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Electronic Supplementary Information

Benzylation of arenes with benzyl ethers promoted by *in situ* prepared superacid BF_3-H_2O

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1. General Methods

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 500/125 MHz spectrometer at 20-25 ^{o}C. ^{1}H NMR chemical shifts were reported in ppm using tetramethylsilane (TMS, δ (ppm) = 0.00 ppm) as the internal standard. The data of ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), coupling constant (*J* value) in Hz, integration and assignment. ^{13}C NMR spectra were reported in parts per million using solvent $CDCl_3$ (δ (ppm) = 77.2 ppm) as an internal standard. Column chromatography were performed using silica gel and analytical thin-layer chromatography (TLC) which was used to monitor the reactions was performed on silica gel plates. All the reagents used were of analytical grade, purchased locally and used without any purification unless otherwise specified.

Toluene distillation: toluene purchased from chemical supplier was firstly dried over 4 Å molecular sieve for one week, and then transferred to distillation apparatus under nitrogen protection. Na slice was added, and after reflux for half a day, dry toluene was collected for use.

2. Experimental Procedures

2.1 Typical procedure for the formation of benzyl ethers

To a solution of benzyl bromide (594.0 μL, 5.0 mmol) in anhydrous THF (10.0 mL) at 0 °C was added sodium hydride (240.0 mg, 10.0 mmol) in several portions, and *n*-octyl alcohol (863.0 μL, 5.5 mmol) were then added. After the suspension was stirred for 30 min at 0 °C, stirring continued at room temperature until completion of reaction. The reaction mixture was quenched by water (10 mL) and extracted with ethylether (10 mL × 3). The extracts were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give crude product, which was chromatographed on a silica gel column using petroleum ether solution as eluent to afford isolated product **1a** (716.3 mg, 65% yield).

The same procedure was utilized for all the synthesis of benzyl ethers **1a-q**.

2.2 Typical procedure for the benzylation of (hetero)arenes with benzyl ether using BF_3-OEt_2 under open-flask conditions.

To a 50 mL round flask filled with 2.0 mL undistilled toluene, benzyl ether **1a** (220.4 mg, 1.0 mmol) and BF_3-OEt_2 (151.0 μL, 1.2 mmol) was added successively. After reaction mixture was stirred in oil bath of 120 ^oC for 2 h in the atmosphere, the excessive toluene was removed by vacuum rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel column using petroleum ether as eluent to afford a colorless liquid product **3a** (180.5 mg, 99% yield).

The same procedure was utilized for all the benzylation reactions unless otherwise noted.

2.3 Typical procedure for the benzylation of naphthalene with benzyl ether using chloroform as solvent

To a 50 mL round flask, benzyl ether **1a** (220.4 mg, 1.0 mmol) and naphthalene (512.8 mg, 4.0 mmol) were dissolved in 2.0 mL of undistilled chloroform. Then BF_3-OEt_2 (151.0 μL, 1.2 mmol) was added. The resulting reaction mixture was transferred into an oil bath of 120 ^oC and stirred for 2 h in the atmosphere. After completion of the reaction, the solvent was removed by vacuum rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel column using petroleum ether as eluent to afford a white solid product **5h** (164.0 mg, 75% yield).

2.4 Typical procedure for the benzylation of toluene with benzyl ether using HBF_4-OEt_2 under an open-flask condition

To a 50 mL round flask filled with undistilled toluene (2.0 mL) was added benzyl ether **1a** (220.4 mg, 1.0 mmol) and HBF_4-OEt_2 (50-55% w/w HBF_4, 162.0 μL, 1.2 mmol) in the atmosphere. Then the reaction mixture was transferred into an oil bath of 120 ^oC and the stirring was turned on. After 2 h, the stirring stopped, reaction mixture cooled to room temperature, and the toluene was removed to get thick residue under reducing pressure. The resulting residue was purified by flash column chromatography on silica gel column using petroleum ether as eluent to afford a colorless oil product **3a** (171.0 mg, 94% yield).

2.5 Typical procedure for the benzylation of toluene with benzyl ether using BF_3-OEt_2 with addition water under N_2 atmosphere

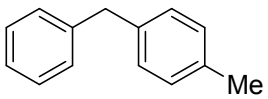
To a 50 mL three-necked bottle filled with anhydrous toluene (2.0 mL), benzyl ether **1a** (220.4 mg, 1.0 mmol), water (3.6 μL, 0.2 mmol) and BF_3-OEt_2 (151 μL, 1.2 mmol) were added successively under nitrogen atmosphere. Reaction mixture was stirred in oil bath of 120 ^oC for 2 h. After completion of the reaction, the toluene was removed by vacuum rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel column using petroleum ether as eluent to afford a colorless oil product **3a** (153.0 mg, 84% yield).

2.6 Typical procedure for the benzylation of toluene with benzyl ether using BF_3-$2H_2O$ under N_2 atmosphere

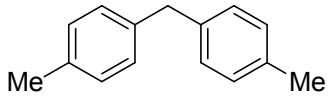
To a 50 mL three-necked bottle filled with anhydrous toluene (2.0 mL), benzyl ether **1a** (220.4 mg, 1.0 mmol) and BF_3-$2H_2O$ (76.2 μL, 1.2 mmol) were added successively under nitrogen atmosphere. Reaction mixture was stirred in oil bath of 120 ^oC for 2 h. After completion of the reaction, the toluene was removed by vacuum rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel column using petroleum ether as eluent to afford a colorless oil product **3a** (46.0 mg, 25% yield).

3. ^1H- and ^{13}C-NMR analytical data

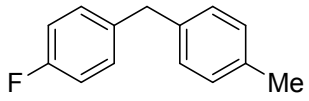
Only the structures of the major products are shown. The ratios of regioisomers were determined by ^{13}C NMR.



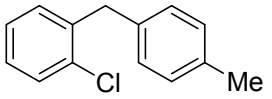
3.1 1-Benzyl-4-methylbenzene (**3a**, prepared from benzyl *i*-octyl ether), colorless oil, 165 mg, 91% yield, *p- : o- : m-* = 51 : 41 : 8. ^1H NMR: ($CDCl_3$, 500 MHz) δ (ppm) 7.25-7.21 (m, 3.21H, ArH), 7.15-7.04 (m, 10.82H, ArH), 6.98-6.95 (m, 0.52H, ArH), 3.94 (s, 1.28H, CH_2), 3.90 (s, 2H, CH_2) 2.28 (s, 2.98H, CH_3) 2.20 (s, 1.98H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 141.6 (*p*), 141.4 (*m*), 141.2 (*m*), 140.5 (*o*), 139.1 (*o*), 138.2 (*p*), 138.1 (*m*), 136.7 (*o*), 135.6 (*p*), 130.4 (*o*), 130.1 (*o*), 129.9 (*m*) 129.3 (*p*), 129.1 (*m*), 129.0 (*p*), 128.97 (*p*), 128.9 (*o*), 128.6 (*p*), 128.5 (*o*), 127.0 (*m*), 126.6 (*o*), 126.14 (*o*), 126.13 (*p*), 126.1 (*o*), 42.0 (*m*), 41.7 (*p*), 39.6 (*o*), 21.6 (*m*), 21.2 (*p*), 19.8 (*o*).



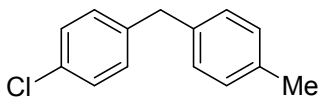
3.2 Di-*p*-tolylmethane (**3b**), colorless oil, 153 mg, 87% yield, *p- : o- : m-* = 64 : 32 : 4. ^{1}H NMR: ($CDCl_3$, 500 MHz) δ (ppm) 7.13-7.11 (m, 1.82H, ArH), 7.08-7.04 (m, 8.99H, ArH), 7.00-6.96 (m, 1.05H, ArH), 3.92 (s, 0.99H, CH_2), 3.88 (s, 2H, CH_2) 2.28 (s, 7.55H, CH_3) 2.22 (s, 1.40H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 139.3 (*o*), 138.5 (*p*), 137.4 (*o*), 136.7 (*o*), 135.6 (*p*), 135.5 (*o*), 130.4 (*o*), 130.0 (*o*), 129.8 (*m*), 129.3 (*p*), 129.2 (*o*), 128.9 (*p*), 128.8 (*o*), 128.5 (*m*), 126.9 (*m*), 126.5 (*o*), 126.1 (*o*), 41.6 (*m*), 41.2 (*p*), 39.2 (*o*), 21.6 (*m*), 21.2 (*p*), 19.8 (*o*).



3.3 1-Fluoro-4-(4-methylbenzyl)benzene (**3c**), colorless oil, 153 mg, 78% yield, *p- : o- : m-* = 53 : 40 : 7. ^{1}H NMR: ($CDCl_3$, 500 MHz) δ (ppm) 7.16-7.01 (m, 9.56H, ArH), 6.97-6.91 (m, 3.51H, ArH), 3.92 (s, 1.33H, CH_2), 3.88 (s, 2H, CH_2) 2.30 (s, 3.02H, CH_3) 2.21 (s, 1.94H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 162.5 (d, *J* = 8.9 Hz) (*p*), 160.5 (d, *J* = 8.8 Hz) (*o*), 141.0 (*m*), 138.9 (*o*), 138.3 (*m*), 138.1 (*p*), 137.2 (*p*), 136.7 (*o*), 136.1 (*o*), 135.9 (*p*), 130.6 (*o*), 130.4 (d, *J* = 7.6 Hz) (*p*), 130.2 (d, *J* = 7.6 Hz) (*o*), 130.0 (*o*), 129.8 (*m*), 129.4 (*p*), 128.9 (*p*), 128.6 (*m*), 127.1 (*m*), 126.8 (*o*), 126.2 (*o*), 126.0 (*m*), 115.4 (*o*), 115.2 (d, *J* = 2.6 Hz) (*p*), 41.2 (*m*), 40.8 (*p*), 38.8 (*o*), 21.6 (*m*), 21.2 (*p*), 19.8 (*o*).

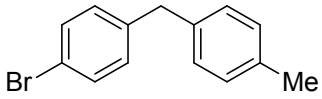


3.4 1-Chloro-2-(4-methylbenzyl)benzene (**3d**), colorless oil, 191 mg, 88% yield, *p- : o- : m-* = 49 : 37 : 14. ^{1}H NMR: ($CDCl_3$, 500 MHz) δ (ppm) 7.38-7.33 (m, 1.54H, ArH), 7.18-7.05 (m, 9.08H, ArH), 7.01-6.97 (m, 1.27H, ArH), 6.88-6.86 (m, 0.59H, ArH), 4.04 (s, 3.12H, CH_2), 2.30 (s, 3H, CH_3) 2.22 (s, 1.68H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 139.6 (m), 139.1 (p), 139.0 (m), 138.2 (o), 137.6 (o), 136.9 (o), 136.6 (*p*), 135.9 (*p*), 134.5 (*o*), 134.3 (*p*), 131.2 (*m*), 131.1 (*o*), 130.4 (*o*), 129.9 (*m*), 129.8 (*o*), 129.7 (*p*), 129.5 (*o*), 129.3 (*p*), 129.0 (*p*), 128.5 (*m*), 127.7 (*p*), 127.6 (*o*), 127.2 (*m*), 126.9 (*p*), 126.8 (*o*), 126.3 (*o*), 126.2 (*m*), 39.2 (*m*), 38.9 (*p*), 36.9 (*o*), 21.6 (*m*), 21.2 (*p*), 19.7 (*o*).

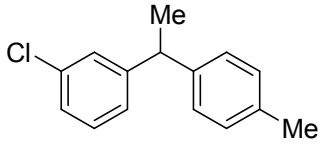


3.5 1-Chloro-4-(4-methylbenzyl)benzene (**3e**), colorless oil, 203 mg, 94% yield, *p- : o- : m-* = 49 : 41 : 10. ^{1}H NMR: ($CDCl_3$, 500 MHz) δ (ppm) 7.21-7.18 (m, 3.38H, ArH), 7.16-7.10 (m, 2.17H, ArH), 7.08-7.03 (m, 4.21H, ArH), 7.02-6.99 (m, 3.09H, ArH), 6.96-6.92 (m, 0.41H, ArH), 3.90 (s, 1.45H, CH_2), 3.85 (s, 2.00H, CH_2), 2.28 (s, 3.00H, CH_3), 2.18 (s, 2.04H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 140.6

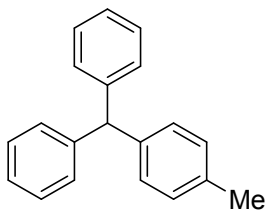
(*m*), 140.0 (*p*), 139.9 (*m*), 139.0 (*o*), 138.5 (*o*), 138.3 (*m*), 137.6 (*p*), 136.7 (*o*), 135.9 (*p*), 131.9 (*p*), 131.8 (*o*), 130.6 (*o*), 130.4 (*m*), 130.3(*p*), 130.2 (*o*), 130.0 (*o*), 129.8 (*m*), 129.4 (*p*), 128.9 (*o*), 128.7 (*p*), 128.6 (*p*), 127.2 (*m*), 126.8 (*o*), 126.3 (*o*), 126.1 (*m*), 41.3 (*m*), 41.0 (*p*), 39.0 (*o*), 21.5 (*m*), 21.2 (*o*), 19.8 (*p*).



