

Supplementary Information

Copper(I) 2-Hydroxyethoxide-Promoted Cross-coupling of Aryl- and Alkenyldimethylsilanes with Organic Halides

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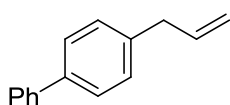
1. General
2. Typical procedure for Copper(I) 2-Hydroxyethoxide-Promoted Cross-coupling (Table 3)
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1. General THF was distilled from sodium and benzophenone. DMF was distilled from calcium hydride under reduced pressure. Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in CDCl_3 on a JEOL JNM-AL300 spectrometer unless otherwise noted. The chemical shifts (δ) were quoted in parts per million from tetramethylsilane for ^1H and CDCl_3 for ^{13}C spectroscopy. IR spectra were obtained on a JASCO FT-IR 460 Plus and reported in cm^{-1} . Mass spectra were recorded on a JEOL MStation MS700.

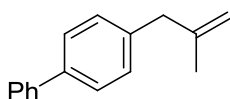
2. Typical procedure for Copper(I) 2-Hydroxyethoxide-Promoted Cross-coupling (Table 3):

CuI (57 mg, 0.3 mmol) and pre-prepared powdered lithium 2-hydroxyethoxide (**10**) (41 mg, 0.6 mmol) were placed in a flask under Ar. A mixture of 4-biphenyldimethylsilane (**8a**) (64 mg, 0.3 mmol) and methallyl chloride (**2b**) (54 mg, 0.6 mmol) in DMF (1.5 mL) was added to the flask at 25 °C under Ar. The mixture was stirred for 16 h at 50 °C. The reaction was quenched by addition of 3.5% aqueous NH_3 and the product was extracted with Et_2O . The extract was washed with H_2O and dried over Na_2SO_4 . The solvent was evaporated under reduced pressure and the residue was purified by PTLC (hexane) to give **6b** (52 mg, 83%).

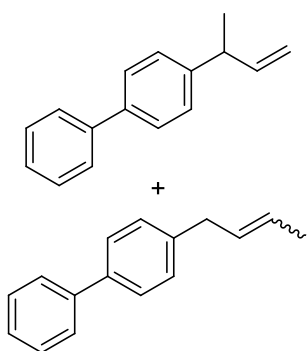
3. Characterization data for compounds 6



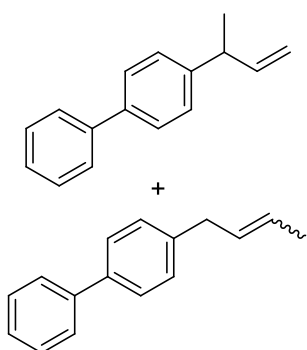
4-Allylbiphenyl (6a)¹: IR (neat) 3058, 3028, 2978, 2902, 1638, 1487, 1432, 1413, 1075, 1008, 914, 761, 738, 696; ^1H NMR 3.44 (d, $J = 6.8$ Hz, 2H), 5.07–5.17 (m, 2H), 6.01 (ddt, $J = 16.9, 10.1, 6.8$ Hz, 1H), 7.25–7.36 (m, 3H), 7.40–7.47 (m, 2H), 7.51–7.61 (m, 4H); ^{13}C NMR 39.8, 115.9, 127.00, 127.03, 127.2, 128.7, 129.0, 137.3, 139.0, 139.1, 141.0.



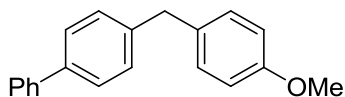
4-(2-Methylprop-2-en-1-yl)biphenyl (6b)²: IR (neat) 3071, 3027, 2969, 2916, 2848, 1650, 1487, 1449, 1407, 889, 759, 741, 693; ^1H NMR 1.72 (s, 3H), 3.36 (s, 2H), 4.78 (br s, 1H), 4.84 (br s, 1H), 7.24–7.29 (m, 2H), 7.30–7.36 (m, 1H), 7.40–7.47 (m, 2H), 7.50–7.56 (m, 2H), 7.56–7.61 (m, 2H); ^{13}C NMR 22.1, 44.2, 112.0, 126.97, 126.99, 127.01, 128.7, 129.3, 138.8, 139.0, 141.0, 145.0.



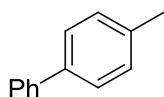
A mixture of 4-(1-methylprop-2-en-1-yl)biphenyl (6c) and 4-(but-2-en-1-yl)biphenyl (6d) [6c: 6d = 8:92 (*E:Z* = 86:14)] (entry 3): IR (neat) 3027, 2966, 2930, 1486, 1449, 1409, 1009, 967, 913, 838, 763, 737, 696; ^1H NMR (500 MHz) 1.40 (d, $J = 7.4$ Hz, 0.24H), 1.70 (dd, $J = 6.0, 1.4$ Hz, 2.37H), 1.75 (d, $J = 4.5$ Hz, 0.39H), 3.35 (d, $J = 6.3$ Hz, 1.58H), 3.44 (d, $J = 5.7$ Hz, 0.26H), 3.48–3.54 (m, 0.08H), 5.04–5.11 (m, 0.16H), 5.51–5.66 (m, 1.84H), 6.03 (ddd, $J = 17.2, 10.3, 6.3$ Hz, 0.08H), 7.21–7.34 (m, 3H), 7.39–7.44 (m, 2H), 7.49–7.60 (m, 4H); ^{13}C NMR 12.9, 17.9, 20.7, 32.7, 38.7, 42.8, 113.2, 125.0, 126.5, 126.99, 127.01, 127.1, 127.2, 127.6, 128.70, 128.72, 128.8, 128.9, 129.9, 138.80, 138.84, 139.1, 140.2, 141.1, 143.1. HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{16}$ $[\text{M}]^+$ 208.1252, found 208.1249.



