fr



6ma (^{1}H)

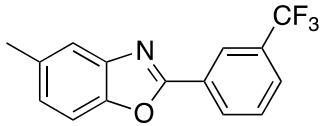


6KO-268 Fr 13C 500MHz

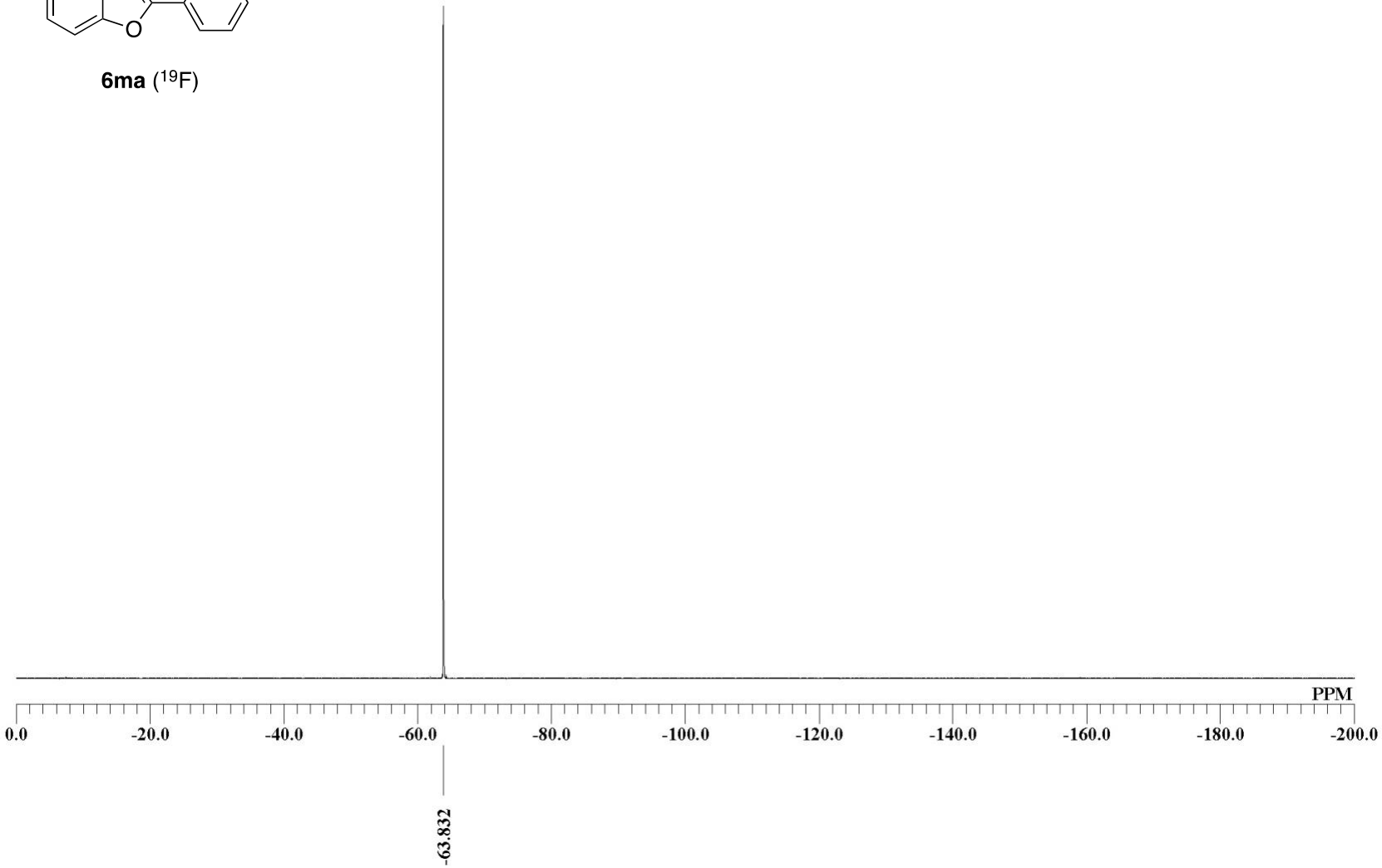


6ma (^{13}C)

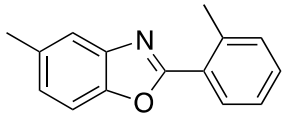
6KO-268 Fr 19F



6ma (^{19}F)

