Supporting Information

Lewis-Base-Catalysed Selective Reductions of Ynones with Mild Hydride Donor

Fritz Schömberg, You Zi, Ivan Vilotijevic

Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich Schiller University Jena, Humboldtstr. 10, 07743 Jena, Germany

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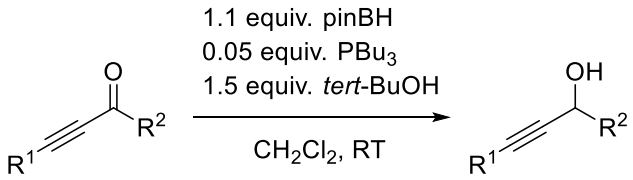
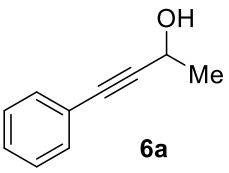
General remarks

Commercially available reagents were used without further purifications with the following exceptions: acetaldehyde, isobutyrylchloride and pivaloylchloride were distilled according to literature procedure,[1] pinacolborane was distilled at 36° C and 56 mbar. Anhydrous dichloromethane was obtained by distillation over calcium hydride under a positive pressure of nitrogen. Anhydrous diethyl ether and tetrahydrofuran were distilled over sodium/benzophenone under a positive pressure of nitrogen. All reactions were carried out using standard Schlenk techniques under a positive pressure of argon or nitrogen. ^{1}H- and ^{13}C NMR-spectra were recorded at 250/63 MHz or 300/75 MHz at 295 K in $CDCl_3$ or CD_3OD on a Bruker Avance I 250 spectrometer and Bruker Fourier 300 system. Chemical shifts (δ) are expressed in parts per million (ppm) with respect to the solvent signal (^{13}C NMR, δC: $CDCl_3$ 77.16, MeOH 49.00 ppm) or the residual nondeuterated solvent signal (^{1}H NMR, δH: $CHCl_3$ 7.26, MeOH 3.31, DMSO 2.50 ppm), respectively. Melting points were determined with a Büchi B-450 device. IR spectra were recorded on a IRAffinity-1 (Shimadzu) spectrometer in ATR modus. Column chromatography was performed using silica gel 60 (40−63 μm) from Macherey-Nagel. Petroleum ether used for purification was light petroleum (bp. 35−70 °C).

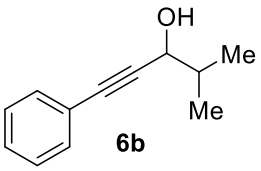
Phosphine catalyzed 1,2-reduction of ynones to propargylic alcohols



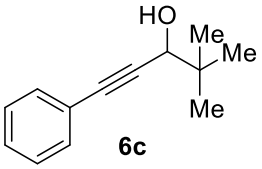
General procedure for the phosphine catalyzed 1,2-reduction of ynone. *For R^1= Ph and R^2= Me.* Ynone **6** (144 mg, 1 mmol) was dissolved in DCM (2.5 mL, 0.4 M) followed by addition of *tert*-BuOH (0.141 mL, 1.5 mmol) and pinBH (0.194 mL, 1.1 mmol) at room temperature. After the addition of tributyl phosphine (13 µL, 0.05 mmol) development of gas was observed. After TLC analysis (10% ethyl acetate in petroleum ether) confirmed full consumption of starting material (10 minutes), reaction mixture was quenched by addition of water (5 mL). The resulting layers were separated, and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 10% ethyl acetate in petroleum ether) to yield the corresponding propargylic alcohol **7** as collorless liquid (132 mg, 90%).



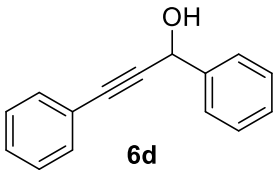
4-phenylbut-3-yn-2-ol (6a): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 - 7.40 (m, 2H), 7.35 - 7.30 (m, 3H), 4.77 (q, *J* = 6.5 Hz, 1H), 2.04 (s, 1H), 1.57 (d, *J* = 6.6 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$): δ 131.8, 128.4, 128.3, 122.6, 90.9, 84, 58.9, 24.5. IR (ATR): ῦ = 3284 (w), 2981 (w), 2231 (w), 753 (s), 689 (s) cm^{-1}. HRMS (ESI-TOF) calcd for $C_{10}H_{10}O$ $[M+Na]^+$ 169.0624, found 169.0623. Analytical data were consistently with those reported in literature.[2]



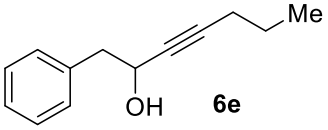
4-methyl-1-phenylpent-1-yn-3-ol (6b): 4-methyl-1-phenylpent-1-yn-3-one **5b** (102 mg, 0.593 mmol), *tert*-BuOH (85 µL, 0.890 mmol), pinBH (98 µL, 0.652 mmol), tributyl phosphine (8 µL, 0.030 mmol) and DCM (1.5 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6b** as colorless liquid (83 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 - 7.42 (m, 2H), 7.34 - 7.30 (m, 3H), 4.41 (d, *J* = 5.3 Hz, 1H), 2.08 - 1.96 (m, 2H), 1.10 (d, *J* = 6.8 Hz), 1.07 (d, *J* = 6.8, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.6, 128.4, 128.3, 122.7, 88.9, 85.6, 68.5, 34.7, 18.2, 17.6. IR (ATR): ῦ = 3313 (w), 2960 (w), 2246 (w), 1598(w) cm^{-1}. HRMS (ESI-TOF) calcd for $C_{12}H_{14}O$ $[M+Na]^+$ 197.0937, found 197.0942. Analytical data were consistently with those reported in literature.[3]



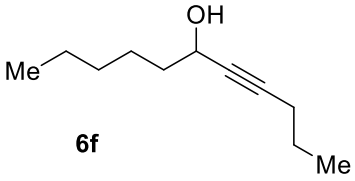
4,4-dimethyl-1-phenylpent-1-yn-3-ol (6c): 4,4-dimethyl-1-phenylpent-1-yn-3-one **5c** (98 mg, 0.527 mmol), *tert*-BuOH (76 µL, 0.791 mmol), pinBH (87 µL, 0.580 mmol), tributyl phosphine (7 µL, 0.026 mmol) and DCM (1.3 mL) were used. 5% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6c** as colorless liquid (4 mg, 4%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 - 7.43 (m, 2H), 7.35 - 7.30 (m, 3H), 1.83 (d, *J* = 5.4 Hz, 1H), 1.10 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$): δ 131.7, 128.4, 128.3, 122.8, 89, 85.7, 71.8, 36.1, 25.4. IR (ATR): ῦ = 3385 (w), 2954 (w), 2256 (w), 1598 (w) cm^{-1}. HRMS (ESI-TOF) calcd for $C_{13}H_{16}O$ $[M+Na]^+$ 211.1093, found 211.1098. Analytical data were consistently with those reported in literature.[4]

1,3-diphenylprop-2-yn-1-ol (6d): 1,3-diphenylprop-2-yn-1-one **5d** (92 mg, 0.446 mmol), *tert*-BuOH (64 µL, 0.669 mmol), pinBH (73 µL, 0.491 mmol), tributyl phosphine (6 µL, 0.022 mmol) and DCM (1.1 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6d** as colorless crystalline solid (73 mg, 80%). 

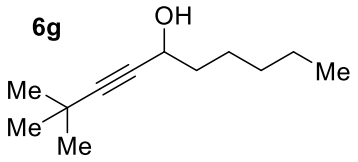
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 - 7.63 (m, 2H), 7.52 - 7.32 (m, 8H), 5.72 (d, *J* = 6.1 Hz, 1H), 2.32 (d, *J* = 6.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.6, 131.8, 128.7, 128.6, 128.5, 128.3, 126.8, 122.4, 88.6, 86.7, 65.3. IR (ATR): ṽ = 3363 (w), 2200 (w), 1598 (w), 754 (s)cm^{-1}. HRMS (ESI-TOF) calcd for $C_{15}H_{12}O$ $[M+Na]^+$ 231.0780, found 231.0782. Analytical data were consistently with those reported in literature.[3]

1-phenylhept-3-yn-2-ol (6e): 1-phenylhept-3-yn-2-one **5e** (149 mg, 0.865 mmol), *tert*-BuOH (124 µL, 1.298 mmol), pinBH (142 µL, 0.952 mmol), tributyl phosphine (11 µL, 0.043 mmol) and DCM (2.2 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **5e** as colorless liquid (120 mg, 84%). 

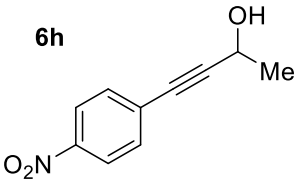
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (m, 5H), 4.58 (ddd, *J* = 5.6, 5.6, 5.6 Hz, 1H), 3.03 (dd, *J* = 4.1, 11.4 Hz, 1H), 2.96 (dd, *J* = 4.6, 11.5 Hz, 1H), 2.19 (dt, *J* = 2.0, 7.1 Hz, 2H),1.84 (d, *J* = 5.1 Hz, 1H), 1.54 (tq, *J* = 7.2, 7.3 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.9, 129.8, 128.3, 126.8, 86.6, 80.7, 63.5, 44.6, 22, 20.7, 13.5. IR (ATR): ṽ = 3455 (w), 2964 (w), 2231 (w), 695 (s) cm^{-1}. HRMS (ESI-TOF) calcd for $C_{13}H_{16}O$ $[M+Na]^+$ 211.1093, found 211.1096.

undec-4-yn-6-ol (6f): undec-4-yn-6-one **5f** (104 mg, 0.626 mmol), *tert*-BuOH (90 µL, 0.939 mmol), pinBH (103 µL, 0.689 mmol), tributyl phosphine (8 µL, 0.031 mmol) and DCM (1.6 mL) were used. 5% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6f** as colorless liquid (80 mg, 76%). 

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.37 - 4.28 (m, 1H), 2.16 (dt, *J* =1.9, 7.0 Hz, 2H), 1.73 (d, *J* =4.7 Hz, 1H), 1.69 - 1.62 (m, 2H), 1.55 - 1.42 (m, 4H), 1.33 - 1.26 (m, 4H), 0.95 (t, *J* =7.3 Hz, 3H), 0.88 (t, *J* =6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 85.3, 81.5, 62.3, 38.2, 31.5, 24.9, 22.6, 22.1, 20.7, 14.0, 13.4. IR (ATR): ṽ = 3340 (w), 2931 (m), 2862 (w), 2214 (w), 1746 (w) cm^{-1}. HRMS (GCMS + p EI) calcd for $C_{11}H_{20}O$ $[M]^+$ 168.1514, found 168.1463. Analytical data were consistently with those reported in literature.[5]

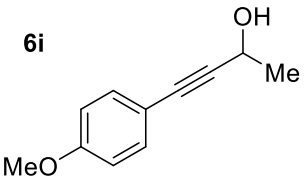
2,2-dimethyldec-3-yn-5-ol (6g): 2,2-dimethyldec-3-yn-5-one **5g** (110 mg, 0.610 mmol), *tert*-BuOH (88 µL, 0.915 mmol), pinBH (100 µL, 0.671 mmol), tributyl phosphine (8 µL, 0.031 mmol) and DCM (1.5 mL) were used. 5% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6g** as colorless liquid (37 mg, 33%). 

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.36 (t, *J* =6.3 Hz, 1H), 1.82 (s, 1H), 1.74 - 1.71 (m, 2H), 1.49 - 1.43 (m, 2H), 1.35 - 1.31 (m, 4H), 1.25 (s, 9H), 0.92 (t, *J* =6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 93.7, 79.9, 62.7, 38.4, 31.4, 31.1, 27.4, 24.9, 22.6, 14.0. IR (ATR): ṽ = 3332 (w, br), 2962 (s), 2927 (s), 2251 (w), 1029 (m) cm^{-1}. HRMS (ESI-TOF) calcd for $C_{12}H_{22}O$ $[M+Na]^+$205.1563, found 205.1567.

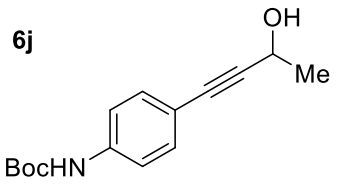
4-(4-nitrophenyl)but-3-yn-2-ol (6h): 4-(4-nitrophenyl)but-3-yn-2-one **5h** (124 mg, 0.656 mmol), *tert*-BuOH (94 µL, 0.984 mmol), pinBH (108 µL, 0.722 mmol), tributyl phosphine (8 µL, 0.033 mmol) and DCM (1.6 mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6h** as pale yellow solid (98 mg, 78%). 

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22-8.14 (*m*, 2H), 7.60 - 7.53 (*m*, 2H), 4.80 (qd, *J* = 4.3, 12.1 Hz, 1H), 2.08 (d, *J* = 5.3 Hz, 1H), 1.59 (d, *J* = 5.8 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$): δ 147.2, 132.5, 129.6, 123.6, 111.7, 96.3, 82.3, 58.7, 24.1. IR (ATR): ṽ = 3216 (w), 2256 (w), 1516 (s), 1343 (s) 867 (m) cm^{-1}. HRMS (ESI-TOF) calcd for $C_{10}H_9NO_3$ $[M+H]^+$ 192.0655, found 192.0657. Analytical data were consistently with those reported in literature.[6]

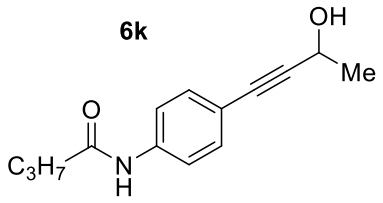
4-(4-methoxyphenyl)but-3-yn-2-ol (6i): 4-(4-methoxyphenyl)but-3-yn-2-one **5i** (157 mg, 0.901 mmol), *tert*-BuOH (129 µL, 1.352 mmol), pinBH (148 µL, 0.991 mmol), tributyl phosphine (11 µL, 0.045 mmol) and DCM (2.3 mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6i** as colorless liquid (130 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 - 7.33 (m, 2H), 6.86 - 6.82 (m, 2H), 4.75 (qd, *J* = 4.2, 10.4 Hz, 1H), 3.82-3.81 (m, 3H), 2.06 (d, *J* = 3.1 Hz, 1H), 1.55 (d, *J* = 6.6 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$): δ 159.7, 133.3, 132.4, 124.8, 118, 114.1, 90.6, 86.8, 32.8. IR (ATR): ῦ = 3357 (w), 2258 (w), 1505 (s), 1290 (s), 1245 (s)cm^{-1}. HRMS (ESI-TOF) calcd for $C_{11}H_{12}O_2$ $[M+H]^+$ 177.0910, found 177.0913. Analytical data were consistently with those reported in literature.[2]



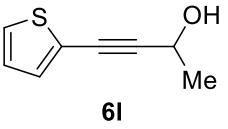
***tert*-butyl (4-(3-hydroxybut-1-yn-1-yl)phenyl)carbamate (6j):** *tert*-butyl (4-(3-oxobut-1-yn-1-yl)phenyl)carbamate **5j** (144 mg, 0.555 mmol), *tert*-BuOH (78 µL, 0.833 mmol), pinBH (91 µL, 0.611 mmol), tributyl phosphine (7 µL, 0.028 mmol) and DCM (1.4 mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6j** as colorless solid (133 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.53 (s, 9H), 1.55 (d, *J* = 6.2 Hz, 3H), 1.92 (d, *J* = 5.9 Hz, 1H), 4.75 (dq, *J* = 6.3, 6.2 Hz, 1H), 7.39 - 7.29 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.3, 139.7, 133.1, 118.9, 117.6, 90.9, 81.6, 59.7, 29.4, 25.1. IR (ATR): ῦ = 3321 (w), 2978 (w), 2238 (w), 1701 (m), 1519 (s) cm^{-1}. HRMS (FTMS-p APCI) calcd for $C_{15}H_{19}NO_3$ $[M-H]^-$ 260.1292, found 260.1292.



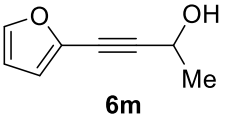
***N*-(4-(3-hydroxybut-1-yn-1-yl)phenyl)butyramide (6k):** *N*-(4-(3-oxobut-1-yn-1-yl)phenyl)butyramide **5k** (139 mg, 0.606 mmol), *tert*-BuOH (85 µL, 0.909 mmol), pinBH (118 µL, 0.788 mmol), tributyl phosphine (8 µL, 0.030 mmol) and DCM (1.5 mL) were used. 40% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6k** as colorless solid (130 mg, 93%). ^{1}H NMR (300 MHz, MeOD): δ 0.99 (t, *J* = 7.4 Hz, 3H), 1.24 (s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H), 1.71 (tq, *J* = 7.4, 7.4 Hz, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 4.68 (q, *J* = 6.7 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (75 MHz, MeOD): δ 12.9, 19.1, 23.3, 38.6, 57.7, 82.6, 90.6, 118.3, 119.3, 131.9, 138.6, 173.3. IR (ATR): ῦ = 3228 (w), 3167 (w), 2873 (w), 2236 (w), 1662 (m), 1539 (m), 1512 (m) cm^{-1}. HRMS (FTMS + p ESI) calcd for $C_{14}H_{17}NO_2$ $[M+H]^+$ 231.1332, found 232.1332.



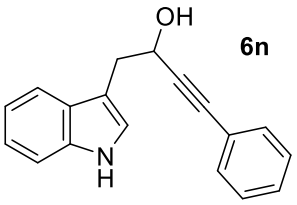
4-(thiophen-2-yl)but-3-yn-2-ol (6l): 4-(thiophen-2-yl)but-3-yn-2-one **5l** (202 mg, 1.345 mmol), *tert*-BuOH (189 µL, 2.018 mmol), pinBH (221 µL, 1.48 mmol), tributyl phosphine (17 µL, 0.067 mmol) and DCM (3.4 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6l** as colorless liquid (186 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 1.56 (d, *J* = 6.6 Hz, 3H), 2.08 (d, *J* = 5.1 Hz, 1H), 4.77 (dq, *J* = 6.2, 6.1 Hz, 1H), 7.00 - 6.95 (m, 1H), 7.27 - 7.24 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.2, 58.9, 77.4, 94.7, 122.5, 127.0, 127.3, 132.3. IR (ATR): ῦ = 3321 (w,br), 2981 (w), 2222 (w), 1192 (m) cm^{-1}. HRMS (GCMS + p EI) calcd for $C_8H_{10}OS$ $[M]^+$ 152.0296, found 152.0293. Analytical data were consistently with those reported in literature.[2]



4-(furan-2-yl)but-3-yn-2-ol (6m): 4-(furan-2-yl)but-3-yn-2-one **5m** (124 mg, 0.924 mmol), *tert*-BuOH (130 µL, 1.386 mmol), pinBH (152 µL, 1.016 mmol), tributyl phosphine (12 µL, 0.046 mmol) and DCM (2.3 mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6m** as colorless liquid (114 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.43 (d, *J* = 1.2 Hz, 1H), 6.62 (d, *J* = 3.4 Hz, 1H), 6.43 (dd, *J* = 1.9, 3.4 Hz, 1H), 4.82 (q, *J* = 6.6 Hz, 1H), 2.09 (s, 1H), 1.60 (d, *J* = 6.6 Hz, 3H) . ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.9, 136.6, 115.4, 110.7, 95.2, 74.4, 58.9, 24.1. IR (ATR): ῦ = 3325 (w), 2985 (w), 2243 (w), 1739 (w), 1211 (m), 740 (s) cm^{-1}. HRMS (GCMS + p EI) calcd for $C_8H_8O_2$ $[M]^+$ 136.0524 found 136.0518.

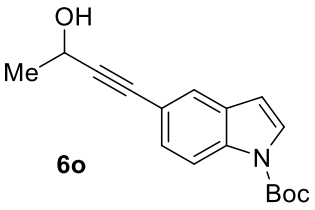


1-(1*H*-indol-3-yl)-4-phenylbut-3-yn-2-ol (6n): 1-(1*H*-indol-3-yl)-4-phenylbut-3-yn-2-one **5n** (123 mg, 0.474 mmol), *tert*-BuOH (67 µL, 0.711 mmol), pinBH (92 µL, 0.616 mmol), tributyl phosphine (6 µL, 0.074 mmol) and DCM (1.2 mL) were used. Ethyl acetate/petroleum ether (3/7) was used as eluent for flash column chromatography to provide propargylic alcohol **6n** as cololorles solid (112 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.78 - 7.73 (m, 1H), 4.91 (t, *J* = 6.1 Hz, 1H), 3.41 - 3.24 (m, 2H), 2.24 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.3, 131.8, 128.5, 128.3, 127.8, 123.6, 122.7, 122.3, 119.7, 119.2, 111.4, 110.5, 90.3, 85.0, 62.9, 34.1. IR (ATR): ṽ = 3410 (w), 3321 (w), 3091 (w), 2251 (w), 1457(m), 1338 (m) cm^{-1}. HRMS (FTMS + p ESI) calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1226. Analytical data were consistently with those reported in literature.[7]



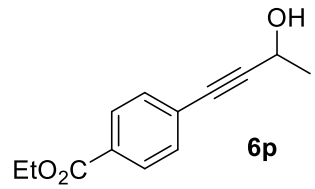
6n

***tert*-butyl 5-(3-hydroxybut-1-yn-1-yl)-1*H*-indole-1-carboxylate (6o):** *tert*-butyl 5-(3-oxobut-1-yn-1-yl)-1*H*-indole-1-carboxylate **5o** (134 mg, 0.473 mmol), *tert*-BuOH (67 µL, 0.710 mmol), pinBH (92 µL, 0.615 mmol), tributyl phosphine (6 µL, 0.024 mmol) and DCM (1.2 mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6o** as colorless solid (112 mg, 83%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.61 (d, *J* = 7.0 Hz, 3H), 1.70 (s, 9H), 2.05 (s, 1H), 4.82 (q, *J* = 6.0 Hz, 1H), 6.55 (d, *J* = 3.7 Hz, 1H), 7.63 (d, *J* = 3.8 Hz, 2H), 7.67 (d, *J* = 1.1 Hz, 1H), 8.10 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.5, 29.1, 59.9, 85.1, 85.7, 90.5, 107.9, 116.1, 117.6, 125.5, 127.6, 128.7, 131.3, 135.9, 150.4. IR (ATR): ṽ = 3309 (w), 2970 (w), 2247 (w), 1732 (s) cm^{-1}. HRMS (FTMS + p APCI) calcd for $C_{17}H_{19}NO_3$ $[M+H]^+$ 286.1438, found 286.1434.



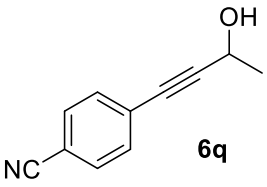
6o

ethyl 4-(3-hydroxybut-1-yn-1-yl)benzoate (6p): ethyl 4-(3-oxobut-1-yn-1-yl)benzoate **5p** (151 mg, 0.698 mmol), *tert*-BuOH (98 µL, 1.05 mmol), pinBH (115 µL, 0.768 mmol), tributyl phosphine (9 µL, 0.035 mmol) and DCM (1.7 mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6q** as colorless solid (134 mg, 74%). ^{1}H NMR (300 MHz, CDCl3): δ = 8.01 - 7.96 (m, 2H), 7.49 - 7.45 (m, 2H), 4.78 (td, *J* = 6.6, 12.0 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.17 (d, *J* =5.4 Hz, 1H), 1.57 (d, *J* = 6.6 Hz, 3H), 1.40 (t, *J* = 6.9 Hz, 3H). ^{13}C-NMR (75 MHz, CDCl3): δ = 166.2, 131.7, 130.1, 129.5, 127.3, 93.9, 83.4, 61.3, 58.8, 24.3, 14.3. IR (ATR): ṽ = 3401(w), 2974 (w), 2237 (w), 1715 (m), 1268 (s), 1095 (s) cm^{-1}. HRMS (ESI-TOF) calcd for $C_{13}H_{14}O_3$ $[M+H]^+$ 219.1016; found 219.1023. Analytical data were consistently with those reported in literature.[8]



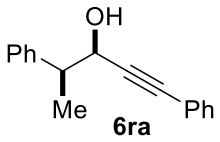
6p

4-(3-hydroxybut-1-yn-1-yl)benzonitrile (6q): 4-(3-oxobut-1-yn-1-yl)benzonitrile **5q** (167 mg, 0.987 mmol), *tert*-BuOH (139 µL, 1.48 mmol), pinBH (162 µL, 1.09 mmol), tributyl phosphine (5 µL, 0.013 mmol) and DCM (2.5 mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6q** as colorless solid (131 mg, 78%). ^{1}H NMR (300 MHz, CDCl3): δ = 7.60 (d, *J* = 9.2 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 4.79 (qd, *J* = 4.0, 10.5 Hz, 1H), 2.15 (d, *J* = 4.0 Hz, 1H), 1.57 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (75 MHz, CDCl3): δ = 132.2, 132, 127.7, 118.4, 111.7, 95.5, 82.5, 58.8, 24.2. IR (ATR): ṽ = 3311 (w), 3245 (w), 2983 (w), 2239 (m), 1370 (m) cm^{-1}. HRMS (FTMS + p APCI) calcd for $C_{11}H_9NO$ $[M+H]^+$ 172.0757; found 172.0760. Analytical data were consistently with those reported in literature.[9]

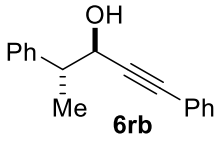


6q

1,4-diphenylpent-1-yn-3-ol (6ra/6rb): 5r (142 mg, 0.606 mmol), *tert*-BuOH (85 µL, 0.909 mmol), pinBH (100 µL, 0.667 mmol), tributyl phosphine (8 µL, 0.030mmol) and DCM (1.5 mL) were used. 5% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide inseparable diasteriomeric mixture of propargylic alcohols **6ra** and **6rb** as colorless liquid (137 mg, 96%, dr = 1:1.8 - *anti*:*syn*). ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 77.36 - 7.18 (m, 10H), 5.60 (d, *J* =6.0 Hz, 1H, minor), 5.57 (d, *J* = 5.9 Hz, 1H, major) 4.53 (dd, *J* = 5.9, 6.4 Hz, 1H, major), 4.47 (dd, *J* = 6.0, 6.7 Hz, 1H, minor), 3.04 - 2.93 (m, 1H), 1.36 - 1.30 (2 x d, *J* = 6.9 major, *J* = 7.0 minor, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.8, 131.7, 128.6, 128.5, 128.3, 128.2, 127.1, 122.6, 88.6, 86.3, 68.0, 46.7, 16.9. IR (ATR): ṽ = 3421 (w, br), 2970 (w), 2245 (w), 1489 (w), 1265 (m) cm^{-1}. HRMS (GCMS + p EI) calcd for $C_{17}H_{16}O$ $[M]^+$ 236.1201, found 236.1194. Analytical data were consistent with those reported in literature.[10] The assignment of *syn*- and *anti*-diastereomer was carried out by comparing chemical shifts and $^3J_{HH}$ coupling constants of the carbinol and the neighboring proton, geminal with the methyl group, to NMR spectra and data of related propargyl alcohols from Brückner *et al.*[11] The corresponding data are highlighted in the tabulated ^{1}H NMR data.

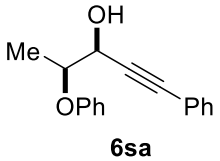


6ra

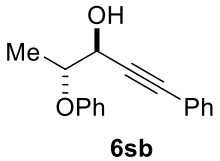


6rb

4-phenoxy-1-phenylpent-1-yn-3-ol (6sa/6sb): 5s (120 mg, 0.479 mmol), *tert*-BuOH (69 µL, 0.719 mmol), pinBH (79 µL, 0.527 mmol), tributyl phosphine (6 µL, 0.024 mmol) and DCM (1.2 mL) were used. 5% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide inseparable diasteriomeric mixture of propargylic alcohols **6sa** and **6sb** as colorless liquid (106 mg, 88% dr = 1:2.1 – *syn*:*anti*). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 - 7.51 (m, 7H), 7.42 - 7.32 (m, 5H), 7.11 - 7.06 (m, 3H), 4.91 (d, *J* = 3.4 Hz, 1H, minor), 4.78 (d, *J* = 6.7 Hz, 1H, major), 4.69 (dq, *J* = 3.4, 6.3 Hz, 1H, minor), 4.62 (dq, *J* = 6.2, 6.2 Hz, 1H, major), 2.77 (s, 1H), 2.63 (s, 1H), 1.57 (d, *J* = 6.8 Hz, 3H, minor), 1.55 (d, *J* = 6.4 Hz, 3H, major). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.5, 157.4, 131.9, 129.6, 128.7, 128.3, 122.4, 122.3, 121.7, 121.6, 116.5, 116.4, 86.6, 86.4, 76.6, 66.8. 65.5, 16.1, 14.6. IR (ATR): ṽ = 3402 (w), 2981 (w), 2230 (w), 1597(w), 1489 (m), 1230 (m) cm^{-1}. HRMS (ESI-TOF) calcd for $C_{17}H_{16}O_2$ $[M+Na]^+$ 275.1043, found 275.1048. The tentative assignment of *syn*- and *anti*-diastereomer was carried out by comparing coupling constance and chemical shifts of the proton geminal to the alcohol and the proton geminal to the phenyl ether (underlined), to NMR spectra and data of related propargyl alcohol from Brückner *et al.*[11] The corresponding data are underlined.

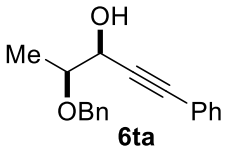


6sa

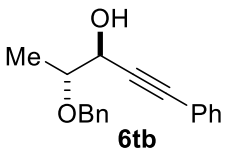


6sb

4-(benzyloxy)-1-phenylpent-1-yn-3-ol (6ta/6tb): 5t (131 mg, 0.496 mmol), *tert*-BuOH (71 µL, 0.744 mmol), pinBH (82 µL, 0.546 mmol), tributyl phosphine (6 µL, 0.025 mmol) and DCM (1.2 mL) were used. 5% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide of propargylic alcohols **6ta** and **6tb** as colorless liquids (113 mg, 86% dr = 1.5:1 - anti:syn). *anti*-product **6ta**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 – 7.23 (m, 10H), 4.71 (d, J = 11.4 Hz, 1H), 4.58 (d, J = 11.4 Hz, 1H), 4.45 (dd, J = 6.6, 4.2 Hz, 1H), 3.72 (dq, *J* = 6.4, 6.5 Hz, 1H), 2.81 (d, J = 4.1 Hz, 1H), 1.34 (d, J = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.2, 131.9, 128.6, 128.3, 127.9, 127.2, 122.6, 87.5, 85.9, 78.3, 71.8, 67.0, 16.3. IR (ATR): ṽ = 3414 (w), 2870 (w), 2278 (w), 1454 (w) cm^{-1}. HRMS (ESI-TOF) calcd for $C_{18}H_{18}O_2$ $[M+Na]^+$ 289.1199, found 289.1202. *syn*-product **6tb**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 - 7.28 (m, 10H), 4.7 (d, *J* =11.7 Hz, 1H), 4.66 (dd, *J* = 4.0, 5.8 Hz, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 3.76 (dq, *J* = 3.8, 6.3 Hz, 1H), 2.47 (d, *J* = 5.8 Hz, 1H), 1.36 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.3, 131.9, 128.6, 128.5, 128.3, 127.9, 127.8, 122.6, 86.9, 86.1, 77.3, 71.1, 65.7, 14.5. IR (ATR): ṽ = 3425 (w), 2873 (w), 2236 (w), 1377 (w) cm^{-1}. HRMS (ESI-TOF) calcd for $C_{18}H_{18}O_2$ $[M+Na]^+$ 289.1199, found 289.1204. Analytical data were consistent with those reported in literature.[10] The assignment of *syn*- and *anti*-diastereomer was carried out by comparing chemical shifts and $^3J_{HH}$ coupling constants of the carbinol and the neighboring proton, geminal with the methyl group, to NMR spectra and data of related propargyl alcohols from Brückner *et al.*[11] The corresponding data are highlighted in the tabulated ^{1}H NMR data.



6ta

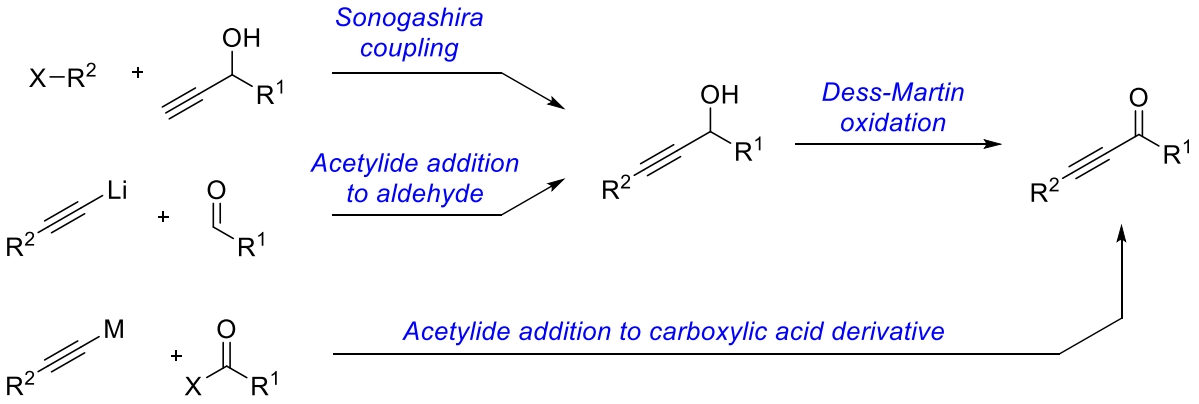


6tb

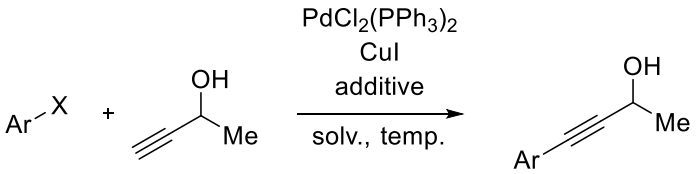
Synthesis of ynones 6-29

The required ynones were prepared via (i) Sonogashira coupling of corresponding aryl halide with but-3-yn-2-ol followed by Dess-Martin oxidation of the resulting propargylic alcohol (ynones **15a**-**19a** and **22a**), (ii) addition of an appropriate lithium acetylide to the corresponding aldehyde followed by Dess-Martin oxidation (ynones **6**, **11a**-**14a**, **20a** and **23**), or (iii) addition of an acetylide to the corresponding acyl chloride (**9a**, **10a**), ester (ynones **26** and **29**) or Weinreb amid (ynone **21a**).

Scheme 1. Summary of synthetic pathways to ynones 6-29.

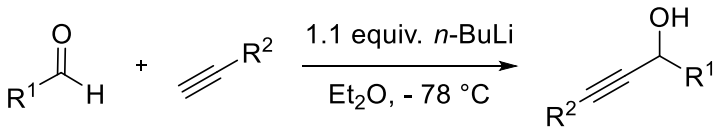


General procedure for Sonogashira coupling:



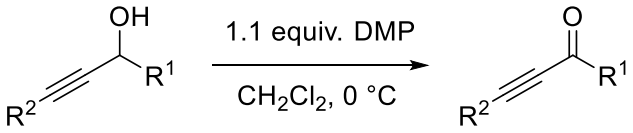
Aryl halide was dissolved in the appropriate solvent. The solution was treated with N_2 (bubbling for 20 minutes) to remove residual oxygen. The additive, but-3-yn-2-ol, $PdCl_2(PPh_3)_2$ and CuI were added and the suspension was heated to appropriate temperature. After the reaction was complete or no further progress was observed by TLC, the mixture was allowed to cool to room temperature. The mixture was filtered through a plug of celite. The solvent was evaporated, and the crude product was purified by flash column chromatography (SiO_2, ethyl acetate in petroleum ether) to provide the corresponding propargylic alcohol.

General procedure for alkyne aldehyde addition:



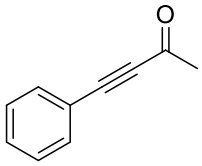
The terminal alkyne was dissolved in Et_2O and cooled to −78 °C. *n*-BuLi was added and the slightly yellow solution was stirred for 30 min. The corresponding aldehyde was added and the mixture was allowed to warm to room temperature and was further stirred for 1 h. Aqueous HCl (1 M) was added and the resulting layers were separated. The aqueous layer was extracted with DCM (3x). The organic layers were combined and dried over Na_2SO_4. The solvent was evaporated, and the crude product was purified by flash column chromatography (SiO_2, ethyl acetate in petroleum ether) to provide the corresponding propargylic alcohol.

General procedure for Dess-Martin-oxidation:



The propargylic alcohol was dissolved in DCM (0.2 M) and cooled to 0 °C. Dess-Martin periodinane (DMP, 1.1 equiv) was added and the mixture was allowed to warm to room temperature. After the reaction was completed, monitored by TLC, aq. NaOH (1.1 equiv, 1 M solution) was added. The layers were separated, and the aqueous layer was extracted with DCM (3 x). The organic layers were combined and dried over Na_2SO_4. The solvent was evaporated, and the crude product was purified by flash column chromatography (SiO_2, ethyl acetate in petroleum ether) to provide the corresponding ynone.

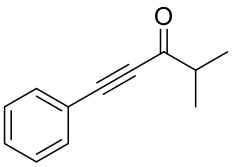
4-phenylbut-3-yn-2-one (5a): Propargylic alcohol **6a** was prepared according to the general procedure for addition of lithium acetylide to aldehydes. Ethynylbenzene (8.34 mL, 75.9 mmol), acetaldehyde (3.88 mL, 69 mmol), *n*-BuLi (30.3 mL, 75.9 mmol, 2.5 M solution in Hexane) and Et_2O (200 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6a** (9.89 g, 98%). Analytical data were identical to the compounds obtained by reduction of corresponding ynone (see SI p. 2).



5a

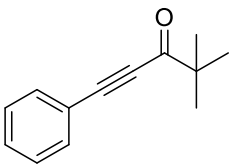
Oxidation of propargylic alcohol **6a** was carried out according to the general procedure for Dess-Martin oxidation: propargylic alcohol **6a** (10.36 g, 70.87 mmol), DMP (33.06 g, 77.95 mmol) and DCM (355 mL) were used. 5% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5a** as pale yellow solid (9.77 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60-7.56 (m, 2H), 7.49 - 7.36 (m, 3H), 2.48 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.7, 134.7, 130.8, 128.6, 119.9, 90.4, 88.0, 32.7. IR (ATR): $\tilde{\nu}$ = 2198 (s),1666 (s) cm^{-1}. MS (EI): m/z = 144 $[M]^{\cdot+}$. Analytical data were consistent with those reported in literature.[12]

4-methyl-1-phenylpent-1-yn-3-one (5b): Synthesized according to the protocol from Müller *et al.*[13] Isobutyryl chloride (3.2 mL, 30 mmol), was dissolved in THF (50 mL). Phenylacetylene (2.2 mL, 20 mmol), $PdCl_2(PPh_3)_2$ (126 mg, 0.2 mmol), CuI (114 mg, 0.6 mmol) NEt_3 (3.5 mL, 25 mmol) were added and the suspension was stirred at room temperature. After the reaction was completed, confirmed by TLC, ethyl acetate (50 mL) was added. The mixture was washed with H_2O (3 x 20 mL) and the organic layers were combined and dried over Na_2SO_4. The solvent was evaporated, and the crude product was purified by flash column chromatography (SiO_2, 3% ethyl acetate in petroleum ether) to provide ynone **5b** as pale yellow solid (2.96 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 - 7.57 (m, 2H), 7.48 - 7.37 (m, 3H), 2.78 (qq, *J* = 7.0, 6.9 Hz, 1H), 1.29 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.5, 133.0, 130.7, 128.5, 120.2, 91.6, 86.9, 43.2, 18.2. IR (ATR): $\tilde{\nu}$ = 2207 (m), 1667 (s) cm^{-1}**.** MS (EI): m/z = 172 $[M]^{\cdot+}$, 129 $[M - CH(CH_3)_2]^{\cdot+}$. Analytical data were consistent with those reported in literature.[14]



5b

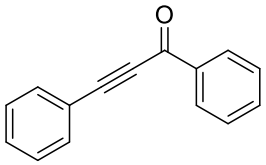
4,4-dimethyl-1-phenylpent-1-yn-3-one (5c): Synthesized according to the protocol from Müller *et al.* [13] Pivaloyl chloride (3.6 mL, 30 mmol), was dissolved in THF (50 mL). Phenylacetylene (2.2 mL, 20 mmol), $PdCl_2(PPh_3)_2$ (126 mg, 0.2 mmol), CuI (114 mg, 0.6 mmol) NEt_3 (3.5 mL, 25 mmol) were added and the suspension was stirred at room temperature. After the reaction was completed, confirmed by TLC, ethyl acetate (50 mL) was added. The mixture was washed with H_2O (3 x 20 mL) and the organic layers were combined and dried over Na_2SO_4. The solvent was evaporated, and the crude product was purified by flash column chromatography (SiO_2, 3% ethyl acetate in petroleum ether) to provide ynone **5c** as pale yellow liquid (2.45 g, 65%). ^{1}H NMR (300 MHz, $CDCl_3$):



5c

δ 7.62 - 7.57 (m, 2H), 7.47 - 7.35 (m, 3H), 1.30 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.8, 133.1, 130.6, 128.5, 120.5, 92.4, 86.1, 45.1, 26.4. IR (ATR): ῦ = 2197 (m), 1661 (s), 1651 (m), 1444(m), 688 (s) cm^{-1}. MS (EI): m/z = 186 $[M]^{\cdot+}$, 171 $[M\text{ -Me}]^{\cdot+}$, 129 $[M\text{ -C}(CH_3)_3]^{\cdot+}$. Analytical data were consistent with those reported in literature.[15]

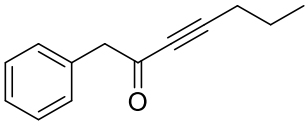
1,3-diphenylprop-2-yn-1-one (5d): Propargylic alcohol **6d** was prepared according to the general procedure for addition of lithium acetylide to aldehydes. Ethynylbenzene (1.01 mL, 10 mmol), benzaldehyde (1.1 mL, 11 mmol), *n*-BuLi (6.9 mL, 11 mmol, 2.5 M solution in Hexane) and Et_2O (27.5 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide alcohol **6d** (1.7 g, 82%). Analytical data were identical to the compound obtained by reduction of corresponding ynone (see SI p 2).