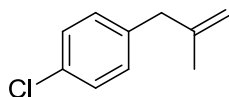
A mixture of 4-(1-methylprop-2-en-1-yl)biphenyl (6c) and 4-(but-2-en-1-yl)biphenyl (6d) [6c: 6d = 51:49 (*E:Z* = 70:30)] (entry 4): IR (neat) 3027, 2966, 2930, 1487, 1449, 1410, 1009, 967, 910, 838, 762, 736, 697; ^1H NMR (500 MHz) 1.40 (d, $J = 7.4$ Hz, 1.53H), 1.70 (dd, $J = 6.0, 1.4$ Hz, 1.02H), 1.75 (d, $J = 4.6$ Hz, 0.45H), 3.35 (d, $J = 6.3$ Hz, 0.68H), 3.44 (d, $J = 5.2$ Hz, 0.30H), 3.51 (dq, $J = 6.3, 7.4$ Hz, 0.51H), 5.04–5.11 (m, 1.02H), 5.51–5.66 (m, 0.98H), 6.03 (ddd, $J = 17.2, 10.3, 6.3$ Hz, 0.51H), 7.21–7.34 (m, 3H), 7.39–7.44 (m, 2H), 7.50–7.60 (m, 4H); ^{13}C NMR 12.9, 17.9, 20.7, 32.7, 38.7, 42.8, 113.2, 125.0, 126.5, 126.99, 127.01, 127.1, 127.2, 127.6, 128.68, 128.72, 128.8, 128.9, 129.9, 138.79, 138.84, 139.1, 140.2, 140.3, 141.0, 141.1, 143.1, 144.6.



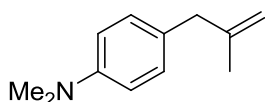
4-(4-Methoxybenzyl)biphenyl (6e)³: IR (neat) 3030, 2924, 2837, 1610, 1509, 1461, 1297, 1240, 1172, 1108, 1030, 849, 801, 766, 697; ¹H NMR 3.79 (s, 3H), 3.97 (s, 2H), 6.82–6.88 (m, 2H), 7.12–7.17 (m, 2H), 7.22–7.27 (m, 2H), 7.28–7.35 (m, 1H), 7.38–7.45 (m, 2H), 7.49–7.59 (m, 4H); ¹³C NMR 40.7, 55.3, 113.9, 126.99, 127.04, 127.2, 128.7, 129.2, 129.9, 133.1, 138.9, 140.7, 141.0, 158.0.



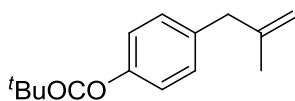
4-Methylbiphenyl (6f)⁴ (Contaminated with biphenyl): IR (neat) 3029, 2921, 1484, 822, 758, 737; ¹H NMR 2.39 (s, 3H), 7.19–7.62 (m, 9H); ¹³C NMR 21.1, 126.9, 127.0, 128.7, 129.5, 137.0, 138.3, 141.1.



1-Chloro-4-(2-methylprop-2-en-1-yl)benzene (6g)³: IR (neat) 3077, 2972, 2914, 1651, 1491, 1442, 1406, 1375, 1093, 1016, 894, 842, 793; ¹H NMR 1.66 (s, 3H), 3.28 (s, 2H), 4.71 (br s, 1H), 4.82 (br s, 1H), 7.09–7.14 (m, 2H), 7.23–7.28 (m, 2H); ¹³C NMR 22.0, 43.9, 112.3, 128.4, 130.2, 131.8, 138.2, 144.6.

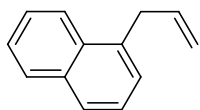


1-(Dimethylamino)-4-(2-methylprop-2-en-1-yl)benzene (6h): IR (neat) 3072, 2969, 2912, 2897, 2799, 1614, 1521, 1443, 1345, 947, 887, 795; ¹H NMR 1.67 (s, 3H), 2.92 (s, 6H), 3.22 (s, 2H), 4.71 (br s, 1H), 4.76 (br s, 1H), 6.67–6.72 (m, 2H), 7.03–7.09 (m, 2H); ¹³C NMR 22.0, 40.9, 43.7, 111.1, 112.9, 127.9, 129.5, 146.0, 149.2. HRMS (FAB) calcd for C₁₂H₁₇N [M]⁺ 175.1361, found 175.1360.

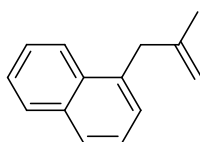


1-(tert-Butoxycarbonyl)-4-(2-methylprop-2-en-1-yl)benzene (6i): IR (neat) 3076, 3005, 2977, 2933, 1713, 1651, 1610, 1476, 1456, 1415, 1392, 1368, 1292, 1255, 1166, 1118, 1020, 893, 851, 752; ¹H NMR 1.59 (s, 9H), 1.66 (s, 3H), 3.35 (s, 2H), 4.73 (s, 1H), 4.83

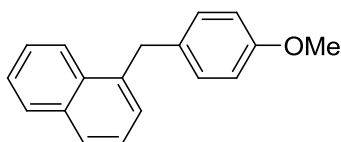
(s, 1H), 7.21–7.26 (m, 2H), 7.89–7.94 (m, 2H); ^{13}C NMR 22.0, 28.2, 44.5, 80.7, 112.5, 128.8, 129.5, 130.0, 144.3, 144.6, 165.8. HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$ $[\text{M}]^+$ 232.1463, found 232.1460.



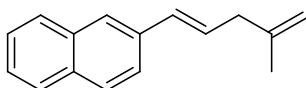
1-Allylnaphthalene (6j)⁵: IR (neat) 3046, 3005, 2977, 2911, 2119, 1926, 1827, 1638, 1597, 1509, 1396, 1257, 994, 914, 776; ^1H NMR 3.85 (d, $J = 6.4$ Hz, 2H), 5.06–5.14 (m, 2H), 6.12 (ddt, $J = 16.7, 10.5, 6.3$ Hz, 1H), 7.32–7.54 (m, 4H), 7.74 (d, $J = 8.1$ Hz, 1H), 7.84–7.89 (m, 1H), 8.00–8.07 (m, 1H); ^{13}C NMR 37.3, 116.2, 124.0, 125.5, 125.6, 125.8, 126.3, 126.9, 128.7, 131.9, 133.8, 136.1, 137.0.