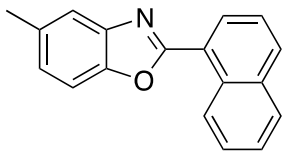


6KO-278 Fr

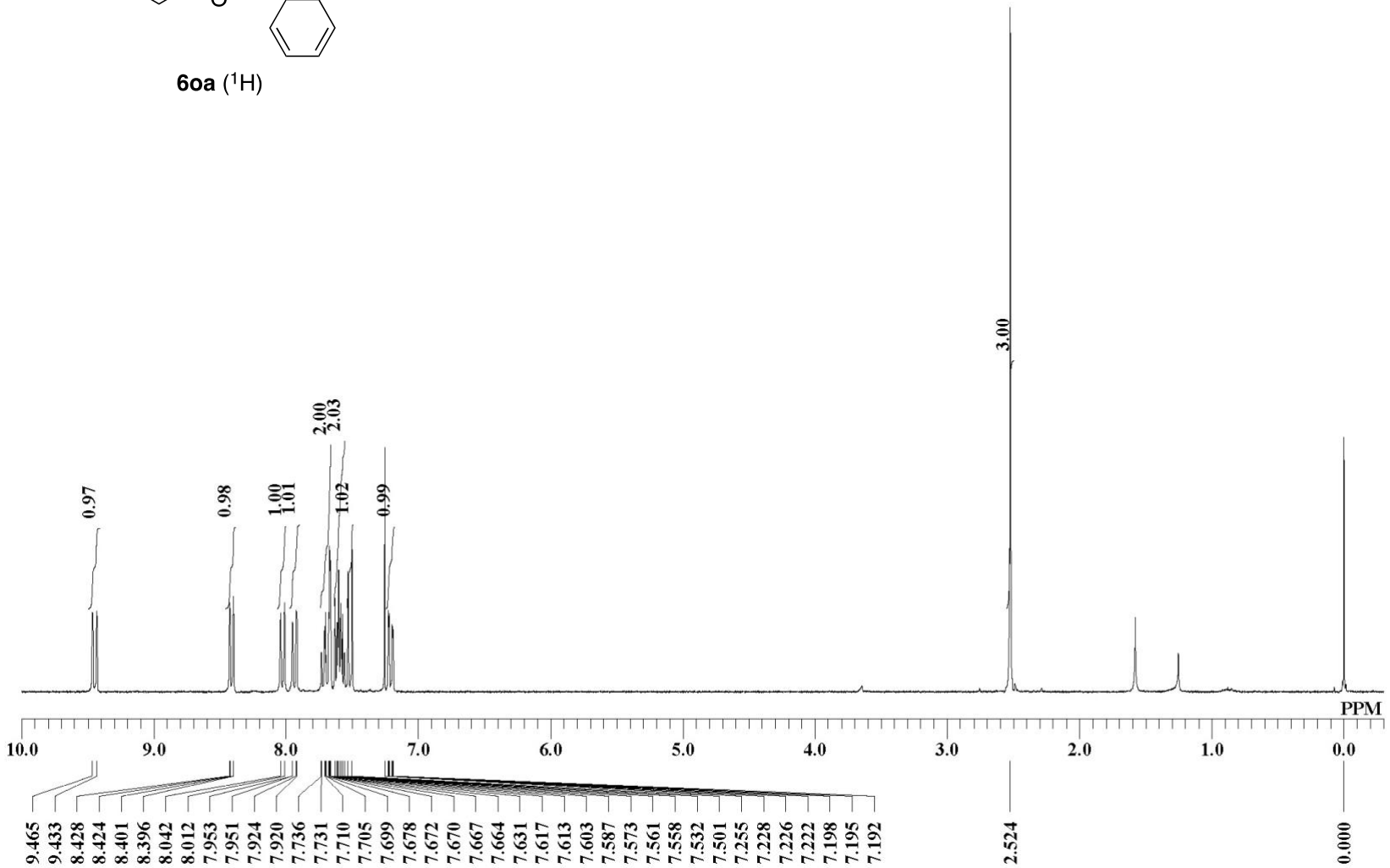


6na (^{1}H)