3.6 1-Bromo-4-(4-methylbenzyl)benzene (**3f**), colorless oil, 254 mg, 97% yield, *p- : o- : m-* = 49 : 41 : 10. ^{1}H NMR: ($CDCl_3$, 500 MHz) δ (ppm) 7.37-7.35 (m, 3.49H, ArH), 7.18-7.11 (m, 2.39H, ArH), 7.09-7.07 (m, 2.38H, ArH), 7.03-7.02 (m, 4.04H, ArH), 6.97-6.93 (m, 1.72H, ArH), 3.90 (s, 1.66H, CH_2), 3.86 (s, 2.00H, CH_2), 2.30 (s, 3.28H, CH_3), 2.20 (s, 2.22H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 140.6 (*p*), 140.4 (*m*), 139.6 (*o*), 138.4 (*o*), 138.3 (*m*), 137.5 (*p*), 136.7 (*o*), 136.0 (*p*), 131.63 (*p*), 131.6 (*p*), 130.8 (*m*), 130.8 (*p*), 130.6 (*p*), 130.0 (*o*), 129.8 (*m*), 129.4 (*o*), 128.9 (*o*), 128.6 (*m*), 127.2 (*m*), 126.9 (*o*), 126.3 (*o*), 126.1 (*m*), 120.0 (*p*), 119.9 (*o*), 41.4 (*m*), 41.0 (*p*), 39.0 (*o*), 21.6 (*m*), 21.2 (*o*), 19.8 (*p*).

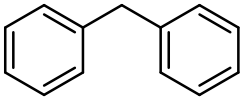


3.7 1-Chloro-3-(1-(p-tolyl)ethyl)benzene (**3g**), colorless oil, 227 mg, 98% yield, *p-* : *o-* : *m-* = 79 : 15 : 6. ^{1}H NMR: ($CDCl_3$, 500 MHz) δ (ppm) 7.24-7.19 (m, 1.39H, ArH), 7.18-7.11 (m, 3.07H, ArH), 7.10-7.06 (m, 4.63H, ArH), 7.01-6.98 (m, 0.39H, ArH), 4.27 (q, *J* = 7.0 Hz, 0.17H, CH), 4.06 (q, *J* = 7.5 Hz, 1.00H, CH), 2.30 (s, 3.09H, CH_2), 2.21 (s, 0.53H, CH_3), 1.58 (d, *J* = 7.0 Hz, 3.23H, CH_3), 1.57 (d, *J* = 6.5 Hz, 0.28H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 148.9 (*p*), 148.7 (*m*), 148.6 (*o*), 145.6 (*m*), 143.2 (*o*), 142.7 (*p*), 138.2 (*m*), 136.2 (*o*), 136.0 (*p*), 134.3 (*p*), 130.7 (*o*), 129.7 (*p*), 129.4 (*p*), 128.6 (*m*), 128.5 (*m*), 128.0 (*o*), 127.9(*p*), 127.6 (*p*), 127.3 (*m*), 126.8 (*o*), 126.5 (*o*), 126.3 (*p*), 126.2 (*o*), 126.1 (*o*), 126.0 (*p*), 124.7 (*m*), 44.7 (*m*), 44.3 (*p*), 41.0 (*o*), 22.1 (*o*), 21.9 (*p*), 21.7 (*m*), 21.1 (*p*), 19.9 (*o*).

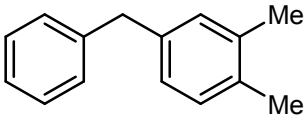


5.8 (P-tolylmethylene)dibenzene (**3h**), colorless oil, 246 mg, 96% yield, *p-* : *o-* : *m-* = 92 : 8 : 0. ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.25 (t, *J* = 7.0 Hz, 4H, ArH), 7.18 (t, *J* = 7.0 Hz, 2H, ArH), 7.11 (d, *J* = 7.0, 4H, ArH), 7.08 (d, *J* = 8.0, 2H, ArH), 7.00 (d, *J* = 7.0, 2H, ArH), 5.50 (s,

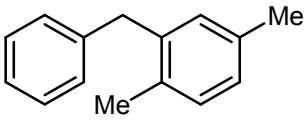
1H, CH), 2.30 (s, 3H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 144.3, 141.1, 136.0, 129.6, 129.5, 129.2, 128.4, 126.4, 56.6, 21.2.



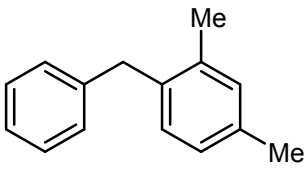
3.9 Diphenylmethane (**5a**), colorless oil, 107 mg, 94% yield. ^1H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.25 (t, *J* = 7.0 Hz, 4H, ArH), 7.18 (t, *J* = 6.5 Hz, 2H, ArH), 7.16 (d, *J* = 8.0 Hz, 4H, ArH), 3.95 (s, 2H, CH_2). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 141.3, 129.1, 128.6, 126.2, 42.1.



3.10 4-Benzyl-1,2-dimethylbenzene (**5b**), colorless oil, 187 mg, 95% yield, (*4-* : *3-* = 66 : 34). ^1H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.24-7.21 (m, 3.01H, ArH), 7.20-7.13 (m, 3.46H, ArH), 7.09 (d, *J* = 8.0 Hz, 1.08H, ArH), 7.05-7.01 (m, 2.06H, ArH), 6.97 (d, *J* = 5.5 Hz, 0.42H, ArH), 6.95 (s, 1.07H, ArH), 6.90 (d, *J* = 8.0 Hz, 1.02H, ArH), 3.99 (s, 0.95H, CH_2), 3.88 (s, 2.00H, CH_2), 2.25 (s, 1.44H, CH_3), 2.19 (s, 6.16H, CH_3) , 2.10 (s, 1.44H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 141.7 (*4-*), 140.9 (*3-*), 138.8 (*3-*), 138.7 (*4-*), 137.1 (*3-*), 136.7 (*4-*), 135.3 (*3-*), 134.3 (*4-*), 130.4 (*3-*), 129.9 (*3-*), 129.0 (*4-*), 128.8 (*4-*), 128.6 (*4-*), 128.5 (*4-*), 128.4 (*3-*), 128.3 (*3-*), 126.5 (*4-*), 126.1 (*4-*), 126.0 (*3-*), 125.6 (*3-*), 41.7 (*4-*), 40.2 (*3-*), 20.8 (*3-*), 19.9 (*4-*), 19.5 (*4-*), 15.5 (*3-*).

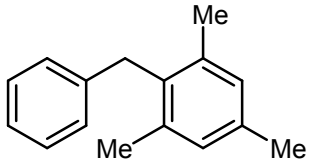


3.11 2-Benzyl-1,4-dimethylbenzene (**5c**), colorless oil, 172 mg, 88% yield. ^1H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.24 (t, *J* = 7.5 Hz, 2H, ArH), 7.16 (t, *J* = 7.0 Hz, 1H, ArH), 7.10 (d, *J* = 7.5 Hz, 2H, ArH), 7.03 (d, *J* = 8.0 Hz, 1H, ArH), 6.95 (d, *J* = 7.5 Hz, 1H, ArH), 6.92 (s, 1H, ArH), 3.93 (s, 2H, CH_2), 2.27 (s, 3H, CH_3), 2.18 (s, 3H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 140.7, 138.8, 135.5, 133.6, 130.9, 130.4, 128.9, 128.5, 127.3, 126.0, 39.6, 21.1, 19.4.

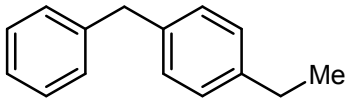


3.12 1-Benzyl-2,4-dimethylbenzene (**5d**), colorless oil, 180 mg, 92% yield, (*4-* : *5-* = 80∶20). ^1H NMR: ($CDCl_3$, 500 MHz) δ (ppm) 7.25-7.18 (m, 2.56H, ArH), 7.17-7.13 (m, 1.29H, ArH), 7.10 (d, *J* = 7.5 Hz, 2.00H, ArH), 7.08-7.03 (m, 0.71H, ArH), 7.00-6.93 (m, 3.42H, ArH), 4.04 (s, 0.53H, CH_2), 3.93 (s, 2.00H, CH_2), 2.29 (s, 3H, CH_3), 2.23 (s, 1.52H, CH_3), 2.18 (s, 3H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 140.9 (*4-*), 139.9 (*5-*), 137.3 (*5-*), 137.0 (*5-*), 136.6 (*4-*), 136.0 (*4-*), 131.3

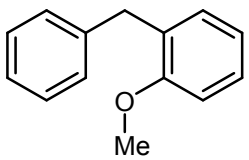
(*4*-), 130.1 (*4*-), 128.8 (*4*-), 128.5 (*4*-), 128.3 (*5*-), 128.0 (*5*-), 126.8 (*4*-), 126.5 (*5*-), 126.0 (*4*-), 125.9 (*5*-), 39.2 (*4*-), 35.2 (*5*-), 21.1 (*4*-), 20.4 (*5*-), 19.8 (*4*-).



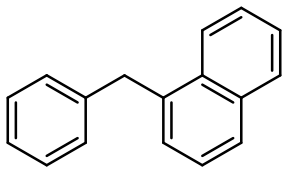
3.13 2-Benzyl-1,3,5-trimethylbenzene (**5e**), colorless oil, 189 mg, 89% yield. ^{1}H NMR: ($CDCl_3$, 500 MHz) δ (ppm) 7.21 (t, *J* = 7.5 Hz, 2H, ArH), 7.13 (t, *J* = 7.5 Hz, 1H, ArH), 7.00 (d, *J* = 7.5 Hz, 2H, ArH), 6.88 (s, 2H, ArH), 4.01 (s, 2H, ArH), 2.28 (s, 3H, CH_3), 2.19 (s, 6H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 140.3, 137.2, 135.8, 134.0, 129.1, 128.5, 128.0, 125.8, 34.9, 21.1, 20.3.



3.14 1-Benzyl-3-ethylbenzene (**5f**), colorless oil, 159 mg, 81% yield, *p*- : *o*- : *m*- = 55 : 35 : 10. ^{1}H NMR: ($CDCl_3$, 500 MHz) δ (ppm) 7.26-7.22 (m, 3.02H, ArH), 7.18-7.13 (m, 4.58H, ArH), 7.12-7.09 (m, 5.14H, ArH), 7.02-6.97 (m, 0.61H, ArH), 4.00 (s, 1.02H, CH_2), 3.92 (s, 2.00H, CH_2), 2.59 (q, *J* = 7.5 Hz, 2.98H, $C\underline{H_2}CH_3$), 1.20 (t, *J* = 7.5 Hz, 2.97H, CH_3), 1.12 (t, *J* = 7.5 Hz, 1.52H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 144.5 (*m*), 142.6 (*o*), 142.1 (*p*), 141.5 (*p*), 141.4 (*m*), 141.2 (*m*), 141.1 (*o*), 138.5 (*p*), 138.3 (*o*), 130.5 (*o*), 129.1 (*p*), 129.0 (*p*), 128.9 (*o*), 128.7 (*m*), 128.6 (*p*), 128.5 (*o*), 128.1 (*p*), 126.8 (*o*), 126.4 (*m*), 126.1 (*p*), 126.05 (*o*), 125.7 *m*), 42.1 (*m*), 41.7 (*p*), 38.9 (*o*), 29.0 (*m*), 28.6 (*p*), 25.9 (*o*), 15.8 (*p*), 15.0 (*o*).

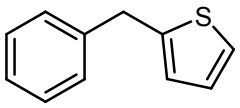


3.15 1-Benzyl-2-methoxybenzene (**5g**), colorless oil, 69 mg, 35% yield, *o*- > 99%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.24 (t, *J* = 7.0 Hz, 2H, ArH), 7.19 (d, *J* = 7.5 Hz, 2H, ArH), 7.17-7.13 (m, 2H, ArH) 7.04 (d, *J* = 7.5 Hz, 1H, ArH), 6.87-6.82 (m, 2H, ArH), 3.96 (s, 2H, CH_2), 3.76 (s, 3H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 157.5, 141.2, 130.5, 129.8, 129.1, 128.4, 127.6, 125.9, 120.6, 110.5, 55.4, 36.0.

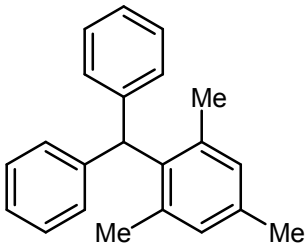


3.16 1-Benzylnaphthalene (**5h**), colorless oil, 164 mg, 75% yield, *1*- : *2*- = 74 : 26. ^{1}HNMR: ($CDCl_3$, 500MHz) δ (ppm) 7.97-7.96 (m, 0.98H, ArH), 7.83-7.82 (m, 1.01H, ArH), 7.75-7.72 (m, 1.98H, ArH), 7.60 (s, 0.36H, ArH), 7.42-7.37 (m, 3.63H, ArH), 7.29-7.20 (m, 4.62H, ArH), 7.17-7.13 (m, 3.29H, ArH), 4.41 (s, 2.00H, CH_2), 4.10 (s, 0.72H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 141.1 (*2*-), 140.8 (*1*-), 138.8 (*2*-), 136.8 (*1*-), 134.1 (*1*-), 133.8 (*2*-), 132.3 (*1*-), 129.2 (*2*-), 128.9 (*1*-), 128.8 (*1*-), 128.7 (*2*-), 128.6 (*1*-), 128.2 (*2*-), 127.8 (*2*-), 127.7 (*2*-), 127.5 (*1*-), 127.3

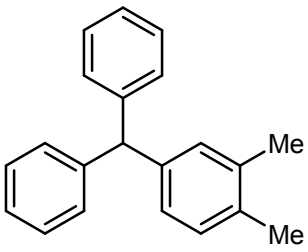
(*1*-), 127.26 (*2*-), 126.3 (*2*-), 126.2 (*1*-), 126.1 (*1*-), 125.7 (*1*-), 125.5 (*2*-), 124.4 (*1*-), 42.3 (*2*-), 39.2 (*1*-).