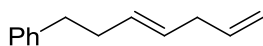
1-(2-Methyl-2-propen-1-yl)naphthalene (6k)⁶: IR (neat) 3067, 1650, 1597, 1509, 1444, 1396, 1260, 1078, 891, 790, 774; ^1H NMR 1.78 (s, 3H), 3.78 (s, 2H), 4.62 (s, 1H), 4.86 (s, 1H), 7.30–7.52 (m, 4H), 7.71–7.77 (m, 1H), 7.81–7.88 (m, 1H), 7.98–8.05 (m, 1H); ^{13}C NMR 22.8, 41.5, 112.2, 124.3, 125.4, 125.5, 125.7, 127.0, 127.2, 128.6, 132.4, 133.8, 135.7, 144.6.



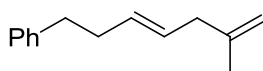
1-(4-Methoxybenzyl)naphthalene (6l): IR (neat) 1176, 1106, 1035, 908, 792, 779, 731; ^1H NMR 3.75 (s, 3H), 4.38 (s, 2H), 6.75–6.85 (m, 2H), 7.05–7.16 (m, 2H), 7.22–7.29 (m, 1H), 7.37–7.48 (m, 3H), 7.71–7.78 (m, 1H), 7.81–7.88 (m, 1H), 7.96–8.03 (m, 1H); ^{13}C NMR 38.1, 55.2, 113.9, 124.2, 125.50, 125.53, 125.9, 127.0, 127.1, 128.6, 129.6, 132.1, 132.7, 133.9, 137.0, 157.9. HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{16}\text{O}$ $[\text{M}]^+$ 248.1201, found 248.1215.



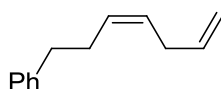
2-[(E)-4-Methyl-1,4-pentadien-1-yl]naphthalene (6m)⁷: IR (neat) 3057, 2969, 2933, 1650, 1627, 1598, 1508, 1438, 1372, 1271, 963, 890, 857, 818, 790, 742; ^1H NMR 1.80 (s, 3H), 2.96 (d, $J = 7.0$ Hz, 2H), 4.82 (br s, 2H), 6.36 (dt, $J = 15.8, 7.1$ Hz, 1H), 6.59 (d, $J = 15.8$ Hz, 1H), 7.38–7.48 (m, 2H), 7.60 (dd, $J = 8.6, 1.6$ Hz, 1H), 7.70 (s, 1H), 7.74–7.82 (m, 3H); ^{13}C NMR 22.5, 41.6, 111.1, 123.6, 125.5, 125.6, 126.1, 127.6, 127.8, 128.1, 128.6, 131.5, 132.7, 133.7, 135.0, 144.5.



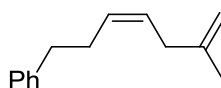
(E)-7-Phenyl-1,4-heptadiene (6n): IR (neat) 3062, 3027, 2925, 2855, 1637, 1604, 1496, 1454, 1433, 1031, 993, 970, 912, 744, 698; ^1H NMR 2.28–2.37 (m, 2H), 2.63–2.79 (m, 4H), 4.94–5.04 (m, 2H), 5.45 (dt, $J = 15.2, 5.5$ Hz, 1H), 5.51 (dt, $J = 15.2, 5.5$ Hz, 1H), 5.82 (ddt, $J = 16.7, 10.4, 6.4$ Hz, 1H), 7.15–7.32 (m, 5H); ^{13}C NMR 34.4, 36.0, 36.7, 114.9, 125.7, 128.2, 128.3, 128.4, 130.7, 137.2, 142.0. Anal. Calcd for $\text{C}_{13}\text{H}_{16}$: C, 90.64; H, 9.36. Found: C, 90.83; H, 9.45.



(E)-2-Methyl-7-phenyl-1,4-heptadiene (6o): IR (neat) 3067, 3027, 2969, 2932, 2854, 1649, 1496, 1454, 970, 888, 743, 698; ^1H NMR 1.68 (s, 3H), 2.29–2.39 (m, 2H), 2.63–2.73 (m, 4H), 4.65 (br s, 1H), 4.70 (br s, 1H), 5.43 (dt, $J = 15.3, 5.7$ Hz, 1H), 5.51 (dt, $J = 15.3, 5.7$ Hz, 1H), 7.15–7.32 (m, 5H); ^{13}C NMR 22.4, 34.4, 36.0, 41.1, 110.2, 125.7, 128.2, 128.3, 128.5, 131.2, 142.0, 145.2.



(Z)-7-Phenyl-1,4-heptadiene (6p): IR (neat) 3063, 3011, 2925, 1637, 1604, 1496, 1454, 1077, 994, 911, 697; ^1H NMR 2.37 (dt, $J = 7.0, 7.8$ Hz, 2H), 2.67 (t, $J = 7.8$ Hz, 2H), 2.74 (t, $J = 6.4$ Hz, 2H), 4.92–5.05 (m, 2H), 5.41 (dt, $J = 10.8, 7.0$ Hz, 1H), 5.51 (dt, $J = 10.8, 7.0$ Hz, 1H), 5.74 (ddt, $J = 17.1, 10.1, 6.2$ Hz, 1H), 7.15–7.33 (m, 5H); ^{13}C NMR 29.1, 31.5, 35.8, 114.6, 125.8, 127.4, 128.3, 128.4, 129.9, 136.9, 141.9.