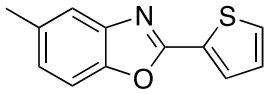
6KO-275 Fr



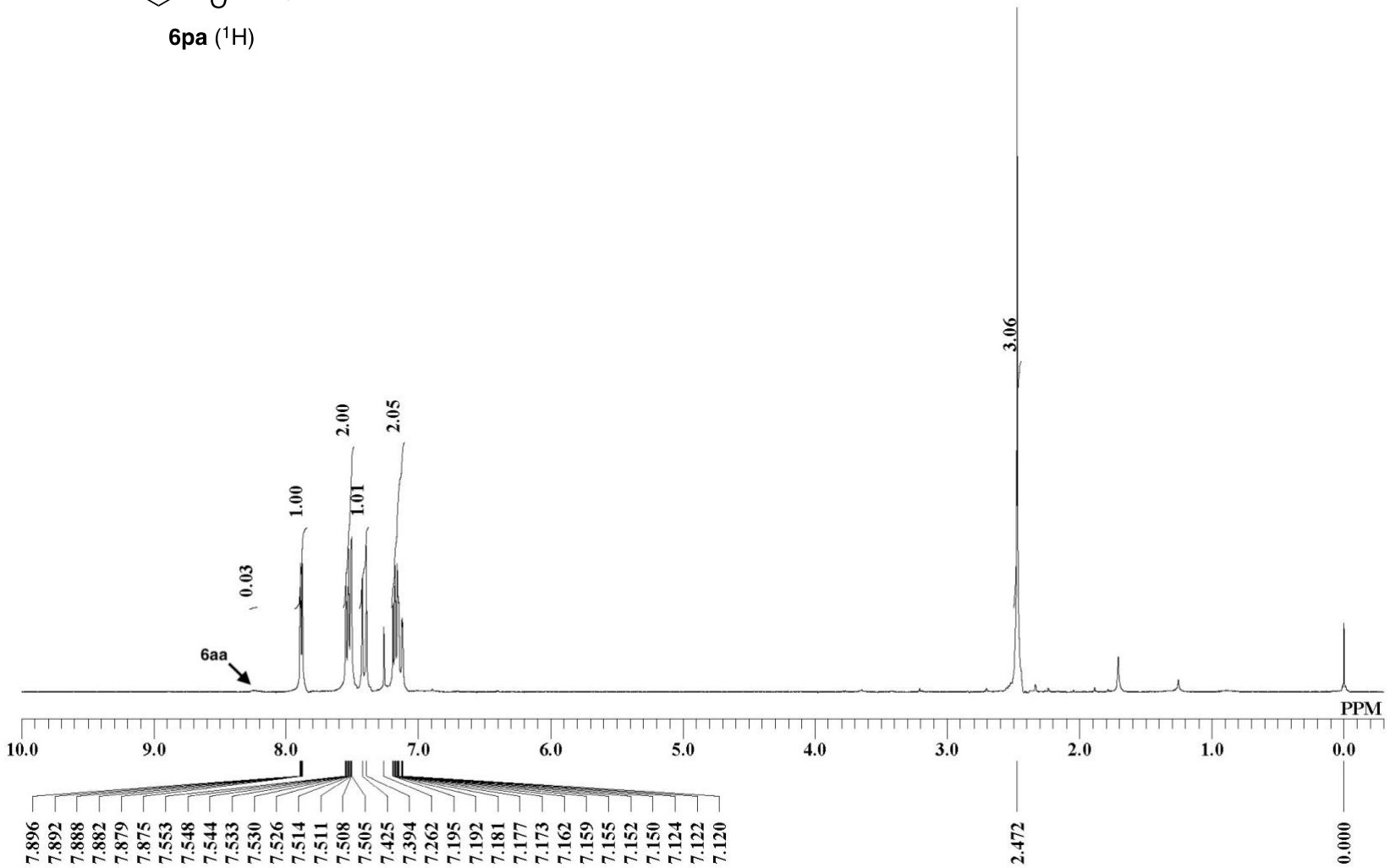
6oa (^{1}H)