5d

Oxidation of propargylic alcohol **6d** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **6d** (1.52 g, 7.3 mmol), DMP (3.14 g, 8.06 mmol) and DCM (37 mL) were used. 5% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5d** as colorless solid (1.36 g, 90%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.28 - 8.23 (m, 2H), 7.74 - 7.42 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.1, 136.9, 134.1, 133.2, 130.9, 129.7, 128.7, 128.6, 120.1, 93.2, 86.9. IR (ATR): ῦ = 3082 (w), (2203) (m), 1631 (m) cm^{-1}. MS (EI): m/z = 206 $[M]^{\cdot+}$, 129 $[M\text{ -Ph}]^{\cdot+}$. Analytical data were consistent with those reported in literature.[16]

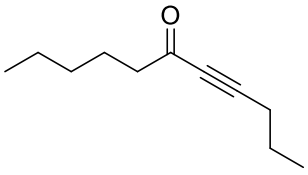
1-phenylhept-3-yn-2-one (5e): Prepared according to the general procedure for addition of lithium acetylide to aldehydes. Pent-1-yne (1.17 mL, 10 mmol), 2-phenylacetaldehyde (1.09 mL, 11 mmol), *n*-BuLi (6.9 mL, 11 mmol, 2.5 M solution in Hexane) and Et_2O (25 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6e** (592 mg, 85%). Analytical data were identical to the compound obtained by reduction of corresponding ynone (see SI p. 3).



5e

Oxidation of propargylic alcohol **6e** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **6e** (1.23 g, 6.35 mmol), DMP (3.05 g, 7.18 mmol) and DCM (32.5 mL) were used. 5% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5e** as colorless liquid (1.07 g, 88%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.42-7.20 (m, 5H), 3.84 (s, 2H), 2.32 (t, *J* = 7.0 Hz, 2H), 1.57 (qt, *J* = 7.2, 7.3 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.2, 135.8, 130.6, 128.7, 127.3, 96.3, 80.8, 52.1, 21.1, 20.9, 13.4. IR (ATR): ῦ = 2971 (w), (2198) (m), 1665 (s), 1052 (s), cm^{-1}. HRMS (ESI,+VE, +HMR): calcd for $C_{13}H_{14}O$ $[M+Na]^+$ 209.0942, found 209.0938.

undec-4-yn-6-one (5f): Prepared according to the general procedure for addition of lithium acetylide to aldehydes. Pent-1-yne (3.1 mL, 31.3 mmol), hexanal (3.5 mL, 28.4 mmol), *n*-BuLi (12.52 mL, 31.3 mmol, 2.5 M solution in Hexane) and Et_2O (42 mL) were used. 5% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6f.** Analytical data were identical to the compound obtained by reduction of corresponding ynone (see SI p. 3).

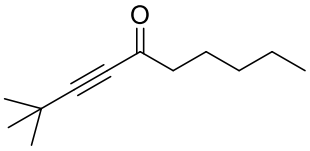


5f

Oxidation of propargylic alcohol **6f** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **6f** (2.68 g, 15.92 mmol), DMP (7.42 g, 17.5 mmol) and DCM (88 mL) were used. 2% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5f** as colorless liquid(2.1 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.47 (t, *J* = 7.4 Hz, 2H), 2.30 (t, *J* = 7.0 Hz, 2H), 1.67 - 1.53 (m, 4H), 1.31 - 1.23 (m, 4H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.85 (t, *J* = 6.9 Hz, 3H) . ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.6, 94.5, 81.1, 45.6, 30.8, 23.9, 22.3, 21.2, 20.9, 13.9, 13.4. IR (ATR): ῦ 2958 (w), 2931 (w), 2210 (m), 1670 (m), 1238 (w) 1165 (m) cm^{-1}. HRMS (FTMS + p

EI) calcd for $C_{11}H_{18}O$ $[M]^+$ 166.1352, found 166.1352. Analytical data were consistently with those reported in literature.[5]

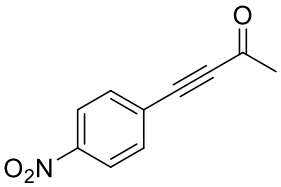
2,2-dimethyldec-3-yn-5-one (5g): Prepared according to the general procedure for addition of lithium acetylide to aldehydes. 3,3-dimethylbut-1-yne (2.57 g, 31.3 mmol), hexanal (3.5 mL, 28.4 mmol), *n*-BuLi (12.52 mL, 31.3 mmol, 2.5 M solution in Hexane) and Et_2O (42 mL) were used. 5% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6g.** Analytical data were identical to the compounds obtained by reduction of corresponding ynone (see SI p. 3).



5g

Oxidation of propargylic alcohol **6g** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **6g** (1.2 g, 6.58 mmol), DMP (3.07 g, 7.24 mmol) and DCM (36 mL) were used. 2% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5g** as colorless liquid (985 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.53 (t, *J* = 7.4 Hz, 2H), 1.74 - 1.63 (m, 2H), 1.37 - 1.29 (m, 13H), 0.92 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.9, 101.5, 79.3, 45.6, 31.2, 30.1, 27.7, 23.9, 22.4, 13.9. IR (ATR): ṽ = 2966 (w), 2931 (w), 2210 (m), 1674 (m), 1261 (m) cm^{-1}. HRMS (GCMS + p EI) calcd for $C_{12}H_{20}O$ $[M+H]^+$ 181.1587, found 181.1587. Analytical data were consistently with those reported in literature.[17]

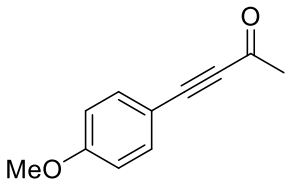
4-(4-nitrophenyl)but-3-yn-2-one (5h): Prepared following the general procedure for Sonogashira coupling. 1-Bromo-4-nitrobenzene (1.49 g, 7.4 mmol), but-3-yn-2-ol (0.87 mL, 8.14 mmol), $PdCl_2(PPh_3)_2$ (104 mg, 0.15 mmol), CuI (56 mg, 0.3 mmol), NEt_3 (59 mL) were used at 80 °C. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6h** (1.38 g, 98%). Analytical data were identical to the compound obtained by reduction of corresponding ynone (see SI p. 3).



5h

Oxidation of propargylic alcohol **6h** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **6h** (200 mg, 1.05 mmol), DMP (488 mg, 1.15 mmol) and DCM (5.3 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5h** as pale yellow solid (180 mg, 88%).^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 - 8.22 (m, 2H), 7.77 - 7.70 (m, 2H), 2.49 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.3, 148.5, 133.8, 126.7. 123.8, 91.2, 86.4, 32.6. IR (ATR)ṽ = 3107 (w), 2206 (m), 1680 (m), 1576 (w), 1336 (s), 853 (s) cm^{-1}. MS (EI): m/z = 189 $[M]^{\cdot+}$, 174 $[M\text{ -Me}]^{\cdot+}$. Analytical data were consistent with those reported in literature.[18]

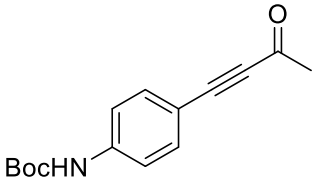
4-(4-methoxyphenyl)but-3-yn-2-one (5i): Prepared following the general procedure for Sonogashira coupling. 4-Iodoanisole (4.08 g, 20 mmol), but-3-yn-2-ol (1.7 mL, 22 mmol), $PdCl_2(PPh_3)_2$ (140 mg, 0.2 mmol), CuI (76 mg, 0.4 mmol), NEt_3 (160 mL) were used at 80 °C. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6i** (2.39 g, 68%). Analytical data were identical to the compound obtained by reduction of corresponding ynone (see SI p. 3).



5i

Oxidation of propargylic alcohol **6i** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **6i** (2.07 g, 11.8 mmol), DMP (5.47 g, 12.9 mmol) and DCM (60 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5i** as pale yellow solid (1.85 g, 90%).^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57-7.50 (m, 2H), 6.93 - 6.87 (m, 2H), 3.85 (s, 3H), 2.44 (s, 3H) . ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.7, 161.7, 135.4, 114.4, 111.7, 91.6, 88.3, 55.5, 32.7. IR (ATR): ṽ = 2981 (w), 2213 (w), 1653 (s), 1250 (s), 836 (s) cm^{-1}. MS (EI): m/z = 174 $[M]^{\cdot+}$, 159 $[M\text{ -Me}]^{\cdot+}$ Analytical data were consistent with those reported in literature.[19]

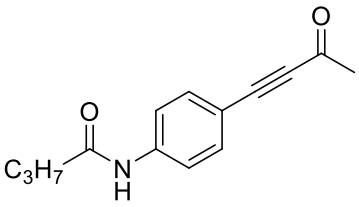
tert-butyl (4-(3-oxobut-1-yn-1-yl)phenyl)carbamate (6j): Prepared following the general procedure for Sonogashira coupling. *tert*-butyl (4-iodophenyl)carbamate (4.58 g, 14.3 mmol), but-3-yn-2-ol (1.36 mL, 17.2 mmol), $PdCl_2(PPh_3)_2$ (300 mg, 0.429 mmol), CuI (266 mg, 1.4 mmol) and NEt_3(50 mL) as solvent were used at 70 °C. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6j** (2.36 g, 63%). Analytical data were identical to the compounds obtained by reduction of corresponding ynone (see SI p. 4).



5j

Oxidation of propargylic alcohol **6j** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **6j** (2.23g, 8,53mmol), DMP (3.98 g, 9.38mmol) and DCM (43mL) were used. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5j** as pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 - 7.39 (m, 4H), 6.70 (s, 1H), 2.44 (s, 3H), 1.53 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.5, 152.6, 140.7, 134.5, 118.2, 113.4, 91.1, 81.1, 32.9, 27.8 . IR (ATR): ṽ = 3363 (s), 2179 (m), 1732 (m), 1149 (s). HRMS (Micro-ESI,+) calcd for $C_{15}H_{17}NO_3$ $[M+Na]^+$ 282.1111, found 282.1106.

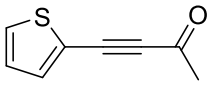
***N-(4-(3-oxobut-1-yn-1-yl)phenyl)butyramide* (5k):** Prepared following the general procedure for Sonogashira coupling. *N*-(4-iodophenyl)butyramide (5.81 g, 20.1 mmol), but-3-yn-2-ol (2.38 mL, 30.1 mmol), $PdCl_2(PPh_3)_2$ (280 mg, 0.4 mmol), CuI (382 mg, 2 mmol), PPh_3 (1.05 g, 4.02 mmol) as additive and NEt_3 (70 mL) as solvent were used at 70 °C. 40% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6k** (2.77 g, 60%). Analytical data were identical to the compounds obtained by reduction of corresponding ynone (see SI p. 4).



5k

Oxidation of propargylic alcohol **6k** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **6k** (0.947 mg, 4.09 mmol), DMP (2.56 g, 5.32 mmol) and DCM (23mL) were used. 30% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5k** as pale yellow solid (0.692 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.62 - 7.48 (m, 4H), 2.46-2.45 (m, 3H), 1.75 (d, *J* = 14.8 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.2, 172.3, 140.4, 134.1, 119.3, 114.8, 90.8, 88.9, 39.7, 32.6, 18.5, 13.7. IR (ATR): ṽ = 3363 (w), 2981 (w), 2179 (m), 1736 (m), 1226 (m) cm^{-1}. HRMS (GCMS + p EI) calcd for $C_{14}H_{14}NO_2$ $[M]^+$229.1103, found 229.1099.

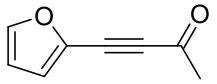
4-(thiophen-2-yl)but-3-yn-2-one (5l): Prepared following the general procedure for Sonogashira coupling. 2-iodothiophene (2.1 mL, 19.04 mmol), but-3-yn-2-ol (1.66 mL, 20.95 mmol), $PdCl_2(PPh_3)_2$ (266 mg, 0.38 mmol), CuI (217 mg, 1.14 mmol), NEt_3 (8 mL, 57.7 mmol) as additive and THF (24 mL) were used at 60 °C. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6l** (2.44 g, 84%). Analytical data were identical to the compounds obtained by reduction of corresponding ynone (see SI p. 4).



5l

Oxidation of propargylic alcohol **6l** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **6l** (2.42 g, 15.91 mmol), DMP (8.09 g, 19.09 mmol) and DCM (96mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5l** as pale yellow liquid (1.98 g, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52-7.48 (m, 2H), 7.08 (dd, *J* = 3.9, 5.0 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.1, 136.8, 131.8, 127.8, 119.8, 92.7, 84.4, 32.5. IR (ATR): ṽ = 3105 (w), 2179 (s), 1662 (s), 1257 (m), 1211 (s) cm^{-1}. HRMS (GCMS + p EI) calcd for C_8H_6OS $[M]^+$ 150.0139, found 150.0134. Analytical data were consistently with those reported in literature.[20]

4-(furan-2-yl)but-3-yn-2-one (5m): A procedure of Paraja *et al.* was followed.[21] To a stirred suspension of Zn dust (1.58 g, 24.14 mmol) in DCM (15 mL) was added PPh_3 (12.68 g, 48.29 mmol). The suspension was cooled to 0 °C and CBr_4 (8.01 g, 48.23 mmol) dissolved in DCM (27 mL) was slowly added over 15 minutes. Furfural (0.5 mL, 6.04 mmol) dissolved in DCM (12 mL) was added dropwise and the mixture was allowed to warm to room temperature. After 15 minutes TLC (SiO_2, petroleum ether) indicated full consumption of furfural. Water (50 mL) was added, the resulting layers were separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organics were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (SiO_2, petroleum ether) to provide the corresponding geminal dibromide. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, *J* = 1.1 Hz, 1H), 7.42 (s, 1H), 6.96 (d, *J* = 3.4 Hz, 1H), 6.47 (dd, *J* = 1.6, 3.4 Hz, 1H). Analytical data were consistent with those reported in literature.[22]

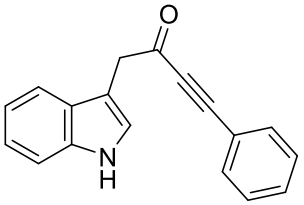


5a

2-(2,2-dibromovinyl)furan (1.36 g, 5.39 mmol) was dissolved in THF (6 mL) and cooled to -78 °C. *n*-BuLi (11.31 mmol) was added dropwise and the solution was stirred for 1h. Acetaldehyde (0.31 mL, 5.39 mmol) was added and the solution was allowed to warm to room temperature. After 1h TLC (30% ethyl acetate in petroleum ether) showed full consumption of starting material. Water (10 mL) was added, the resulting layers were separated and the aqueous layer was extracted with dichloromethane (3 x 5 mL). The combined organics were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (SiO_2, 30% ethyl acetate in petroleum ether) to provide the propargylic alcohol **6m**. Analytical data were identical to the compound obtained by reduction of corresponding ynone (see SI p. 4).

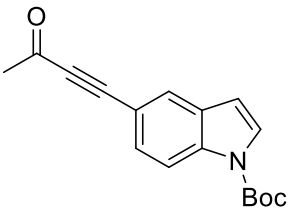
Oxidation of propargylic alcohol **6m** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **6m** (1.25 g, 9.18 mmol), DMP (4.28 g, 10.09 mmol) and DCM (51mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5a** as pale yellow liquid (0.775 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J* = 1.1 Hz, 1H), 6.96 (d, *J* = 3.4 Hz, 1H), 6.50 (dd, *J* = 1.9, 3.5 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.8, 147.1, 135.2, 121.9, 111.9, 93.7, 80.4, 31.9. IR (ATR): ṽ = 3132 (w), 2179 (m), 1654 (m), 711 (s) cm^{-1}. HRMS (FTMS + p EI) calcd for $C_8H_6O_2$ $[M]^+$ 134.0368, found 134.0364.

1-(1*H*-indol-3-yl)-4-phenylbut-3-yn-2-one (5n): A procedure of Fedoseev and Van der Eycken was followed.[23] The spectral data for the prepared ynone matched the reported compound. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.41 (m, 5H), 7.24 (m, 4H), 4.13 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.7, 137.4, 134.1, 131.7, 129.4, 128.5, 124.6, 123.3, 120.9, 120.1, 112.3, 108.6, 93.0, 89.1, 78.2, 43.3. IR (ATR): ṽ =3410 (w), 2202 (m), 1662 (w), 1084 (S), 743 (s) cm-1.



5n

***tert*-butyl 5-(3-oxobut-1-yn-1-yl)-1*H*-indole-1-carboxylate (5o):** Prepared following the general procedure for Sonogashira coupling. *tert*-butyl 5-bromo-1*H*-indole-1-carboxylate (7.26 g, 24.5 mmol), but-3-yn-2-ol (3.88 mL, 49.1 mmol), $PdCl_2(PPh_3)_2$ (428 mg, 0.61 mmol), CuI (163 mg, 0.86 mmol), NEt_3 (16.89 mL, 122.5 mmol) as additive and THF (65 mL) as solvent were used at 95 °C. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6o** (791 mg, 11% - not optimized). Analytical data were identical to the compounds obtained by reduction of corresponding ynone.

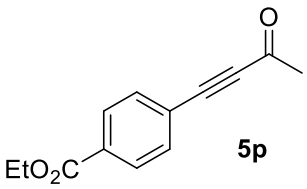


5o

Oxidation of propargylic alcohol **6o** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **6o** (0.791 mg, 2.77 mmol), DMP (1.53 g, 3.6 mmol) and DCM (20 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5o** as colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 1.0 Hz, 1H), 7.65 (d, *J* = 3.7 Hz, 1H), 7.51 (dd, *J* = 1.5, 8.6 Hz, 1H), 6.58 (d, *J* = 3.7 Hz, 1H), 2.47

(s, 3H), 1.68 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.7, 149.3, 136.1, 130.6, 129.0, 127.5, 126.7, 115.6, 113.8, 107.1,92.1, 87.9, 84.6, 32.8, 28.2. IR (ATR): ṽ = 2175 (m), 1735 (m), 1662 (m), 1361 (s) cm^{-1}. HRMS (ESI, +VE, +HMR) calcd for $C_{17}H_{17}NO_3$ $[M+Na]^+$ 306.1106, found 306.1109.

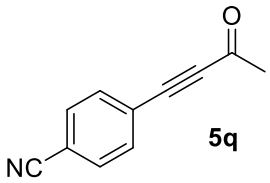
ethyl 4-(3-oxobut-1-yn-1-yl)benzoate (5p): Prepared following the general procedure for Sonogashira coupling. ethyl 4-bromobenzoate (2.85 mL, 17.5 mmol), but-3-yn-2-ol (1.52 mL, 19.2 mmol), $PdCl_2(PPh_3)_2$ (246 mg, 0.35 mmol), CuI (133 mg, 0.7 mmol), NEt_3 (140 mL) as solvent were used at 95 °C. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6p**. Analytical data were identical to the compounds obtained by reduction of corresponding ynone.



5p

Oxidation of propargylic alcohol **6p** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **6p** (4.02 g, 18.4 mmol), DMP (8.61 g, 20.3 mmol) and DCM (92 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5p** as colorless solid (2.82 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.0 - 8.03 (*m*, 2H), 7.65 - 7.60 (*m*, 2H), 4.39 (*q*, *J* = 7.1 Hz, 2H), 2.47 (*s*, 3H), 1.40 (*t*, *J* = 7.3 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 184.3, 163.8, 132.8, 132.1, 128.1, 124.3, 89.8, 88.5, 65.5, 32.8, 14.3. IR (ATR): ṽ = 2983 (w), 2310 (m), 1668 (m), 1648 (w), 1270 (s), 769 (s) cm^{-1}. MS (EI): m/z = 216 $[M]^{\cdot+}$, 201 $[M -Me]^{\cdot+}$, 171 $[M -OMe]^{\cdot+}$. Analytical data were consistent with those reported in literature.[18]

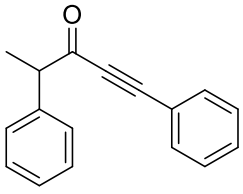
4-(3-oxobut-1-yn-1-yl)benzonitrile (5q): Prepared following the general procedure for Sonogashira coupling. 4-bromobenzonitrile (2.08 g, 11.42 mmol), but-3-yn-2-ol (0.805 mL, 10.2 mmol), $PdCl_2(PPh_3)_2$ (130 mg, 0.185 mmol), CuI (72 mg, 0.39 mmol), NEt_3 (91 mL) as solvent were used at 95 °C. 20% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide propargylic alcohol **6q** (1.61 g, 83%). Analytical data were identical to the compounds obtained by reduction of corresponding ynone.



5q

Oxidation of propargylic alcohol **6q** was carried out according to the general procedure for Dess-Martin oxidation: Propargylic alcohol **6q** (1.43 g, 8.4 mmol), DMP (3.9 g, 9.2 mmol) and DCM (42 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5q** as colorless solid (1.22 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 - 7.63 (m, 4H), 2.48 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 184, 133.3, 132.4, 124.8, 118, 114.1, 90.6, 86.8, 32.8. IR (ATR): ṽ = 2983 (w), 2310 (m), 1668 (m), 1648 (w), 1270 (s), 769 (s) cm^{-1}. MS (EI): m/z = 169 $[M]^{\cdot+}$, 154 $[M -Me]^{\cdot+}$. Analytical data were consistent with those reported in literature.[9]

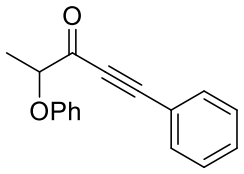
1,4-diphenylpent-1-yn-3-one (5r): Prepared according to the general procedure for addition of lithium acetylide to aldehydes. Ethynylbenzene (3.62 mL, 33 mmol), 2-phenylpropanal (3.53 mL, 30 mmol), *n*-BuLi (13.2 mL, 33 mmol, 2.5 M solution in Hexane) and Et_2O (45 mL) were used. 10% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide a mixture of propargylic alcohol **6ra/6rb.** Analytical data were identical to the compounds obtained by reduction of corresponding ynone.



5r

Oxidation of mixture of propargylic alcohol **6ra/6rb** was carried out according to the general procedure for Dess-Martin oxidation: Mixture of propargylic alcohols **6ra/6rb** (1.57 g, 6.64 mmol), DMP (3.09 g, 7.3 mmol) and DCM (35 mL) were used. 5% ethyl acetate in petroleum ether was used as eluent for flash column chromatography to provide ynone **5r** as colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 - 7.28 (m, 10H), 3.93 (q, *J* = 7.1 Hz, 1H), 1.56 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.3, 139.5, 133.0, 130.7, 128.8, 128.5, 128.4, 127.5, 93.0, 87.4, 54.8, 17.1. IR (ATR): ṽ = 2978 (w), 2194 (m), 1662 (s) cm^{-1}. HRMS (GCMS + p EI) calcd for $C_{17}H_{14}O$ $[M]^+$ 234.1045, found 234.1039.

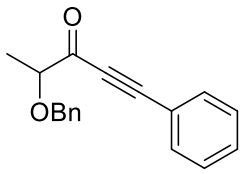
4-phenoxy-1-phenylpent-1-yn-3-one (5s): To a suspension of Phenol (2.53 g, 26.9 mmol) and K_2CO_3 (8.26 g, 59.8 mmol) in Acetone (200 mL) was added methyl 2-bromopropanoate (5 g, 29.9 mmol). After 48 h the solvent was evaporated, DCM (100 mL) and water (100 mL) were added and the layers were separated. The aqueous layer was extracted with DCM (3 x 50 mL). The organic layers were combined and dried over Na_2SO_4. The solvent was evaporated, and the crude product was purified by flash column chromatography (SiO_2, 10% ethyl acetate in petroleum ether) to provide the phenyl ether **5sc** as colorless liquid (3.69 g, 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 - 7.23 (m, 2H), 6.98 - 6.93 (m, 1H), 6.87 - 6.83 (m, 2H), 4.75 (q, *J* = 6.9 Hz, 1H), 3.74 (s, 3H), 1.61 (d, *J* = 7.0 Hz, 3H). Analytical data were consistent with those reported in literature.[24]



5s

To a solution of ethynyl benzene (2.35 mL, 21.4 mmol) in THF (22 mL), at -78 °C was added *n*-BuLi (8 mL, 20.2 mmol, 2.5 M in hexane). After stirring for 30 minutes, a solution of phenyl ether **5sc** (3.5 g, 19.4 mmol) in THF (12 mL) was added dropwise. The mixture was allowed to reach room temperature and stirred for further 30 minutes. HCl aq. (21 mL (1 M) was added, the layers were separated, and the aqueous layer was extracted with DCM (3 x 10 mL). The organic layers were combined and dried over Na_2SO_4. The solvent was evaporated, and the crude product was purified by flash column chromatography (SiO_2, 10% ethyl acetate in petroleum ether) to provide ynone **5s**. ^{1}H NMR (300 MHz, CDCl3): δ 7.53 - 7.46 (m, 3H), 7.40 - 7.29 (m, 4H), 7.04 - 6.94 (m, 3H), 4.88 (q, J = 6.8 Hz, 1H), 1.70 (d, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3): δ 188.4, 157.7, 133.4, 131.2, 129.7, 128.7, 121.6, 119.7, 115.3, 95.6, 85.8, 78.9, 17.9. IR (ATR): $\tilde{\nu}$ = 2989 (w), 2194 (s), 1666 (m), 1489 (m), 1230 (m) cm^{-1}. HRMS (ESI-TOF) calcd for $C_{17}H_{14}O_2$ $[M+Na]^+$ 273.0886, found 273.0889.

4-(benzyloxy)-1-phenylpent-1-yn-3-one (5t): Ethyl lactate (5.5 mL, 42.3 mmol) was dissolved in THF/DMF (160 mL, v/v = 1:1) and cooled to 0 °C. NaH (1.01 g, 42.3 mmol) was added and stirred for 40 minutes. TBAI (0.77 g, 2.1 mmol) and benzyl bromide (5.06 mL, 42.3 mmol) were added. After 40 h the reaction shows no further progress and 42.3 mL HCl-solution (42.3 mL, 1 M) and water (50 mL) was added and stirred for 10 minutes. The layers were separated, and the aqueous layer was extracted with DCM (3 x). The organic layers were combined and dried over Na_2SO_4. The solvent was evaporated, and the crude product was purified by flash column chromatography (SiO_2, 10% ethyl acetate in petroleum ether) to provide the benzyl ether **5tc** (3.4 g, 39%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 - 7.32 (m, 5H), 4.76 (d, *J* = 12.2 Hz, 1H), 4.51 (d, *J* = 12.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 1H), 1.49 (d, *J* = 6.7 Hz, 3H), 1.35 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.9, 139.7, 129.4, 128.9, 128.8, 75.0, 72.9,61.9, 19.7,15.3. Analytical data were consistent with those reported in literature.[25]



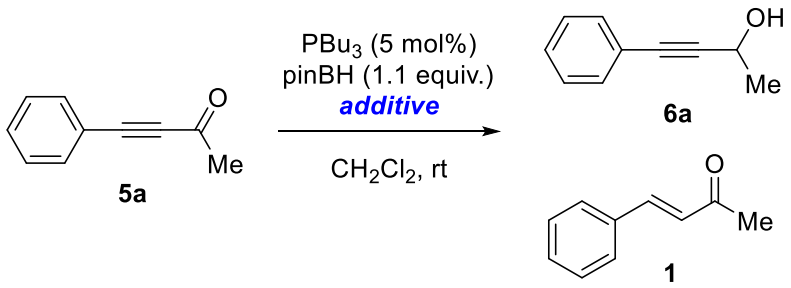
5t

To a solution of ethynyl benzene (2.03 mL, 18.5 mmol) in THF (20 mL), at -78 °C was added *n*-BuLi (8 mL, 20.2 mmol, 2.5 M in hexane). After stirring for 30 minutes, a solution of benzyl ether **5tc** (3.21 g, 15.4 mmol) in THF (10 mL) was added dropwise. The mixture was allowed to reach room temperature and stirred for further 30 minutes. HCl aq. (21 mL (1 M) was added, the layers were separated, and the aqueous layer was extracted with DCM (3 x 10 mL). The organic layers were combined and dried over Na_2SO_4. The solvent was evaporated, and the crude product was purified by flash column chromatography (SiO_2, 10% ethyl acetate in petroleum ether) to provide ynone **5t** as colorless solid. ^{1}H NMR (300 MHz, CDCl3): δ 7.61 (t, J = 4.1 Hz, 2H), 7.51 - 7.34 (m, 8H), 4.83 (d, J = 11.7 Hz, 1H), 4.58 (d, J = 11.7 Hz, 1H), 4.19 (q, J = 6.8 Hz, 1H), 1.55 (d, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3): δ 190.1, 137.7, 133.4, 131.1, 128.8, 128.6, 128.0, 127.9, 119.4, 94.3, 86.3, 80.9, 72.3, 17.8. IR (ATR): $\tilde{\nu}$ = 2978 (w), 2194 (s), 1670 (s), 1068 (m) cm^{-1}. HRMS (GCMS + p EI) calcd for $C_{18}H_{16}O_2$ $[M]^+$ 264.1150, found 264.1146. Analytical data were consistent with those reported in literature.[26]

Selected results of optimization studies

Table 1.

Effects of additives on reaction selectivity and isolated yield of the 1,2-reduction product.

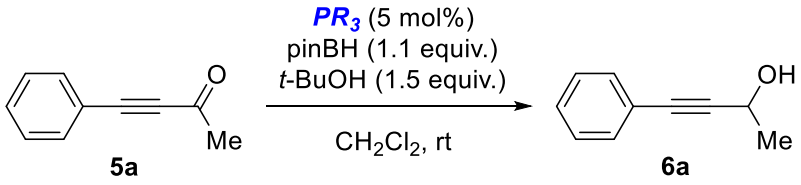


Entry	*t*-BuOH (equiv.)	**6a** (%)[a]	**1** (%)[a]	**5a** (%)[a]
1	-	62	14	24
2	0.5	81	12	3
3	1.1	80	0	3
4	1.5	87	0	0
5	2.1	87	0	0

[a] Yield determined by ^{1}H NMR spectroscopy of crude product mixtures after quenching reactions at designated time point using triphenylmethane as internal standard.

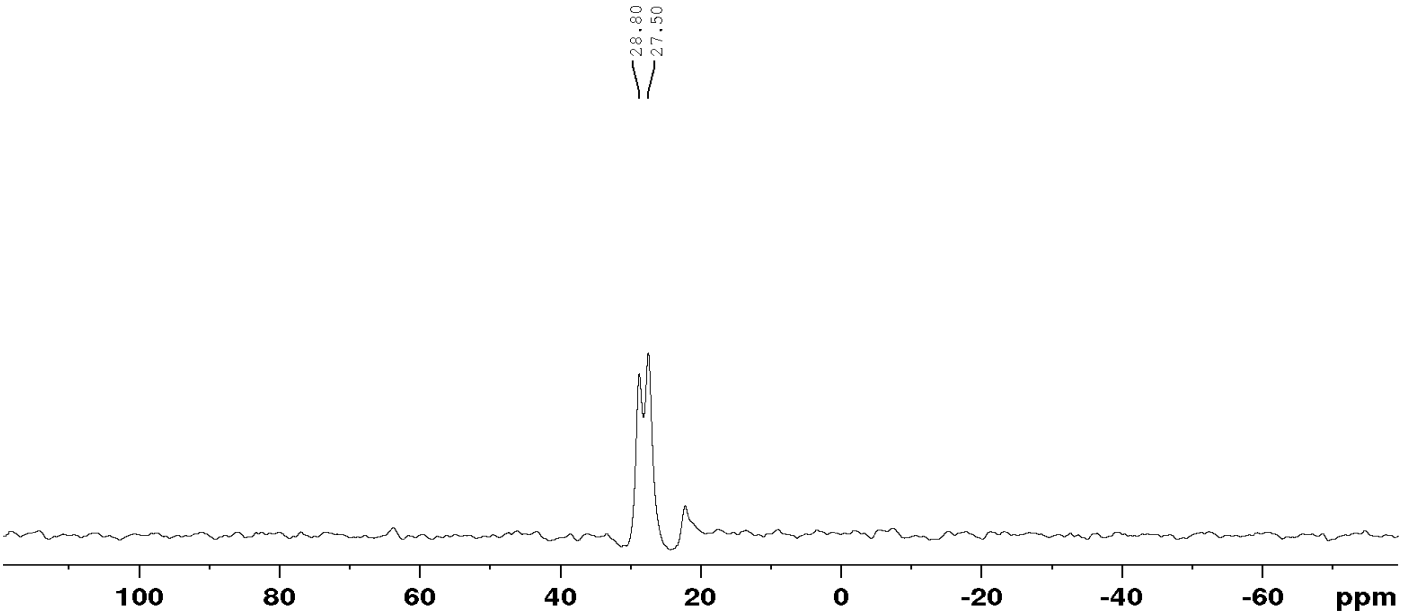
Table 2.

Optimization of the phosphine catalyst.

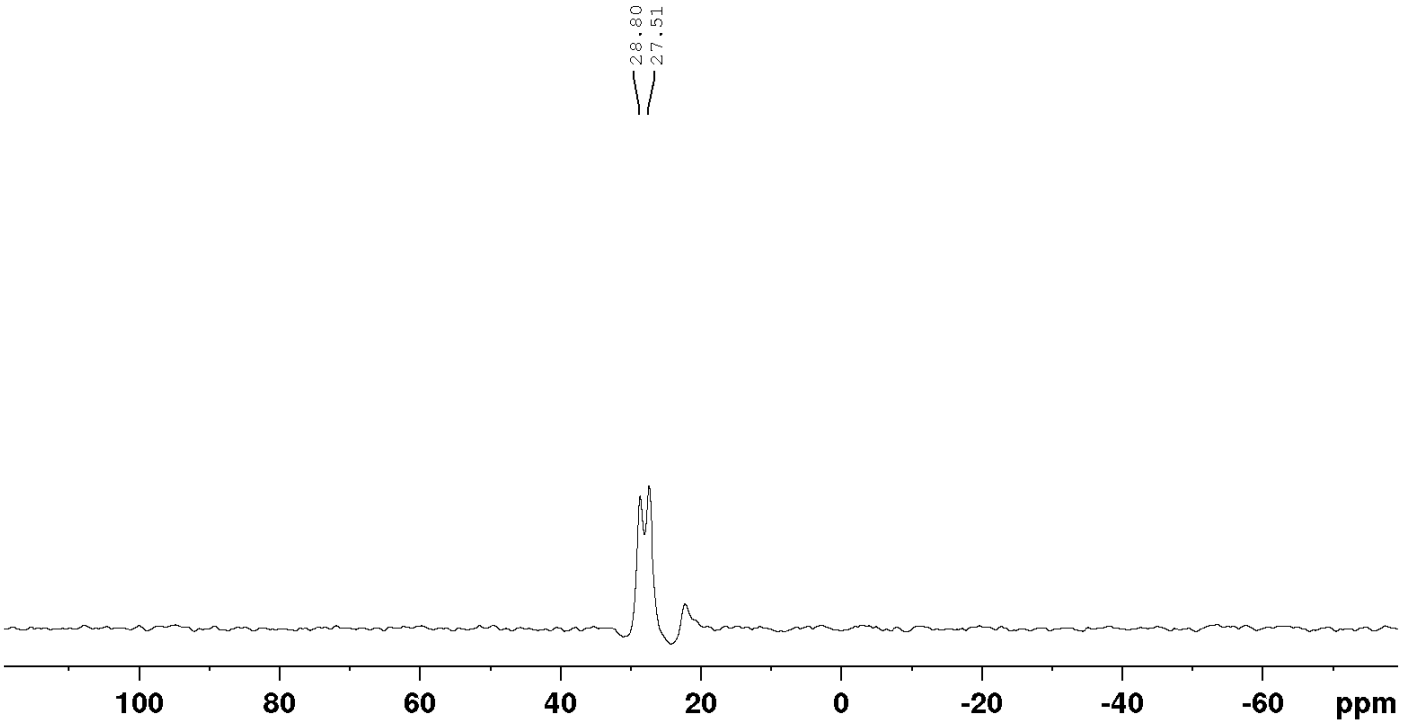


Entry	Catalyst	Reaction time	Isolated yield (%)	
			6a	**5a**
1	PPh3	24 h	55	28
2	PMePh2	24 h	68	10
3	PCy3	24 h	14	23
4	P(*t*-Bu)3	24 h	3	89
5	PMe3	10 min	89	0
6	PBu3	10 min	89	0

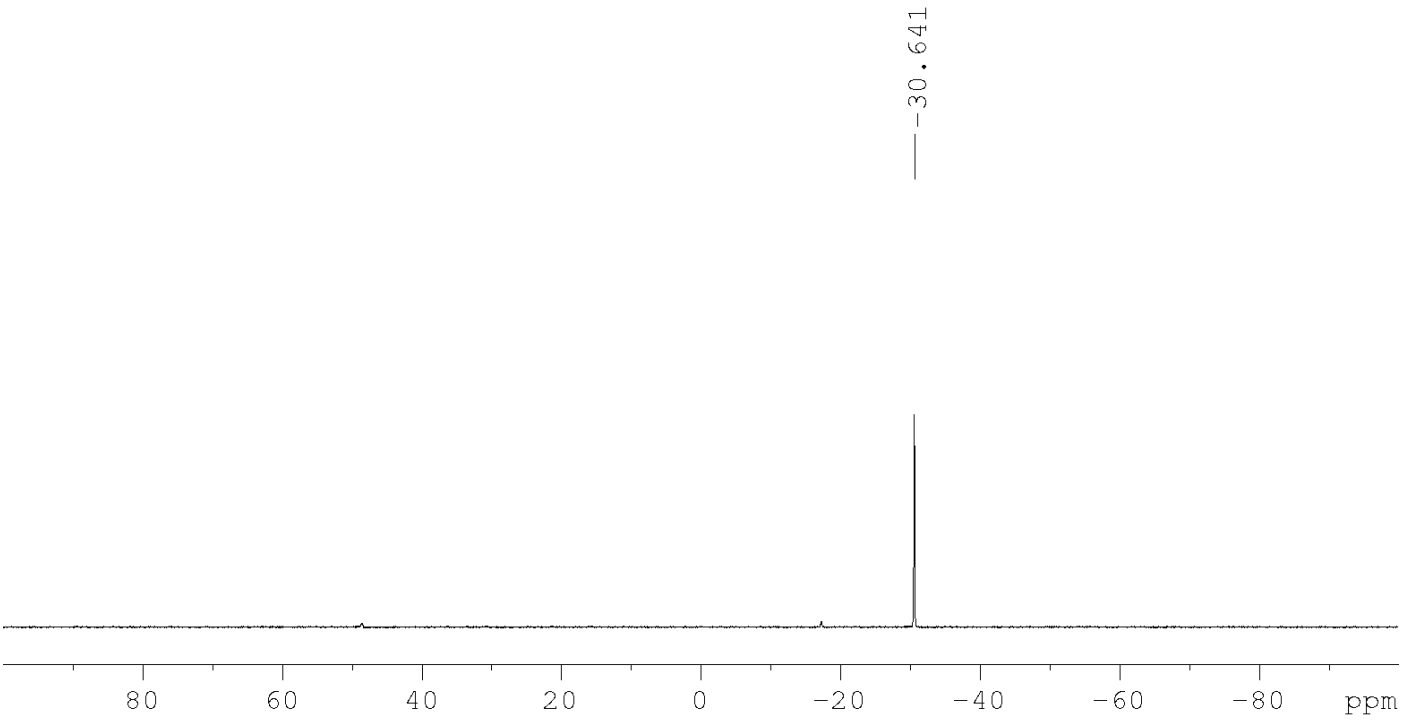
Selected NMR spectra of mixtures of starting components



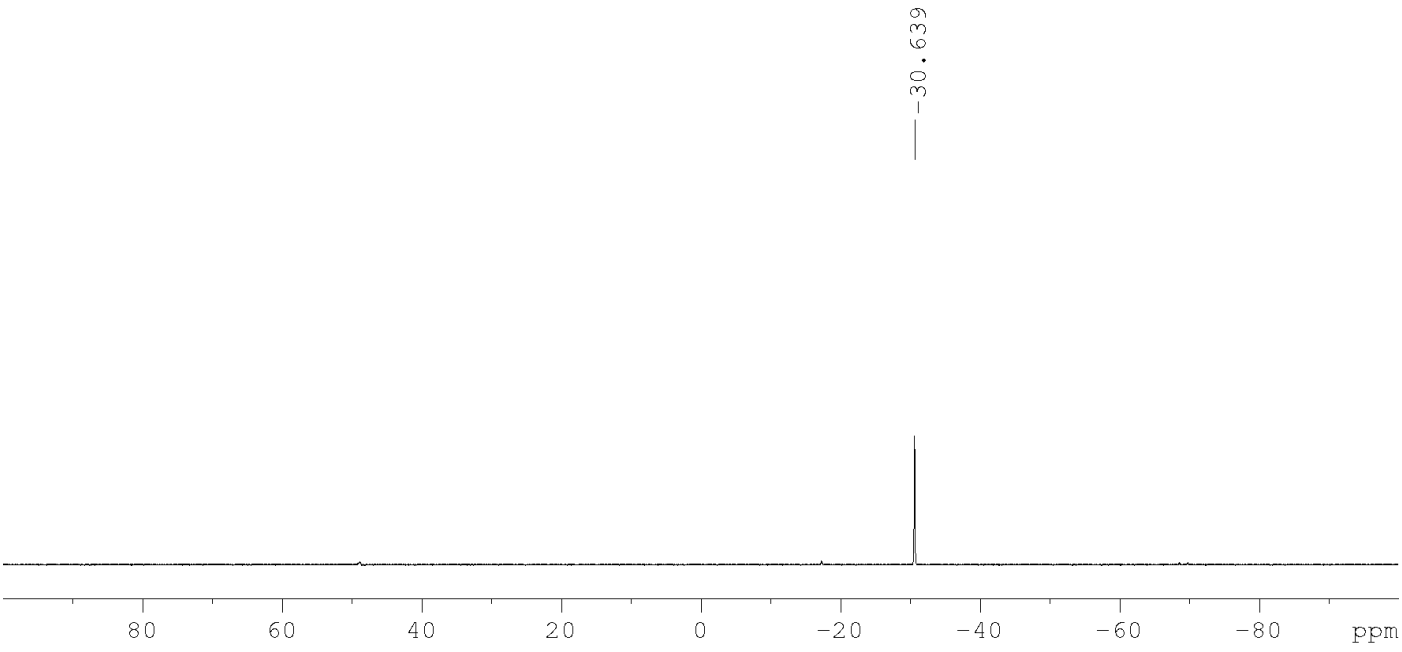
^{11}B-NMR spectrum of pinacolborane in $CDCl_3$.