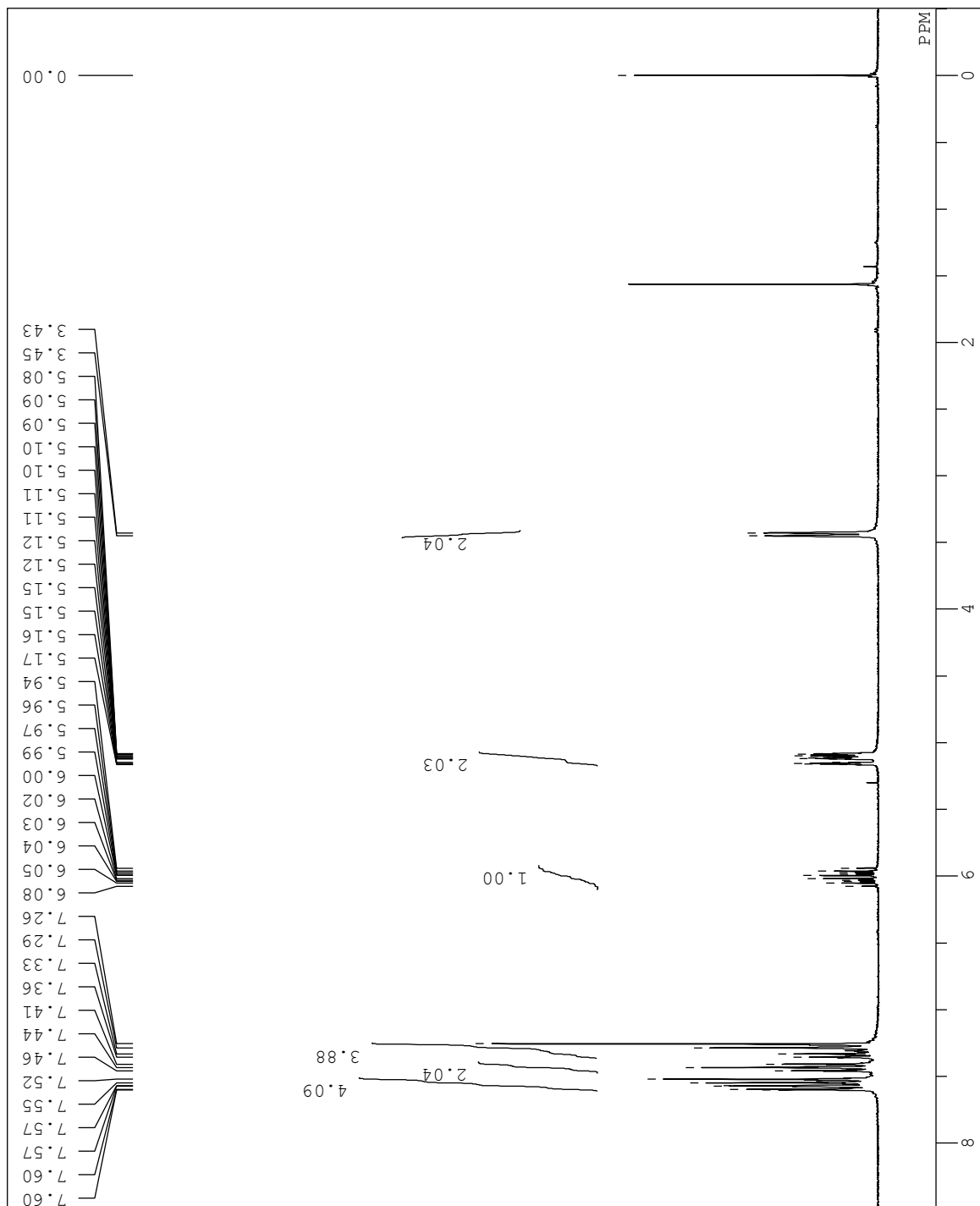
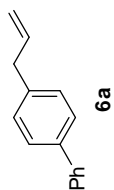