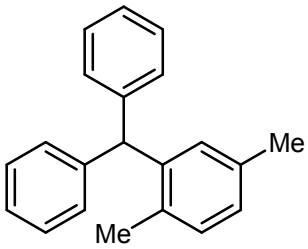
3.17 2-Benzylthiophene (**5i**), colorless oil, 87 mg, 50% yield, *2*- : *3*- = 52 : 48. ^{1}HNMR: ($CDCl_3$, 500MHz) δ (ppm) 7.30-7.27 (m, 4.23H, ArH), 7.25-7.19 (m, 7.31H, ArH), 7.13 (d, *J* = 5.0 Hz, 1H, ArH), 6.92-6.90 (m, 3.06H, ArH), 6.792-6.786 (m, 1.00H, ArH), 4.15 (s, 2.10H, CH_2), 3.97 (s, 2.14H, CH_2). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 144.2 (*2*-), 141.6 (*3*-), 140.8 (*3*-), 140.6 (*2*-), 128.9 (*3*-), 128.8 (*2*-), 128.7 (*2*-), 128.6 (*3*-), 127.0 (*2*-), 126.6 (*2*-), 126.3 (*3*-), 125.8 (*3*-), 125.3 (*2*-), 124.1 (*2*-), 121.4 (*3*-), 36.7 (*3*-), 36.2 (*2*-).



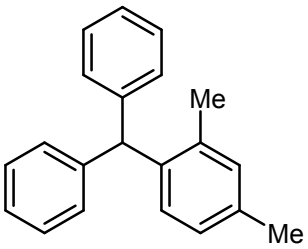
3.18 (Mesitylmethylene)dibenzene (**5j**), colorless oil, 279 mg, 97% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.25 (t, *J* = 7.5 Hz, 4H, ArH), 7.18 (t, *J* = 7.0 Hz, 2H, ArH), 7.09 (d, *J* = 7.0 Hz, 4H, ArH), 6.85 (s, 2H, ArH), 5.99 (s, 1H, ArH), 2.27 (s, 3H, CH_3), 1.99 (s, 6H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 142.7, 137.8, 137.3, 136.2, 130.3, 129.5, 128.3, 126.1, 51.2, 22.2, 21.0.



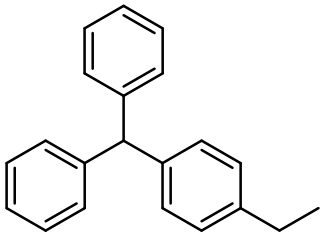
3.19 ((3,4-Dimethylphenyl)methylene)dibenzene (**5k**). Colorless oil, yield: 250 mg (92%), (*4*->99%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.26 (t, *J* = 7.5 Hz, 4H, ArH), 7.18 (t, *J* =7.0 Hz, 2H, ArH), 7.11 (d, *J* = 7.5 Hz, 4H, ArH), 7.03 (d, *J* = 7.5 Hz, 1H, ArH), 6.91 (1H, s, ArH), 6.82 (d, *J* = 7.5 Hz, 1H, ArH), 5.48 (1H, s, CH), 2.21 (3H, s, CH_3), 2.18 (3H, s, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 144.2, 141.3, 136.4, 134.4, 130.7, 129.5, 129.4, 128.2, 126.8, 126.1, 56.5, 19.8, 19.3.



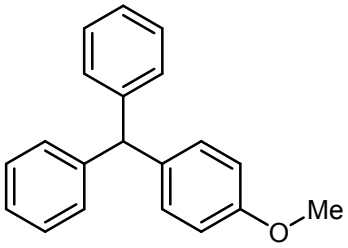
3.20 ((2,5-Dimethylphenyl)methylene)dibenzene (**5l**), colorless oil, 169 mg, 62% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.27 (t, *J* = 7.5 Hz, 4H, ArH), 7.20 (t, *J* = 7.5 Hz, 2H, ArH), 7.06-7.04 (m, 5H, ArH), 6.95 (d, *J* = 7.5 Hz, 1H, ArH), 6.62 (s, 1H, ArH), 5.64 (s, 1H, CH), 2.20 (s, 3H, CH_3), 2.16 (s, 3H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 143.7, 142.3, 135.2, 133.6, 130.5, 130.3, 129.8, 128.4, 127.2, 126.4, 53.7, 21.4, 19.7.



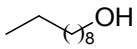
3.21 ((2,4-Dimethylphenyl)methylene)dibenzene (**5m**), colorless oil, 187 mg, 69% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.25 (t, *J* = 7.0 Hz, 4H, ArH), 7.18 (t, *J* = 7.0 Hz, 2H, ArH), 7.05 (d, *J* = 7.0 Hz, 4H, ArH), 6.98 (s, 1H, ArH) 6.89 (d, *J* = 7.5 Hz, 1H, ArH), 6.69 (d, *J* = 7.5 Hz, 1H, ArH), 5.63 (s, 1H, CH), 2.28 (s, 3H, CH_3), 2.17 (s, 3H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 143.8, 139.6, 136.6, 136.0, 131.4, 129.8, 129.6, 128.4, 126.6, 126.3, 53.4, 21.1, 20.0.



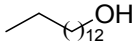
3.22 ((4-Ethylphenyl)methylene)dibenzene (**5n**), colorless oil, 234 mg, 86% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.25 (t, *J* = 7.5 Hz, 4H, ArH), 7.18 (t, *J* = 7.5 Hz, 2H, ArH), 7.12-7.09 (m, 6H, ArH), 7.02 (d, *J* = 8.0 Hz, 2H, ArH), 5.51 (s, 1H, CH), 2.60 (q, *J* = 7.5 Hz, 2H, CH_2), 1.21 (t, *J* = 7.5 Hz, 3H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 144.3, 142.3, 141.3, 129.6, 129.5, 128.4, 127.9, 126.4, 56.7, 28.6, 15.7.



3.23 ((4-Methoxyphenyl)methylene)dibenzene (**5o**), colorless oil, 266 mg, 97% yield, *p*->99%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.26 (t, *J* = 7.5 Hz, 4H, ArH), 7.18 (t, *J* = 7.0 Hz, 2H, ArH), 7.10 (d, *J* = 7.5 Hz, 4H, ArH), 7.02 (d, *J* = 8.5 Hz, 2H, ArH), 6.81 (d, *J* = 8.0 Hz, 2H, ArH), 5.49 (s, 1H, CH), 3.75 (s, 3H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 158.2, 144.4, 136.3, 130.5, 129.5, 128.4, 126.4, 113.8, 56.2, 55.4.

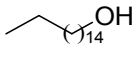


3.24 Decan-1-ol (**4j**), colorless oil, 120 mg, 76% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 3.62 (t, 2H, *J* = 7.0 Hz, C$\underline{H}_2$OH), 2.17 (s, 1H, OH), 1.56 (quin, *J* = 7.0 Hz, 2H, C$\underline{H}_2$CH$_2$OH), 1.31-1.27 (m, 14H, CH$_3$(C$\underline{H}_2$)$_7$CH$_2$CH$_2$OH), 0.88 (t, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 63.0, 32.9, 32.0, 29.8, 29.7, 29.6, 29.5, 25.9, 22.8, 14.2.



3.25 Tetradecan-1-ol (**4k**), white solid, 206 mg, 96% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 3.63 (t, *J* = 6.5 Hz, 2H, C$\underline{H}_2$OH), 1.93 (s, 1H, OH), 1.55 (quin, *J* = 7.0 Hz, 2H, C$\underline{H}_2$CH$_2$OH), 1.34-1.26 (m, 22H, CH$_3$(C$\underline{H}_2$)$_{11}$CH$_2$CH$_2$OH), 0.88 (t, *J* = 6.5 Hz, 3H,

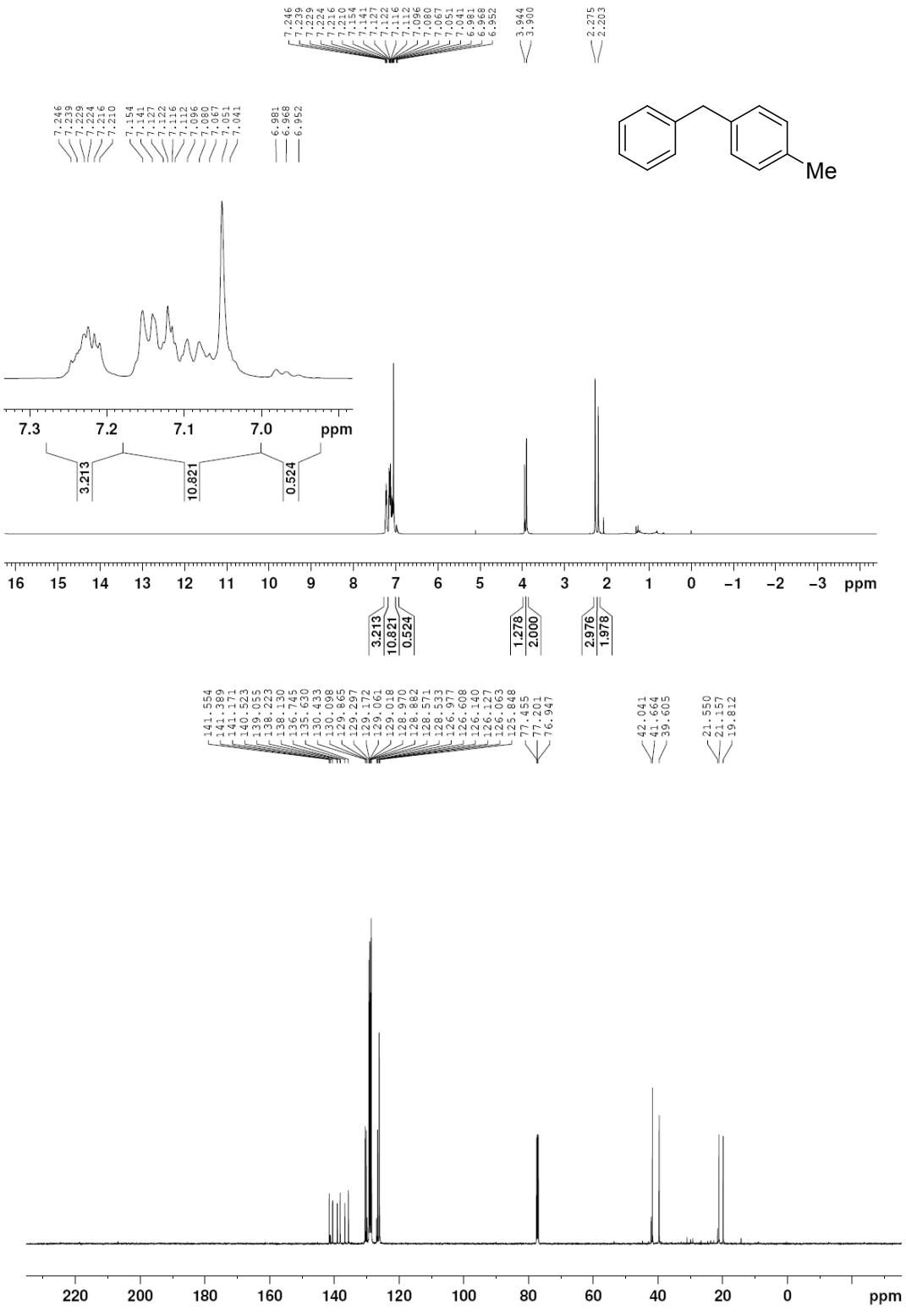
CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 63.2, 32.9, 32.1, 29.8, 29.79, 29.6, 29.5, 25.9, 22.9, 14.3.



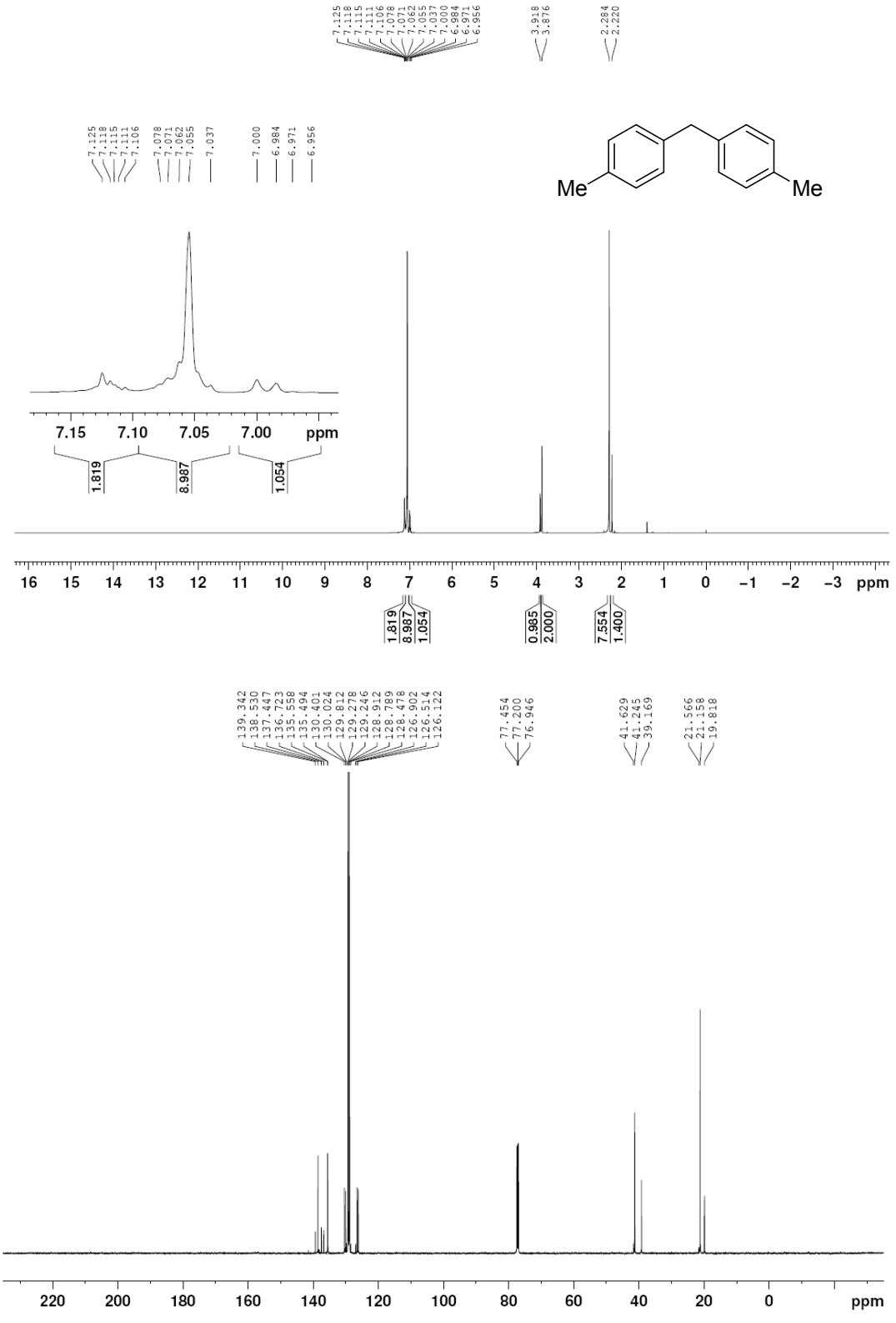
3.26 Hexadecan-1-ol (**4l**), white solid, 233 mg, 76% yield. ^1H NMR ($CDCl_3$, 500 MHz) δ (ppm) 3.63 (t, 2H, J = 6.5 Hz, C<u>H</u>$_2$OH), 1.56 (m, quin, J = 7.0 Hz, 2H, C<u>H</u>$_2$CH$_2$OH), 1.34-1.26 (m, 26H, CH_3(C<u>H</u>$_2$)$_{13}$CH$_2$CH$_2$OH), 0.88 (t, J = 7.0 Hz, 3H, CH_3). ^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 63.2, 33.0, 32.1, 29.9, 29.8, 29.6, 29.5, 25.9, 22.9, 14.3.