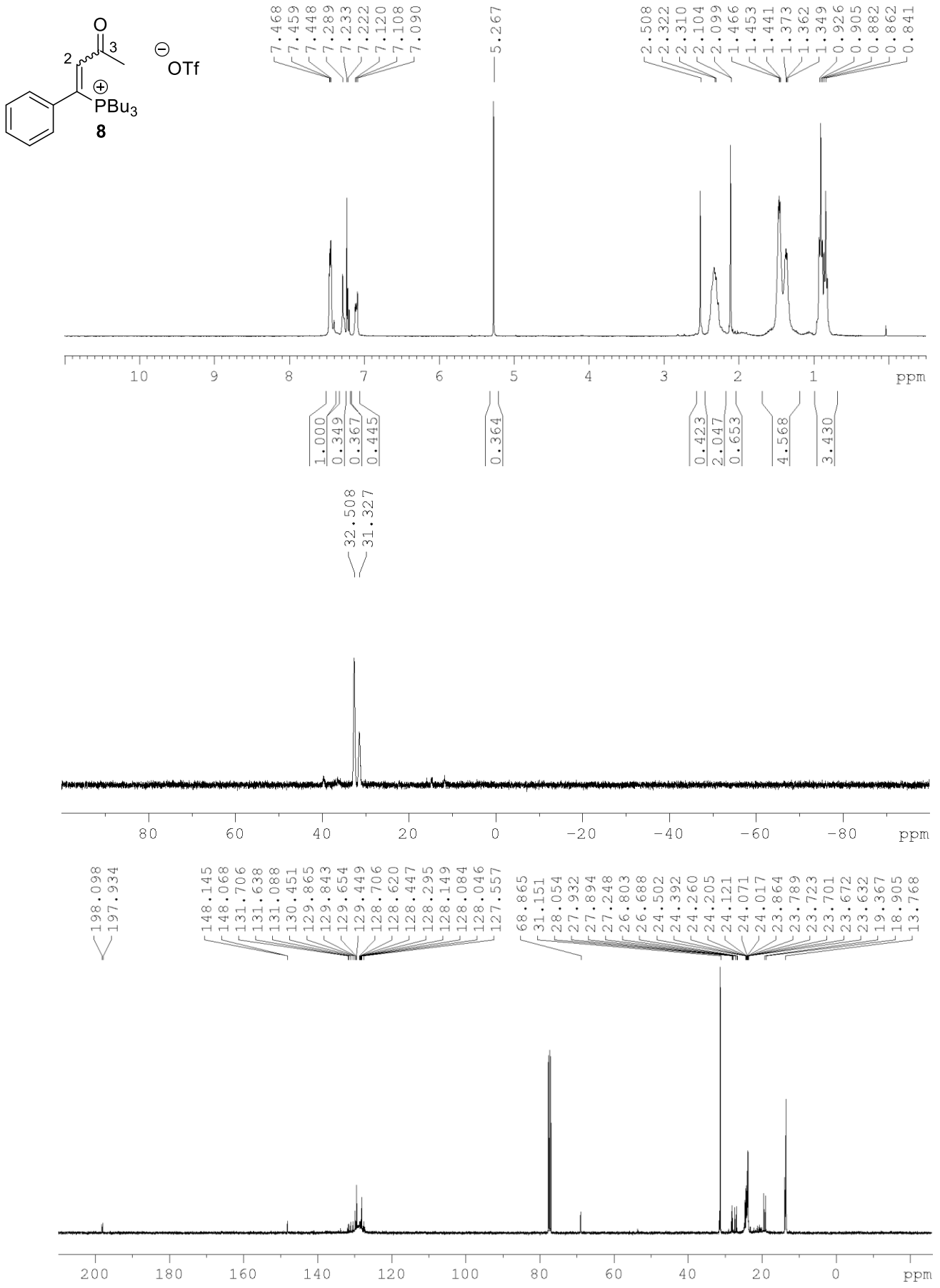
^{11}B-NMR spectrum of a 1:1 (40 mmol each) mixture of PBu_3 and pinBH in $CDCl_3$. ^{11}B-signal relates to pure pinBH and indicates that there is no interaction between the PBu_3 and pinBH.[27]



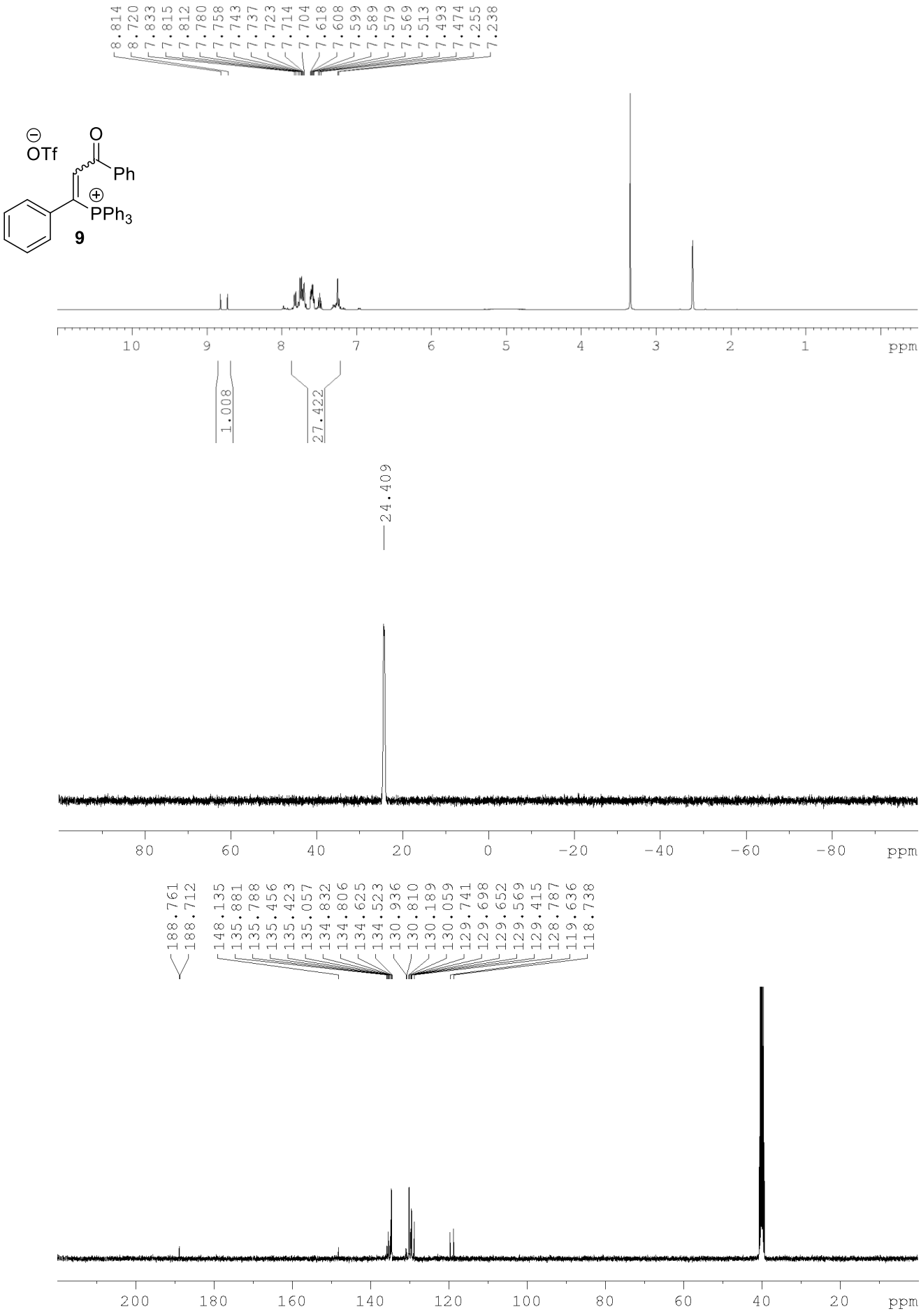
^{31}P-NMR spectrum PBu_3 in $CDCl_3$.



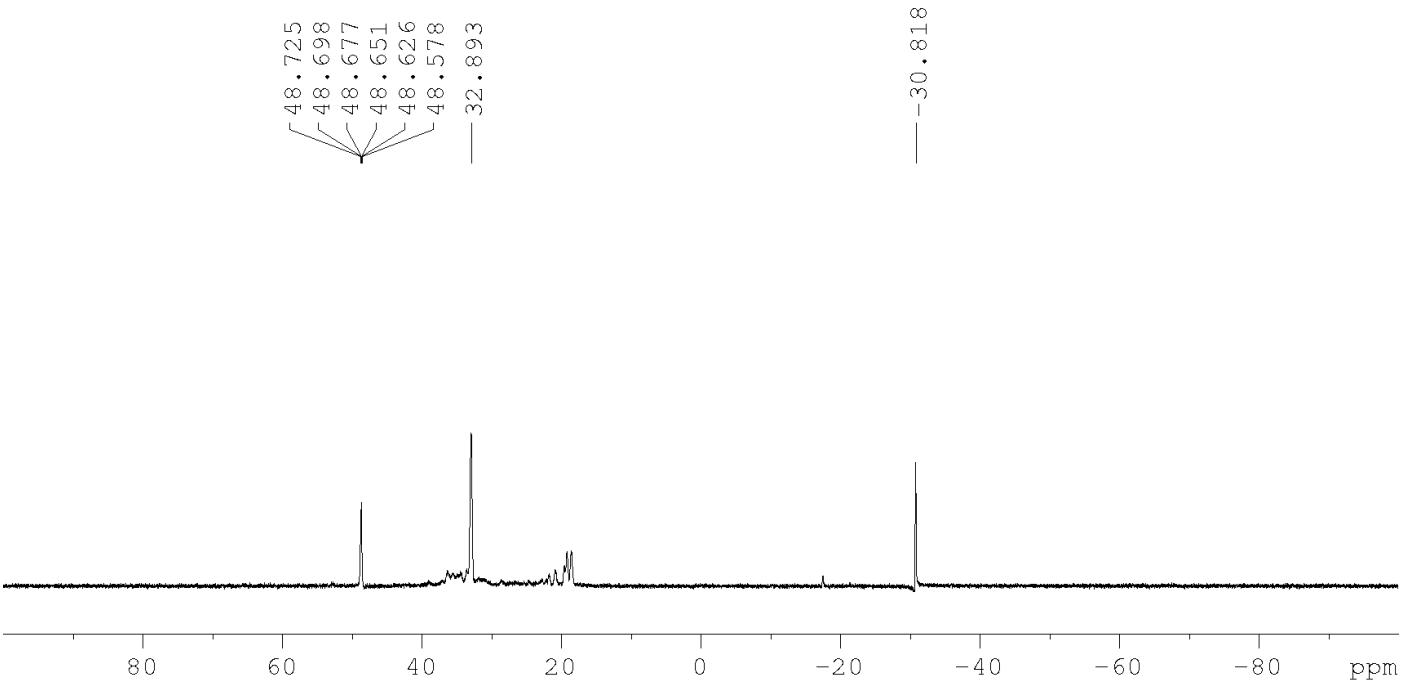
^{31}P-NMR spectrum of a 1:1 (40 mmol each) mixture of PBu_3 and pinBH in $CDCl_3$. ^{31}P-signal relates to pure PBu_3 and indicates that there is no interaction between the PBu_3 and pinBH.[28]



^{1}H-, ^{31}P- and ^{13}C-NMR of the equimolar mixture of **5a**, triflic acid and PBu_3 in $CDCl_3$. Phosphorus resonances are assigned to vinylphosphonium salt **8**; the two signals are attributed to *E* and *Z* isomers.[29] ^{13}C-NMR spectrum shows the characteristic splitting due to $^{1}J_{CP}$ and $^{2}J_{CP}$.



^{1}H-, ^{31}P- and ^{13}C-NMR spectra of salt **9** in $(CD_3)_2SO$. The crude sample of **9** was produced by mixing equimolar quantities of ynone **5a**, triflic acid and PBu_3 in $CDCl_3$.[29]



^{31}P-NMR spectra of a 1:1:1 (0.35 mmol each) mixture of **5a,** PBu_3, *t*-BuOH in $CDCl_3$. The singlet at 32.9 ppm corresponds to the vinylphosphonium cation in **8** produced by conjugate addition of phosphine to ynone followed by proton quench.[29] The signal at -30.8 ppm is assigned to free PBu_3. Other multiplets may arise from phosphine addition to side products that are produced under these conditions and related compounds.

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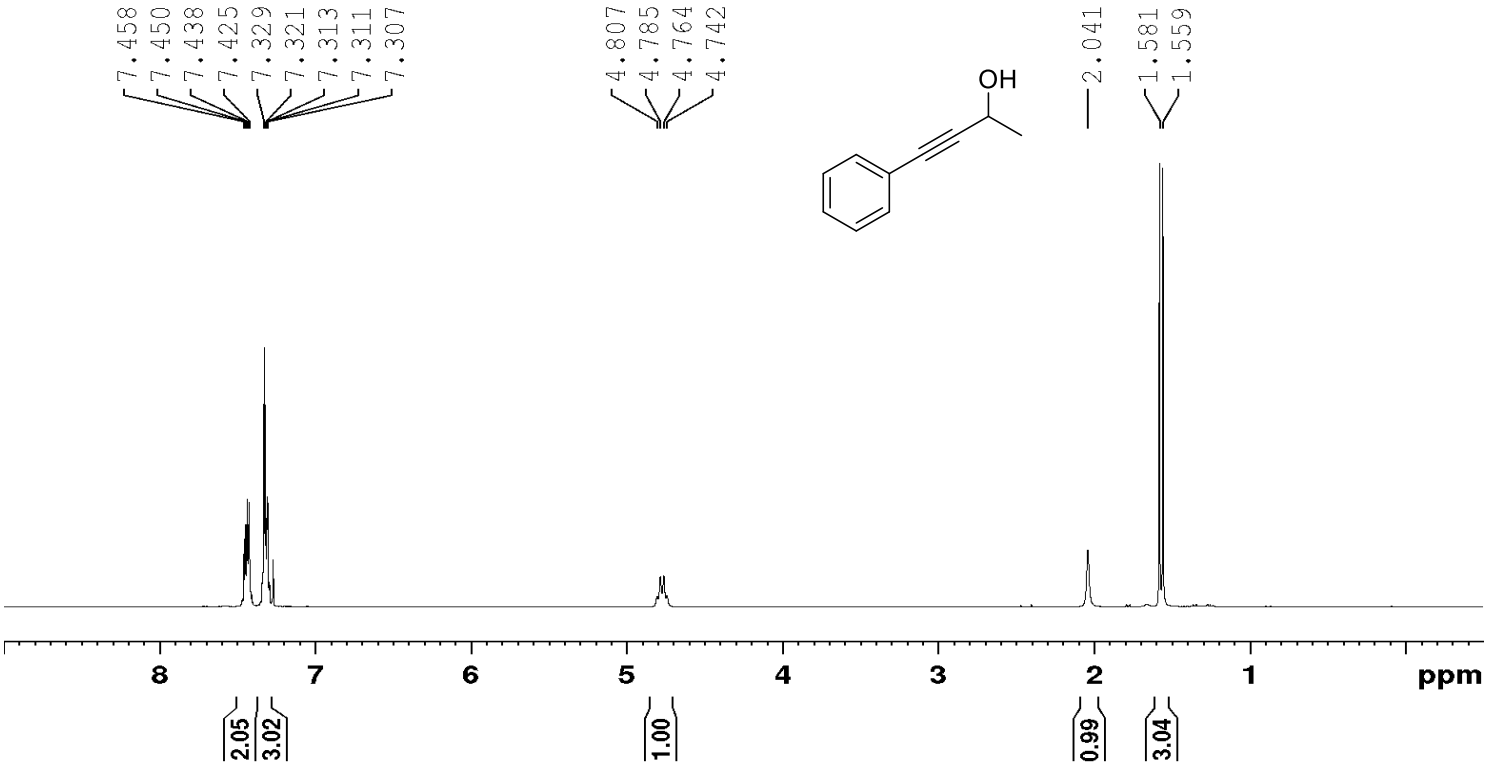
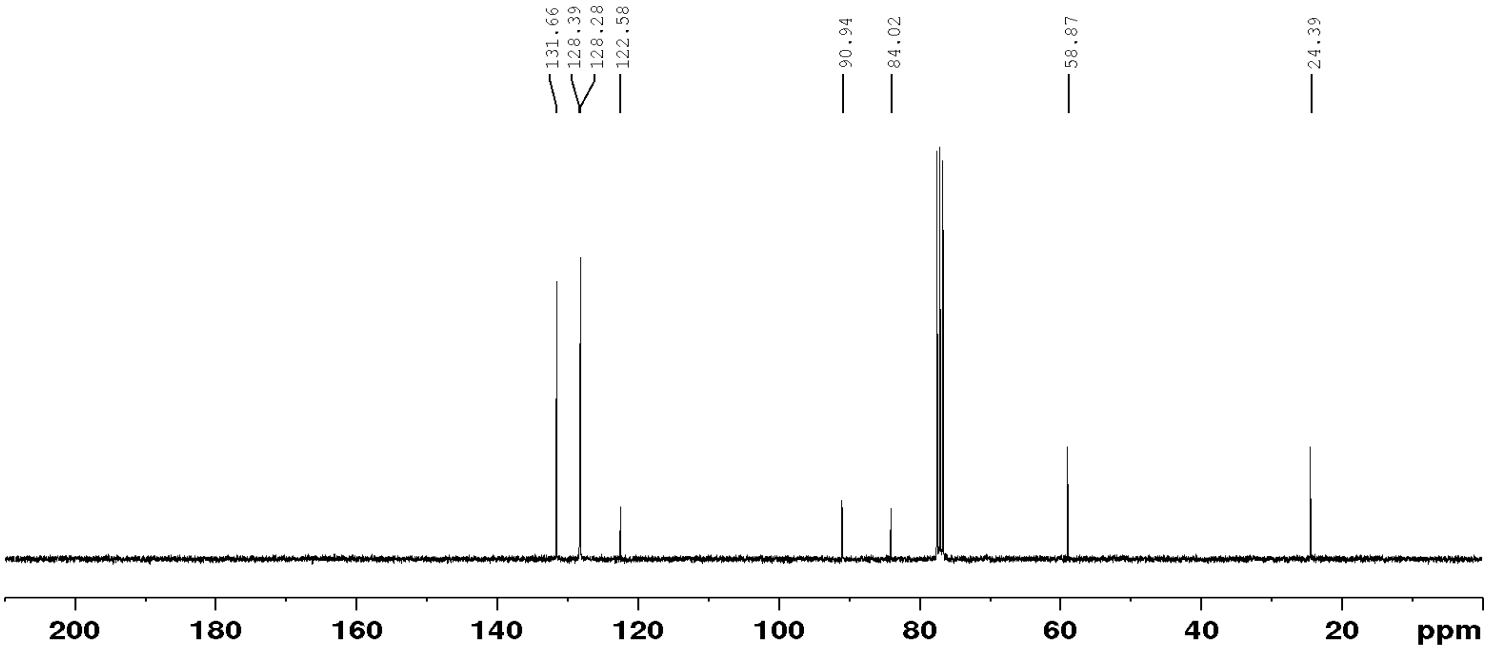
Copies of NMR spectra

4-phenylbut-3-yn-2-ol (6a)





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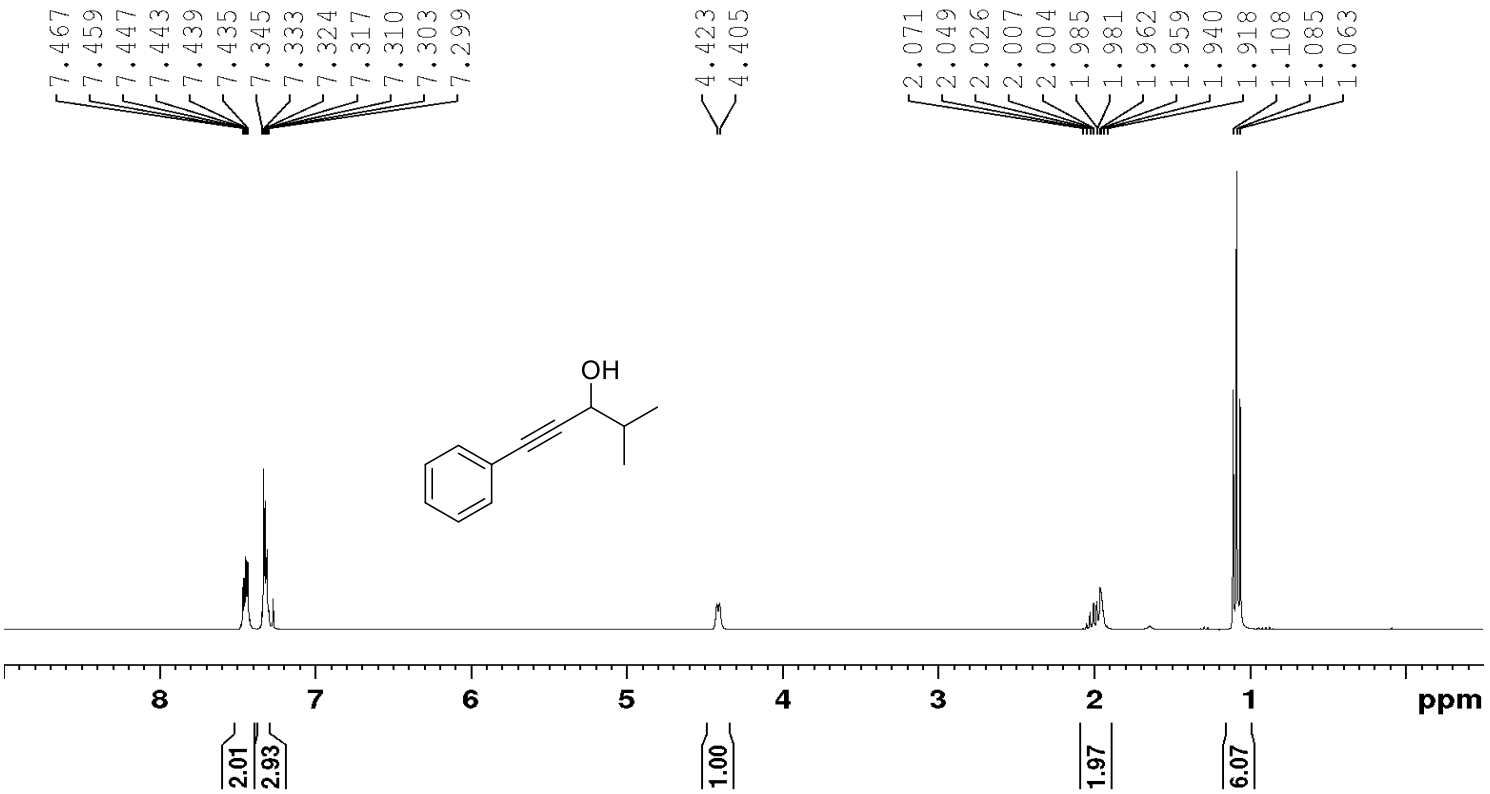
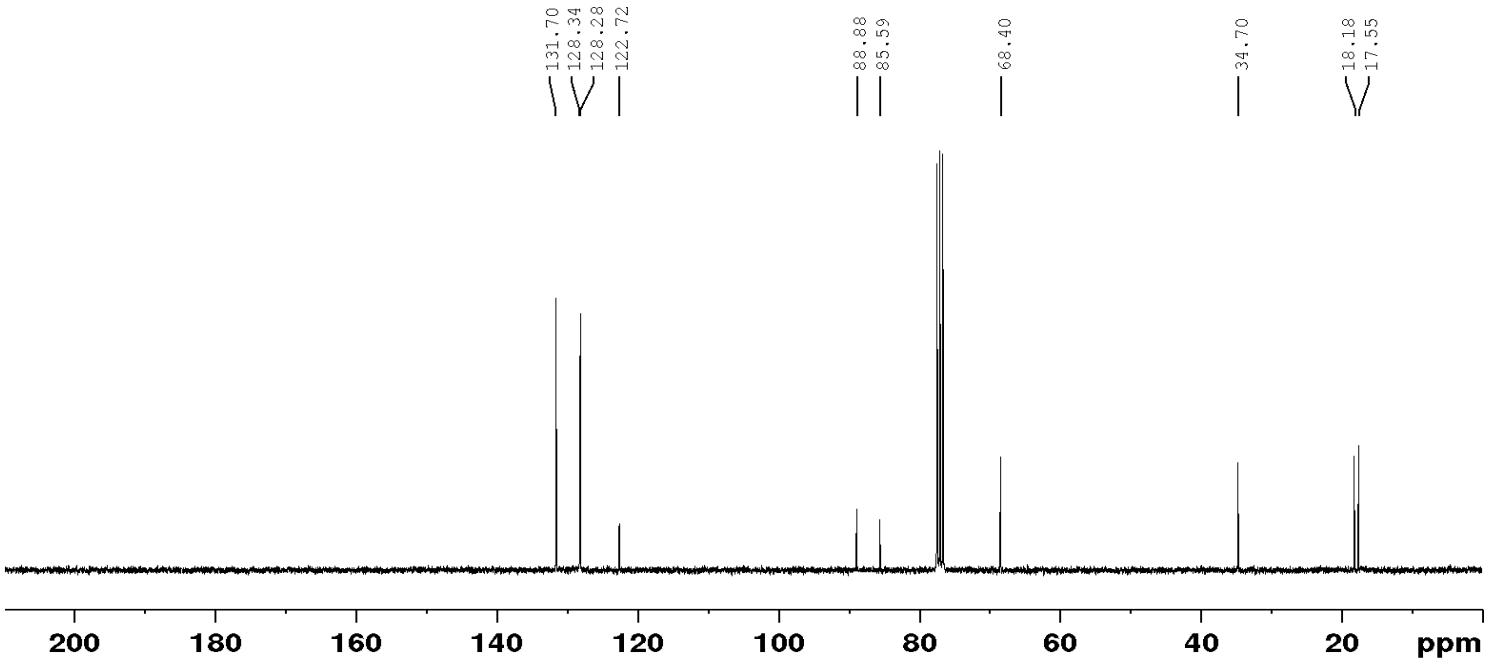
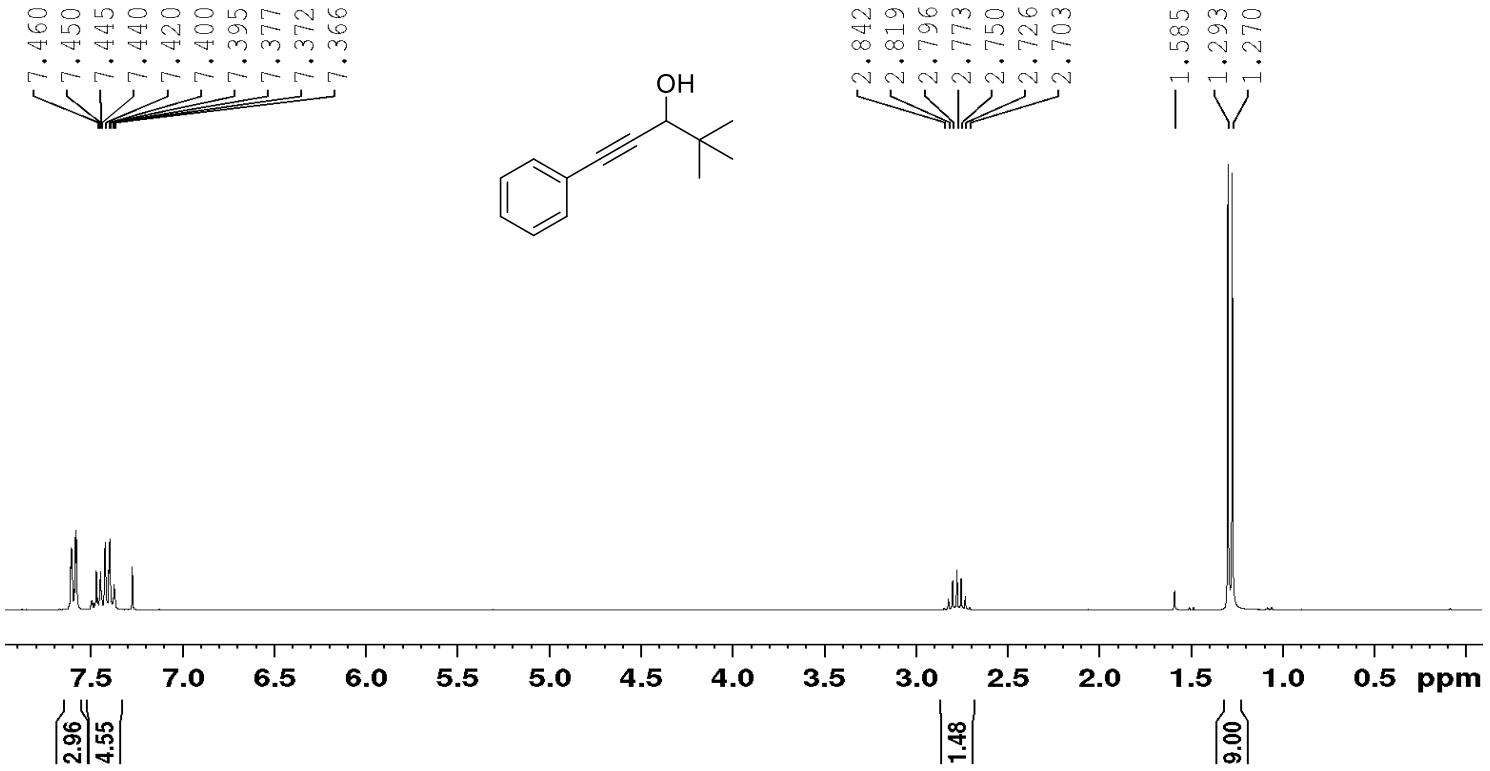
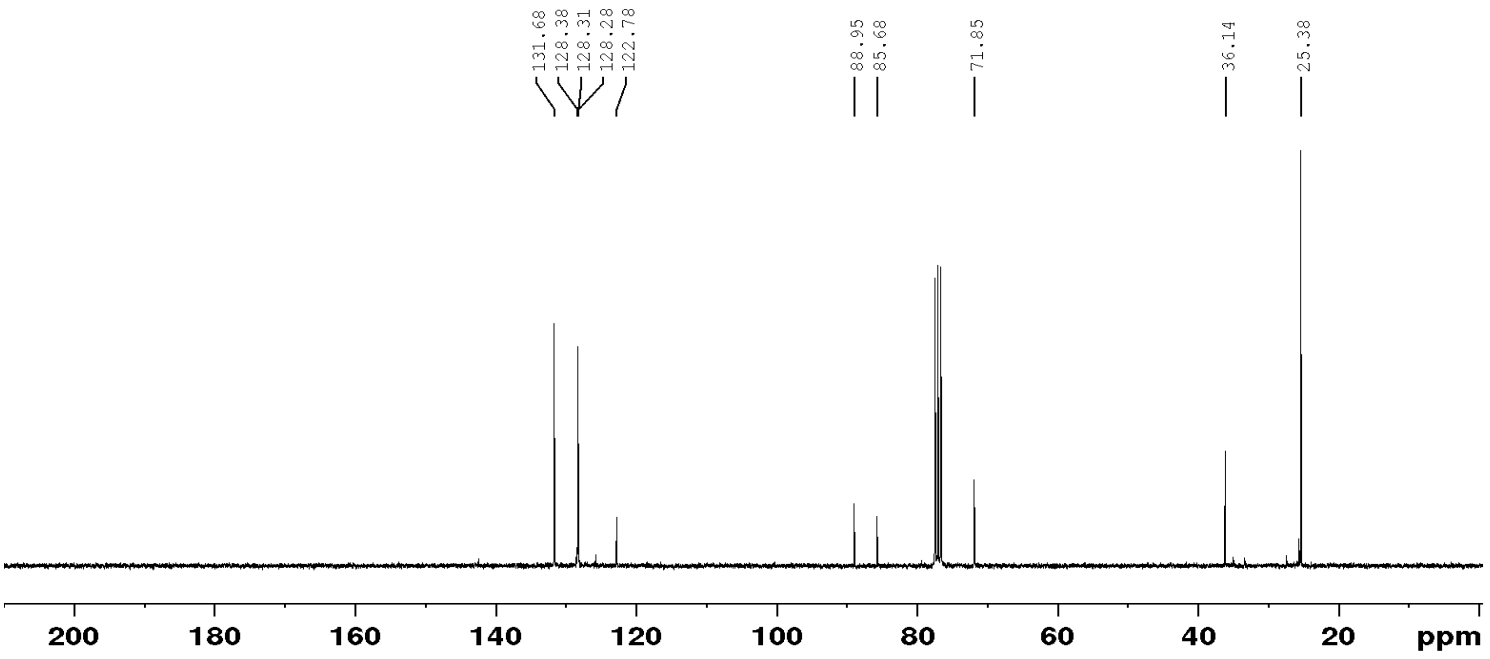


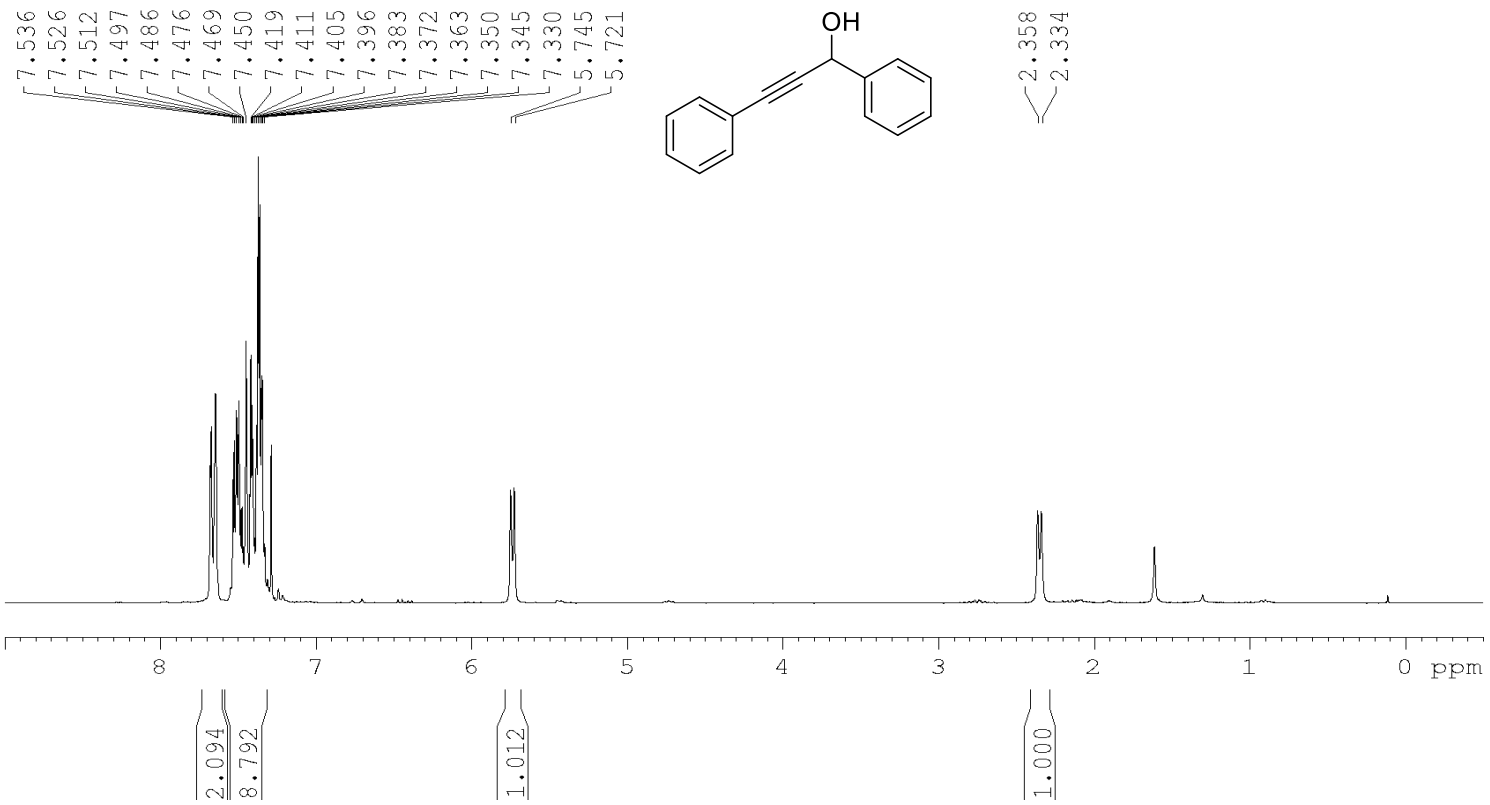


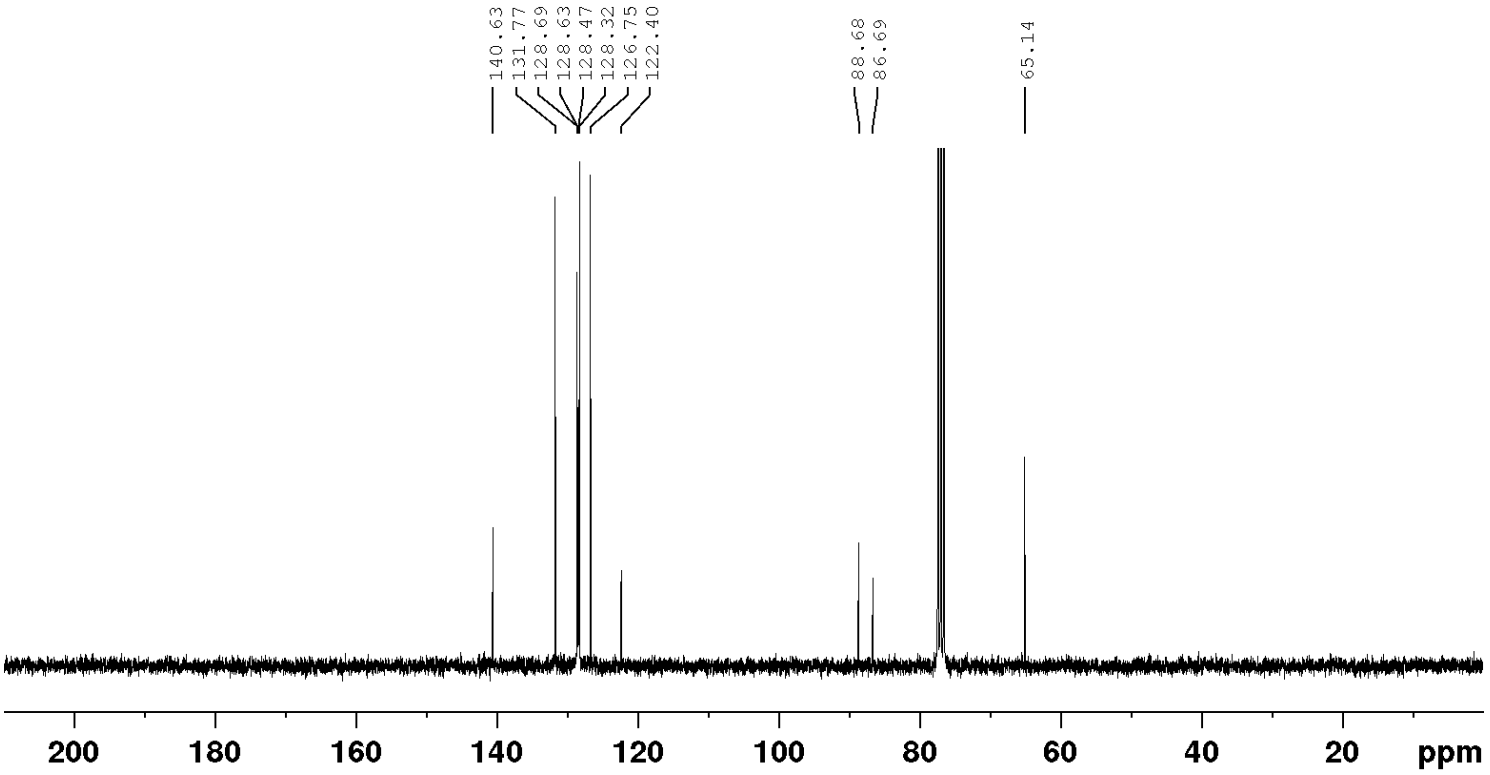
4,4-dimethyl-1-phenylpent-1-yn-3-ol (6c)