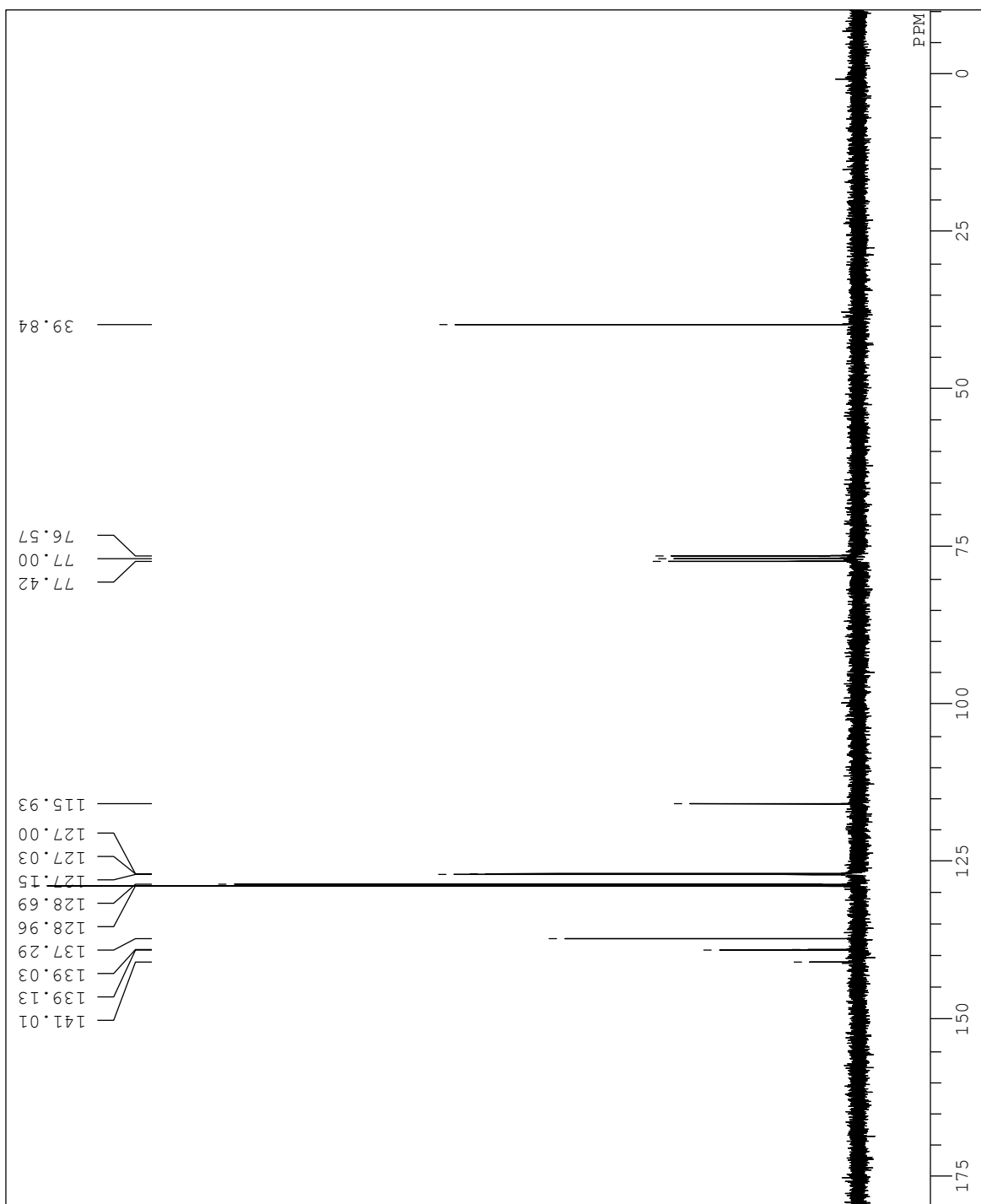
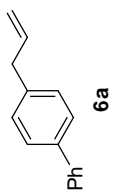
(Z)-2-Methyl-7-phenyl-1,4-heptadiene (6q): IR (neat) 3064, 3026, 2933, 1649, 1604, 1496, 1453, 1373, 888, 698; ^1H NMR 1.69 (s, 3H), 2.33–2.42 (m, 2H), 2.63–2.73 (m, 4H), 4.68 (br s, 1H), 4.70 (br s, 1H), 5.44 (dtt, $J = 10.8, 7.2, 1.1$ Hz, 1H), 5.53 (dtt, $J = 10.8, 7.2, 1.1$ Hz, 1H), 7.15–7.32 (m, 5H); ^{13}C NMR 22.5, 29.1, 35.6, 35.9, 110.2, 125.8, 127.6, 128.3, 128.4, 130.2, 142.0, 144.7.

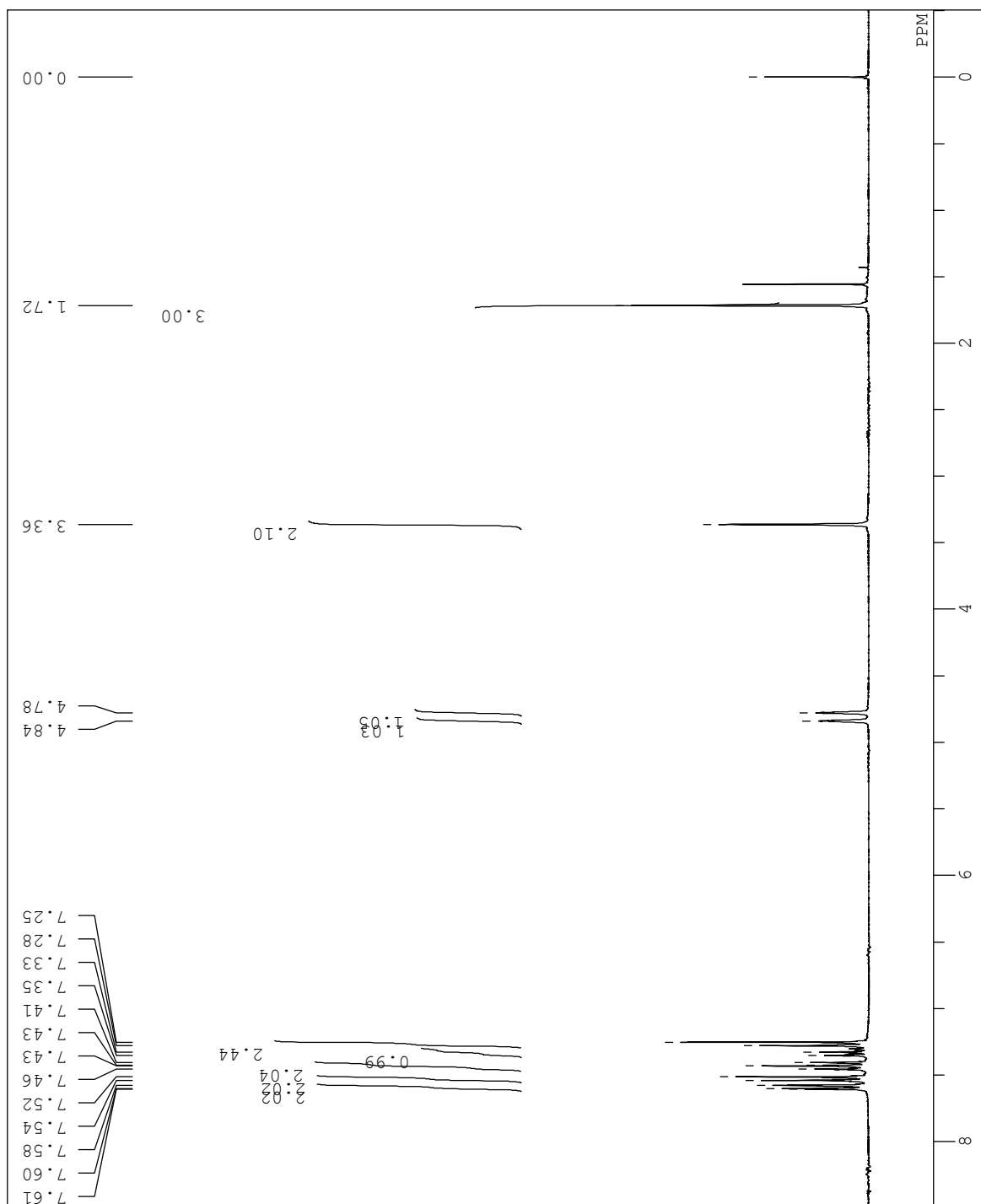
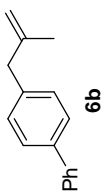
5. References