4. ^{1}H- and ^{13}C-NMR spectra

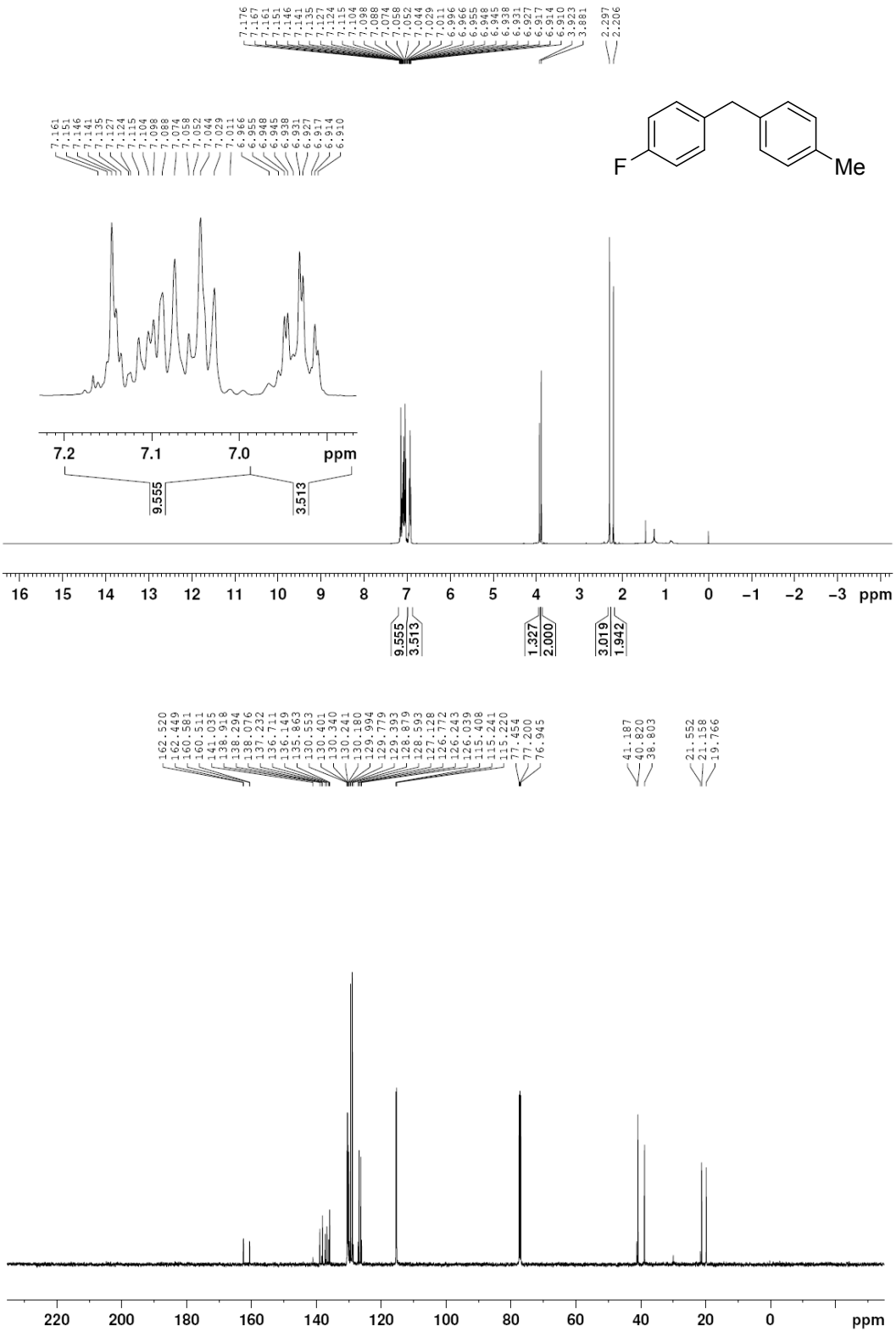
1-Benzyl-4-methylbenzene (**3a**)



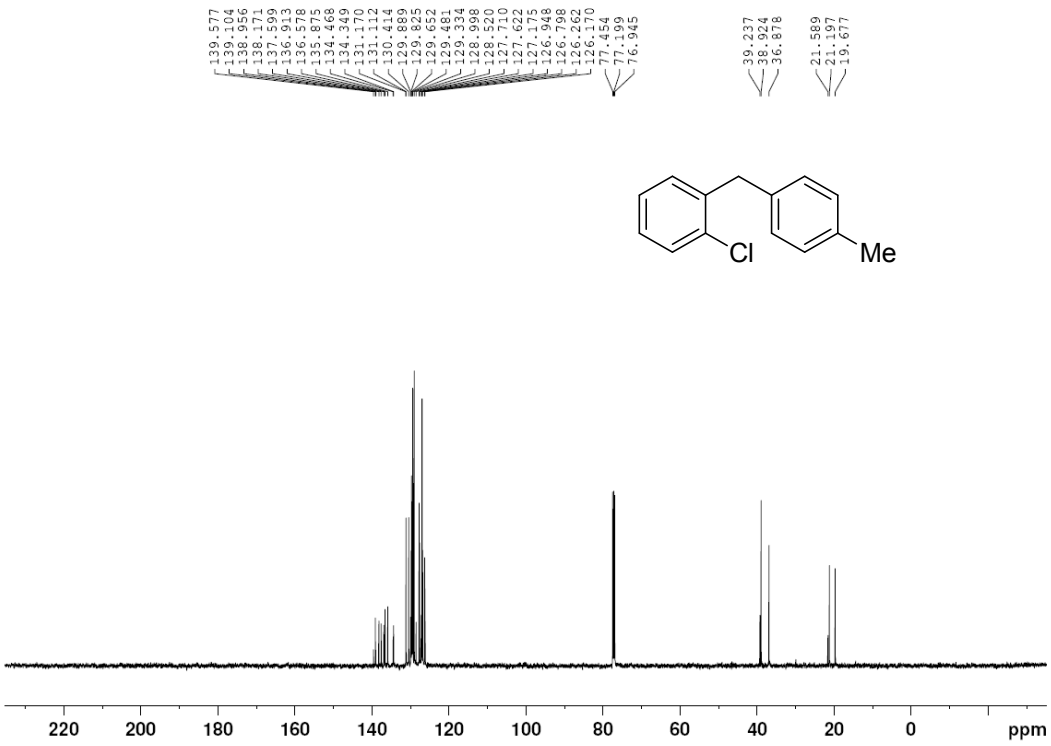
Di-*p*-tolylmethane (**3b**)

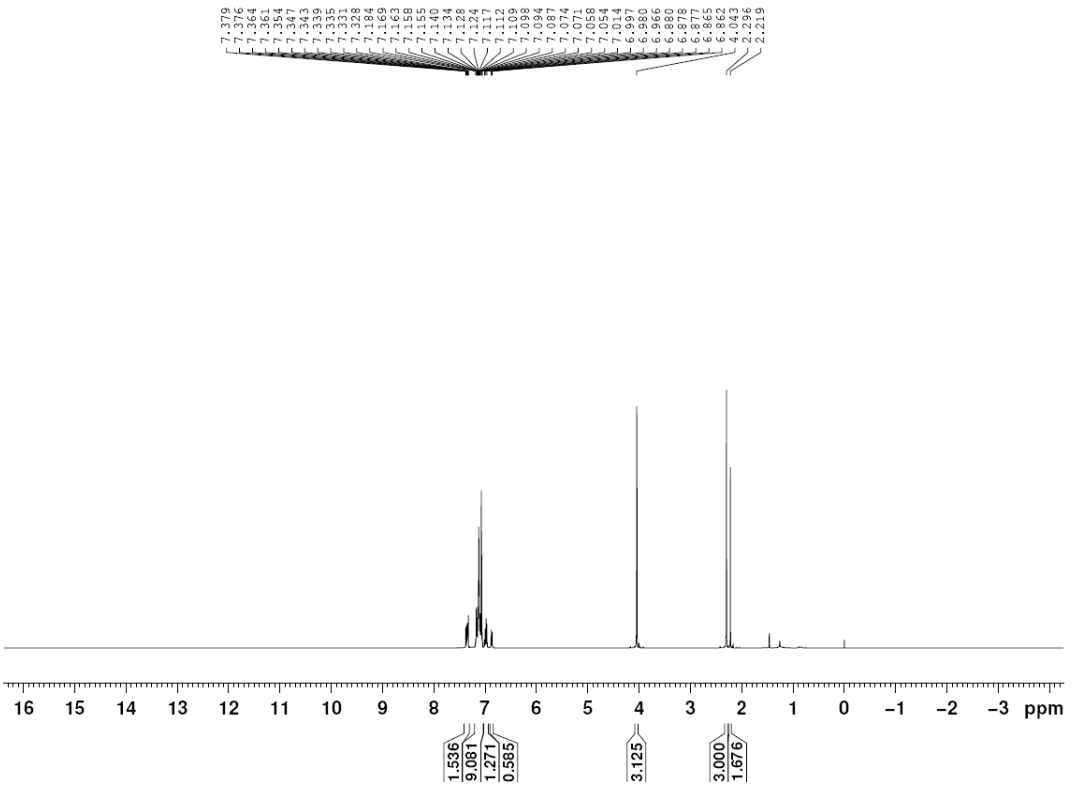


1-Fluoro-4-(4-methylbenzyl)benzene (**3c**)

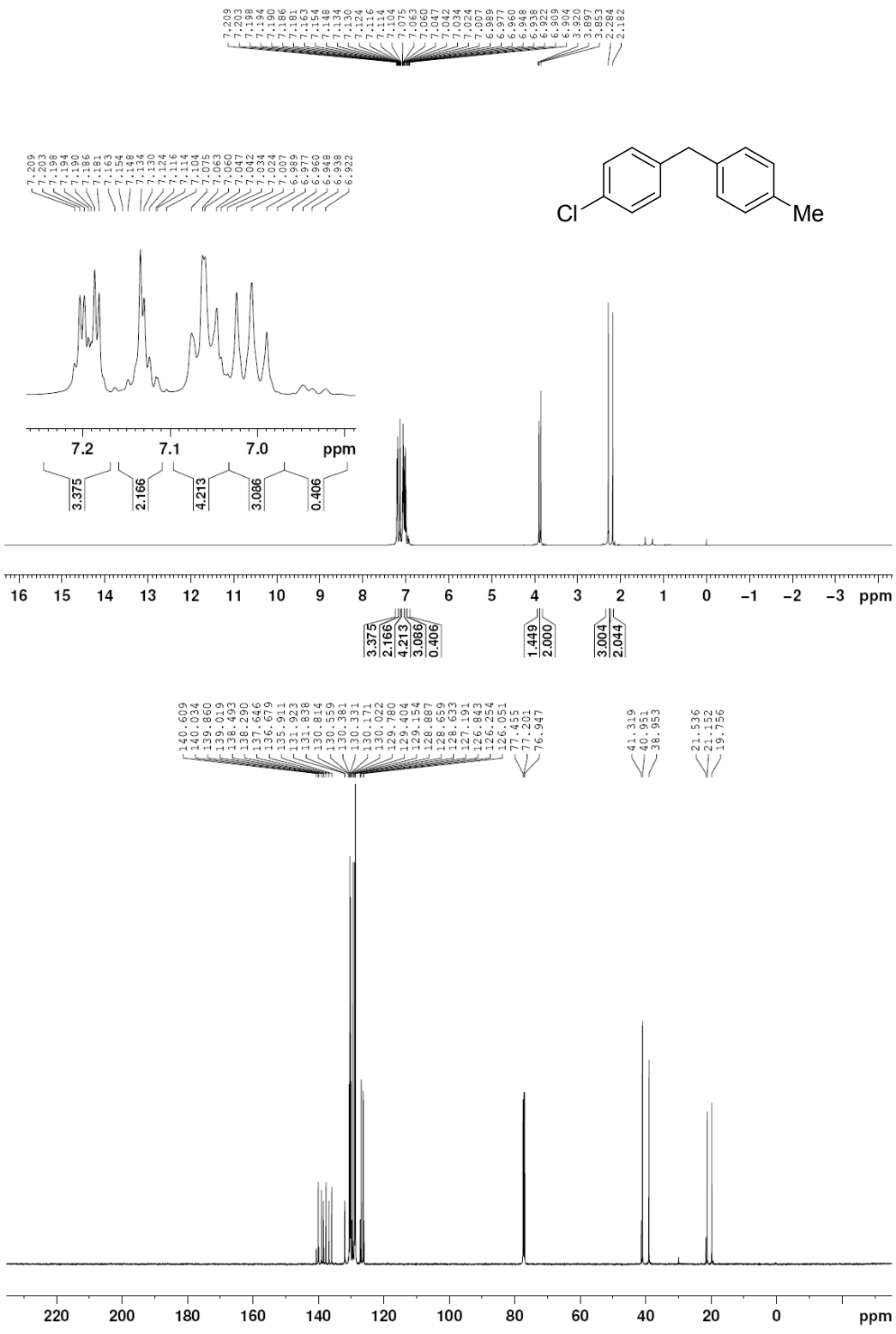


1-Chloro-2-(4-methylbenzyl)benzene (**3d**)