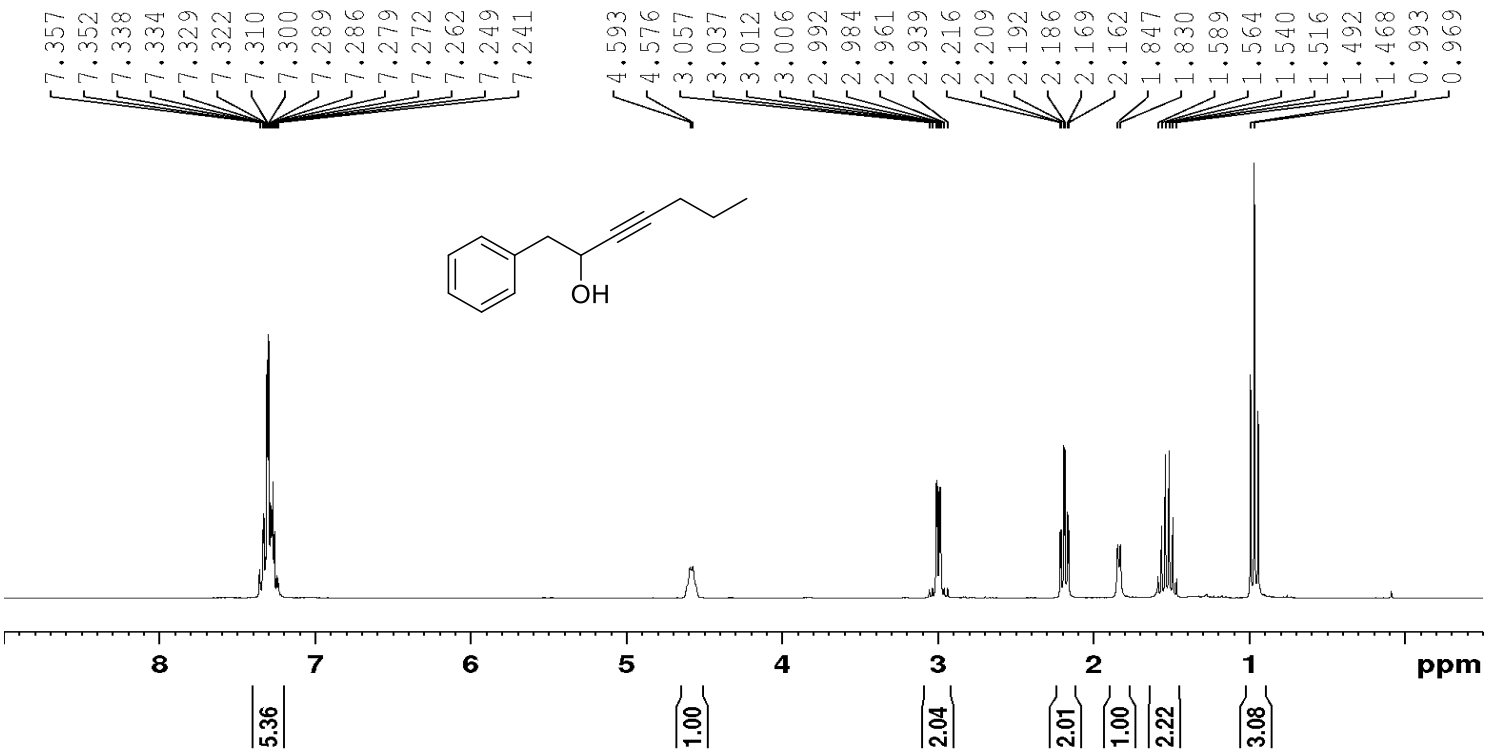


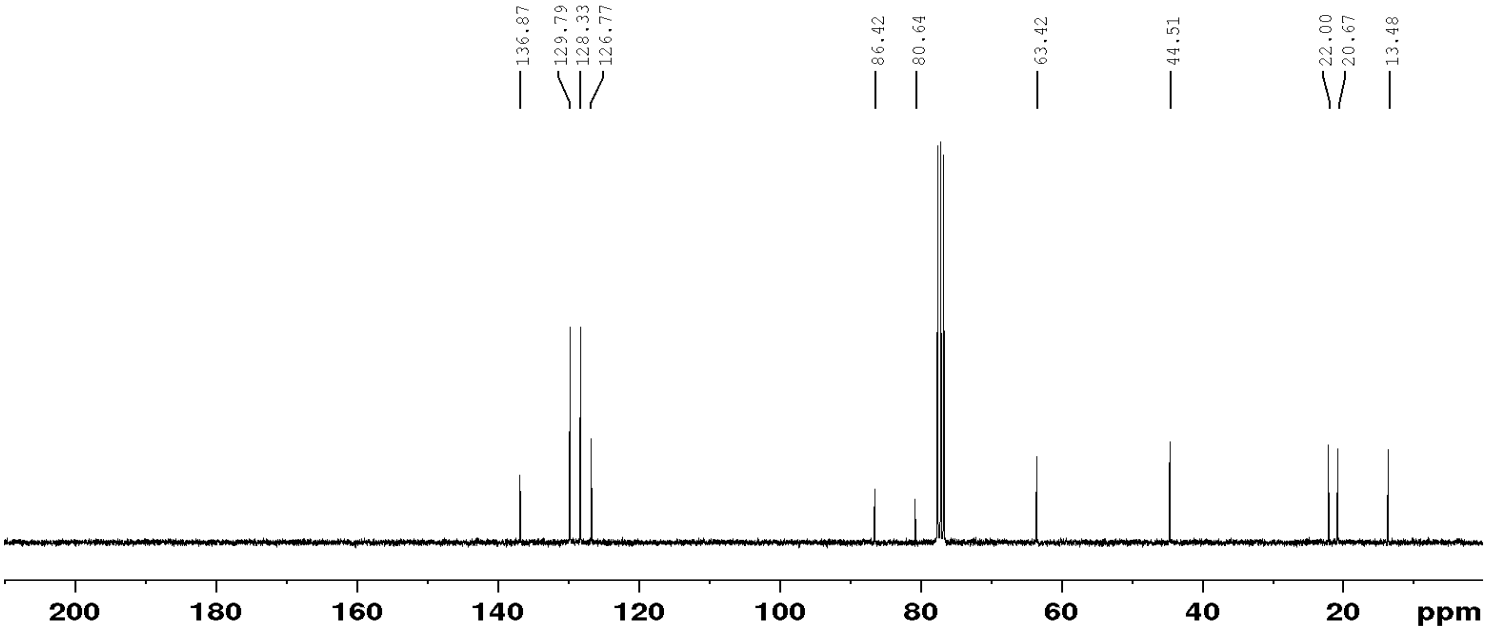
1,3-diphenylprop-2-yn-1-ol (6d)



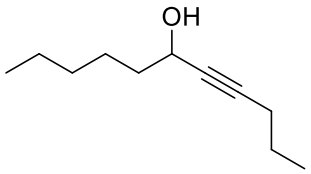


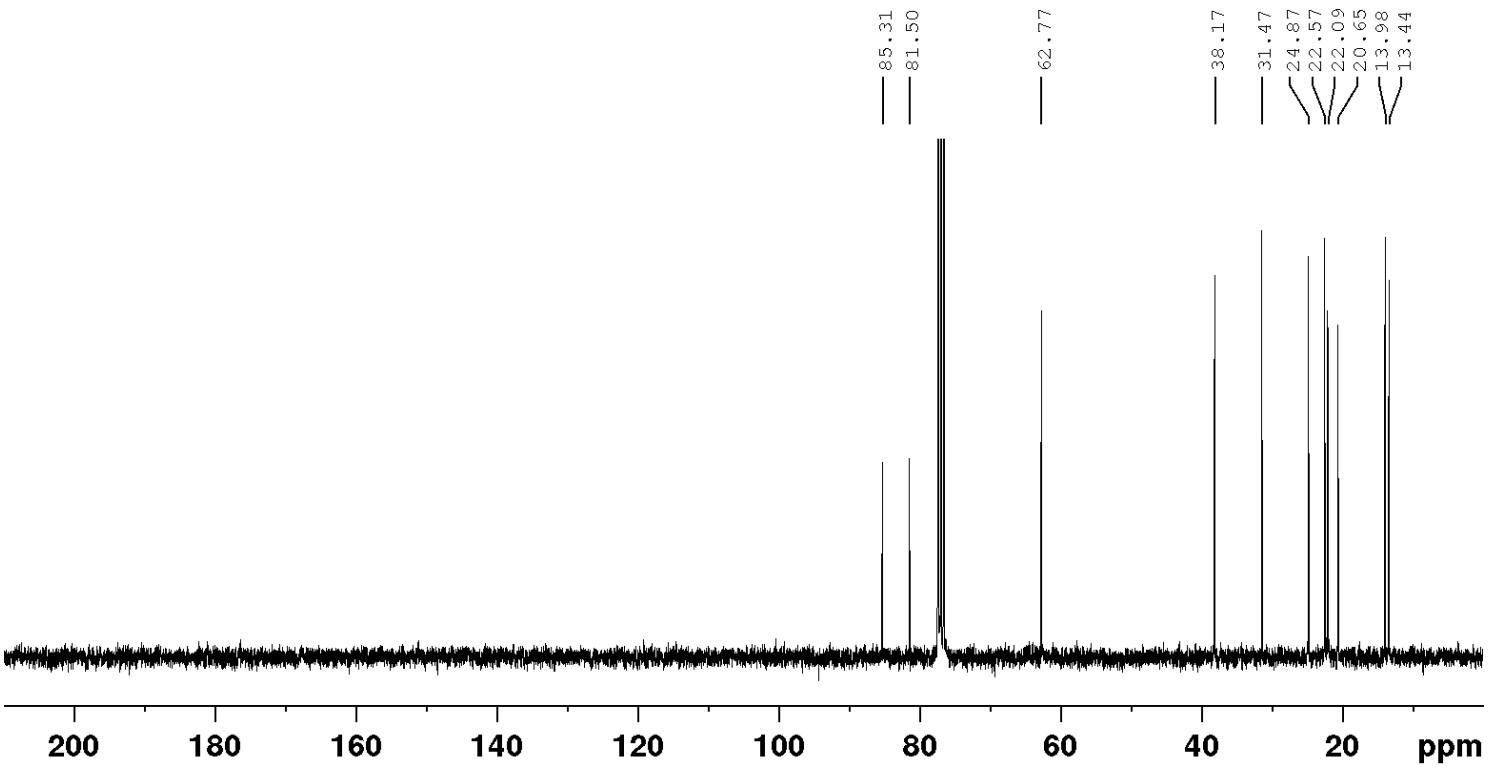
1-phenylhept-3-yn-2-ol (6e)



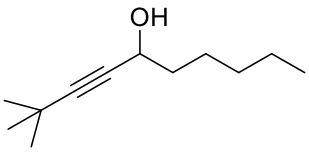


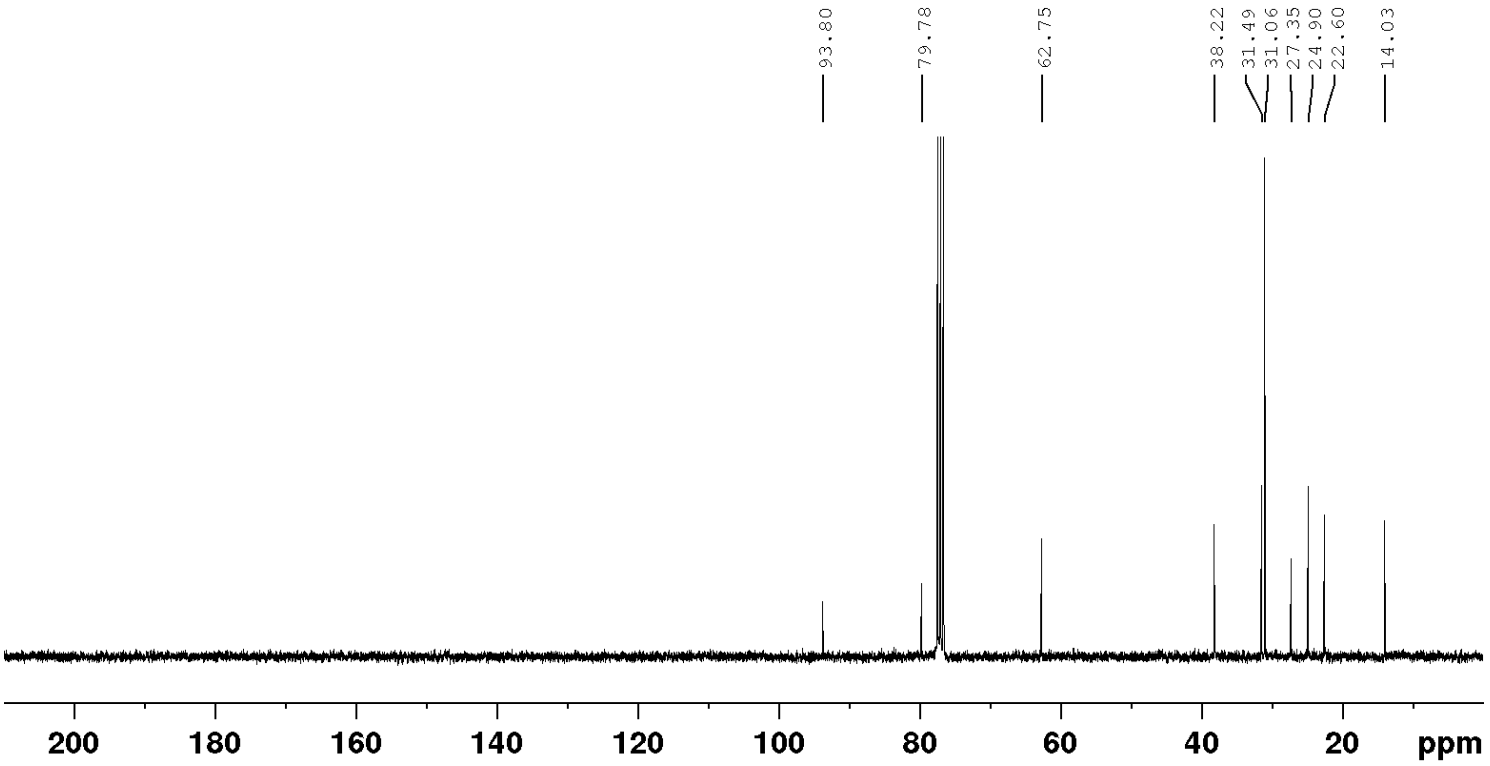
undec-4-yn-6-ol (6f)



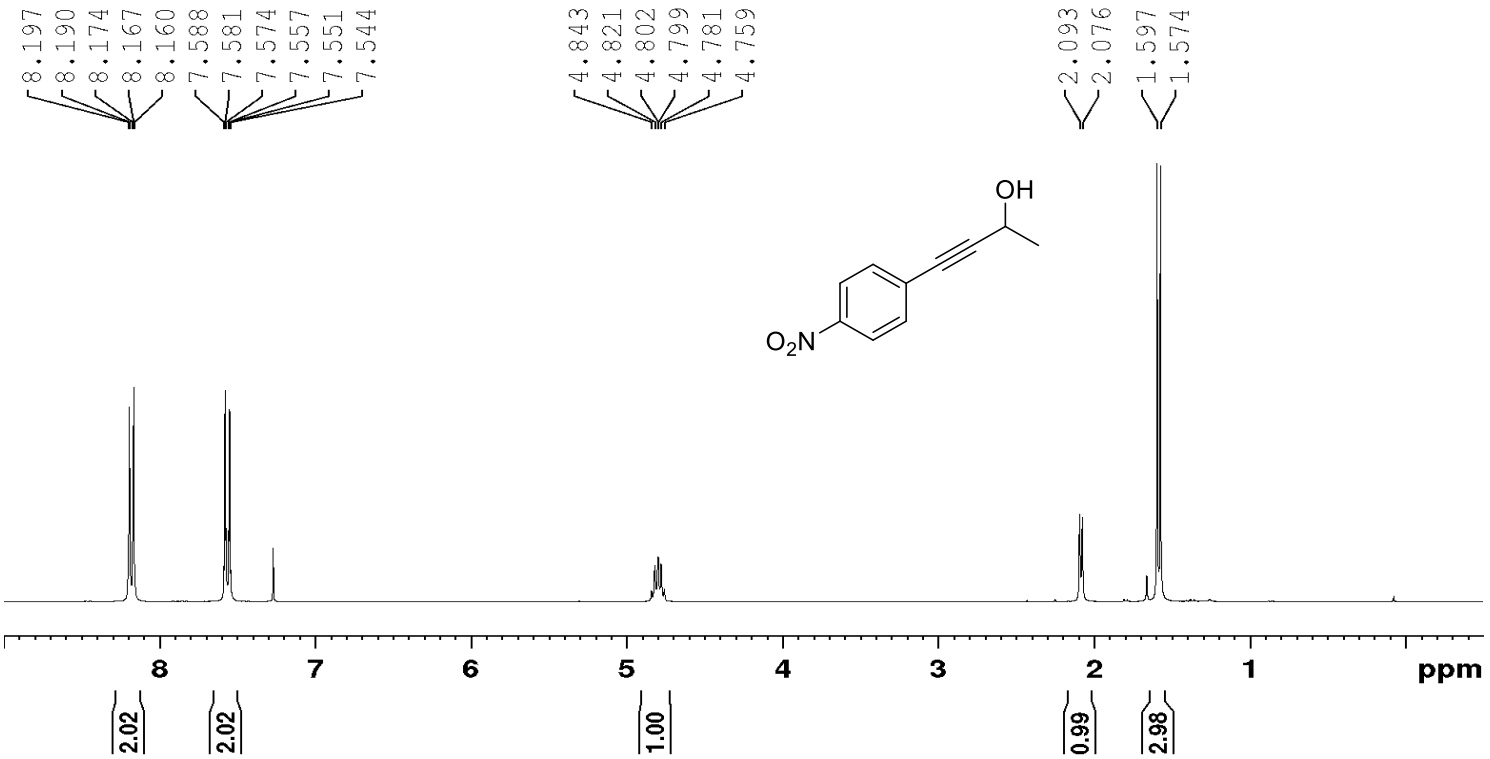


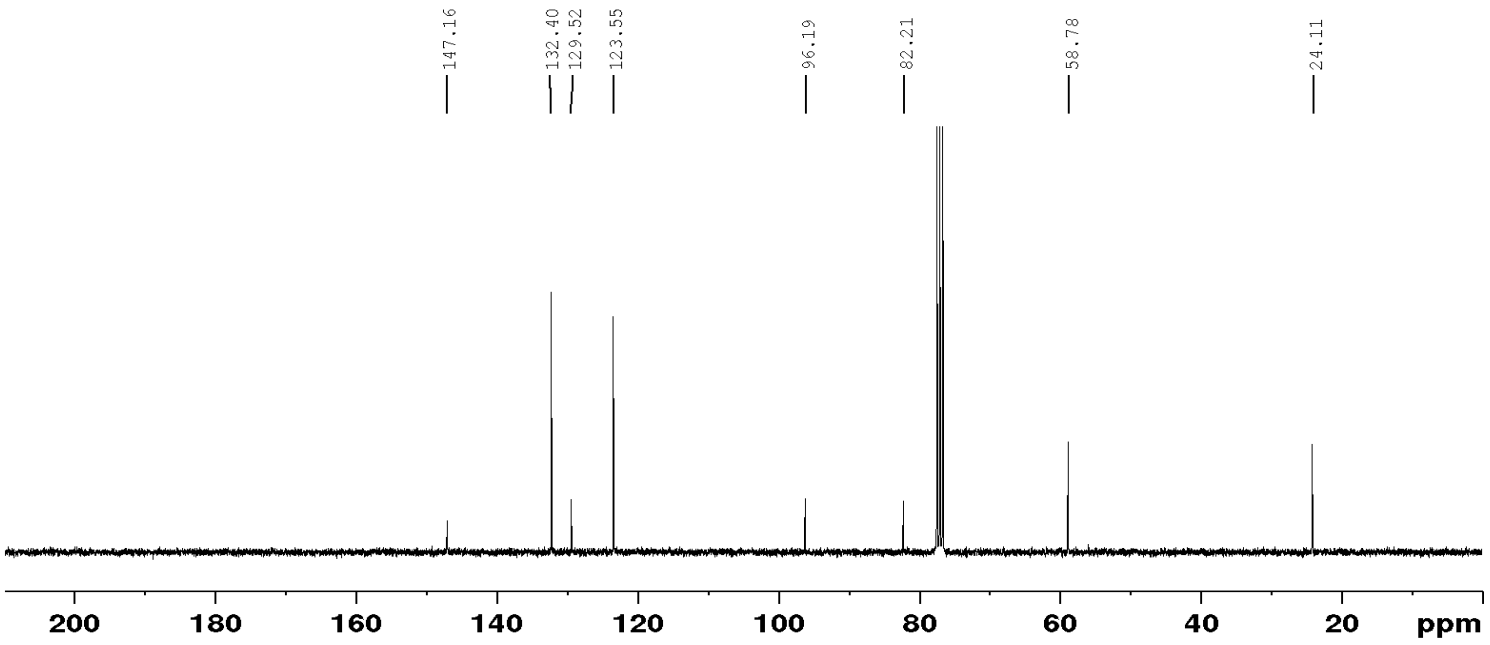
2,2-dimethyldec-3-yn-5-ol (6g)



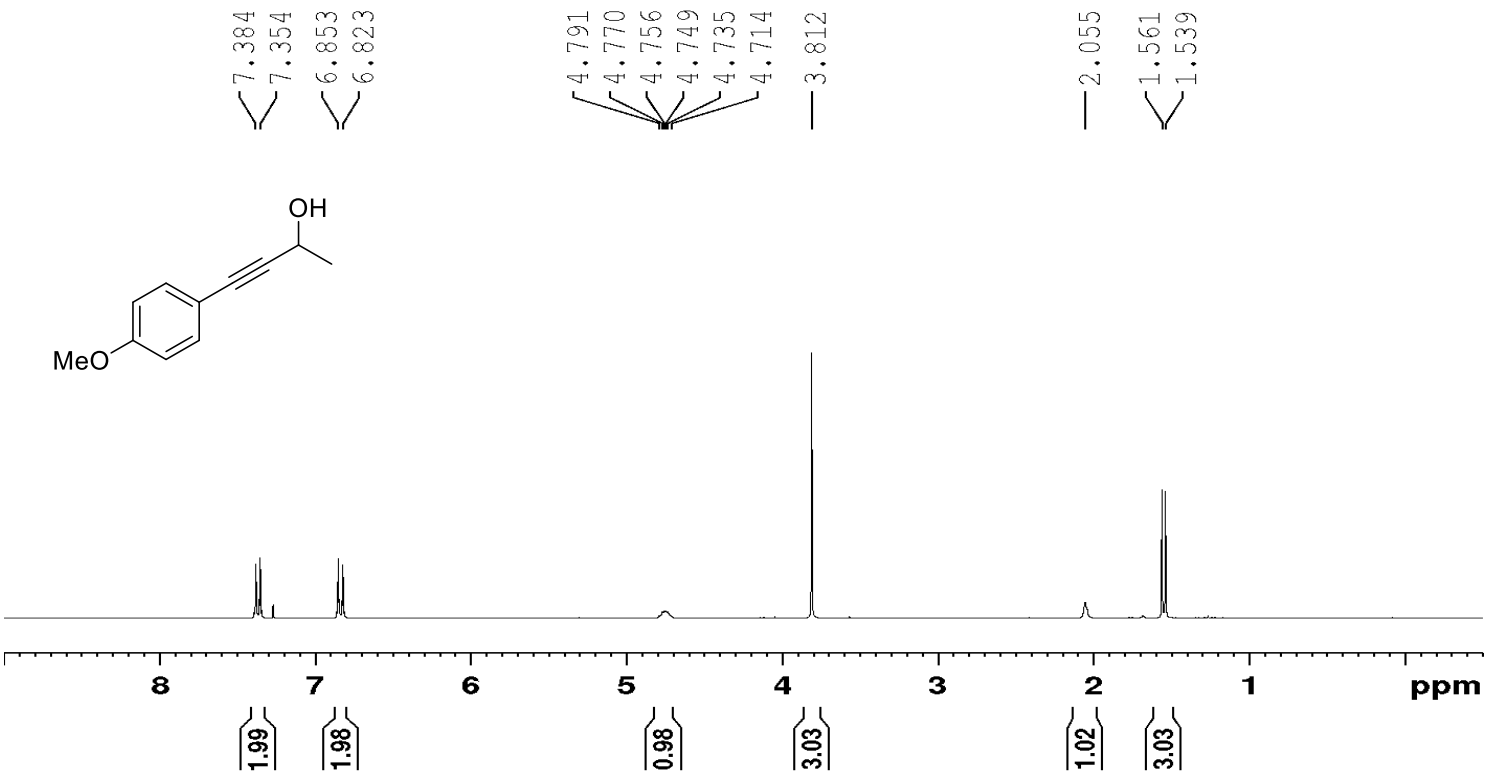


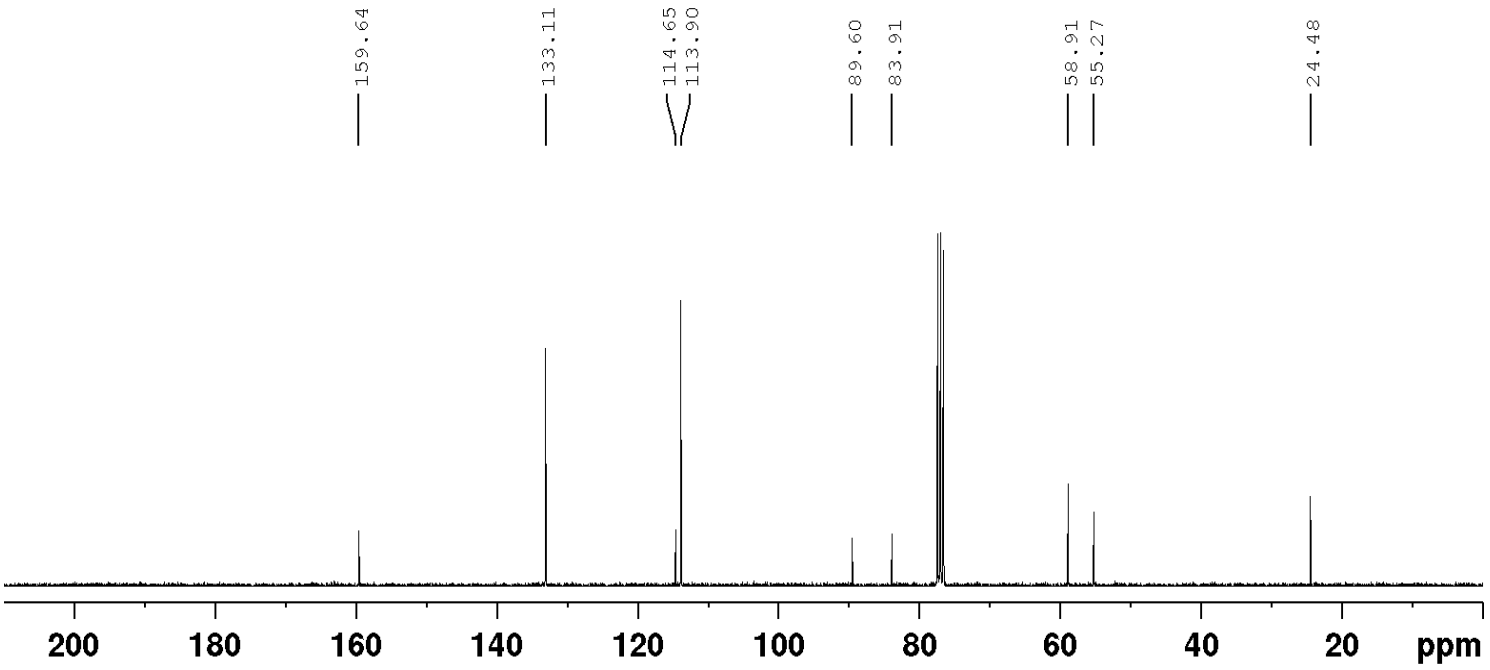
4-(4-Nitrophenyl)but-3-in-2-ol (6h)



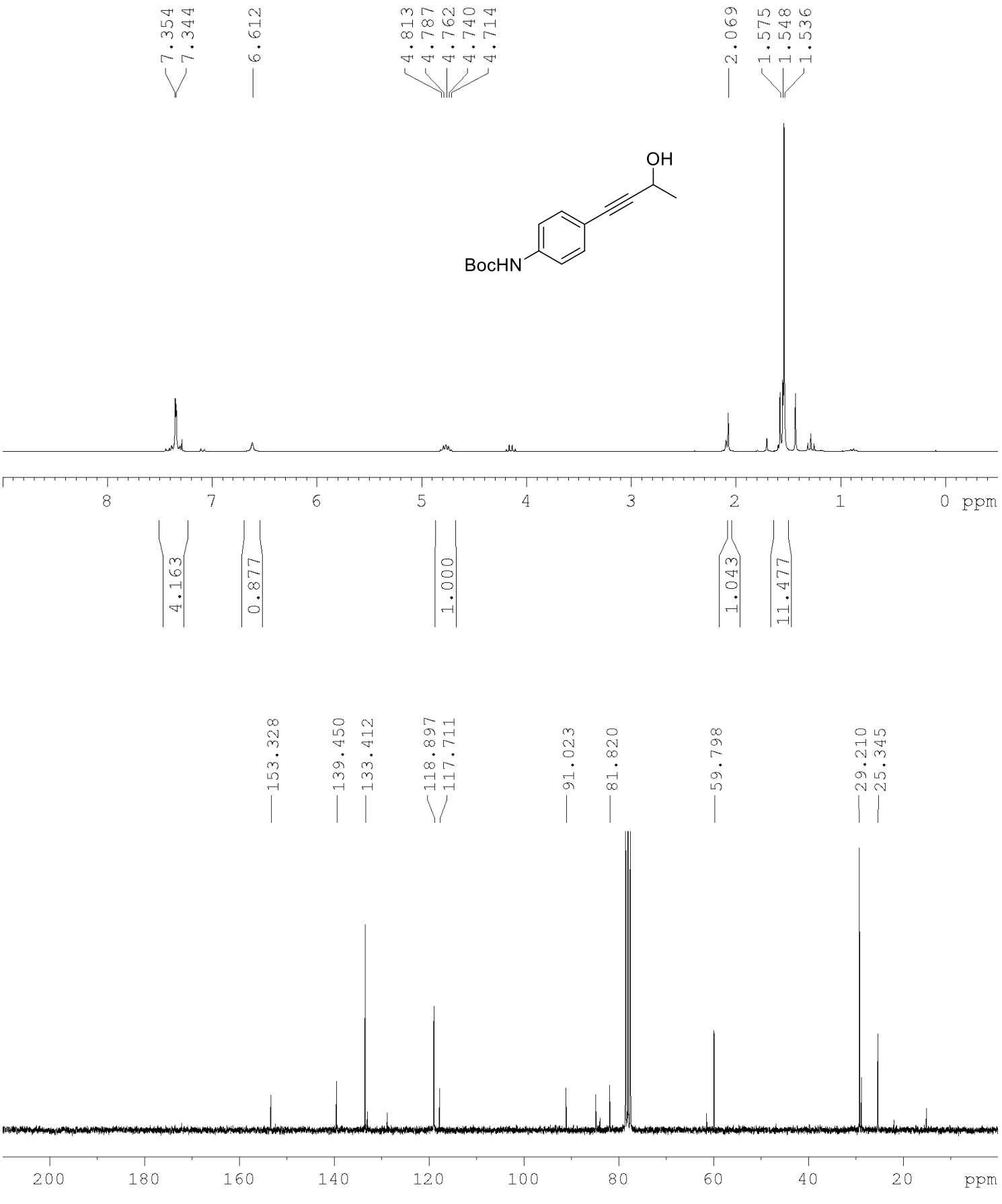


4-(4-Methoxyphenyl)but-3-in-2-ol (6i)