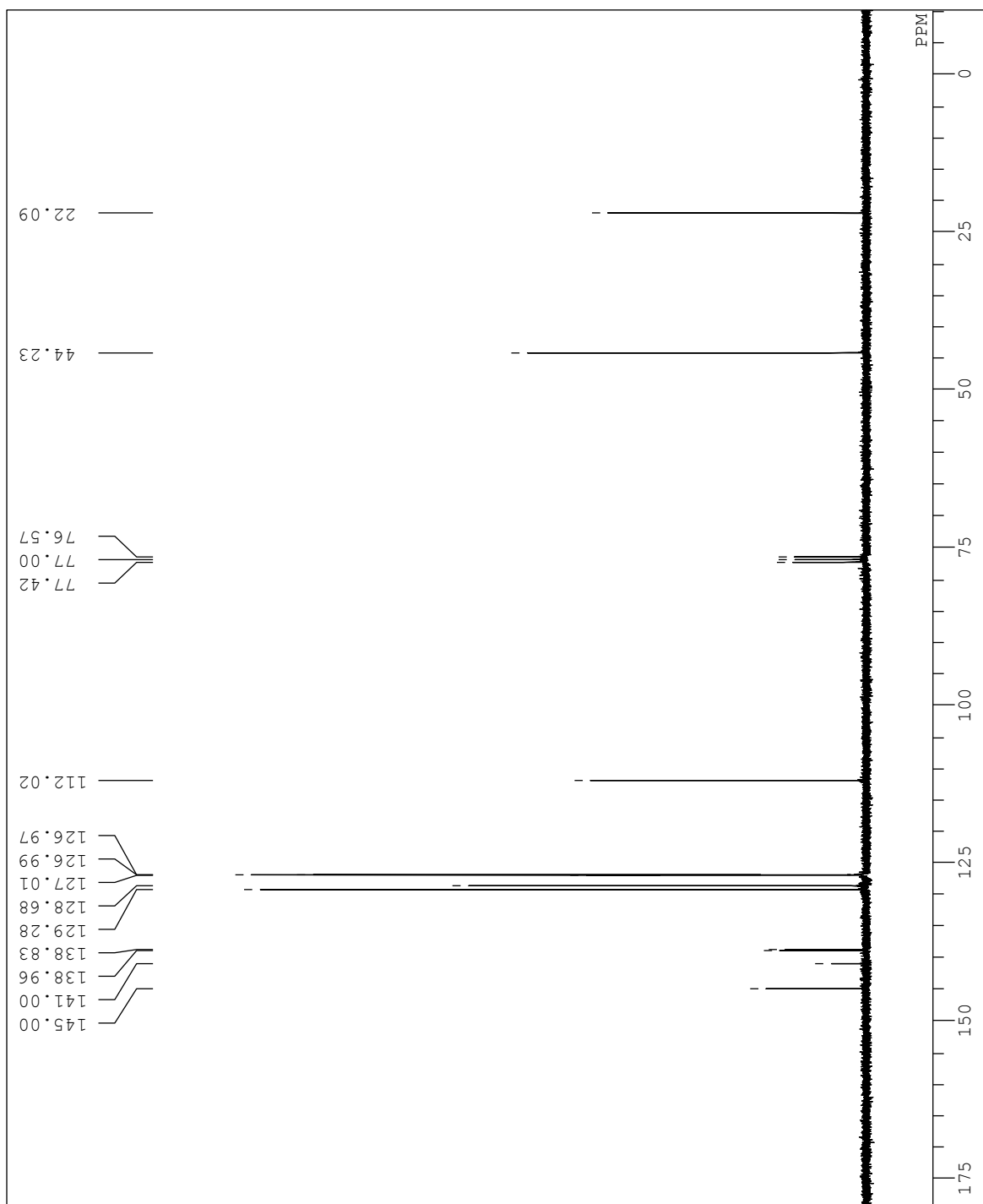
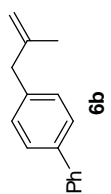
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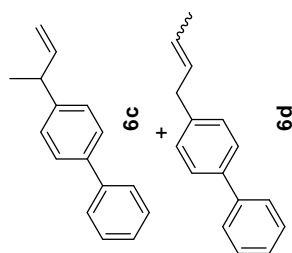
5. ^1H and ^{13}C NMR spectra for compounds 6