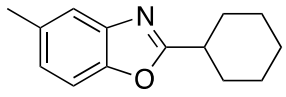
6KO-274 Fr



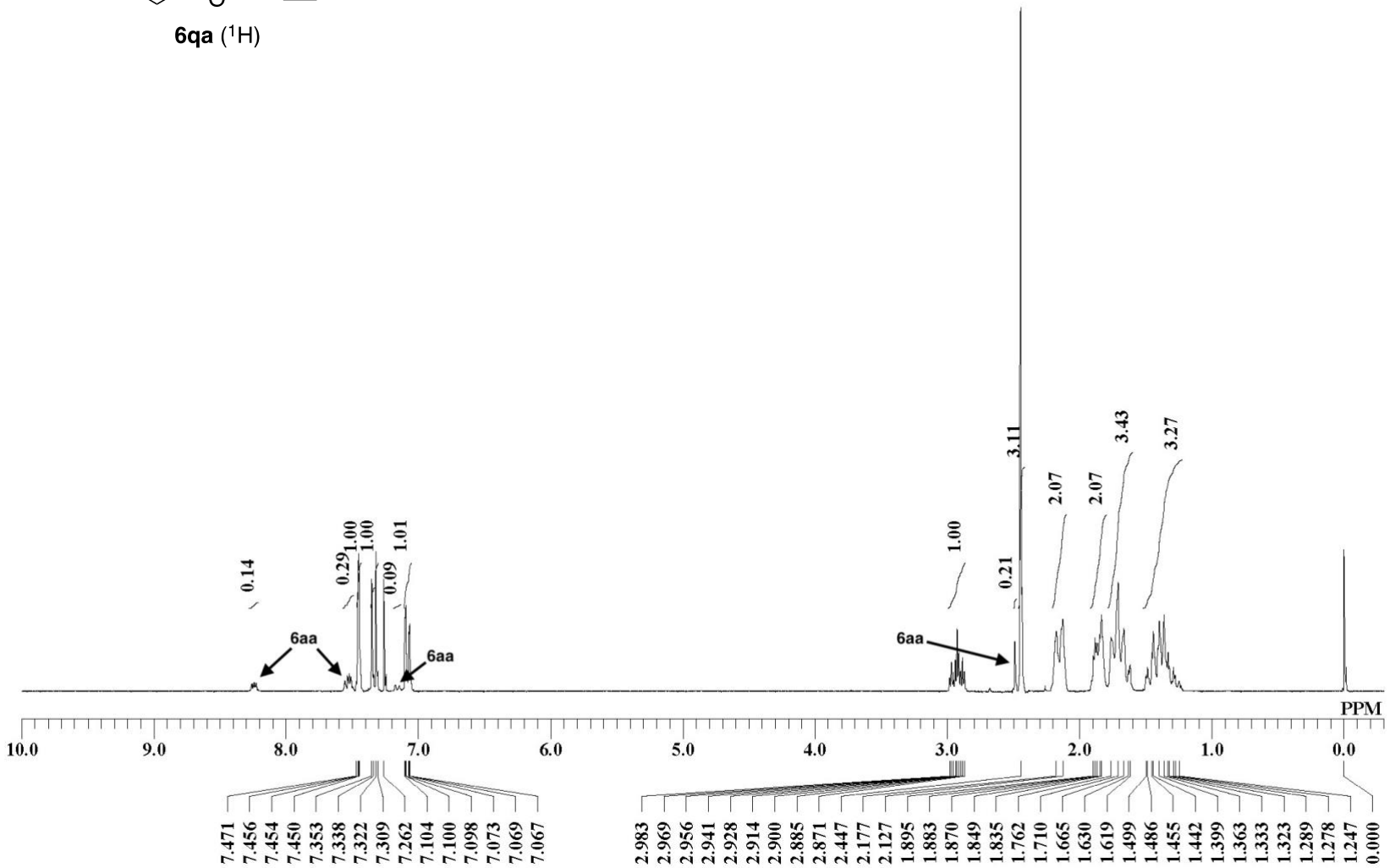
6pa (^{1}H)



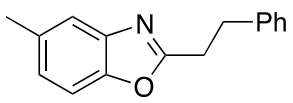
6KO-266 Fr



6qa (^{1}H)