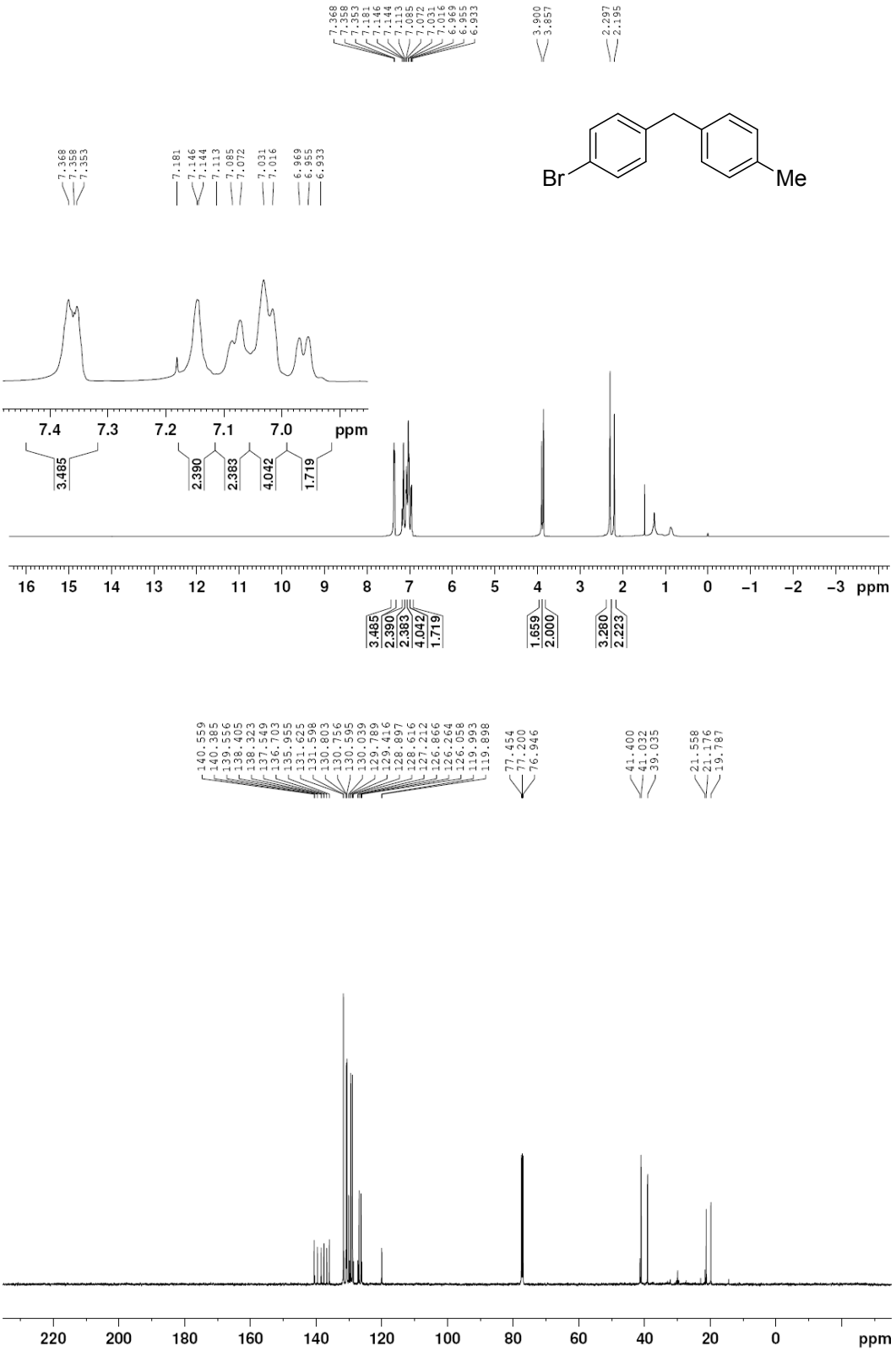




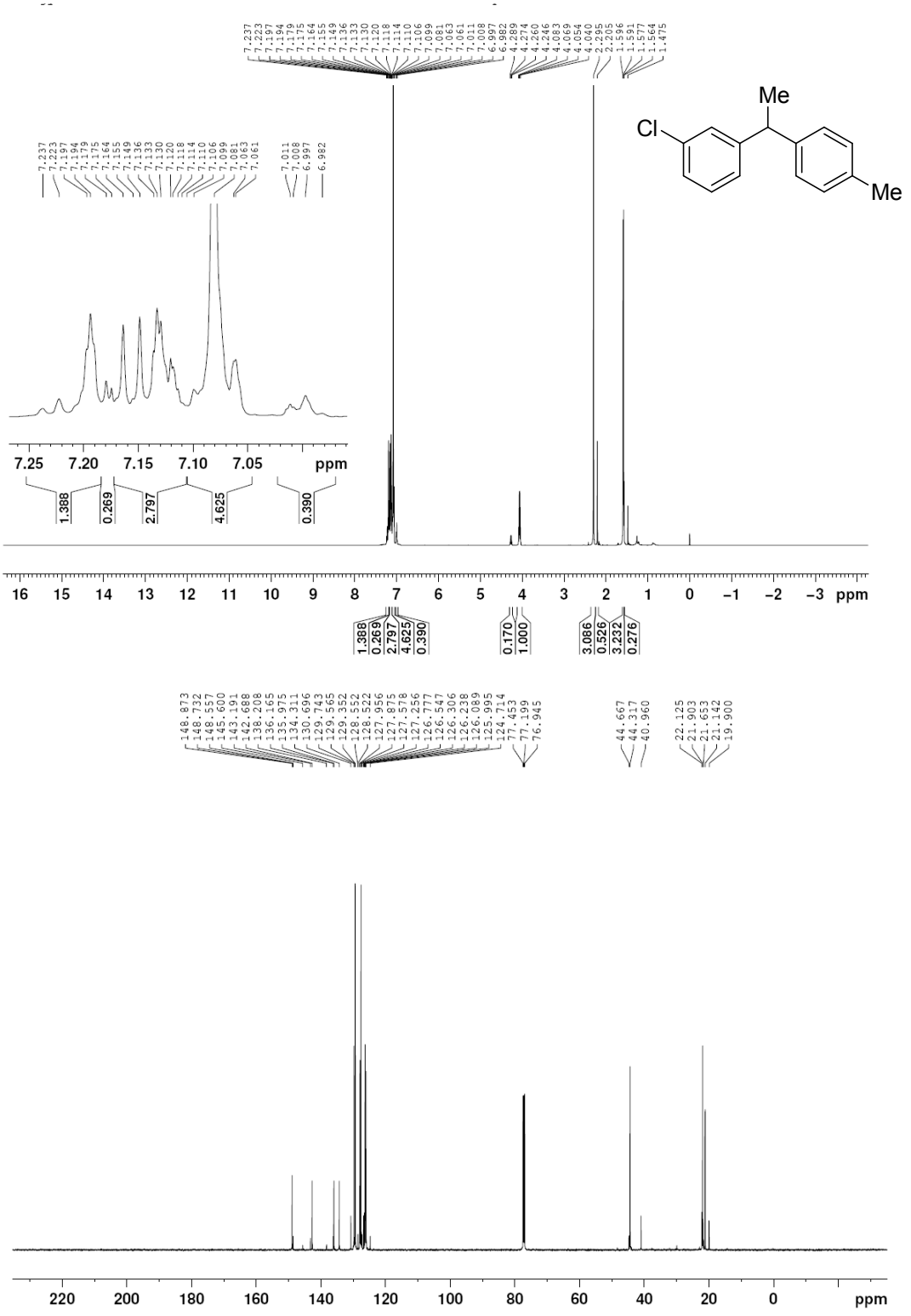
1-Chloro-4-(4-methylbenzyl)benzene (**3e**)



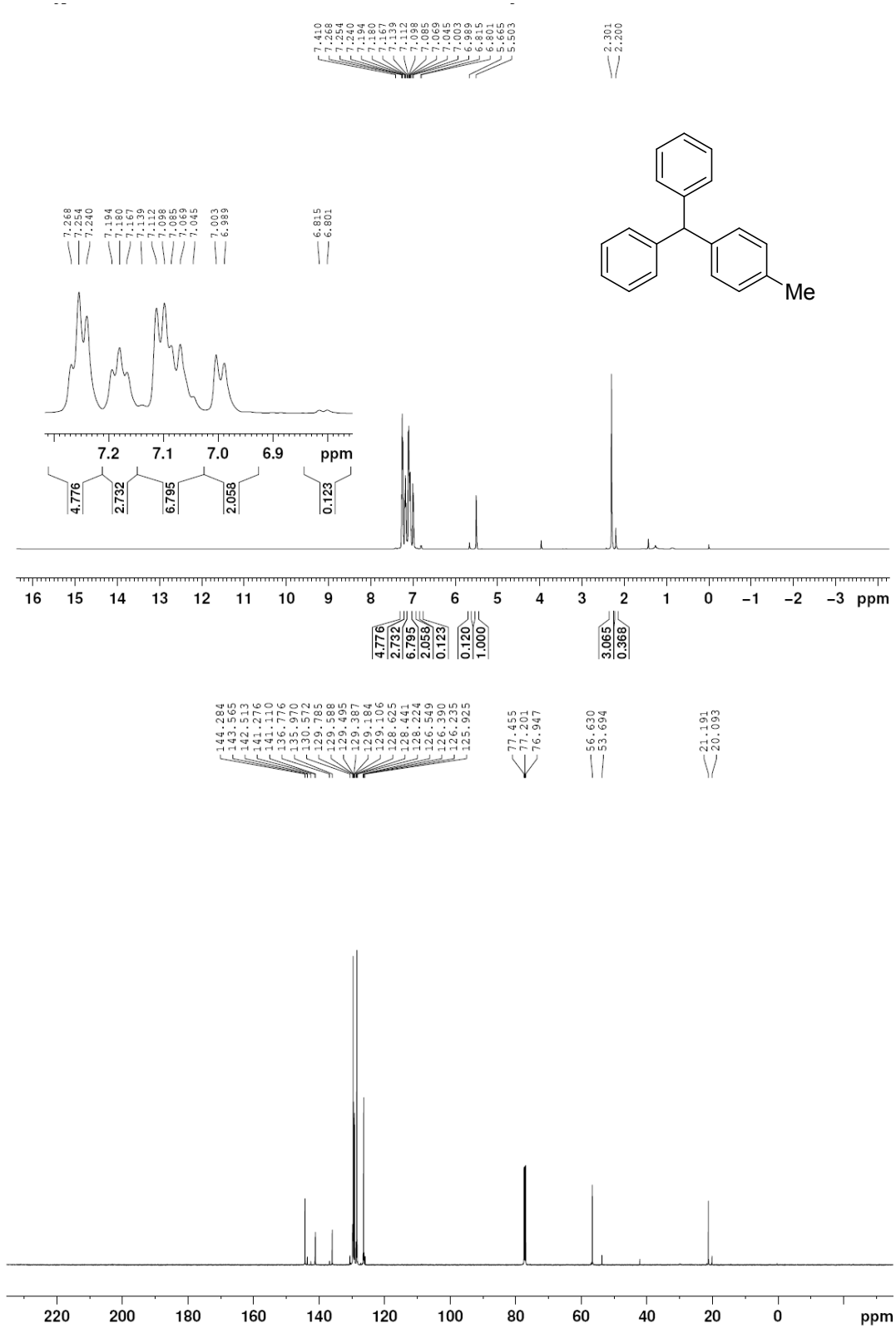
1-Bromo-4-(4-methylbenzyl)benzene (**3f**)