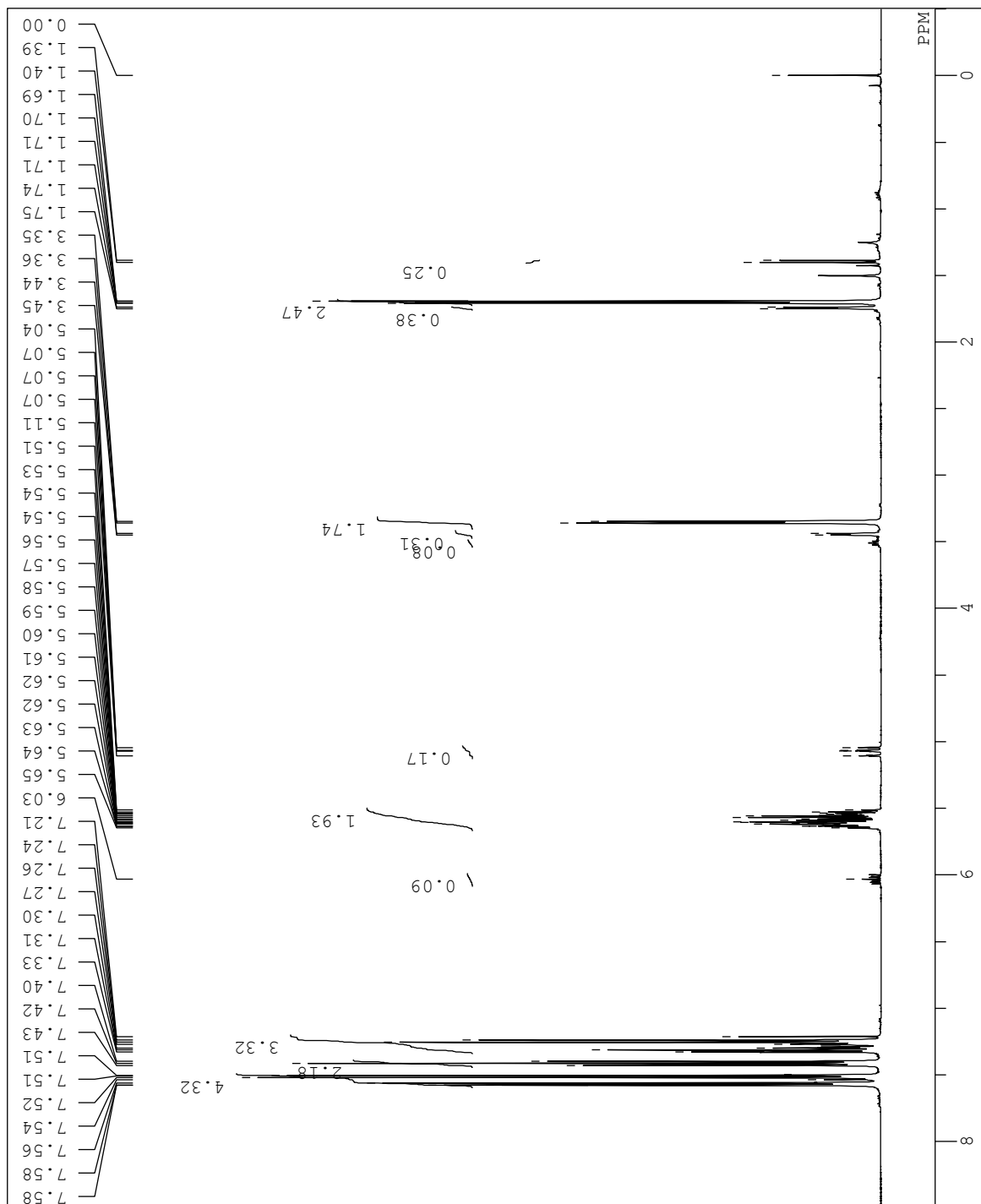


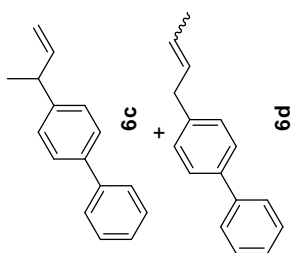




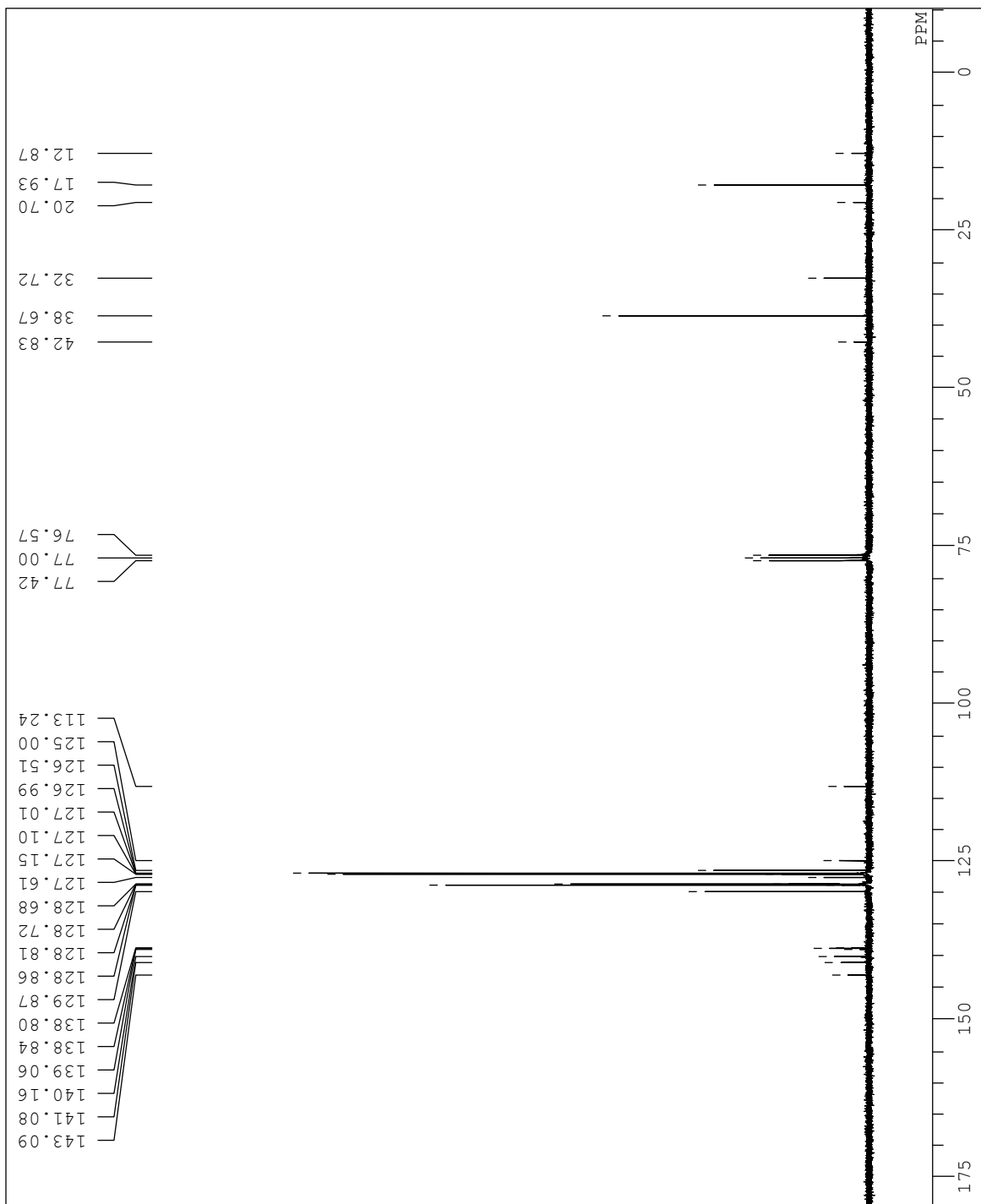


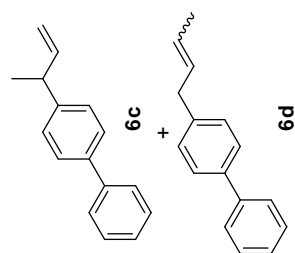
6c:6d = 8:92 (E:Z : 86:14)
 (Table 3, entry 3)