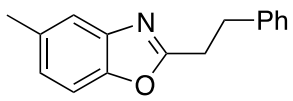


6KO-261 Fr2

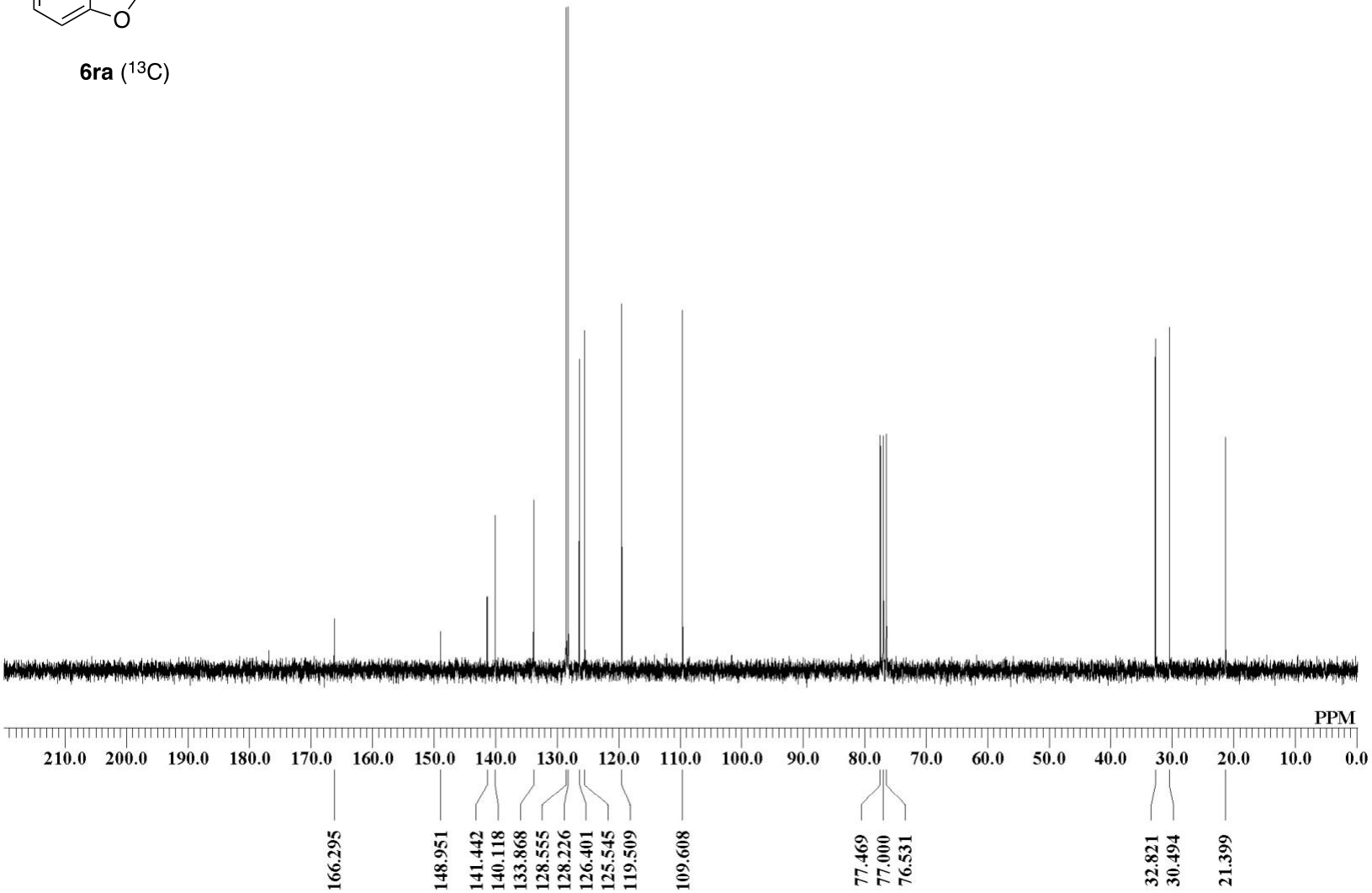


6ra (^{1}H)

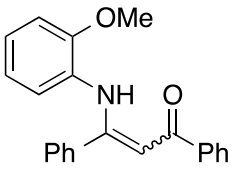
6KO-261 Fr 13C



6ra (^{13}C)

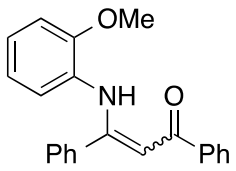


6KO-305 Fr2



7 (^{1}H)

6KO-305 Fr 13C



7 (^{13}C)