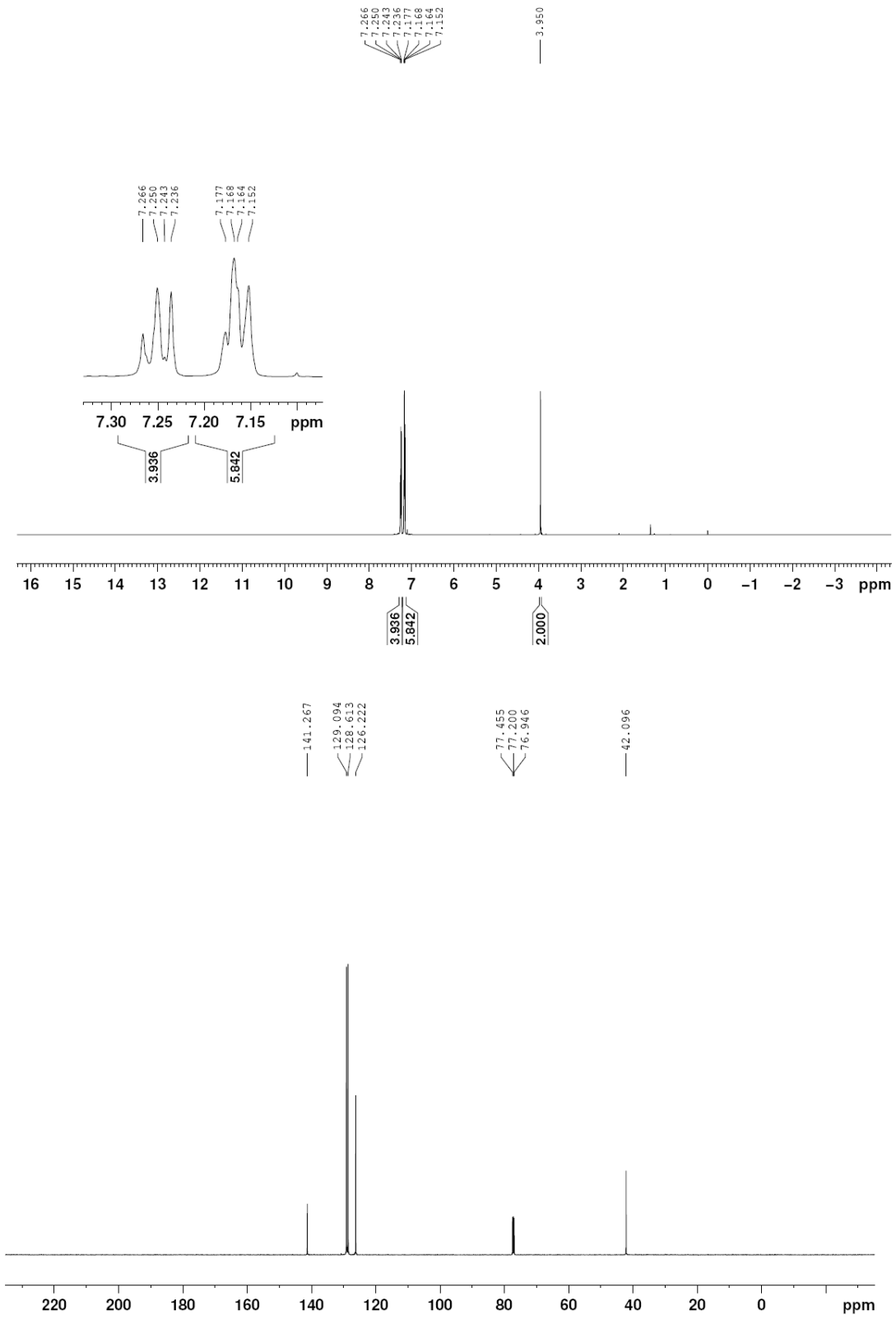
1-Chloro-3-(1-(p-tolyl)ethyl)benzene (**3g**)



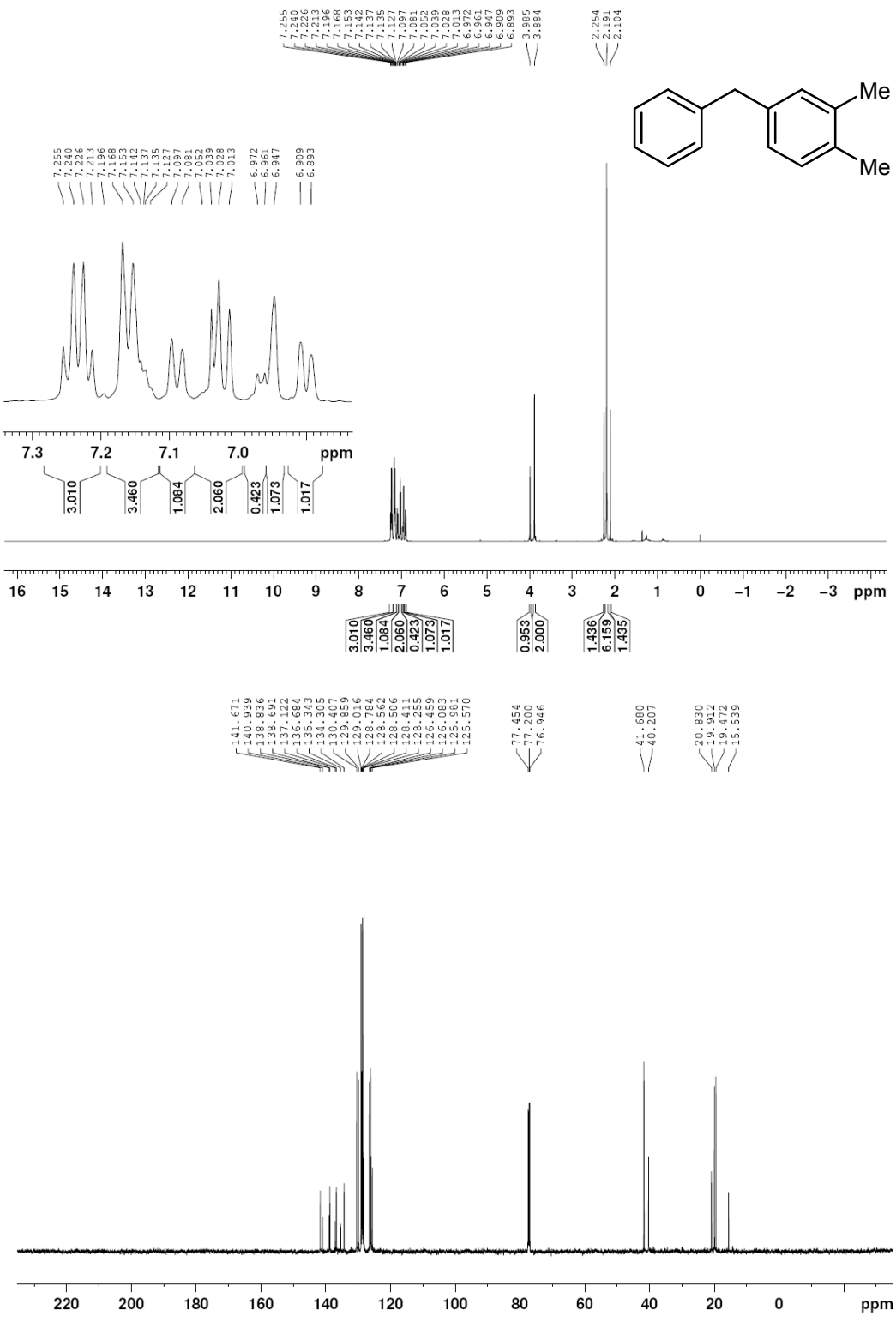
(P-tolylmethylene)dibenzene (**3h**)



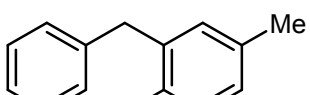
Diphenylmethane (**5a**)

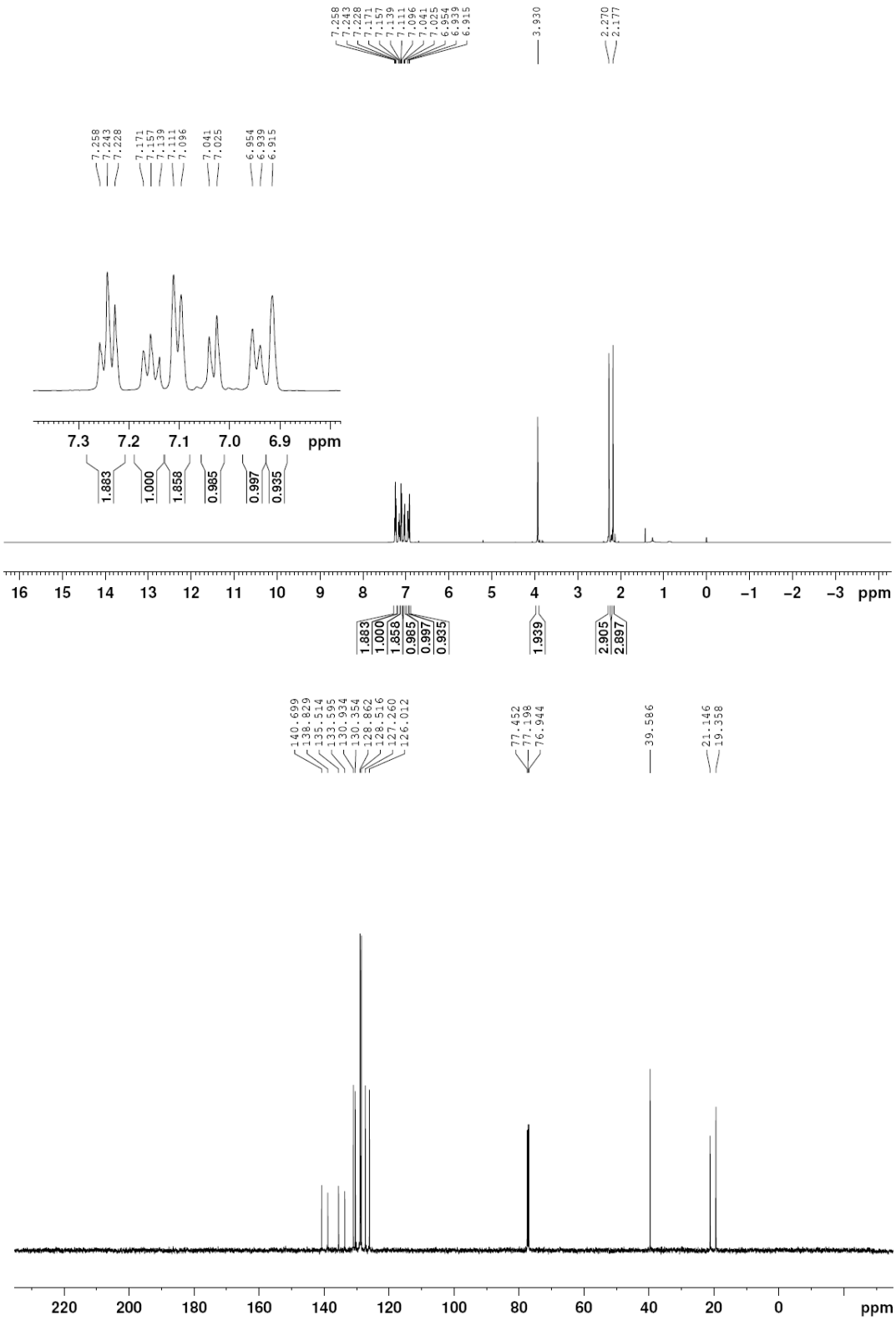


4-Benzyl-1,2-dimethylbenzene (**5b**)

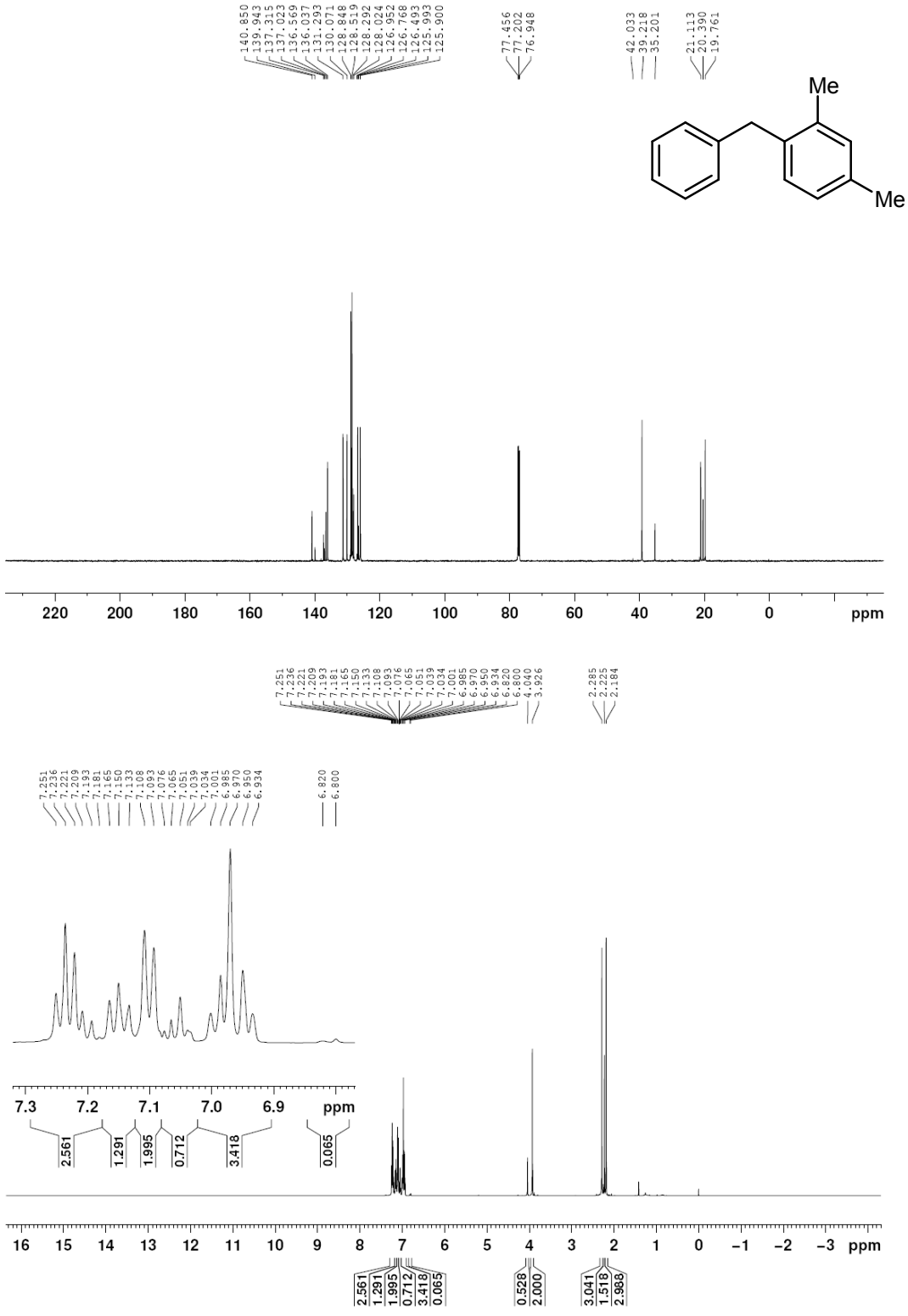


2-Benzyl-1,4-dimethylbenzene (**5c**)