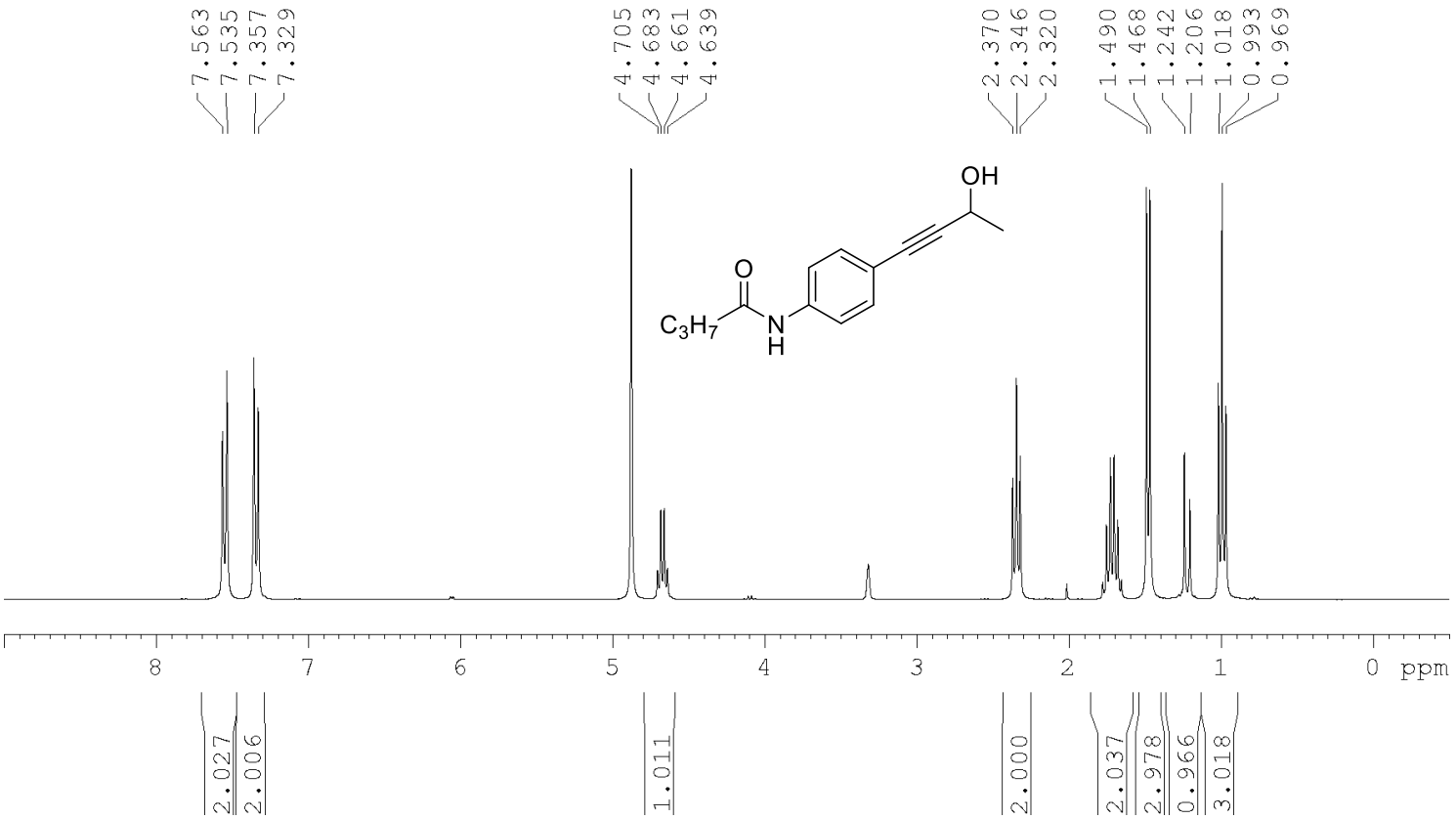


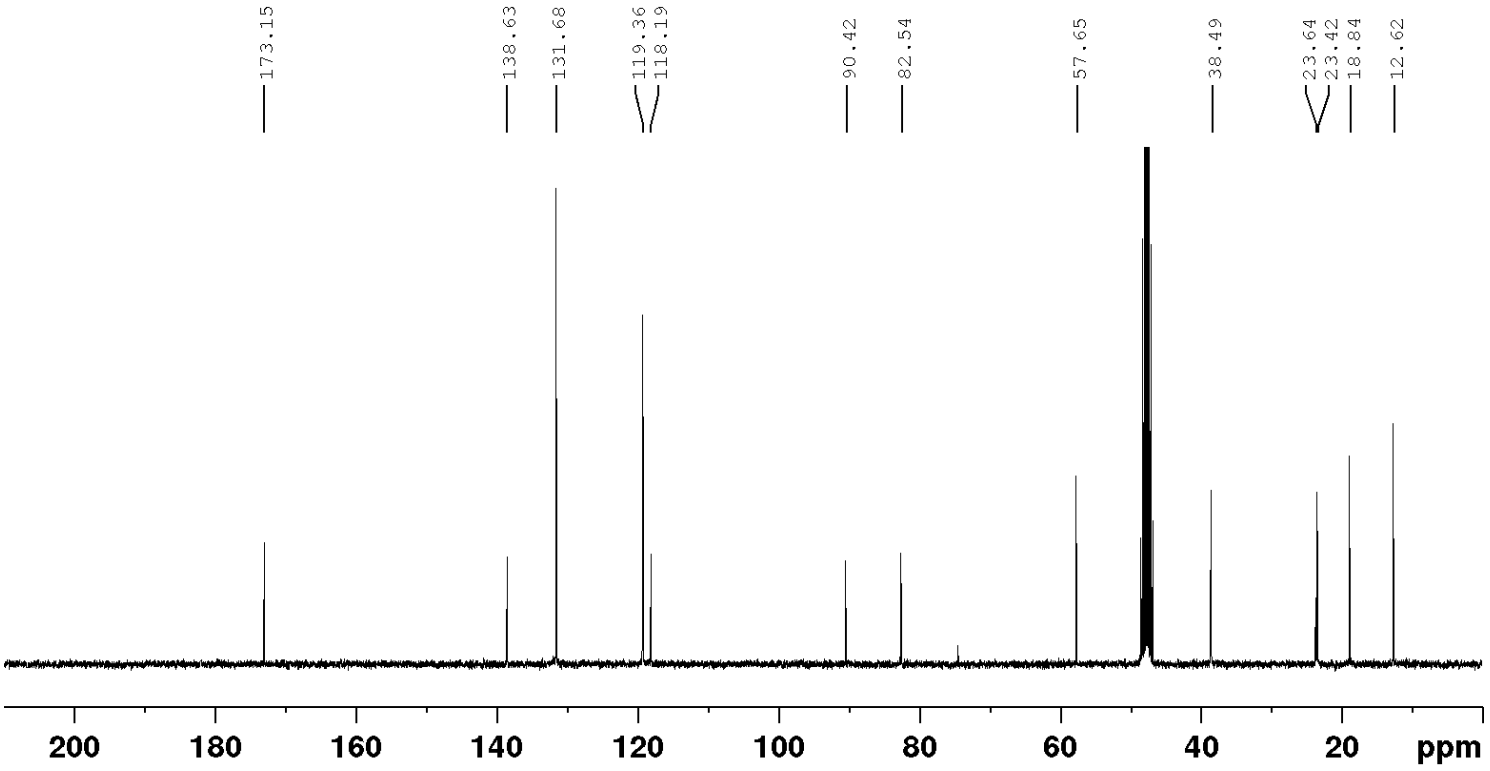


***tert*-butyl (4-(3-hydroxybut-1-yn-1-yl)phenyl)carbamate (6j)**

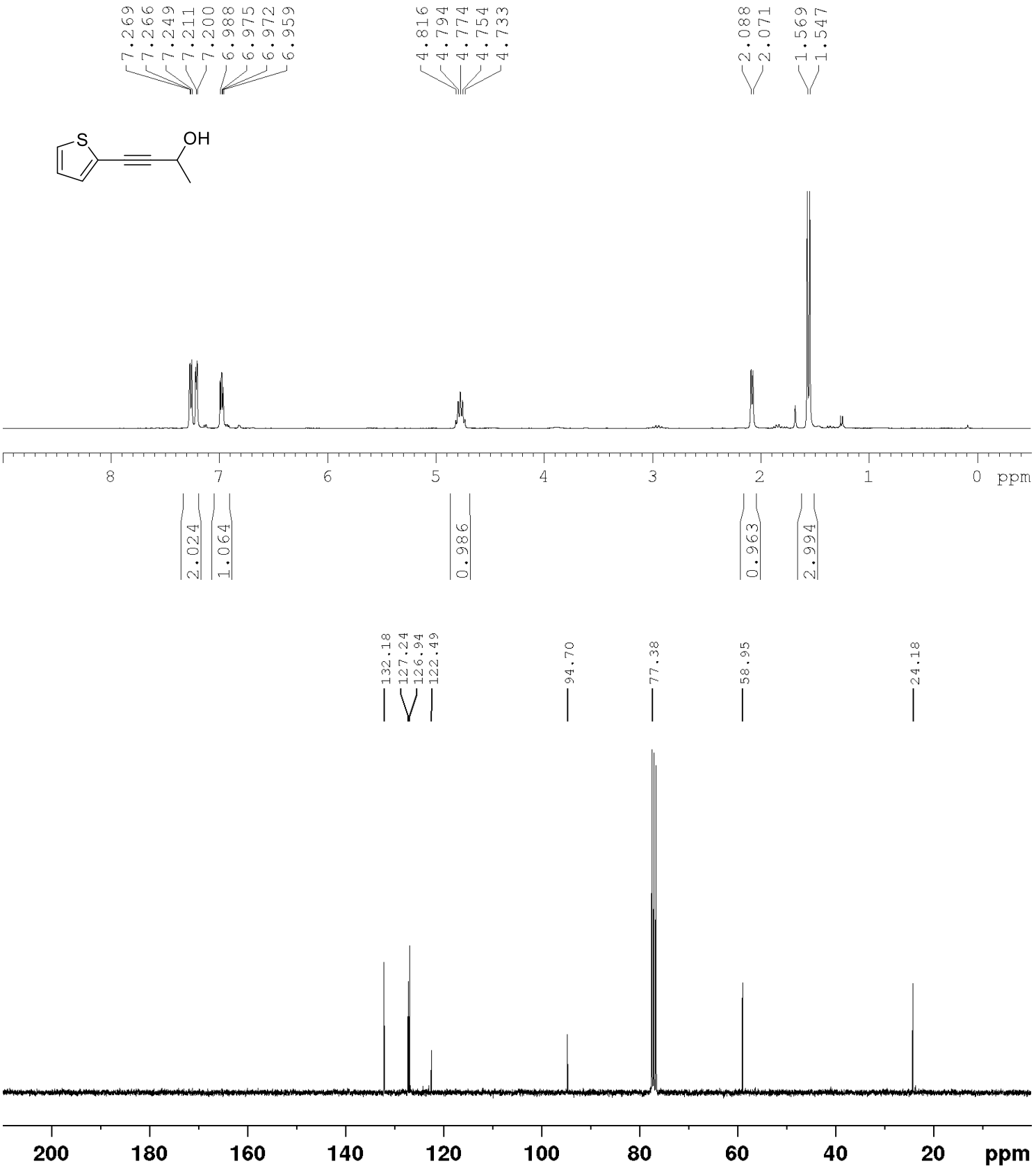


***N*-(4-(3-hydroxybut-1-yn-1-yl)phenyl)butyramide (6k)**

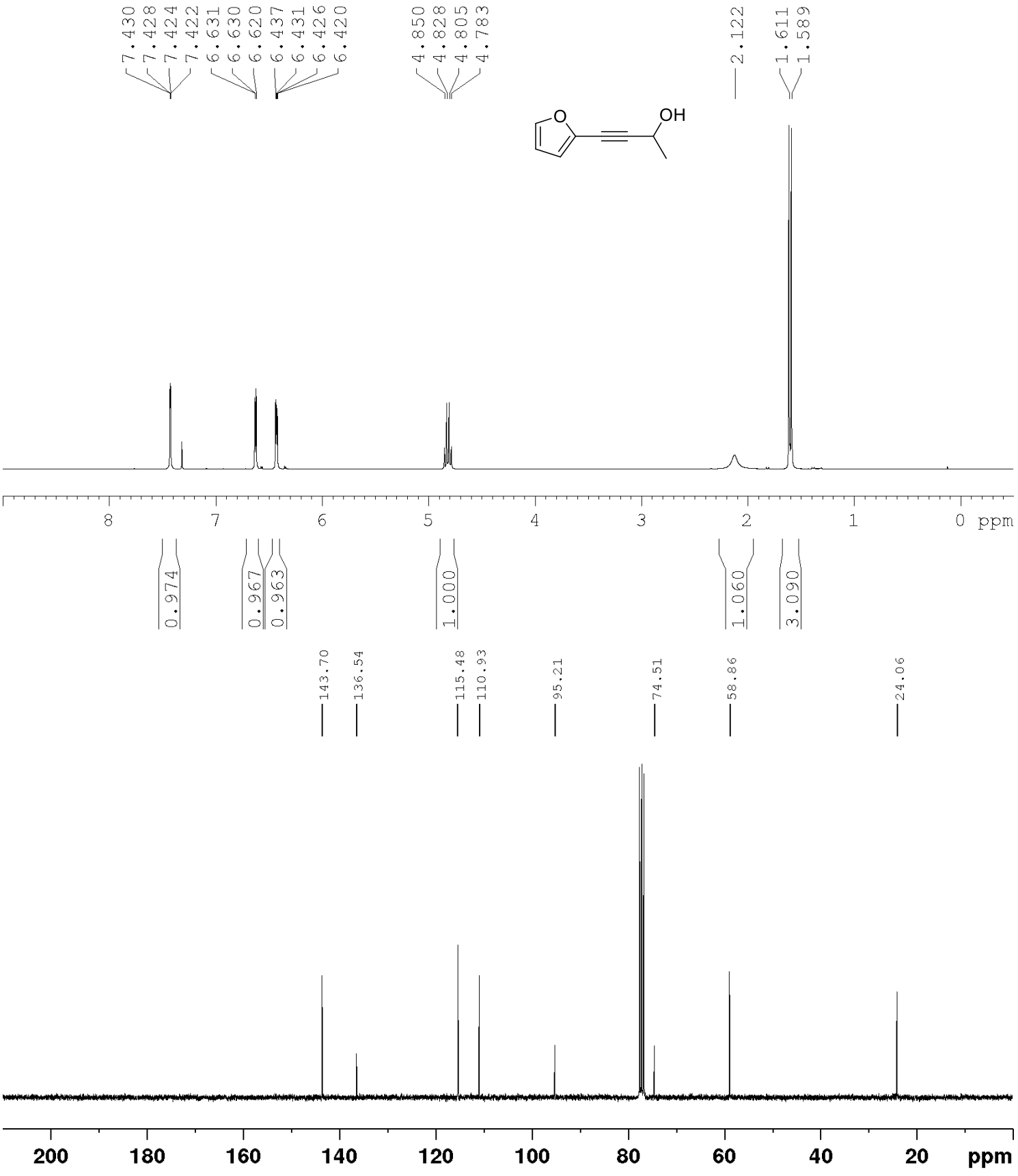




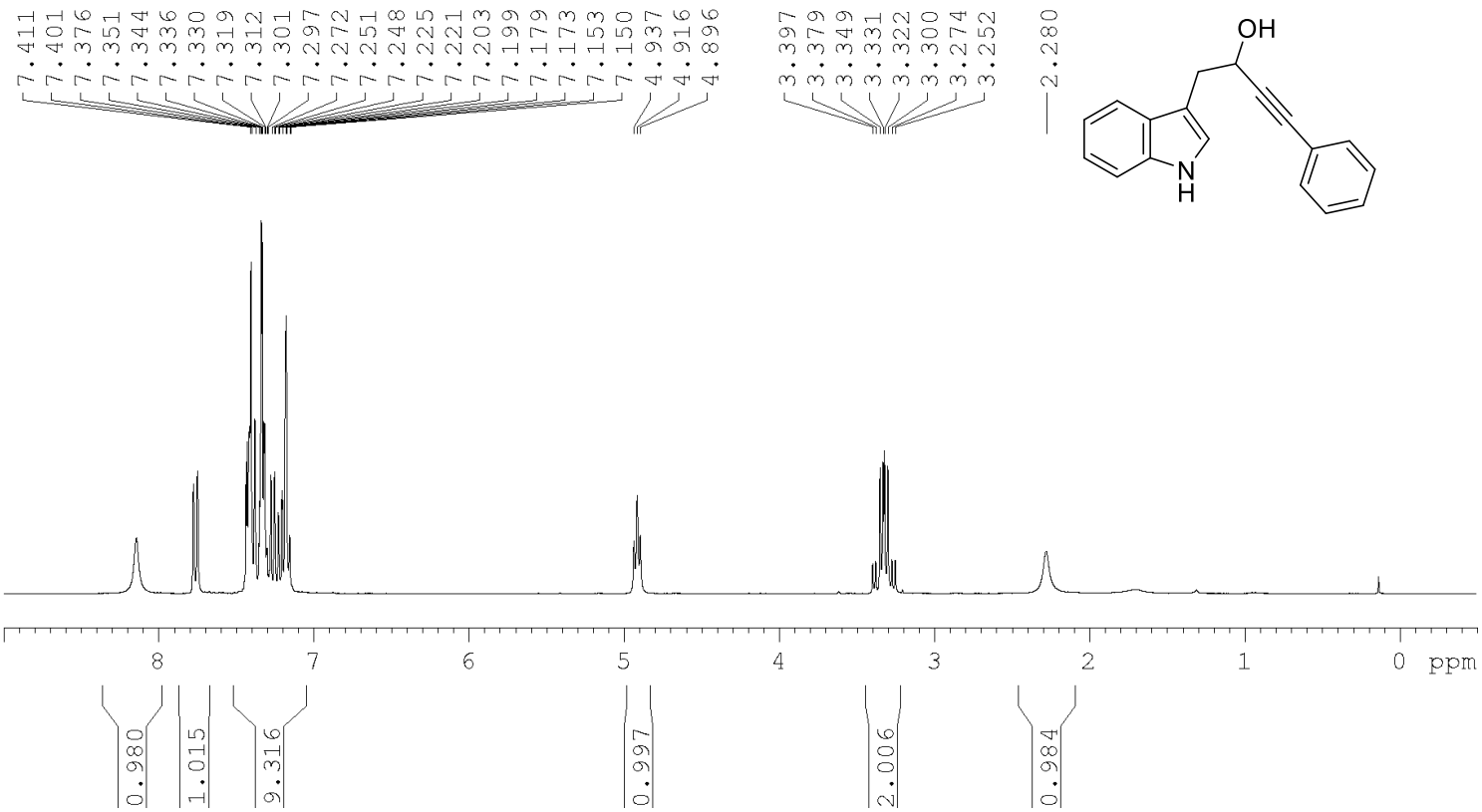
4-(thiophen-2-yl)but-3-yn-2-ol (6l)

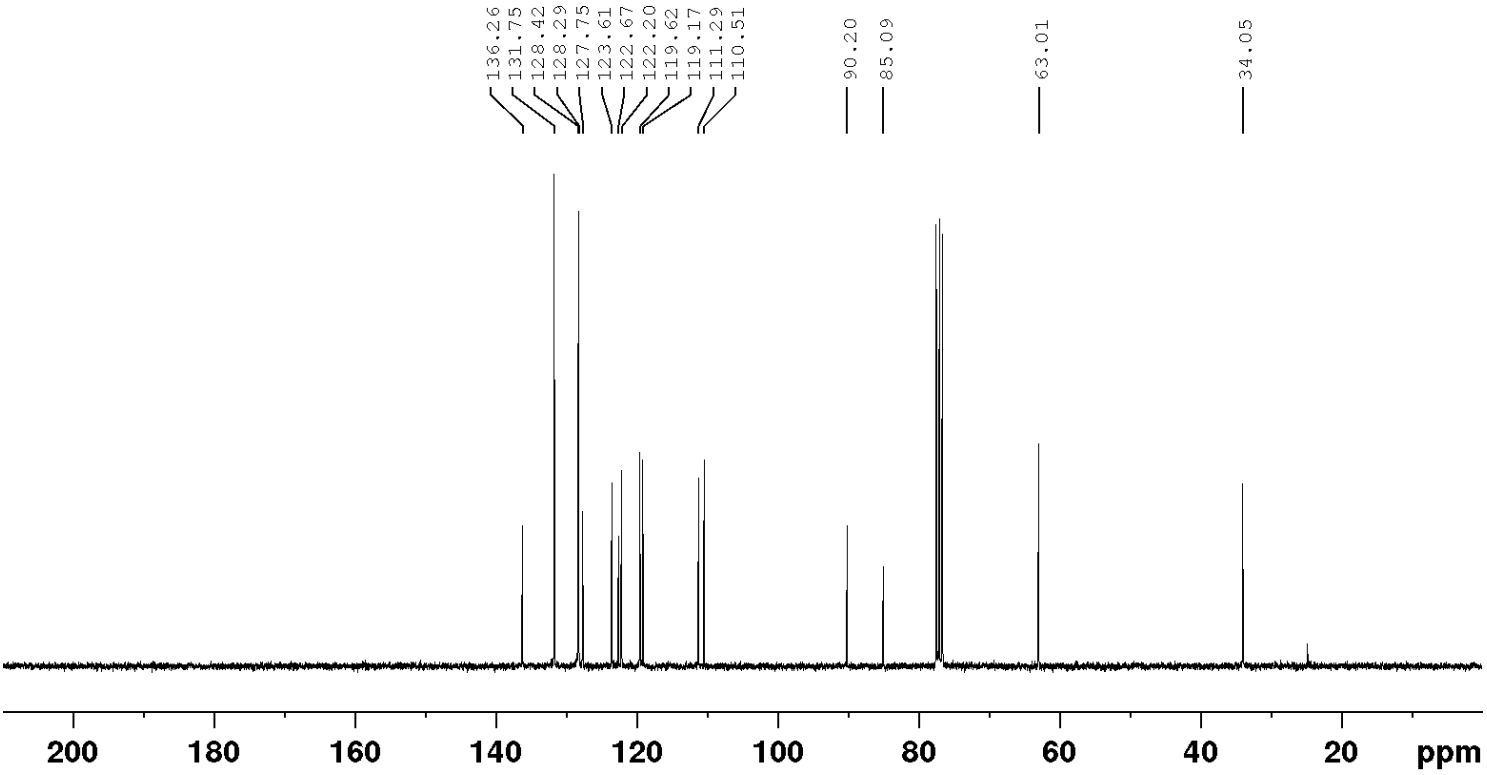


4-(furan-2-yl)but-3-yn-2-ol (6m)

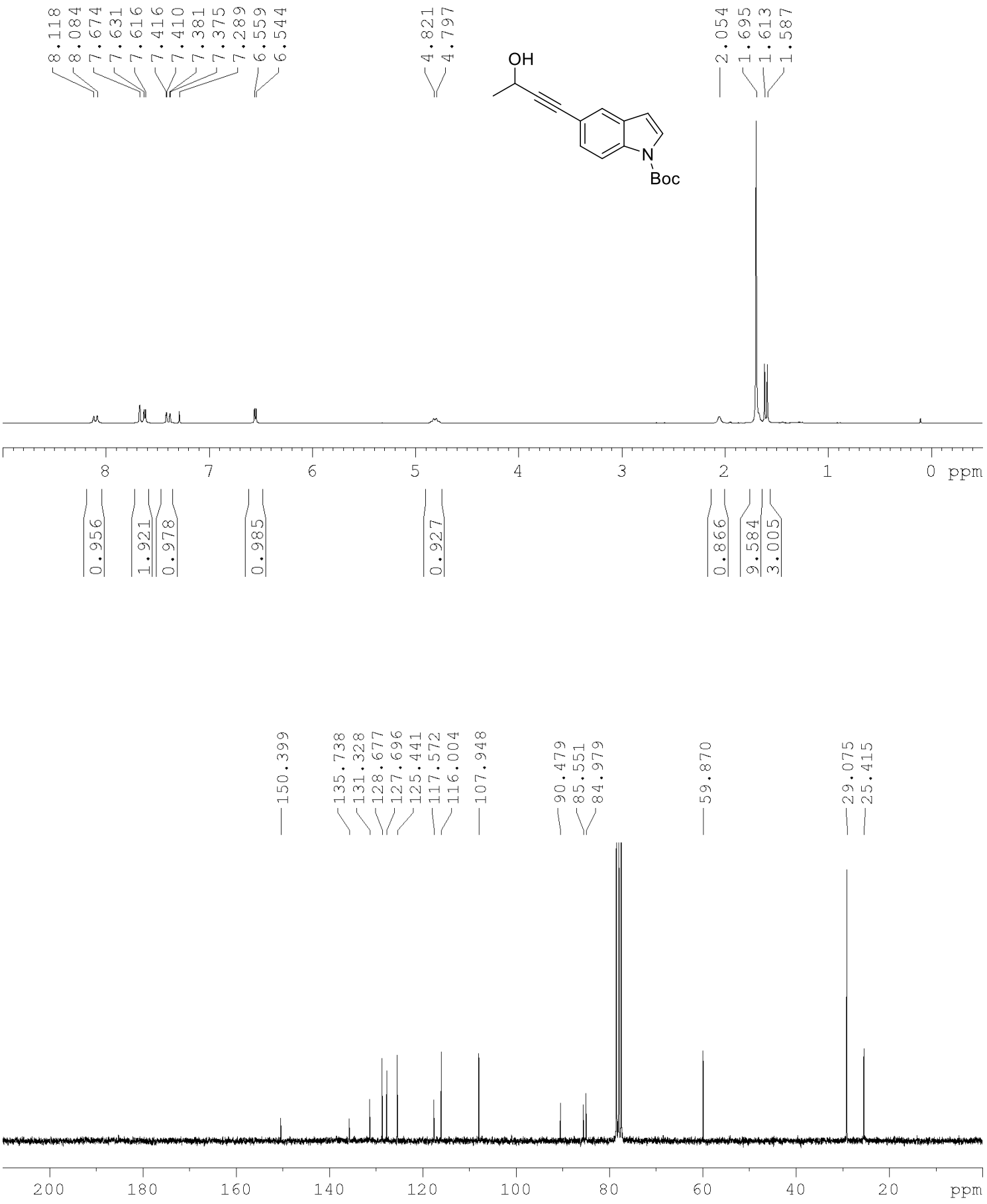


1-(1*H*-indol-3-yl)-4-phenylbut-3-yn-2-ol (6n)

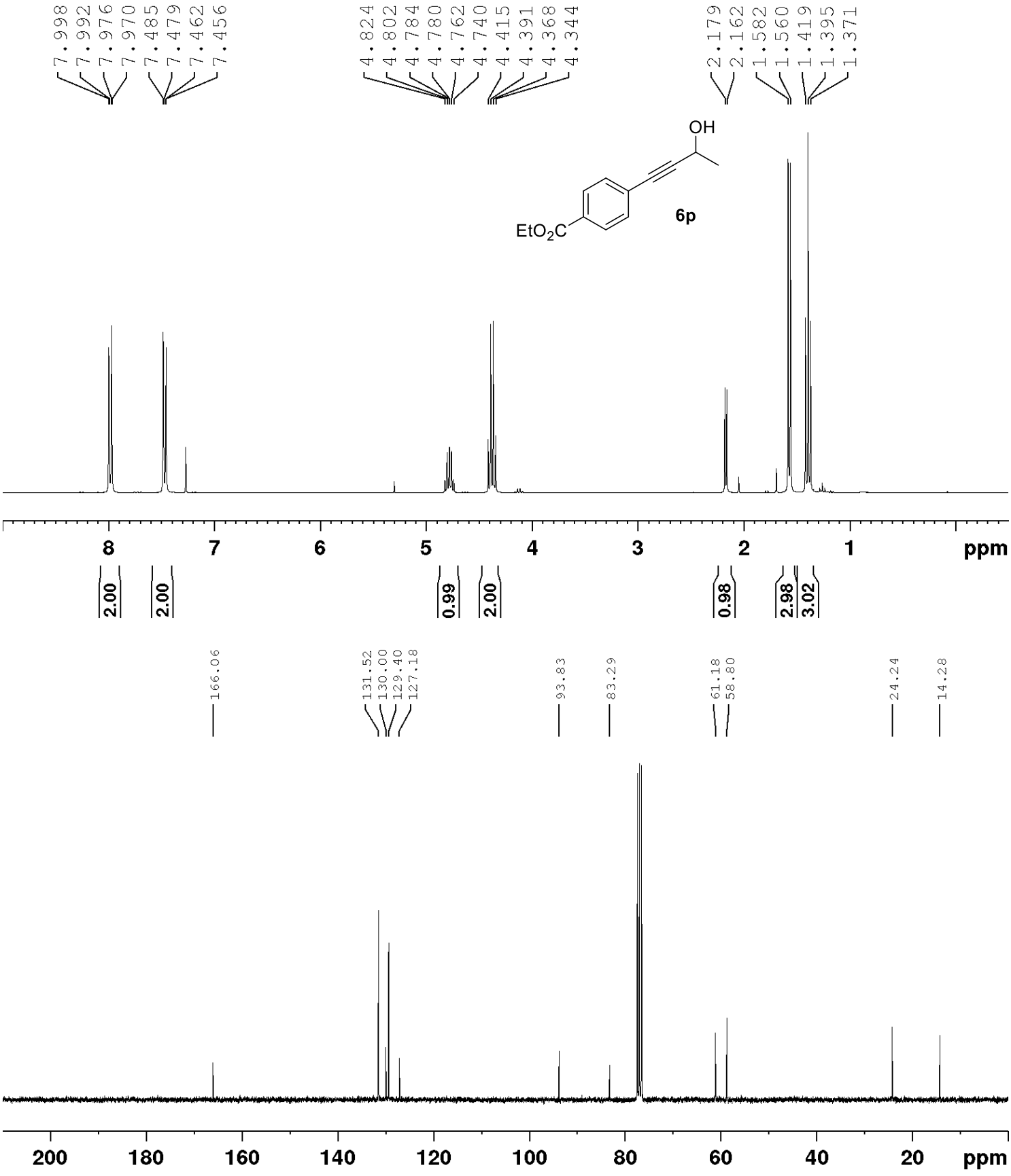




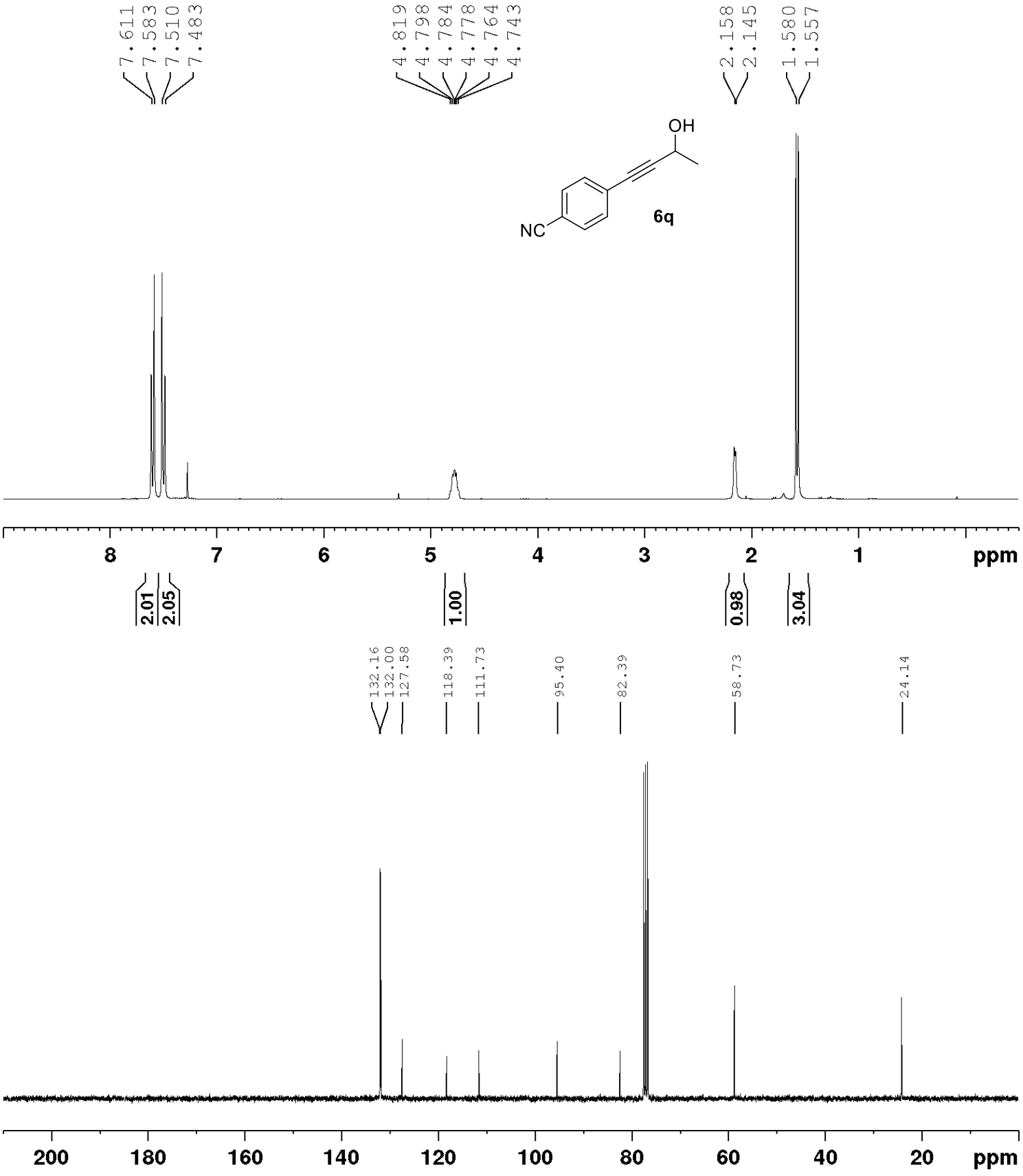
***tert*-butyl 5-(3-hydroxybut-1-yn-1-yl)-1*H*-indole-1-carboxylate (6o)**



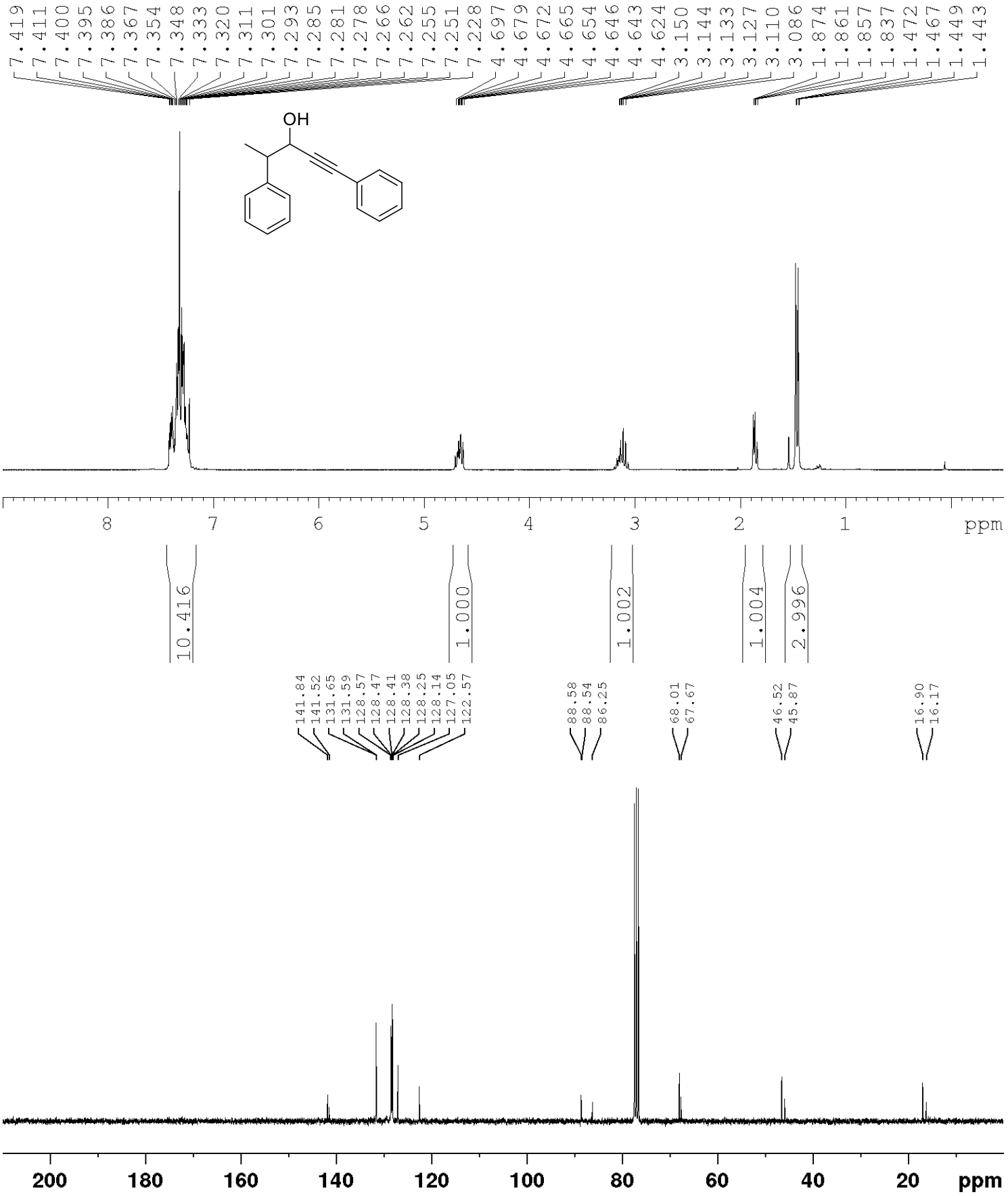
ethyl 4-(3-hydroxybut-1-yn-1-yl)benzoate (6p)



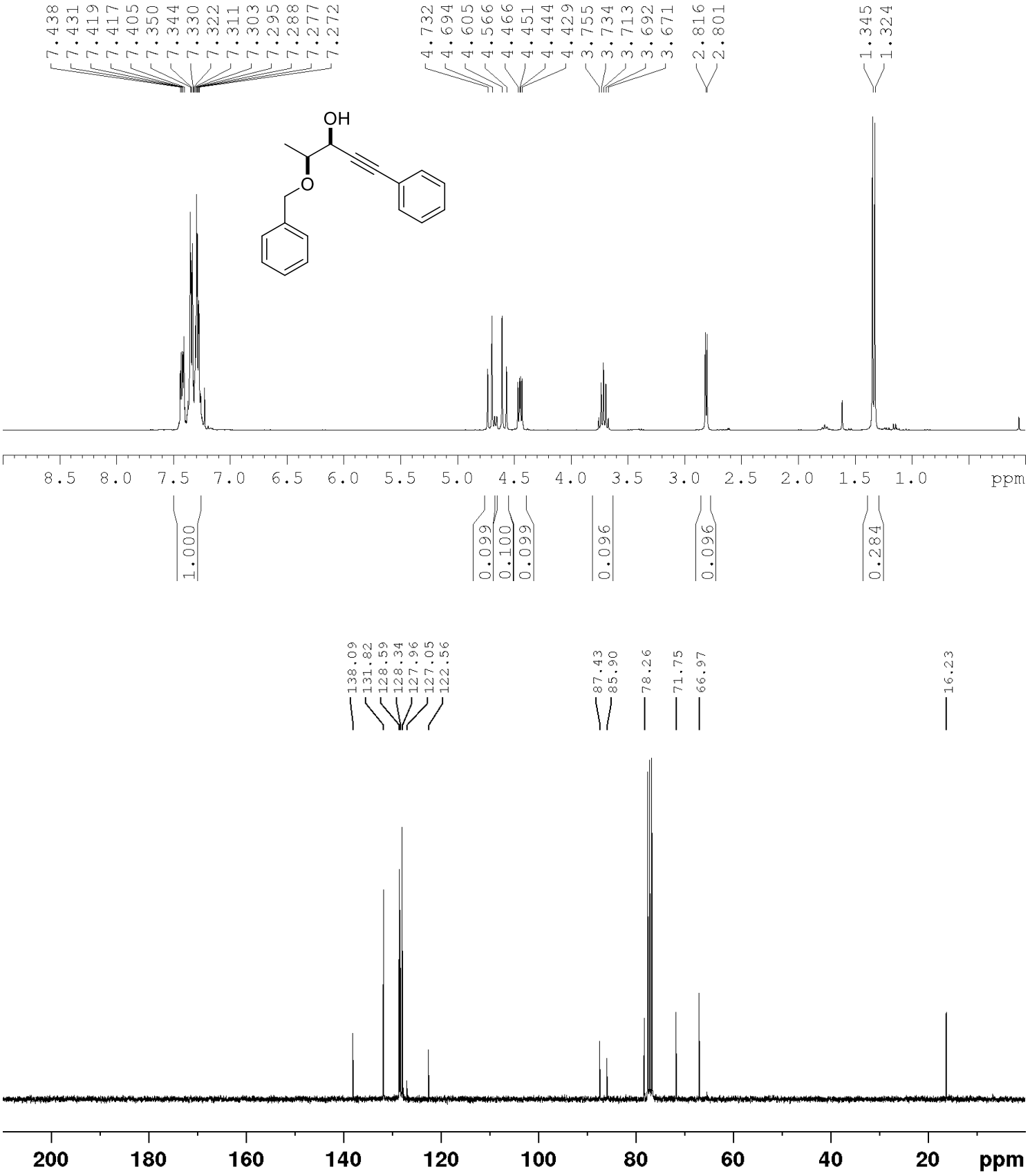
4-(3-hydroxybut-1-yn-1-yl)benzonitrile (6q)



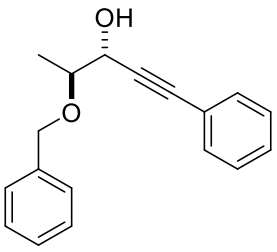
1,4-diphenylpent-1-yn-3-ol (6ra/6rb)



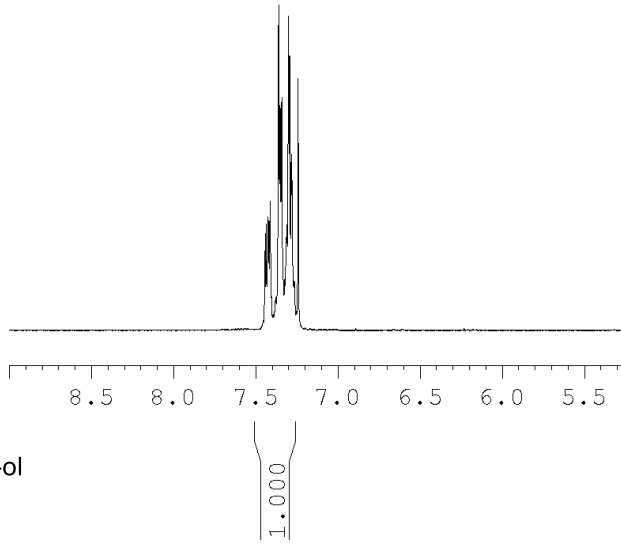
***syn*-4-phenoxy-1-phenylpent-1-yn-3-ol (6ta)**