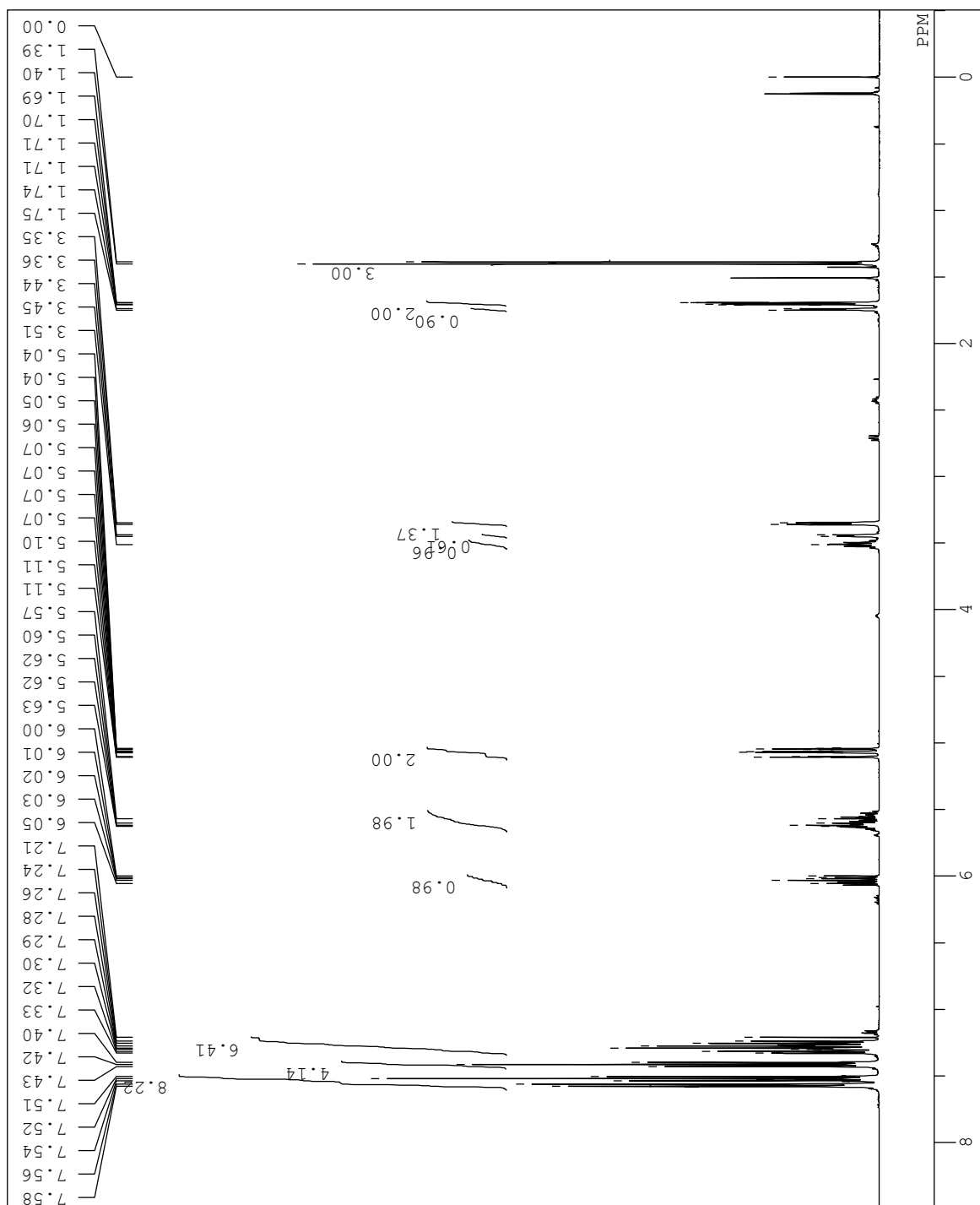


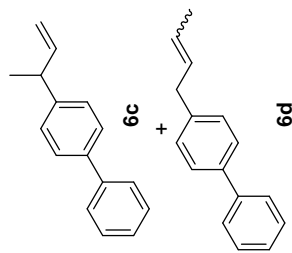
6c:6d = 8:92 (*E:Z* : 86:14)
 (Table 3, entry 3)





6c:6d = 51:49 (E:Z : 70:30)
 (Table 3, entry 4)





6c:6d = 51:49 (*E:Z*: 70:30)
 (Table 3, entry 4)