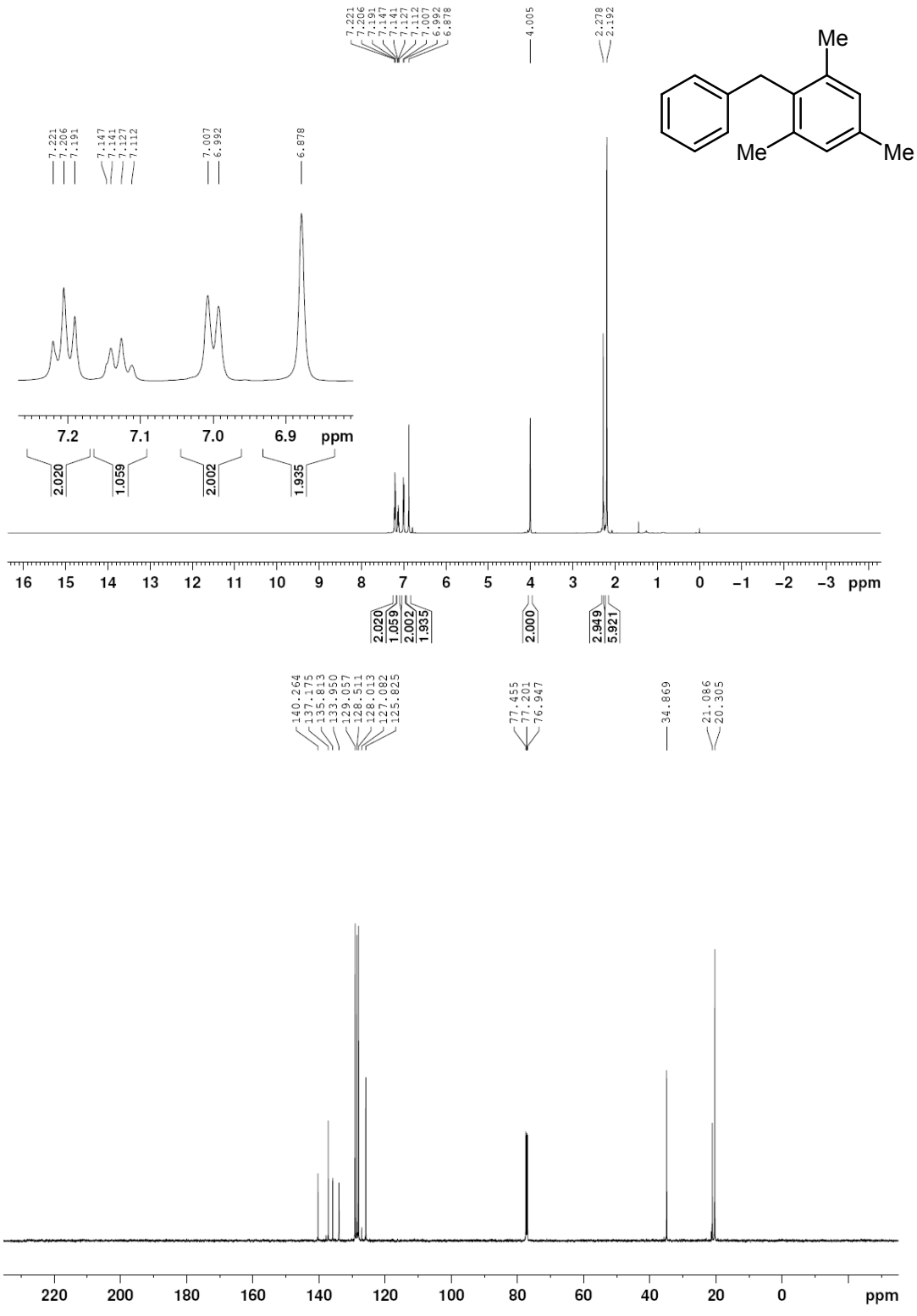




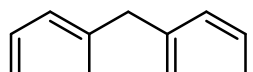
1-Benzyl-2,4-dimethylbenzene (**5d**)

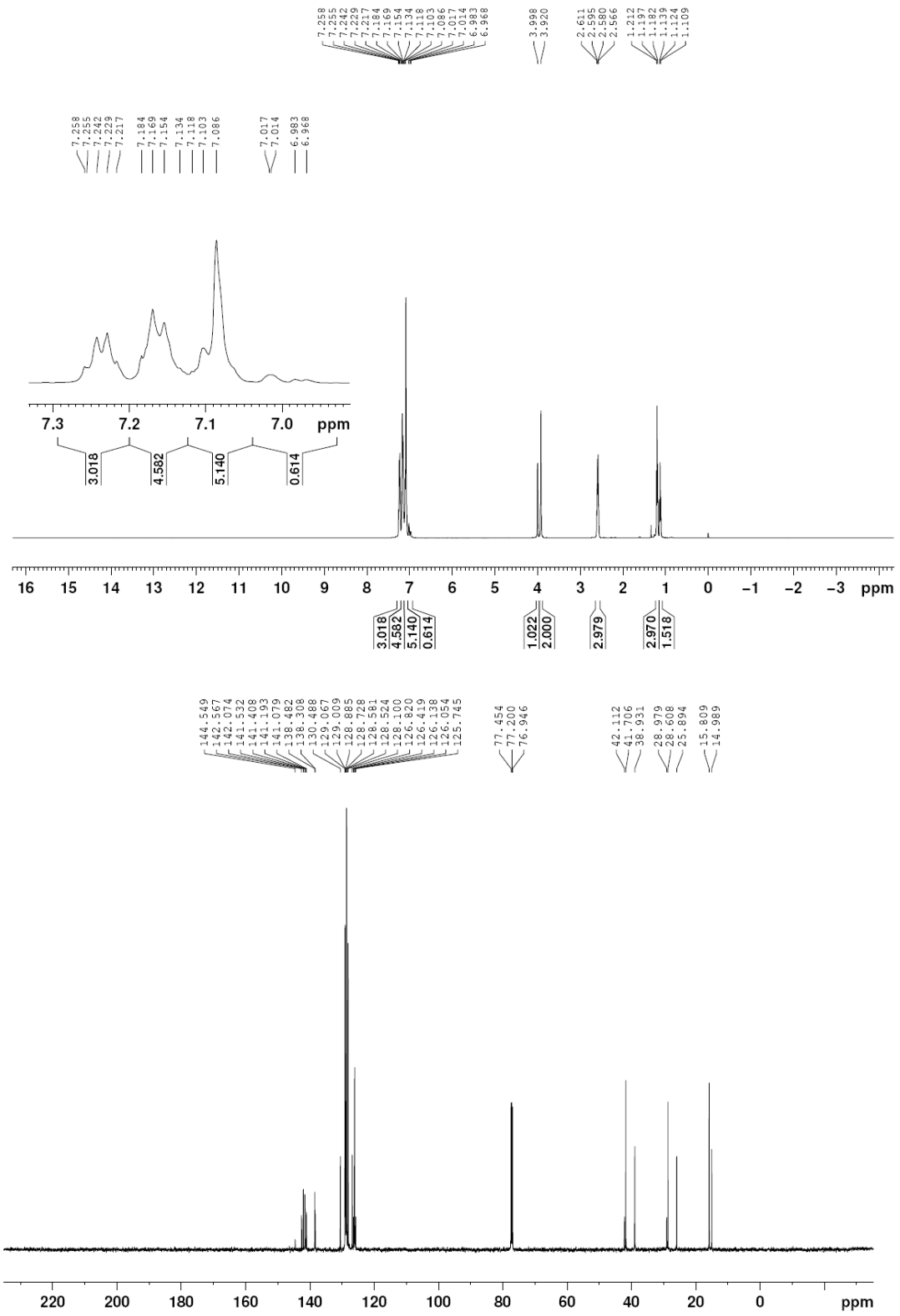


2-Benzyl-1,3,5-trimethylbenzene (**5e**)

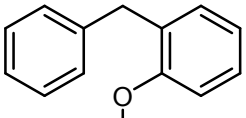


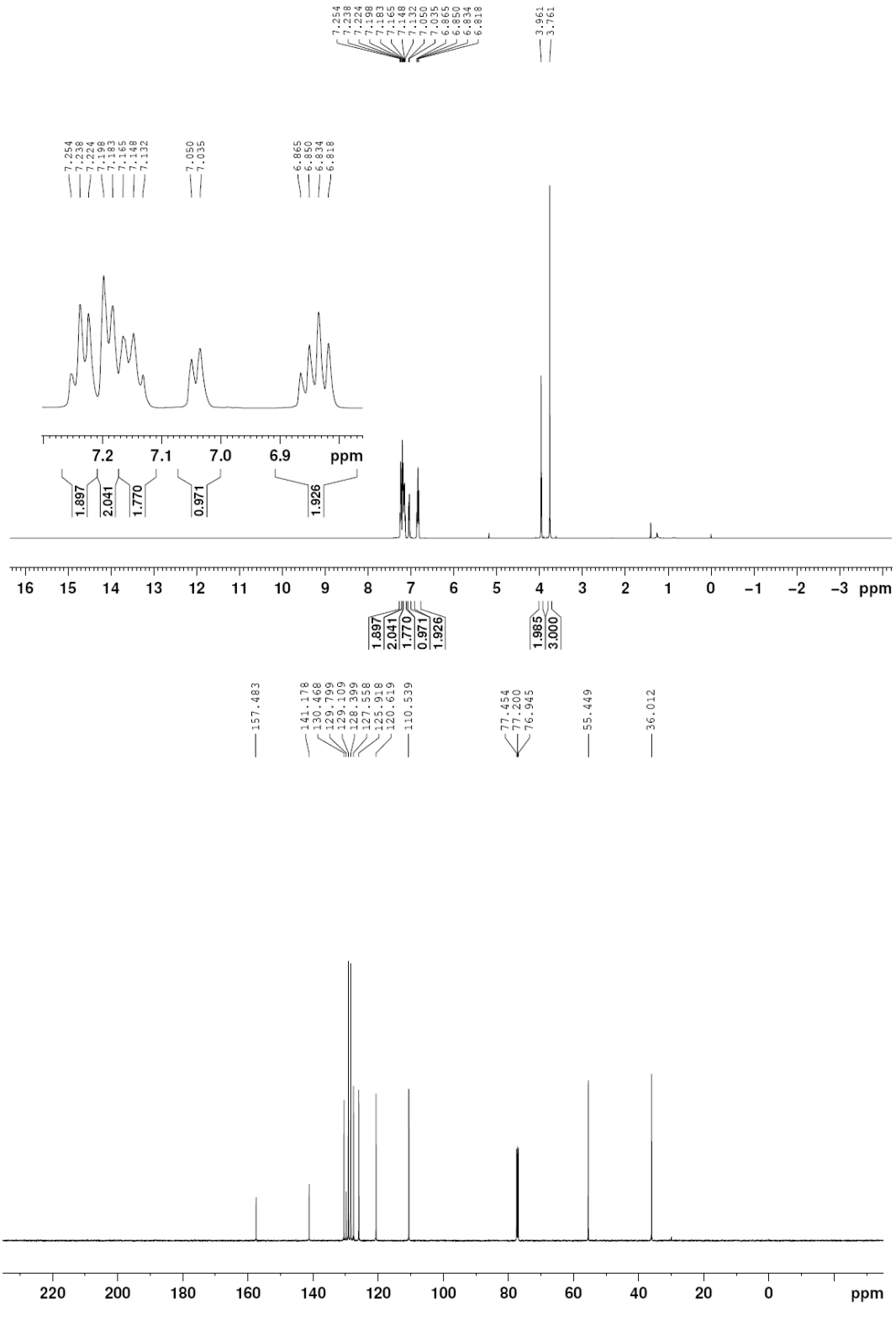
1-Benzyl-3-ethylbenzene (**5f**)