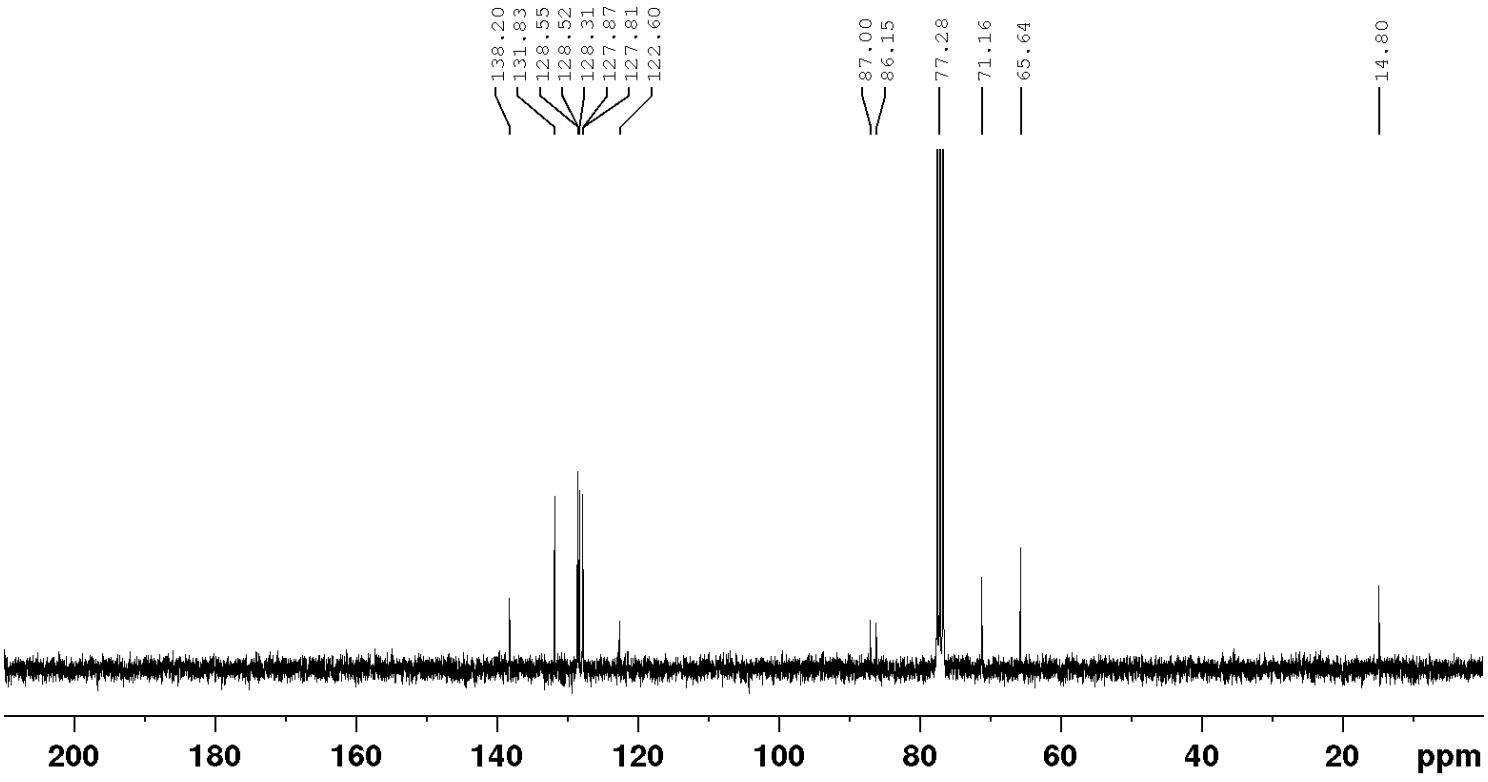


***trans*-4-phenoxy-1-phenylpent-1-yn-3-ol (6tb)**

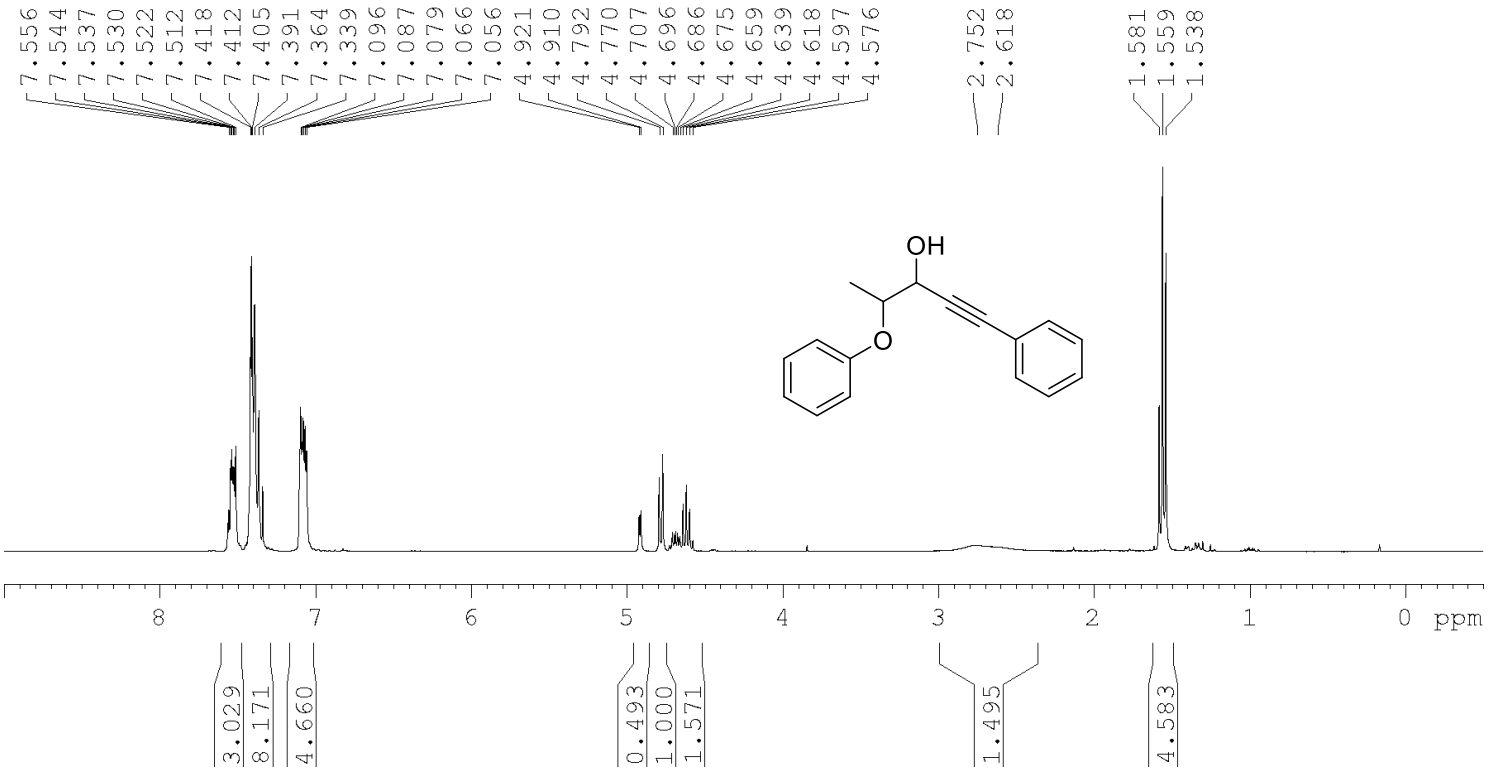


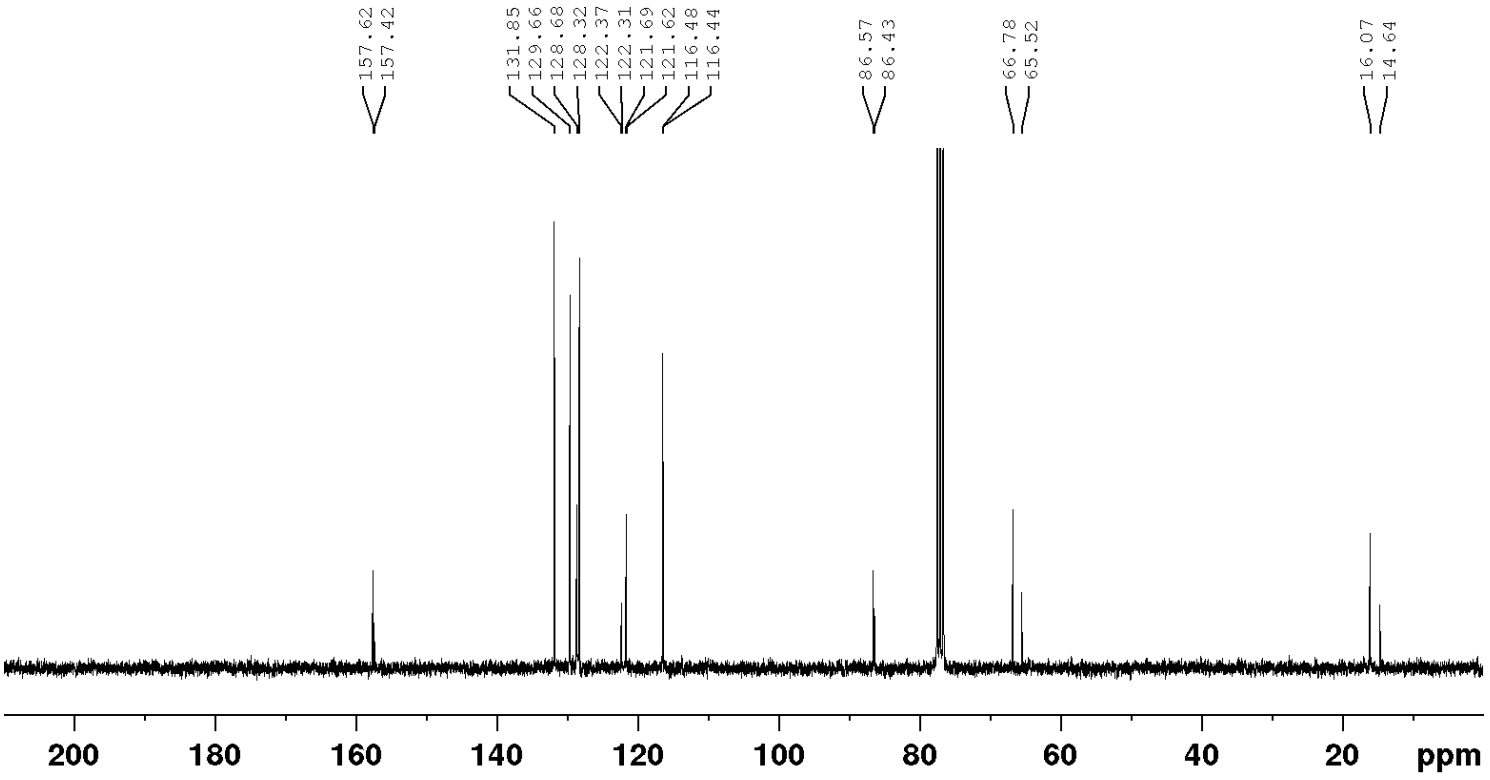
(3*R*,4*S*)-4-(benzyloxy)-1-phenylpent-1-yn-3-ol



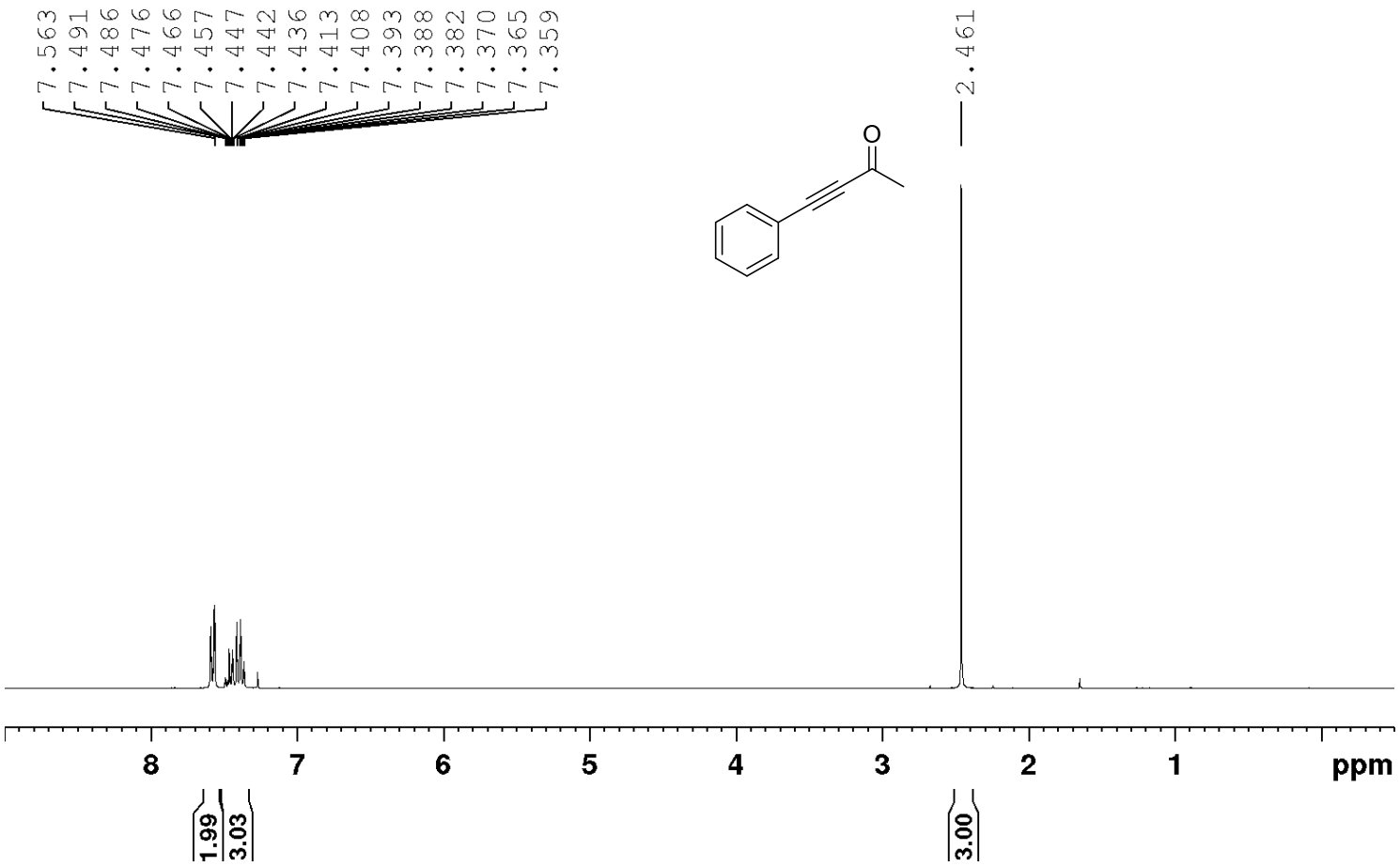


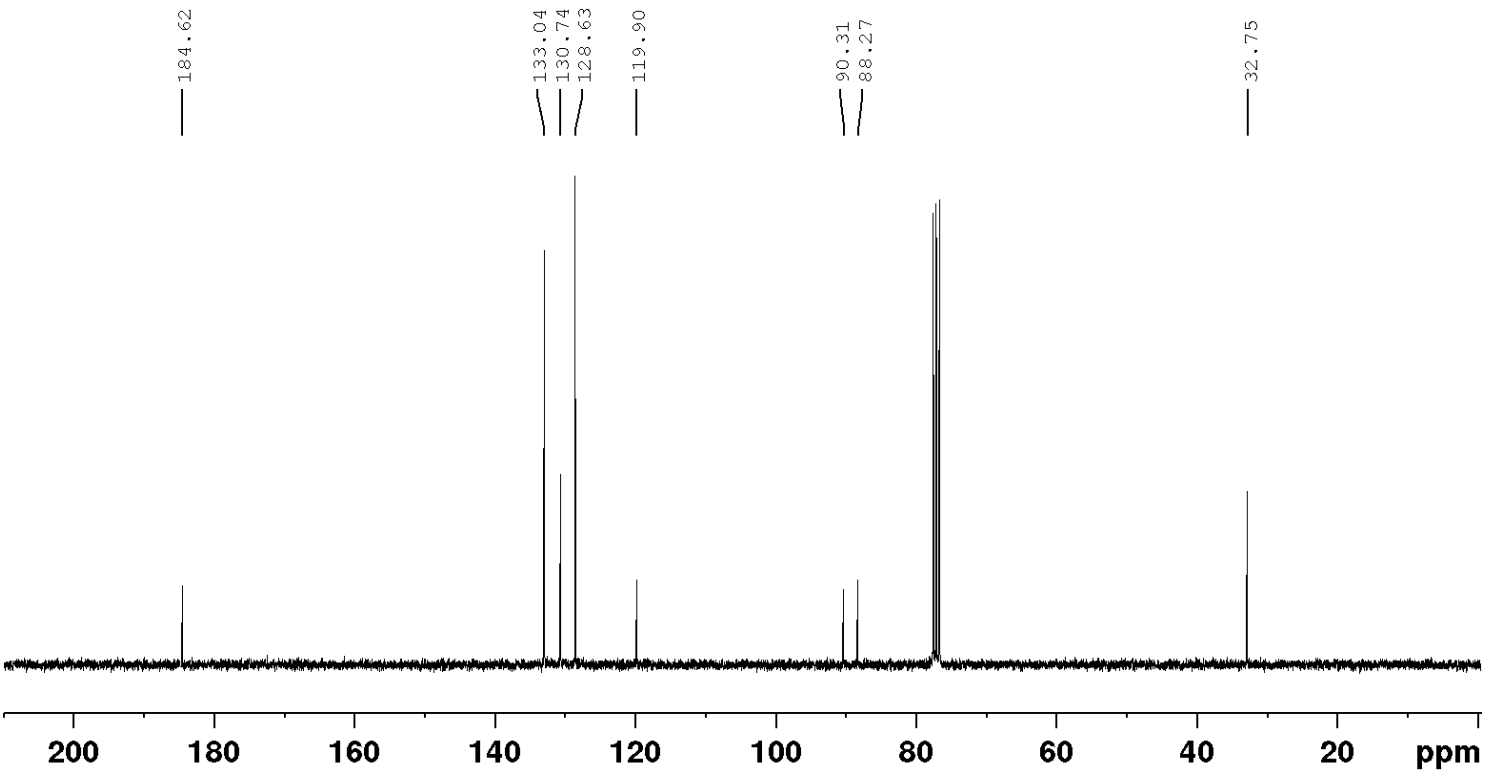
4-phenoxy-1-phenylpent-1-yn-3-ol (6sa/6sb)



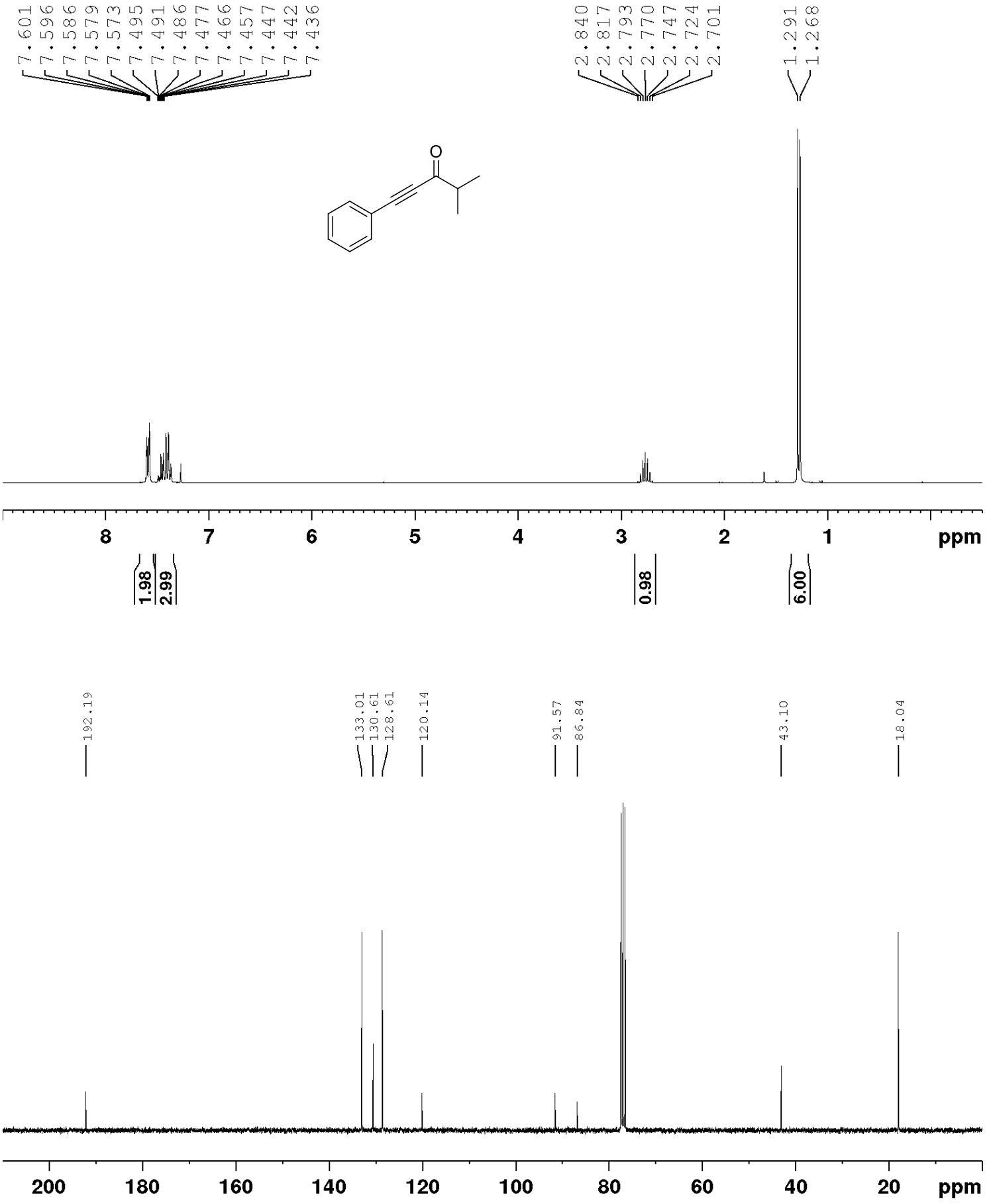


4-Phenylbut-3-in-2-on (5a)

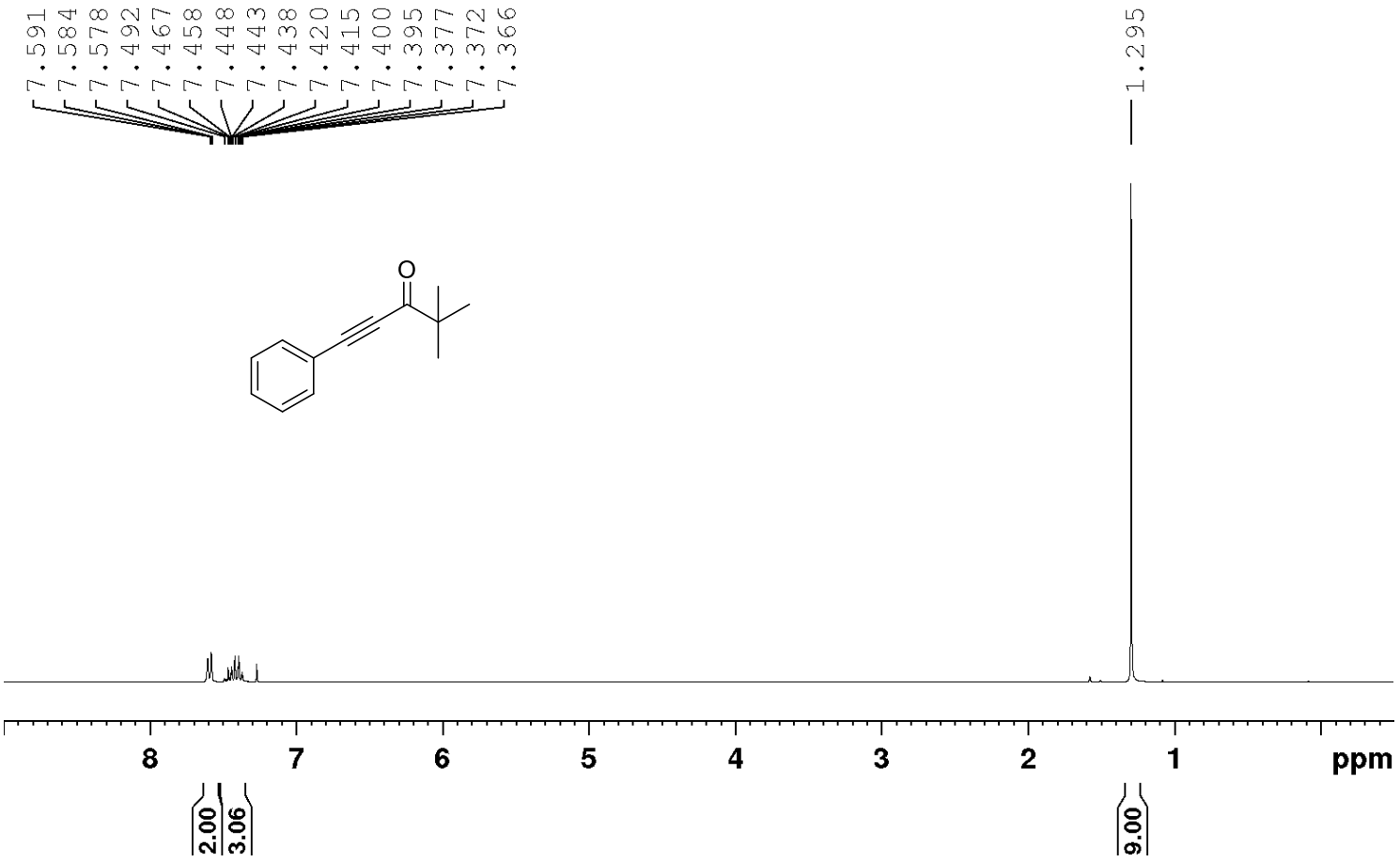


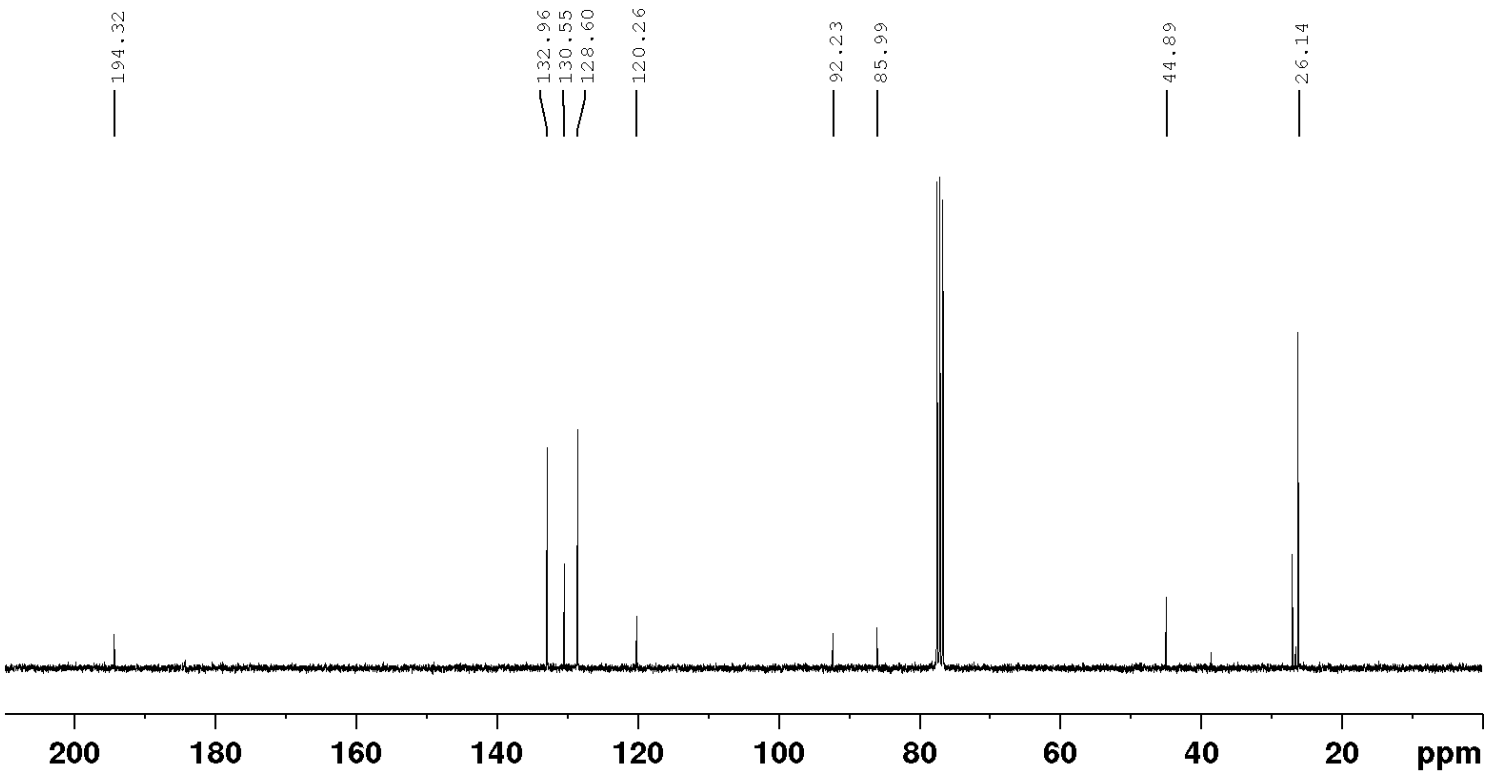


4-Methyl-1-phenylpent-1-in-3-on (5b)

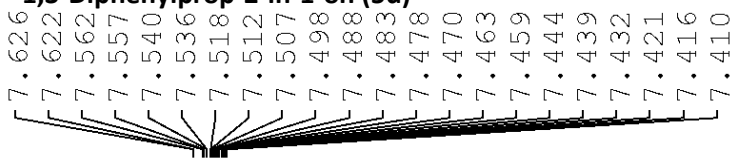


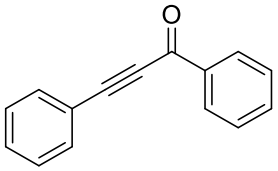
4,4-Dimethyl-1-phenylpent-1-in-3-on (5c)

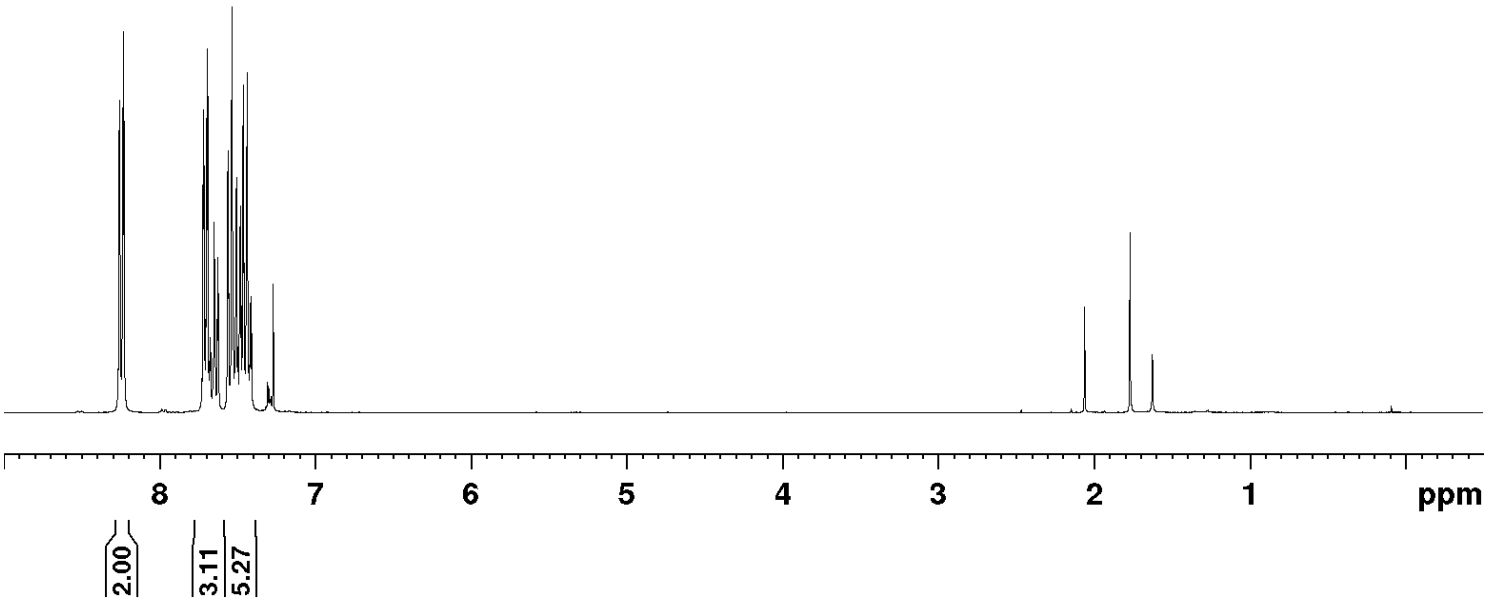


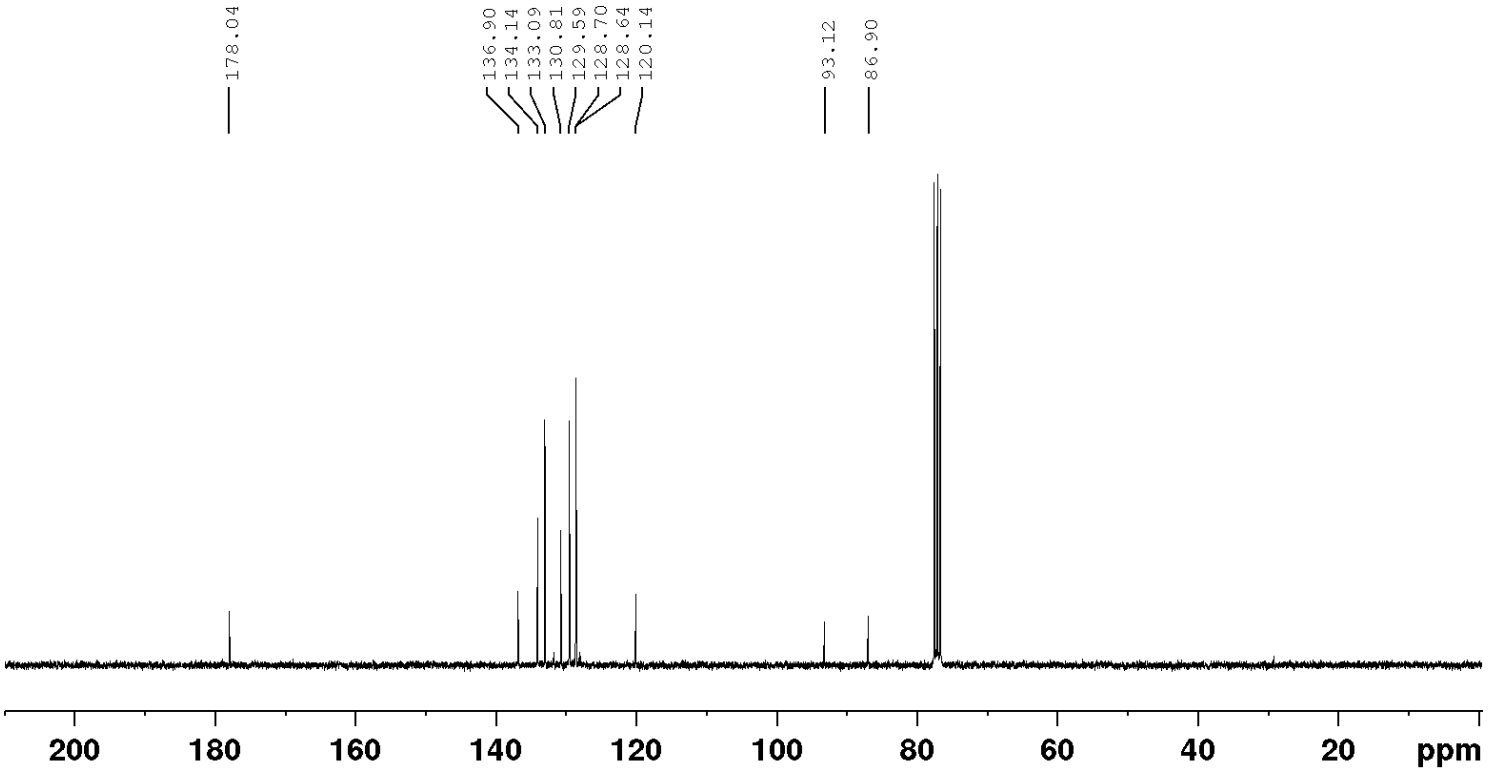


1,3-Diphenylprop-2-in-1-on (5d)

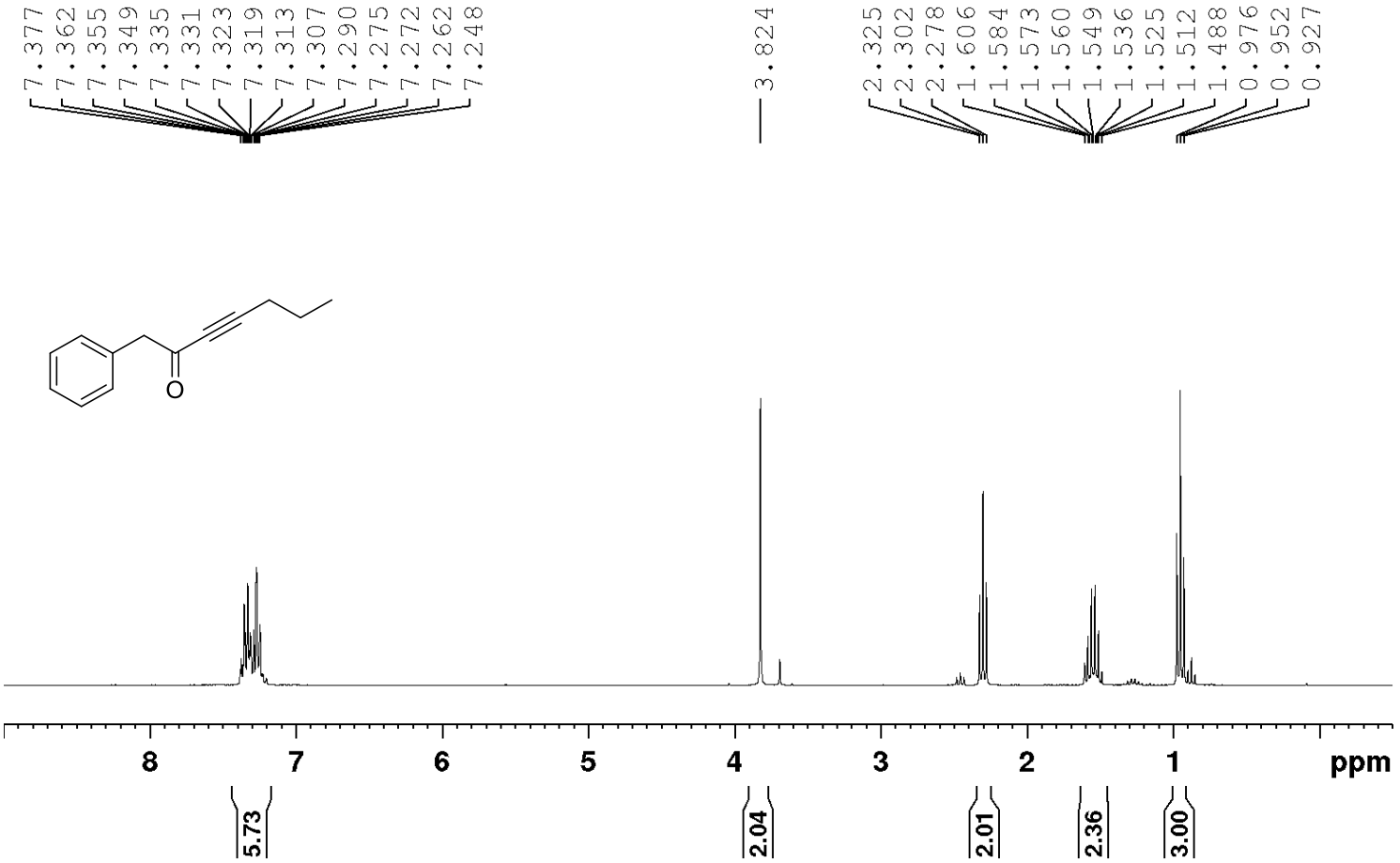


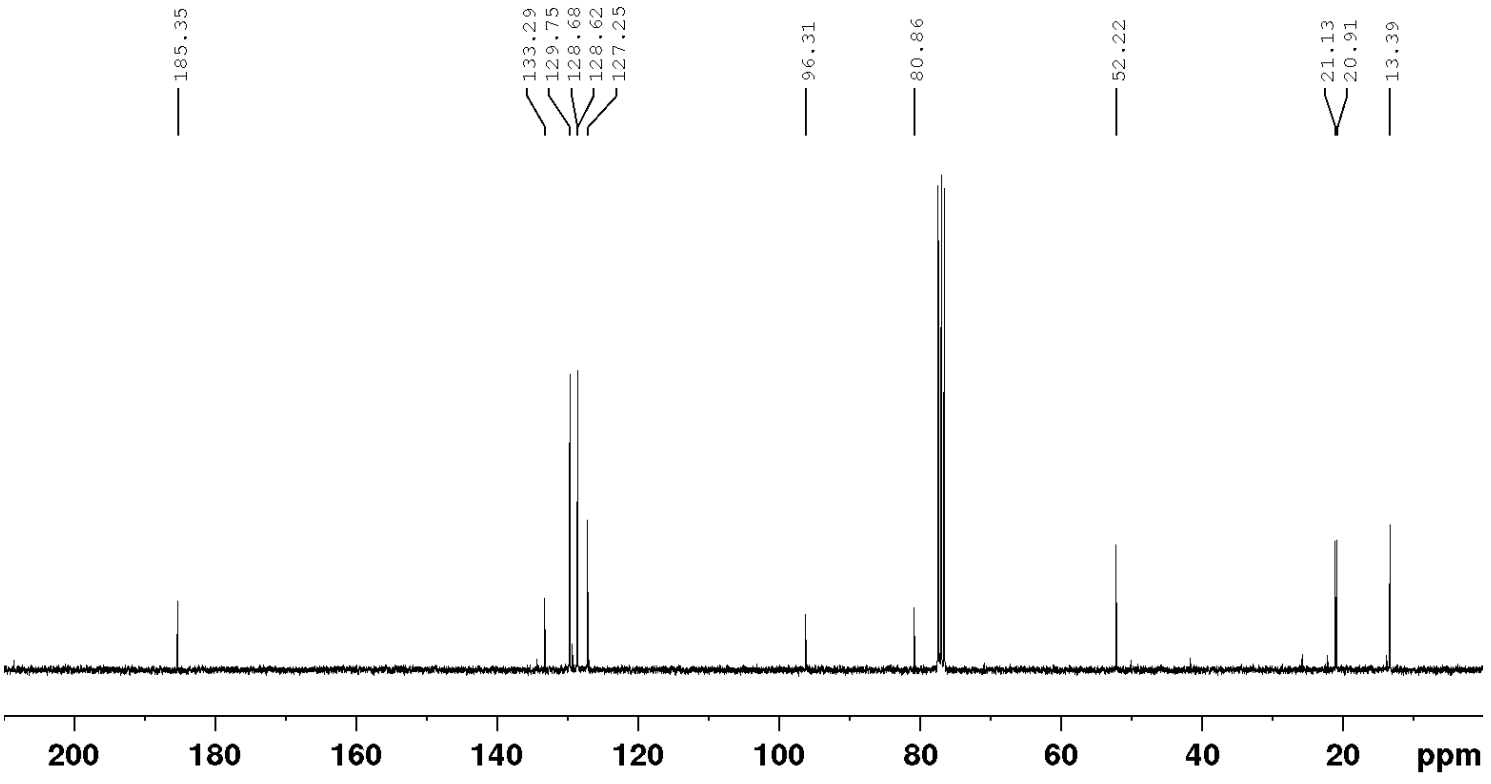




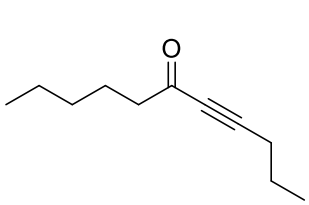


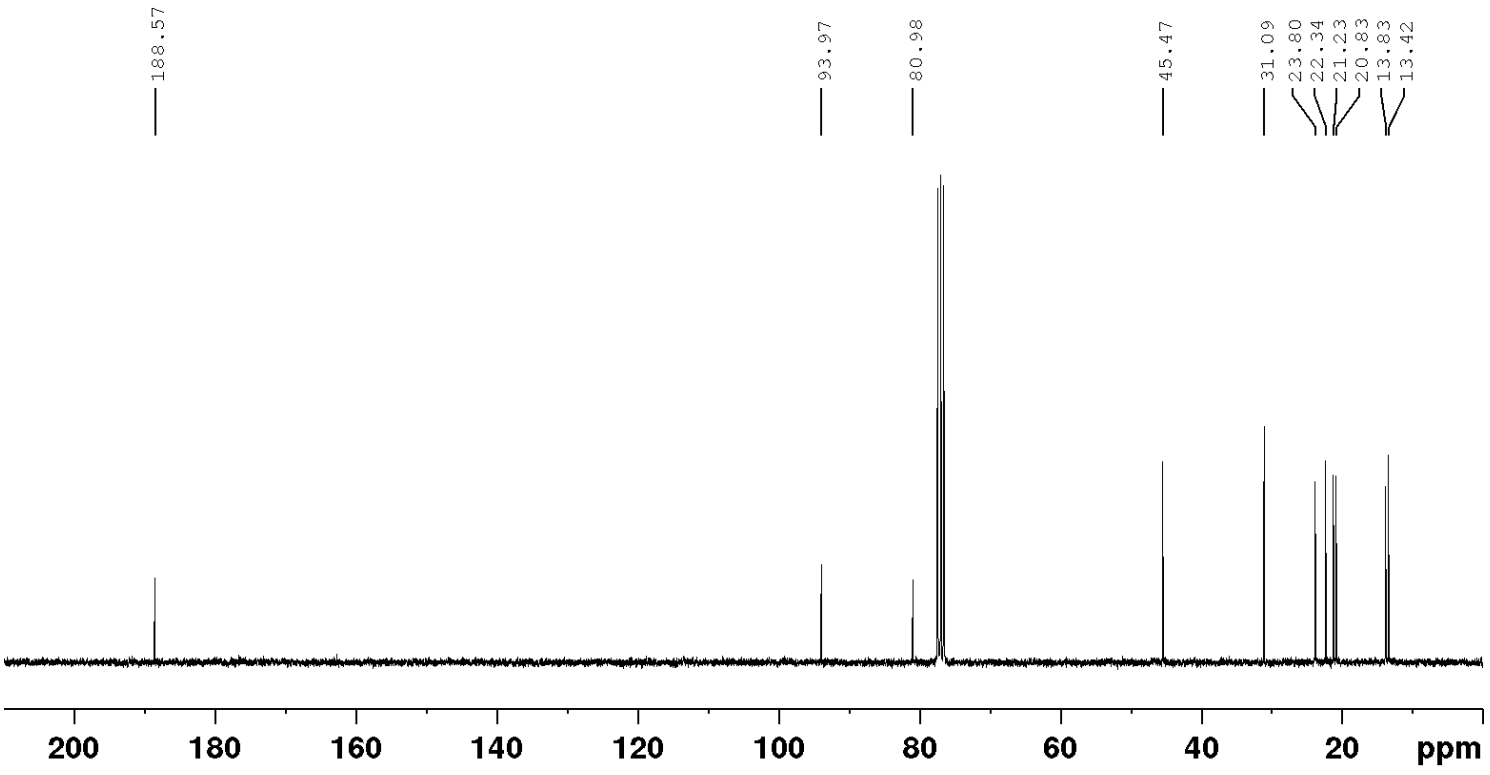
1-Phenylhept-3-in-2-on (5e)



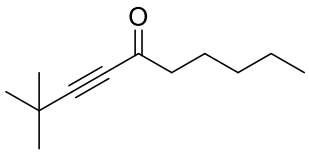


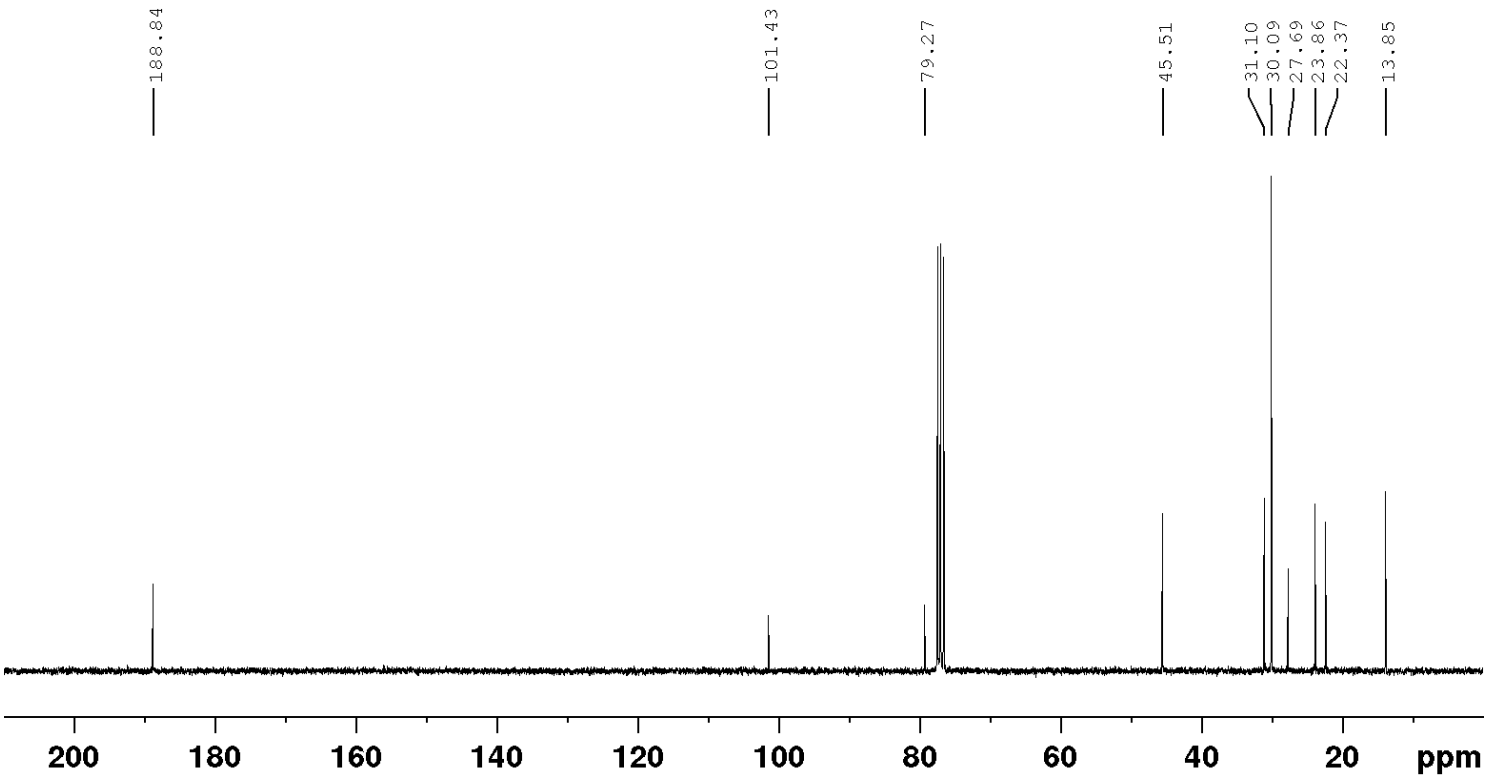
undec-4-yn-6-one (5f)



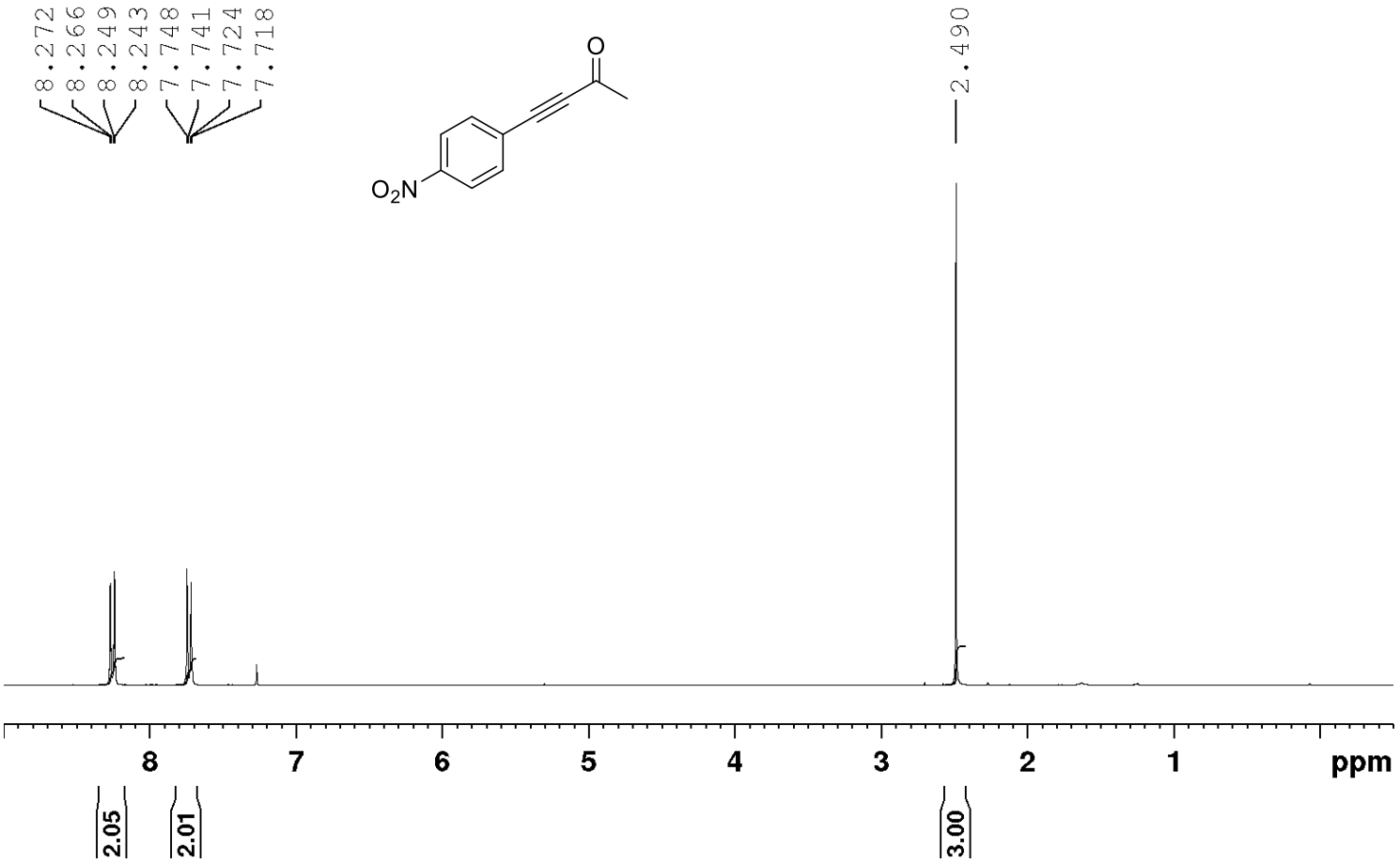


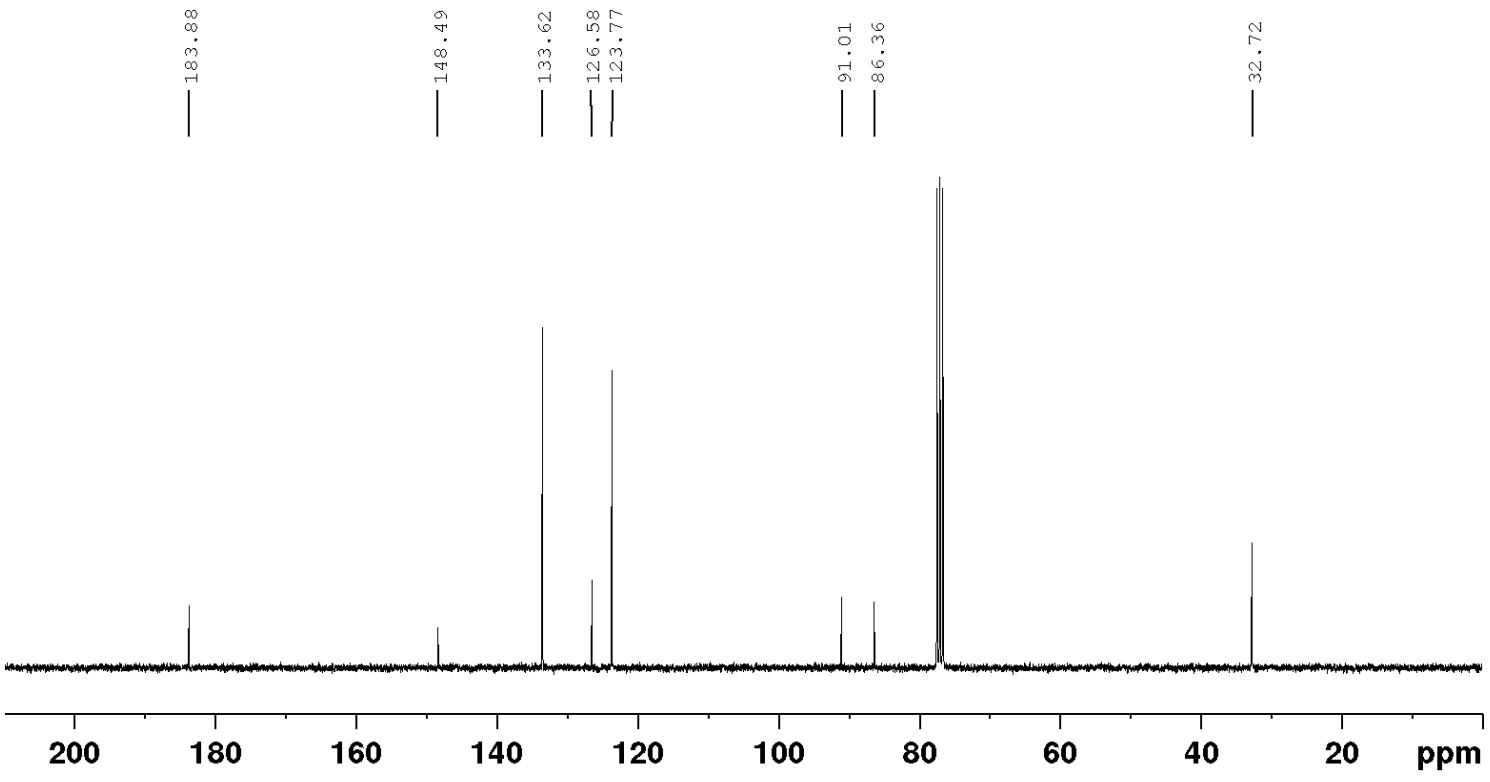
2,2-dimethyldec-3-yn-5-one (5g)



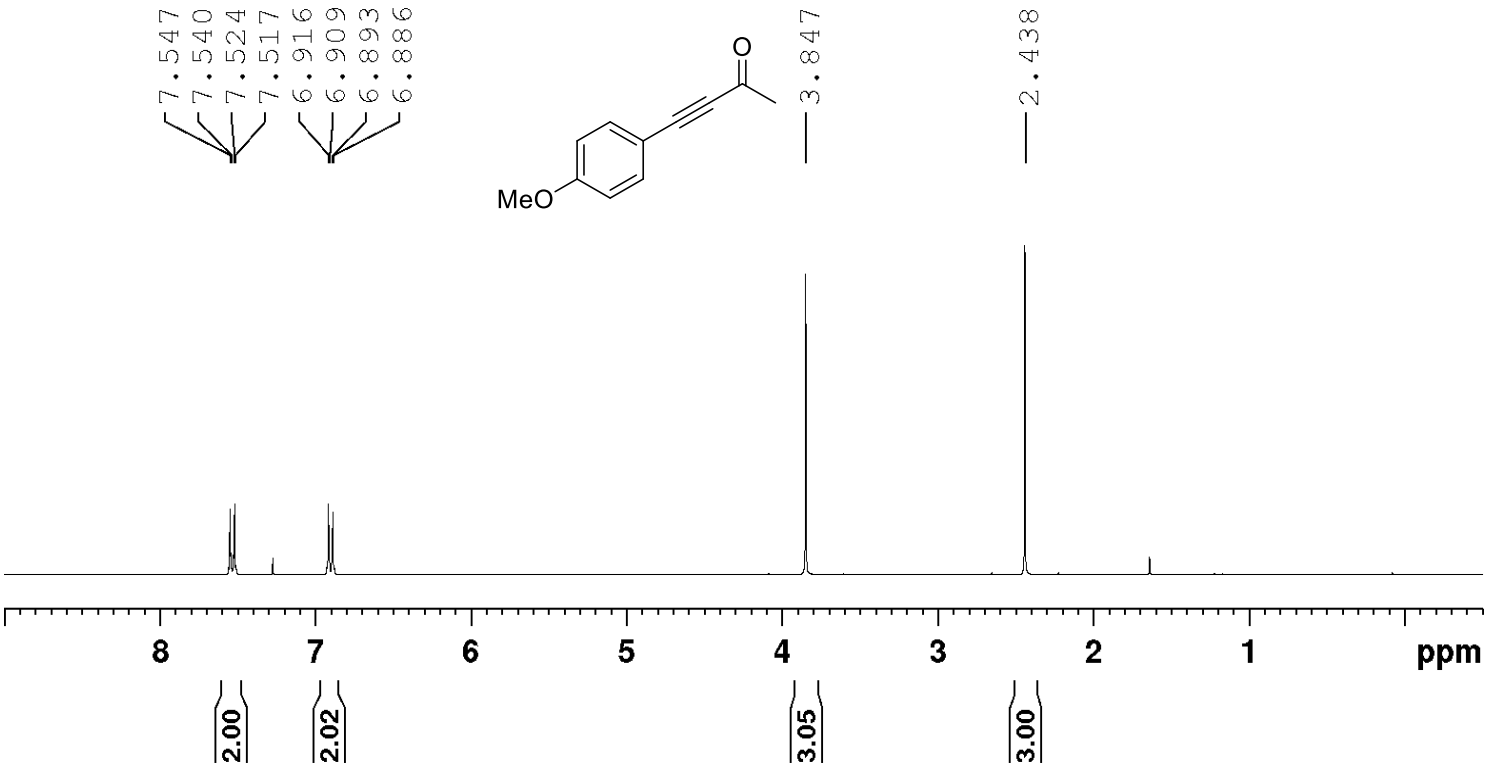


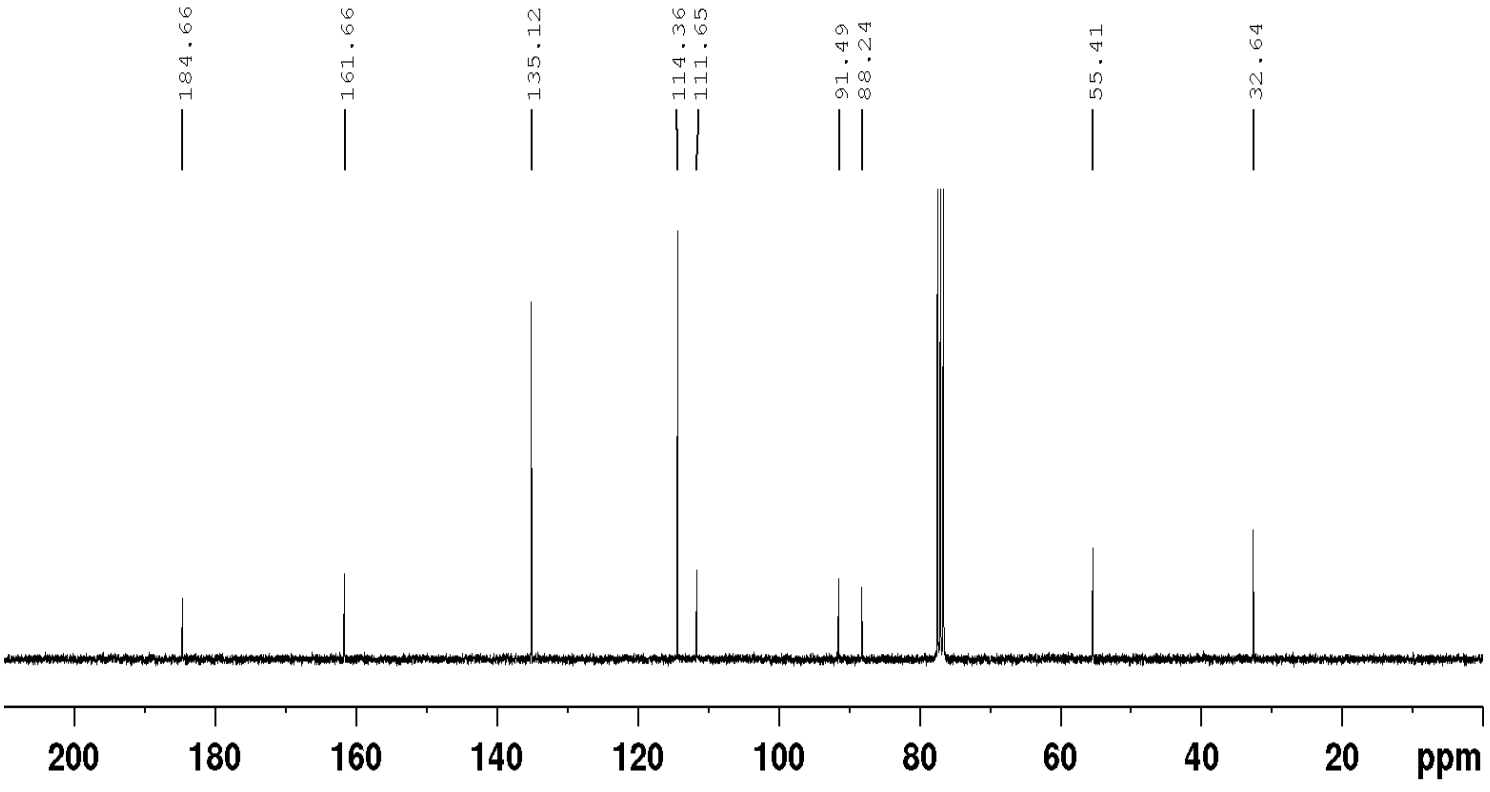
4-(4-Nitrophenyl)but-3-in-2-on (5h)



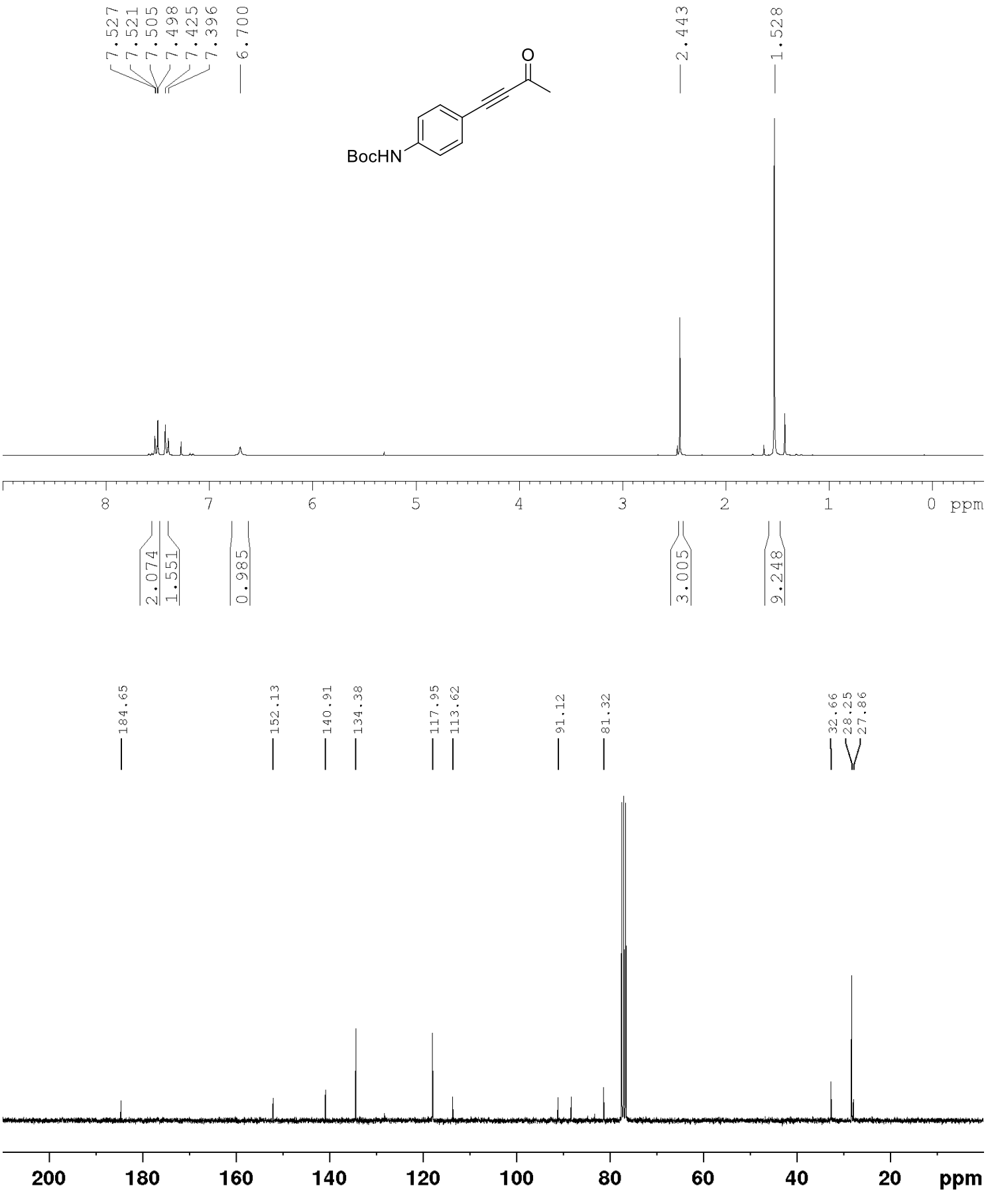


4-(4-Methoxyphenyl)but-3-in-2-on (5i)

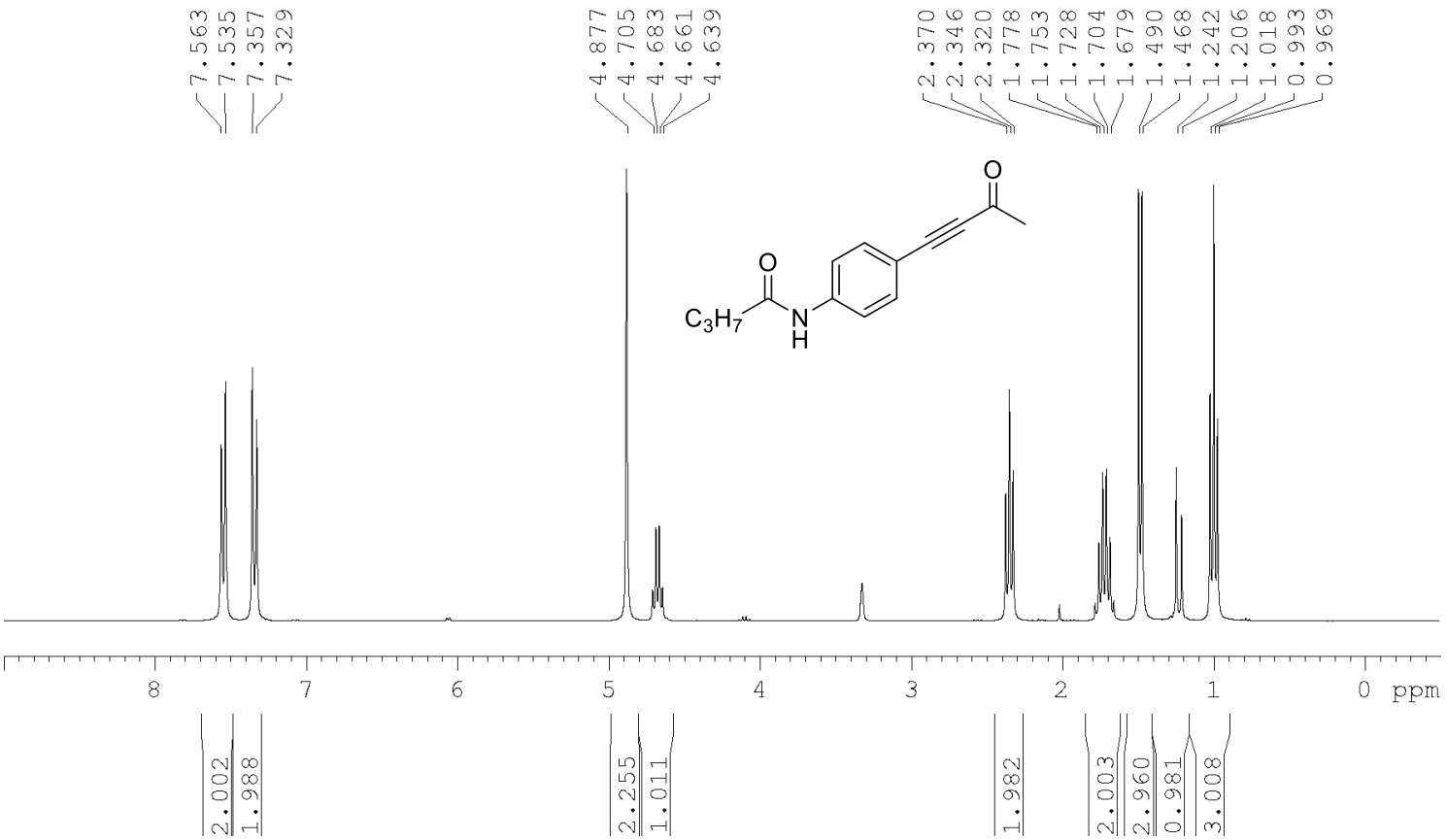


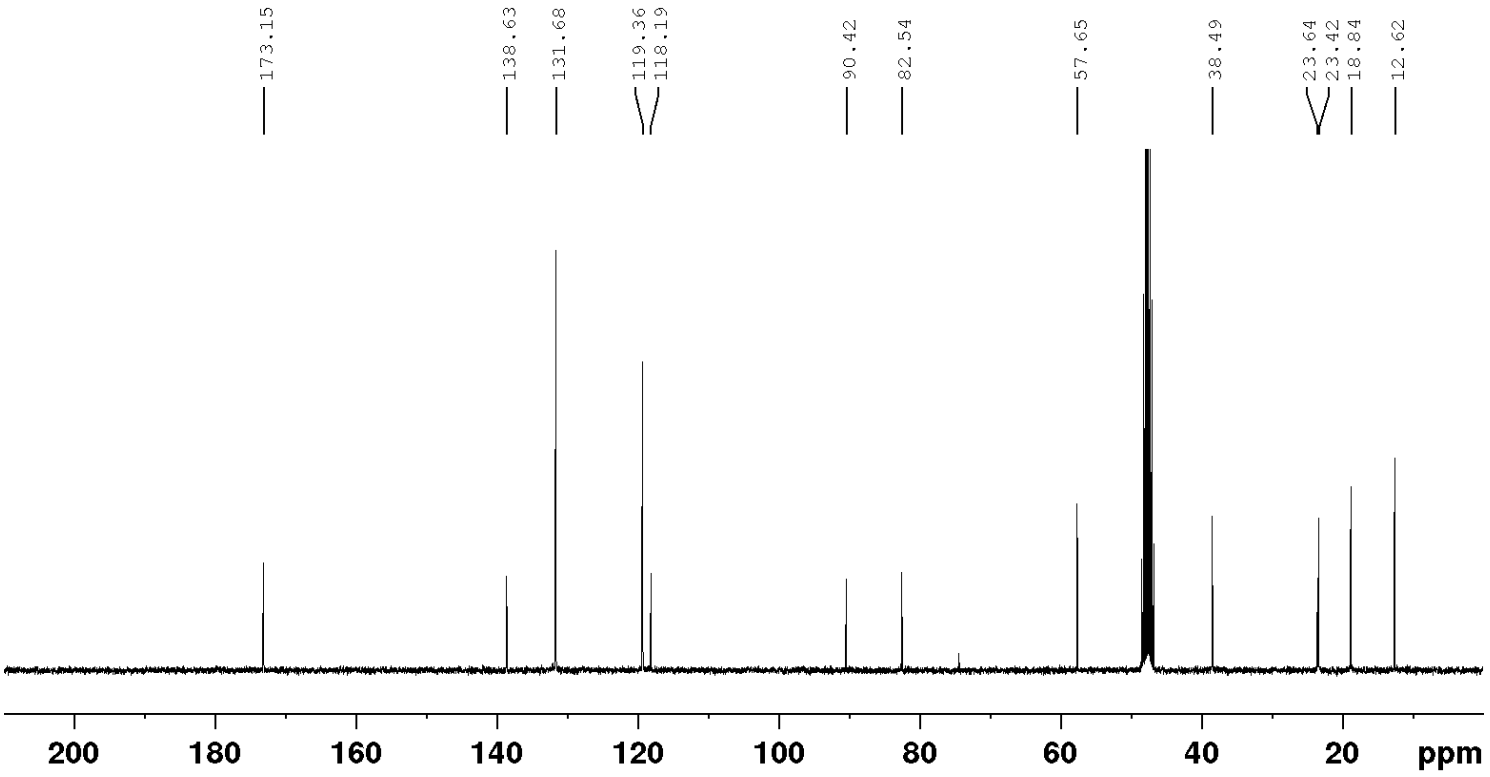


***tert*-butyl (4-(3-oxobut-1-yn-1-yl)phenyl)carbamate (5j)**

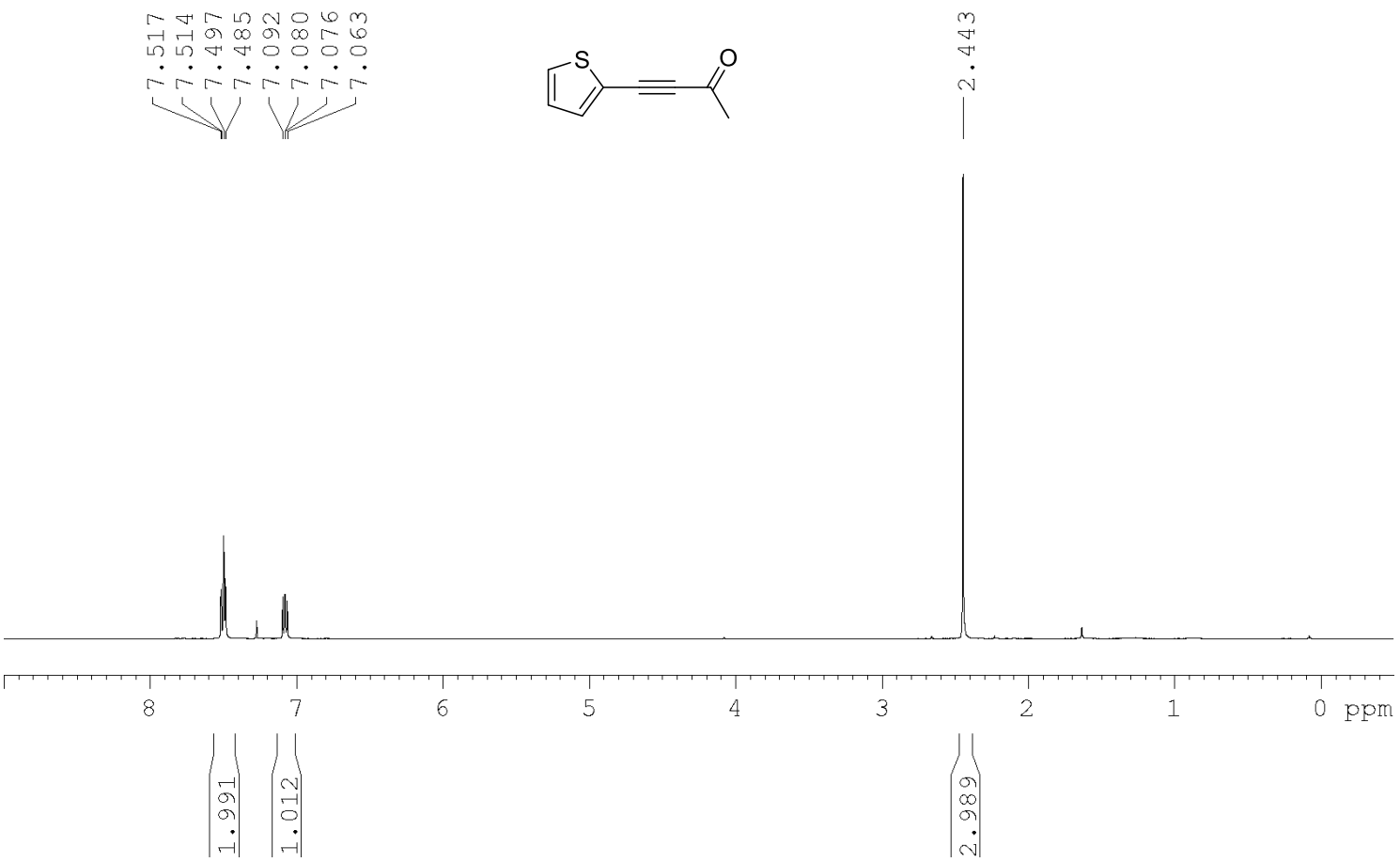


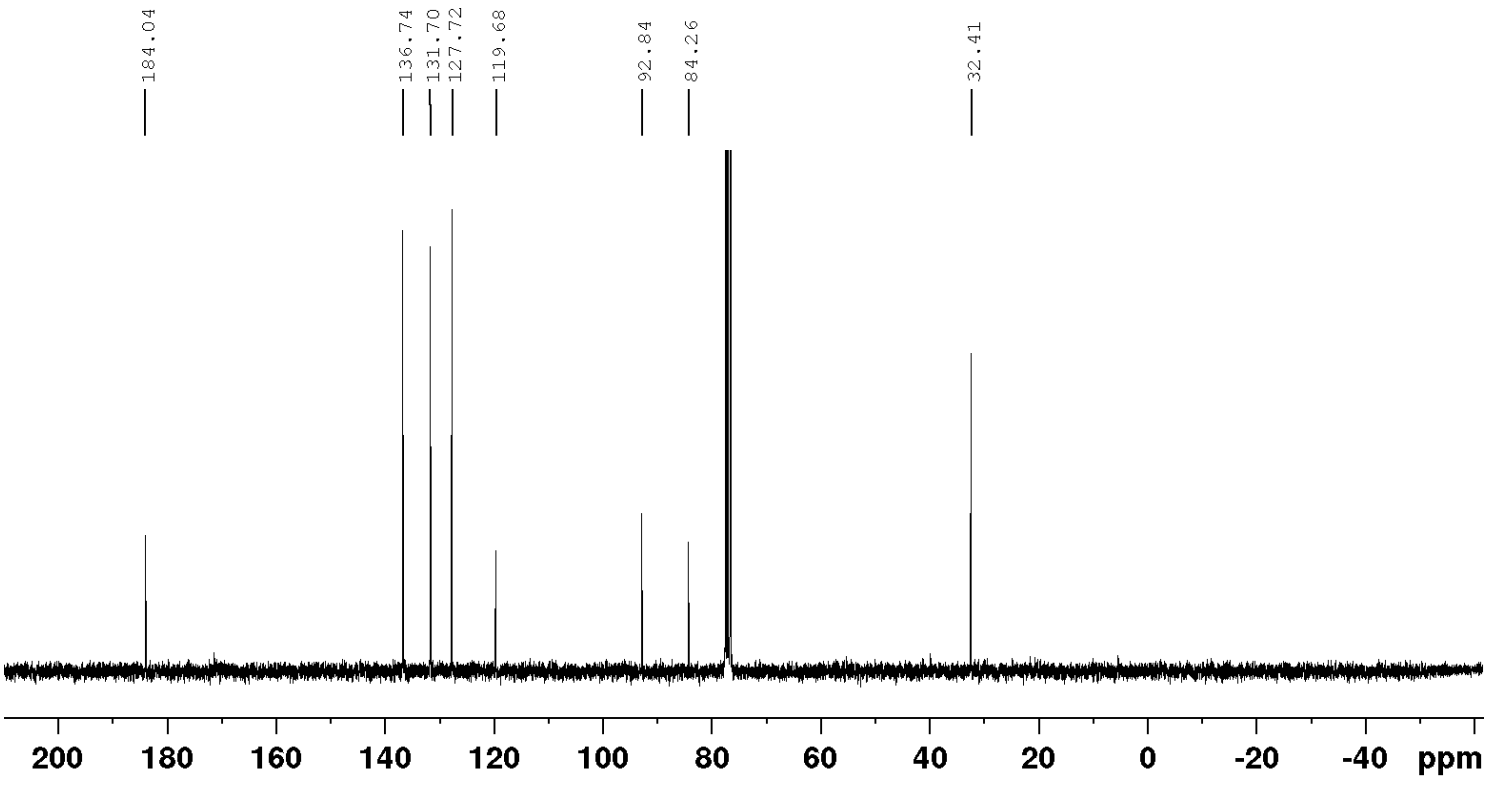
***N*-(4-(3-oxobut-1-yn-1-yl)phenyl)butyramide (5k)**



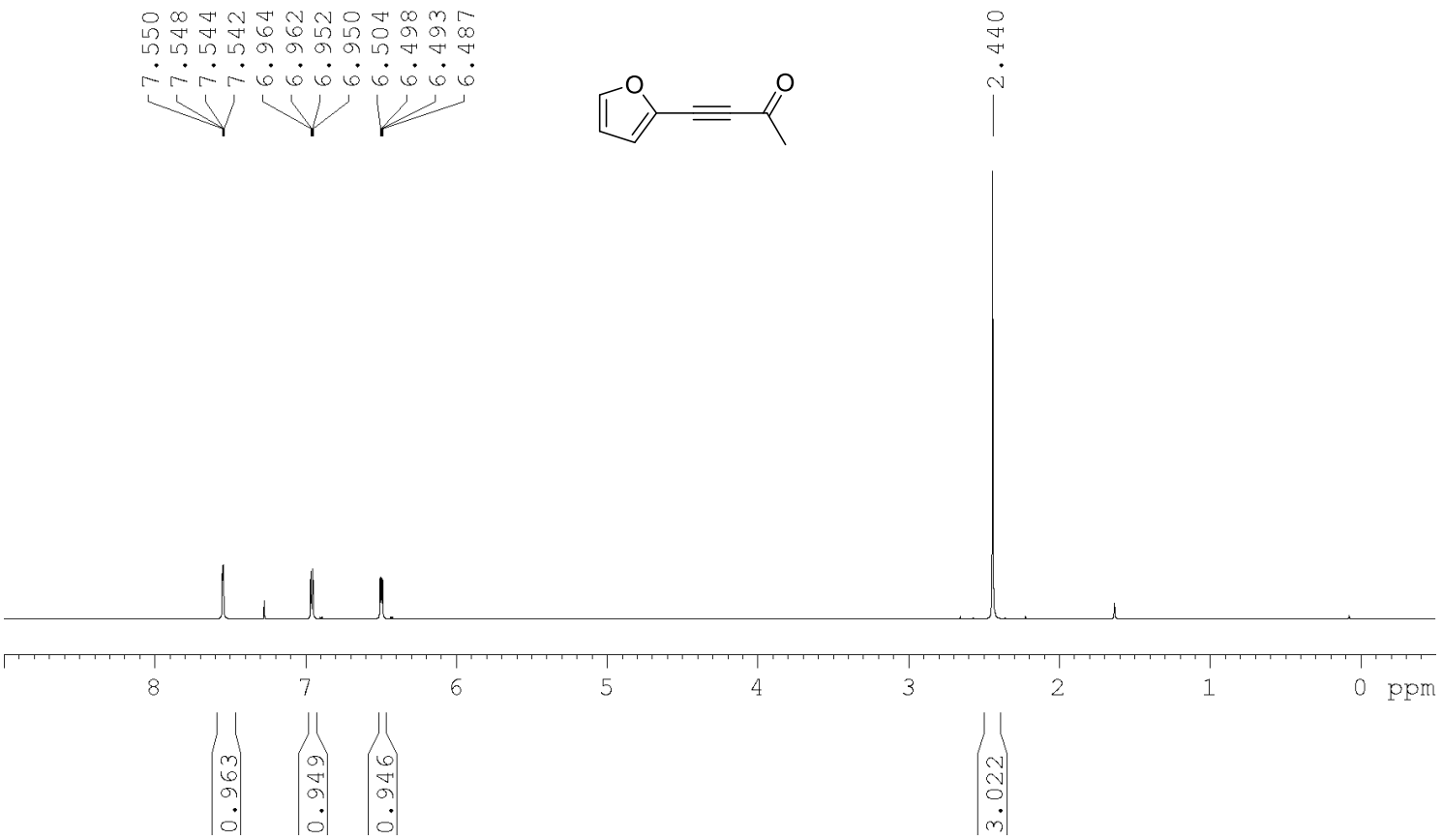


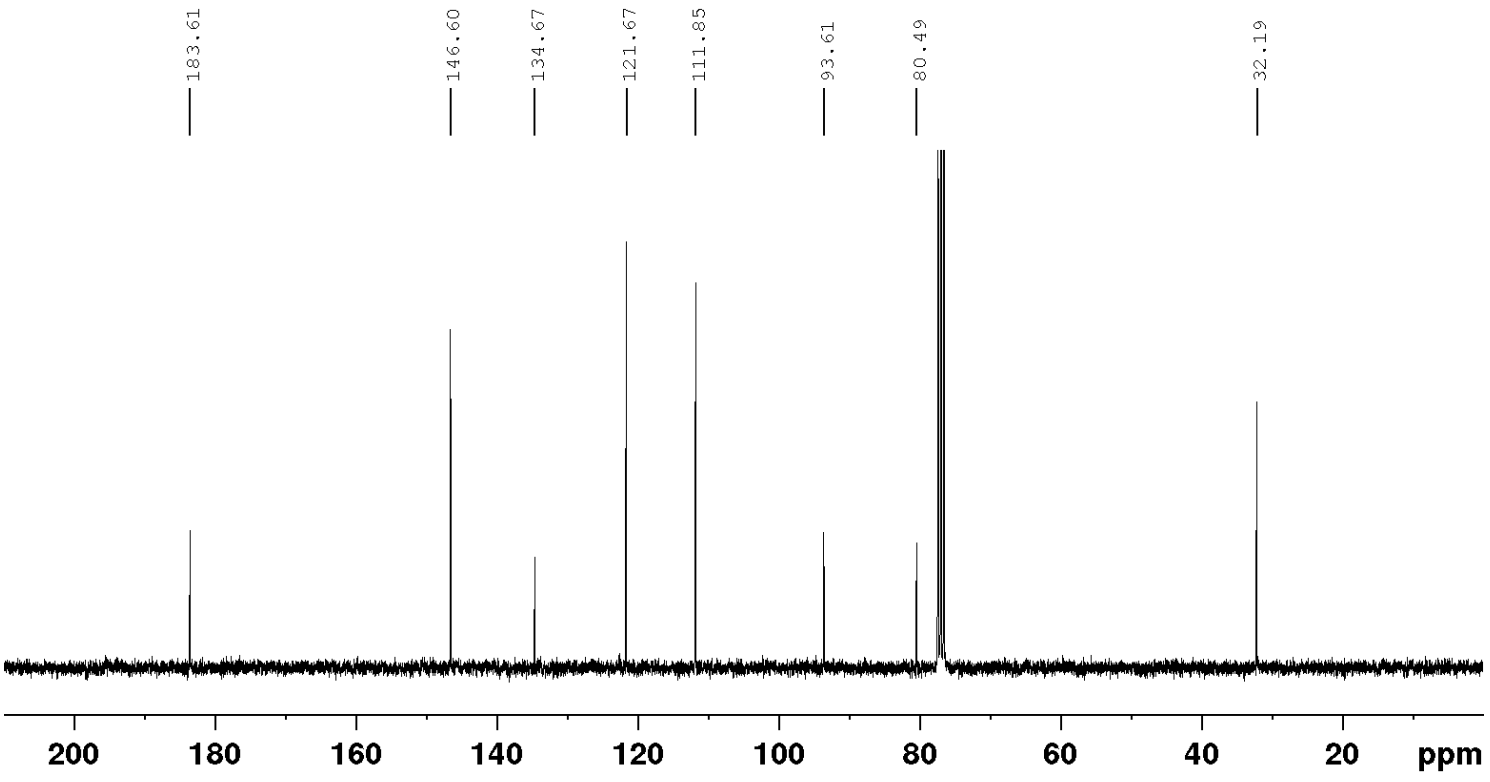
4-(thiophen-2-yl)but-3-yn-2-one (5l)



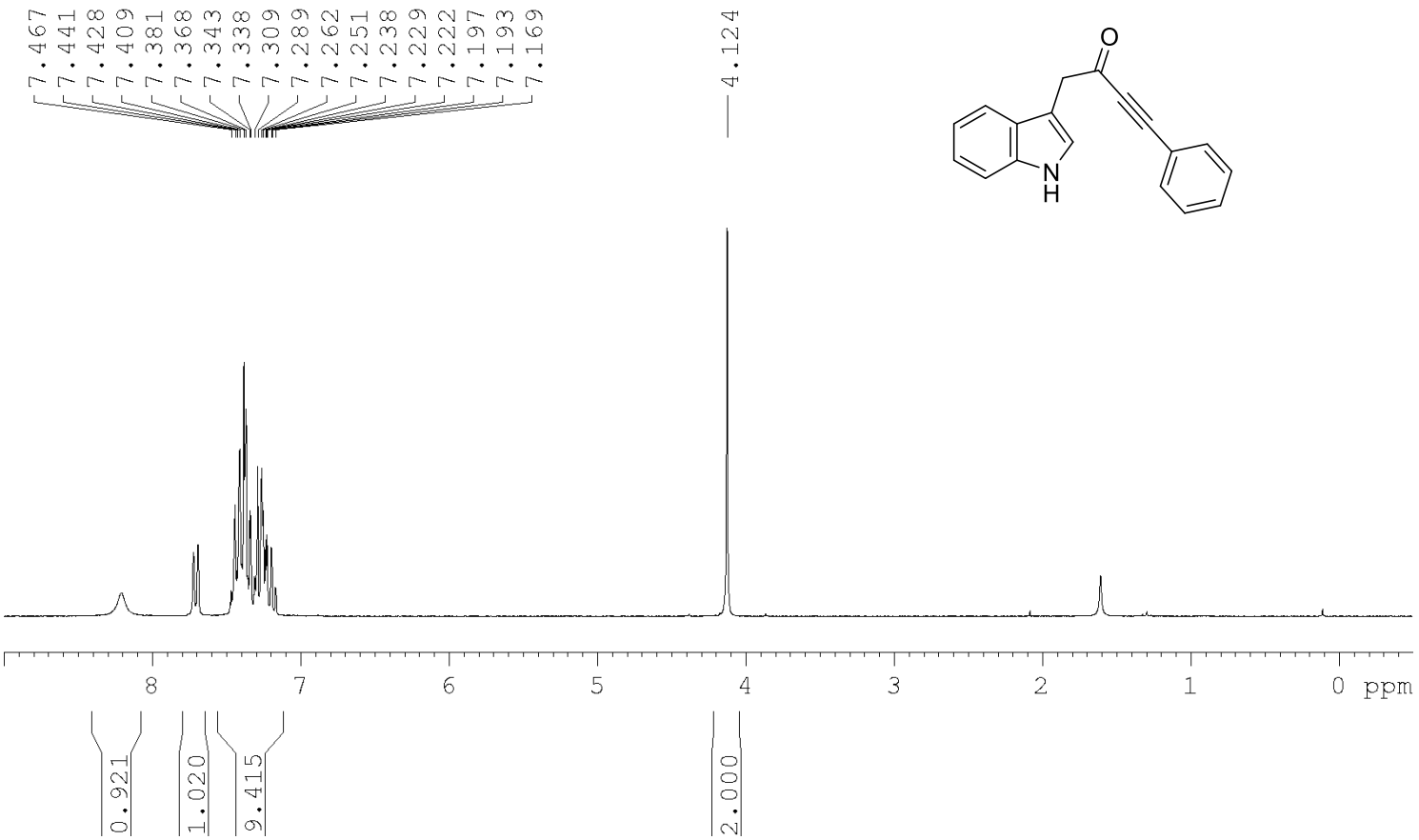


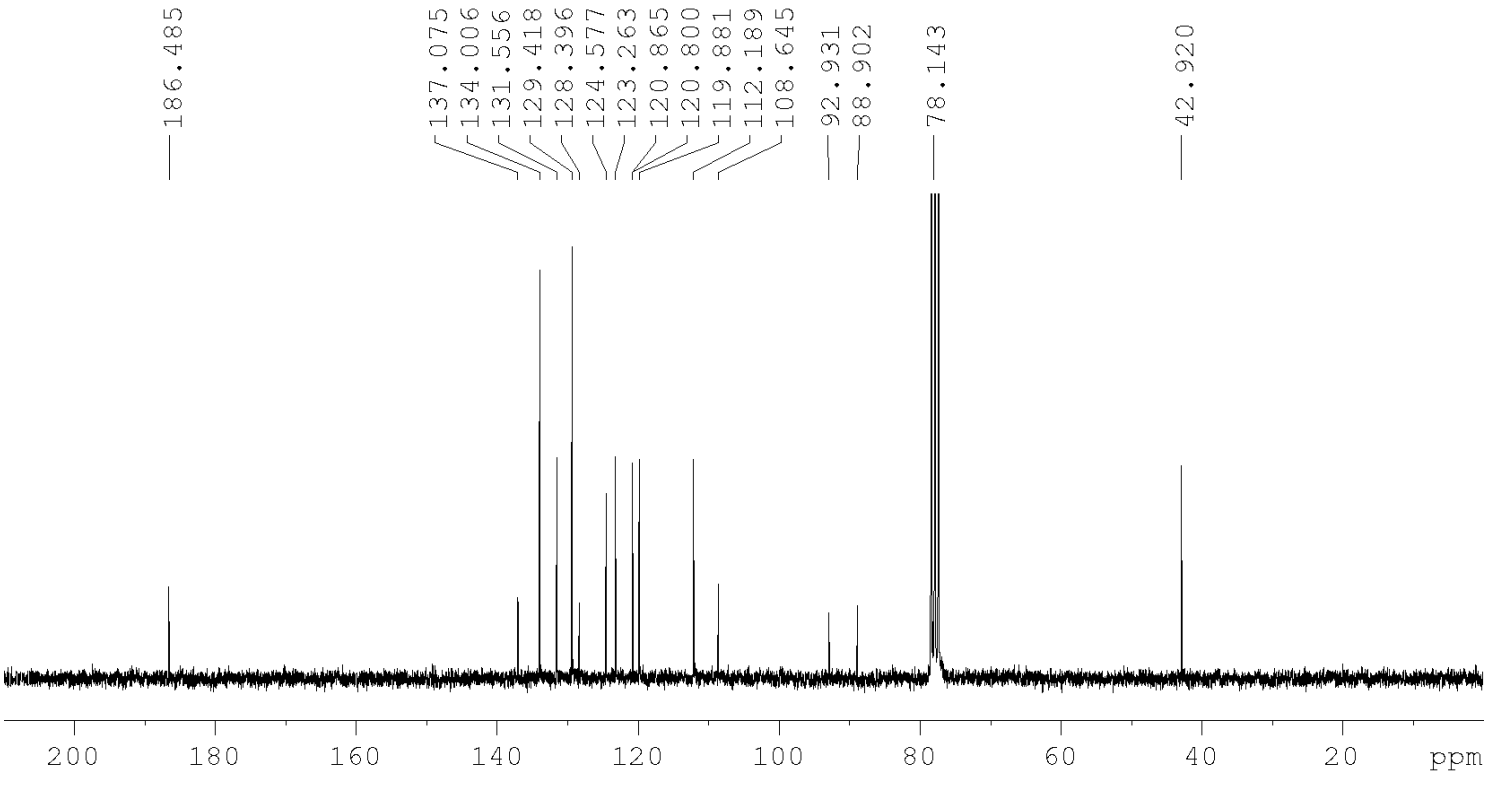
4-(furan-2-yl)but-3-yn-2-one (5m)



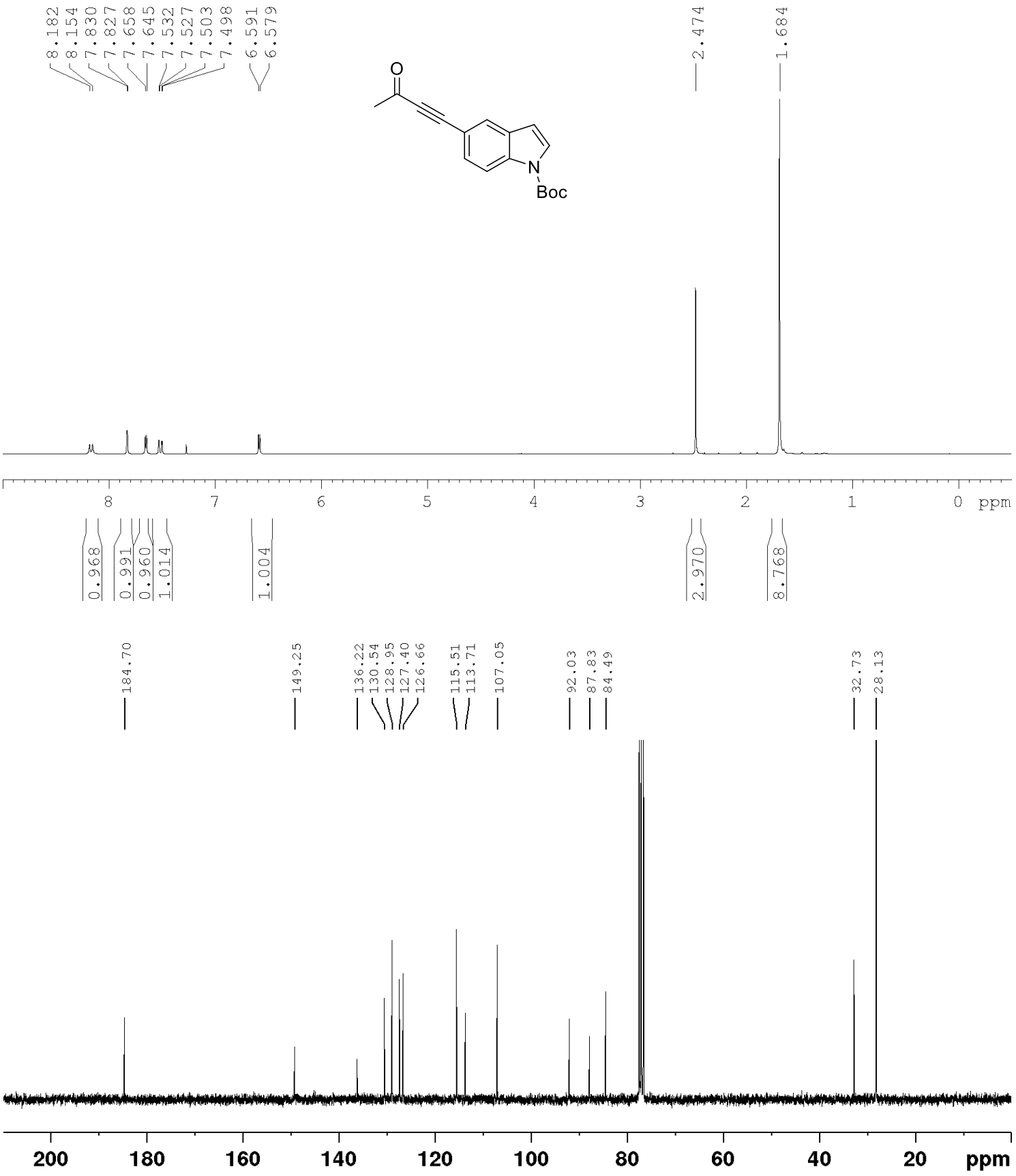


1-(1*H*-indol-3-yl)-4-phenylbut-3-yn-2-one (5n)

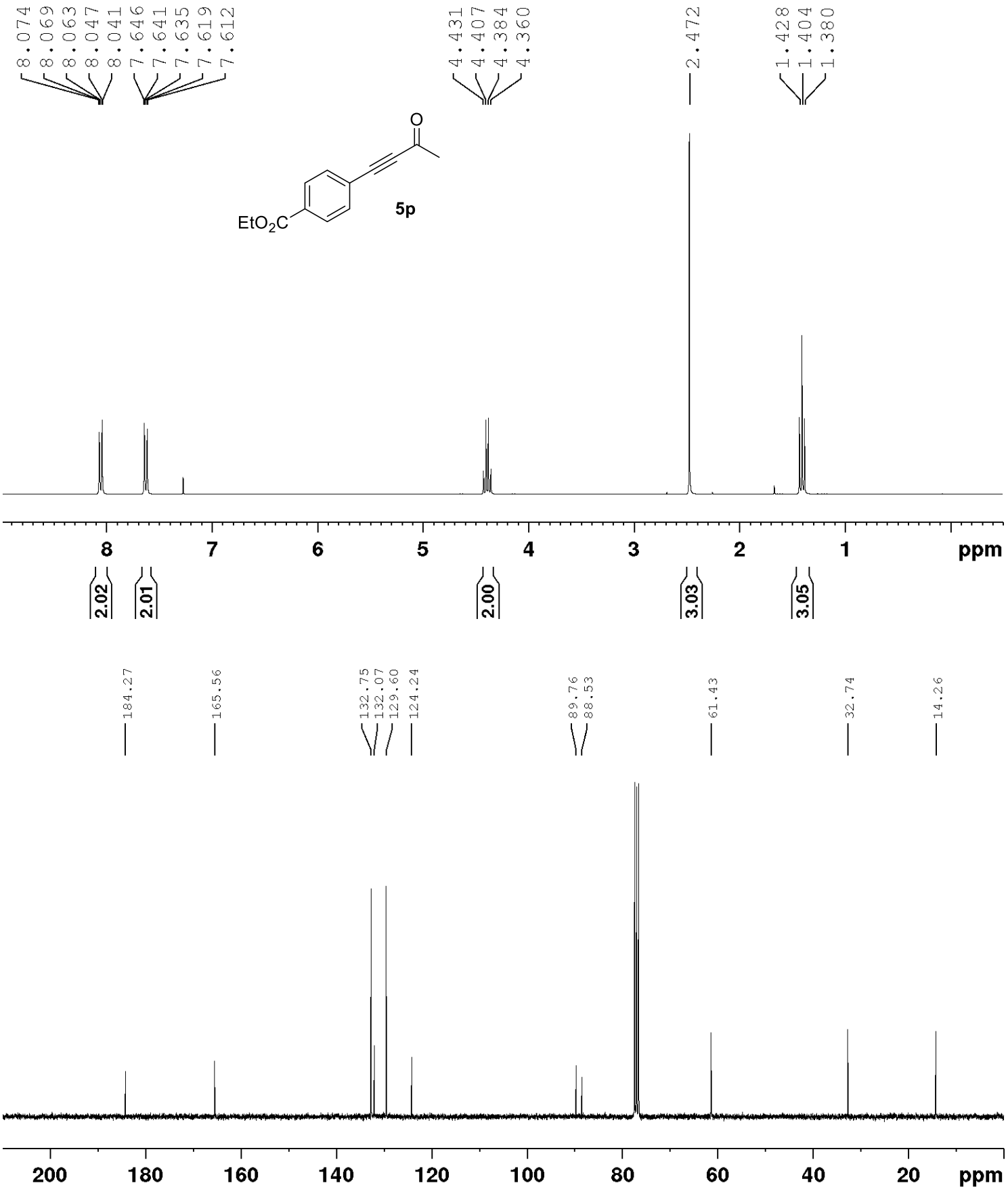




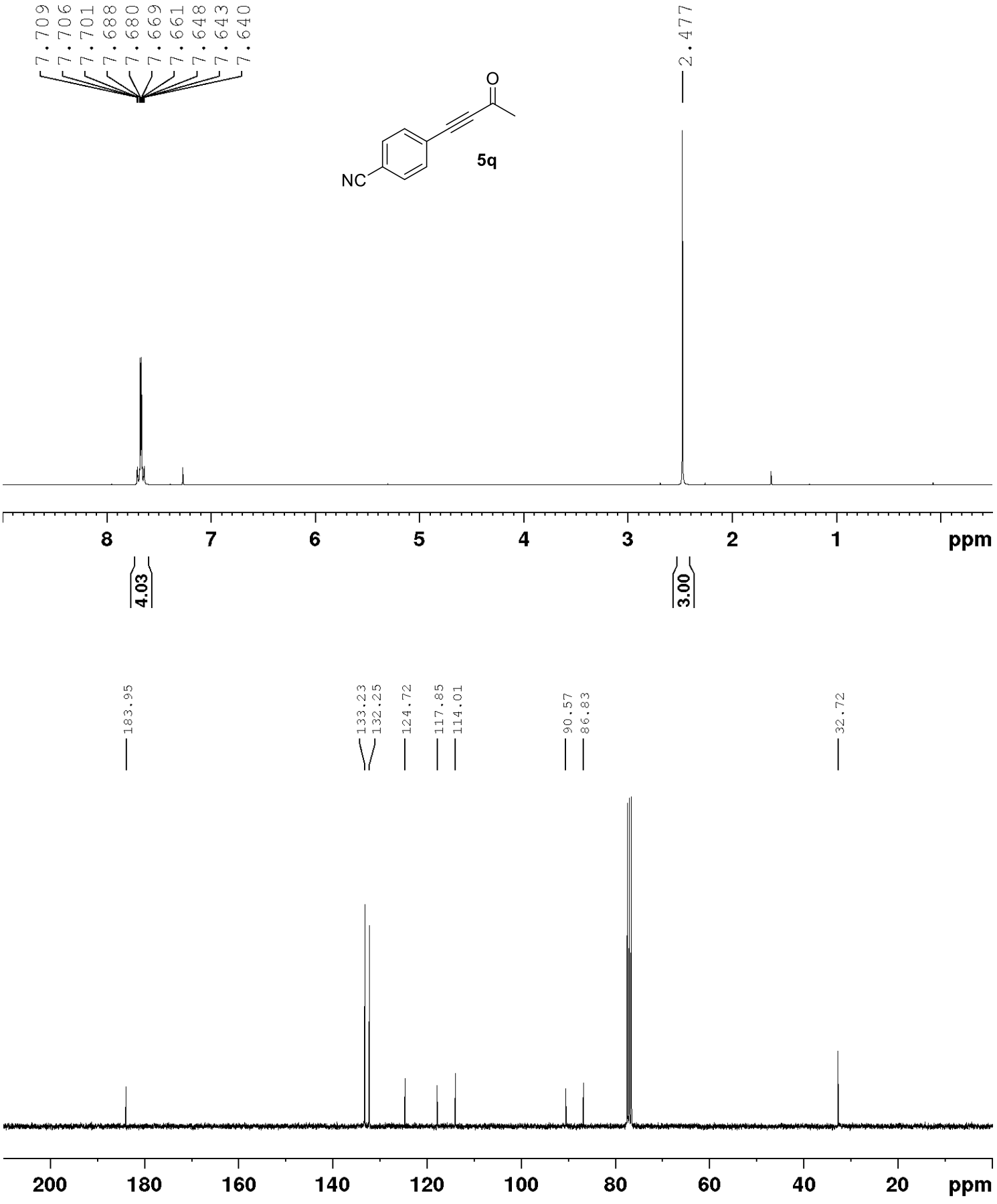
***tert*-butyl 5-(3-oxobut-1-yn-1-yl)-1*H*-indole-1-carboxylate (5o)**



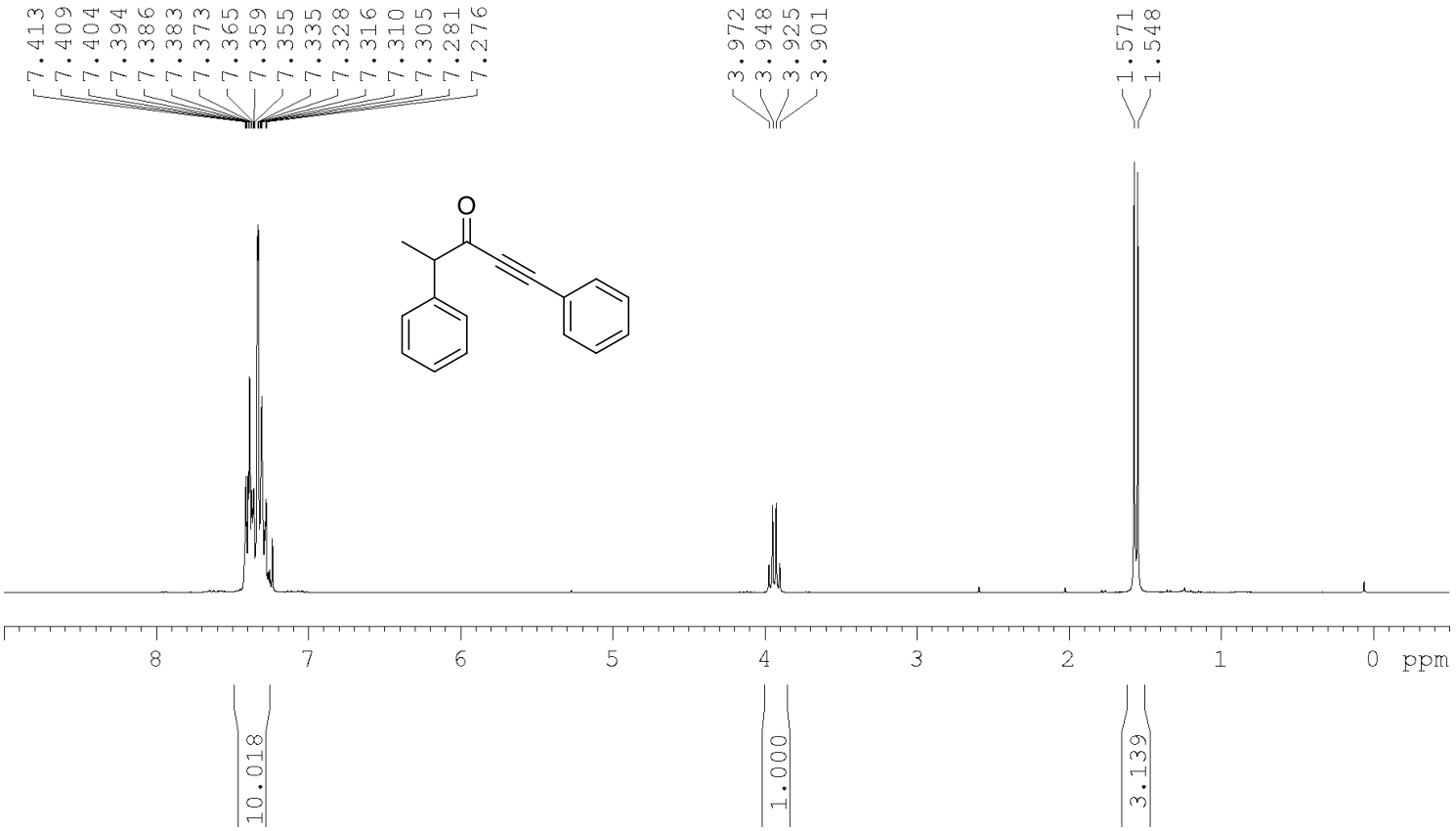
ethyl 4-(3-oxobut-1-yn-1-yl)benzoate (5p)

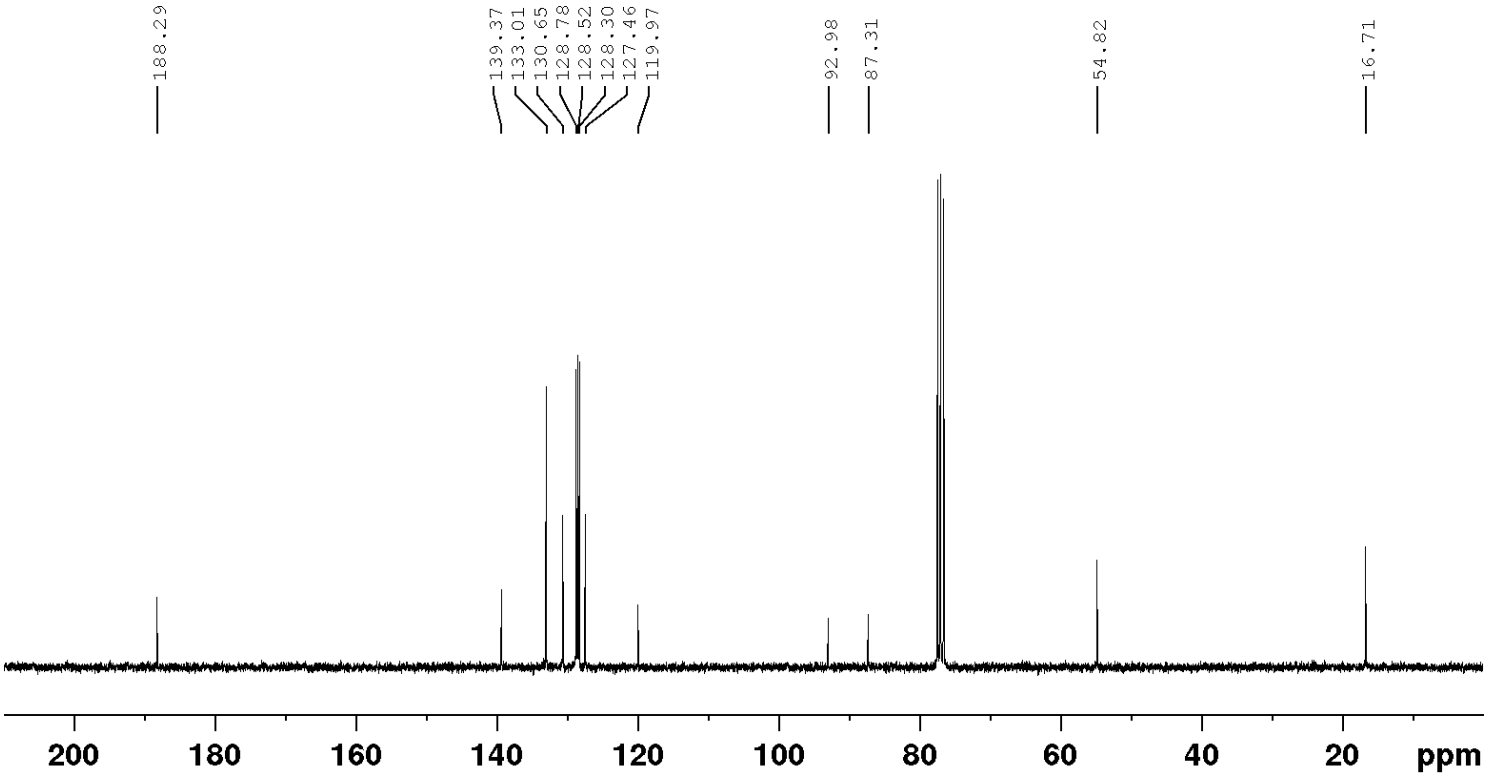


4-(3-oxobut-1-yn-1-yl)benzonitrile (5q)

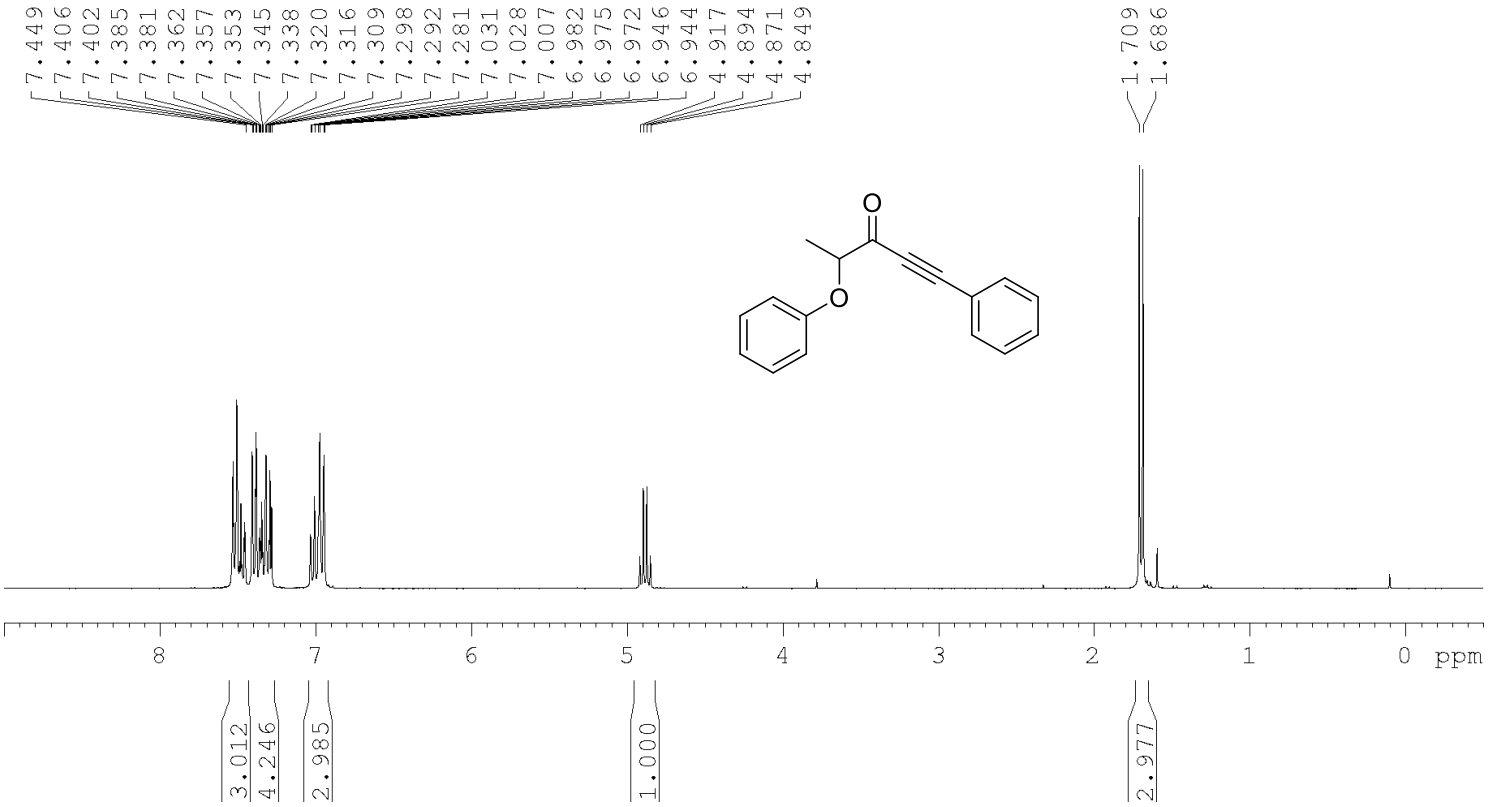


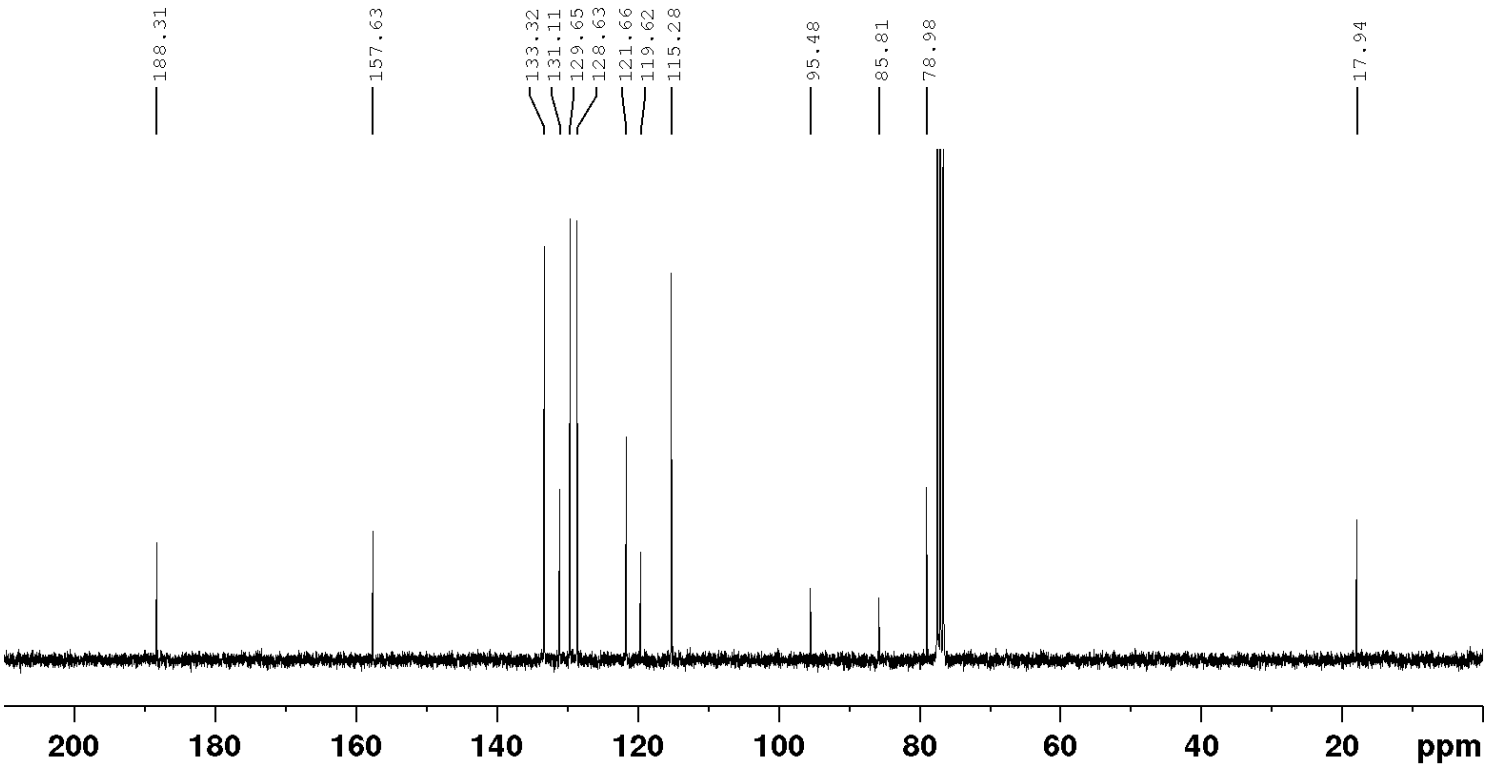
1,4-diphenylpent-1-yn-3-one (5r)





4-phenoxy-1-phenylpent-1-yn-3-one (5s)





4-(benzyloxy)-1-phenylpent-1-yn-3-one (5t)