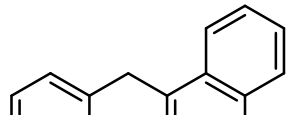


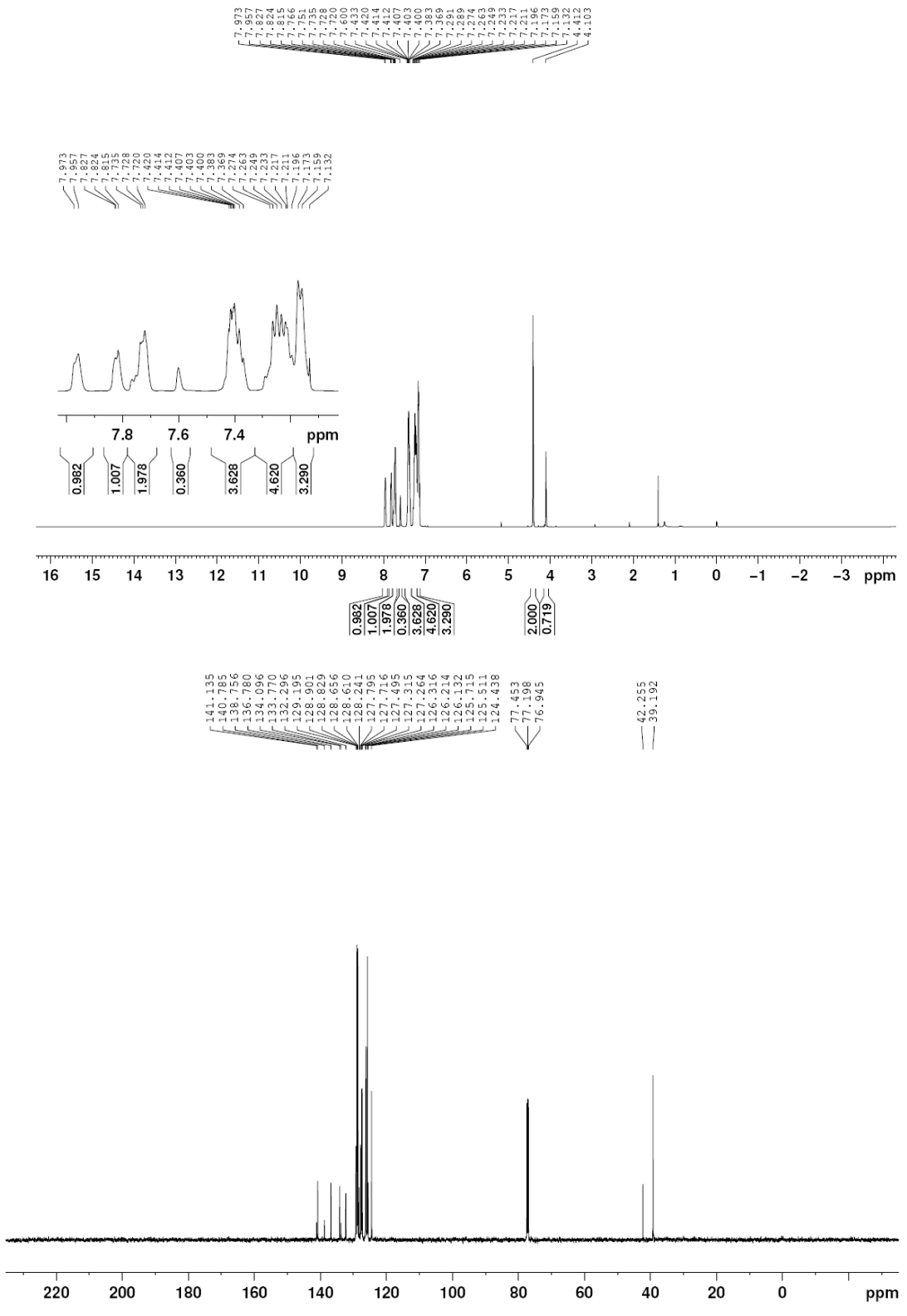
1-Benzyl-2-methoxybenzene (**5g**)



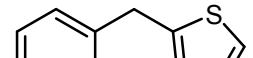


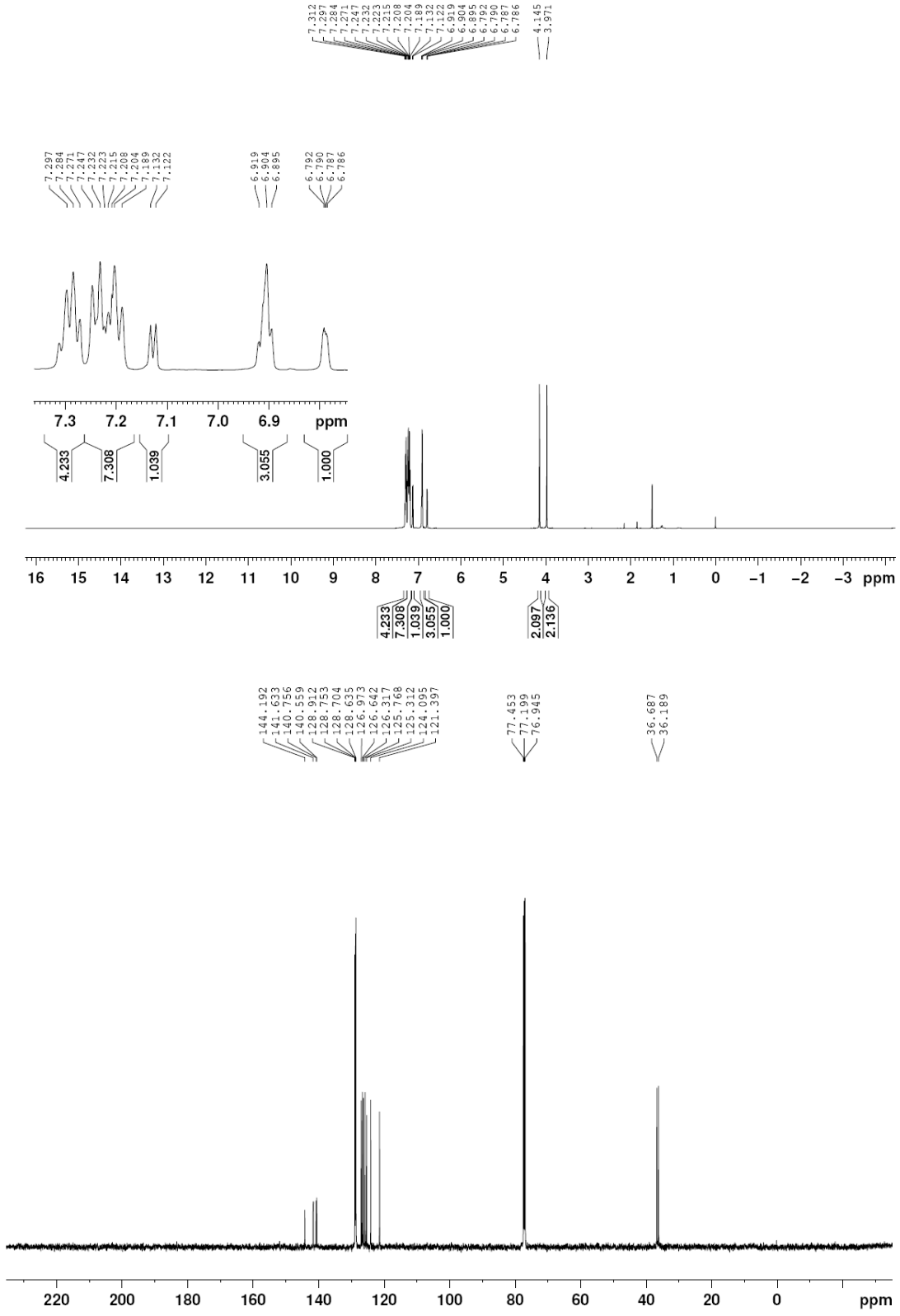
1-Benzylnaphthalene (**5h**)



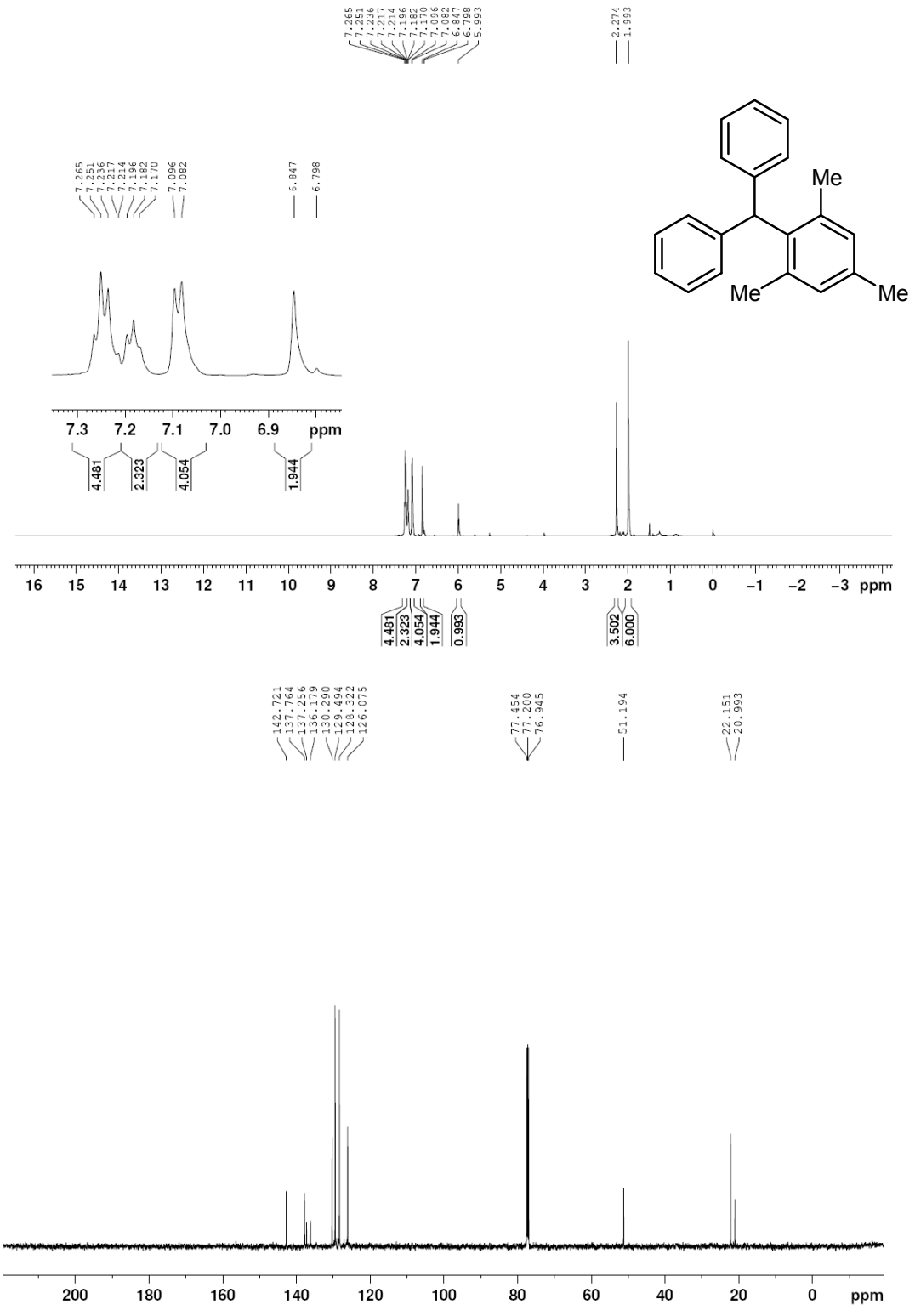


2-Benzylthiophene (**5i**)

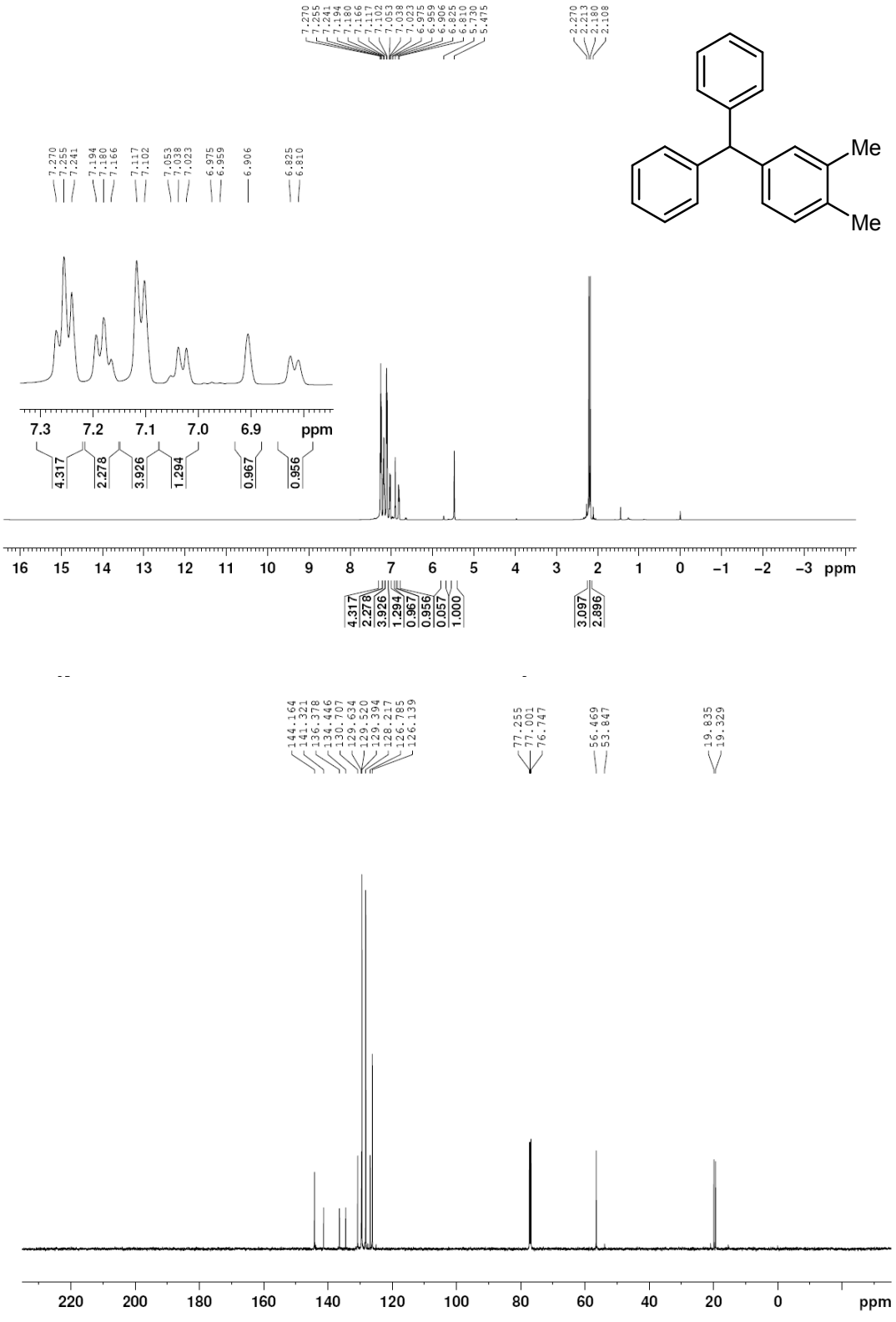




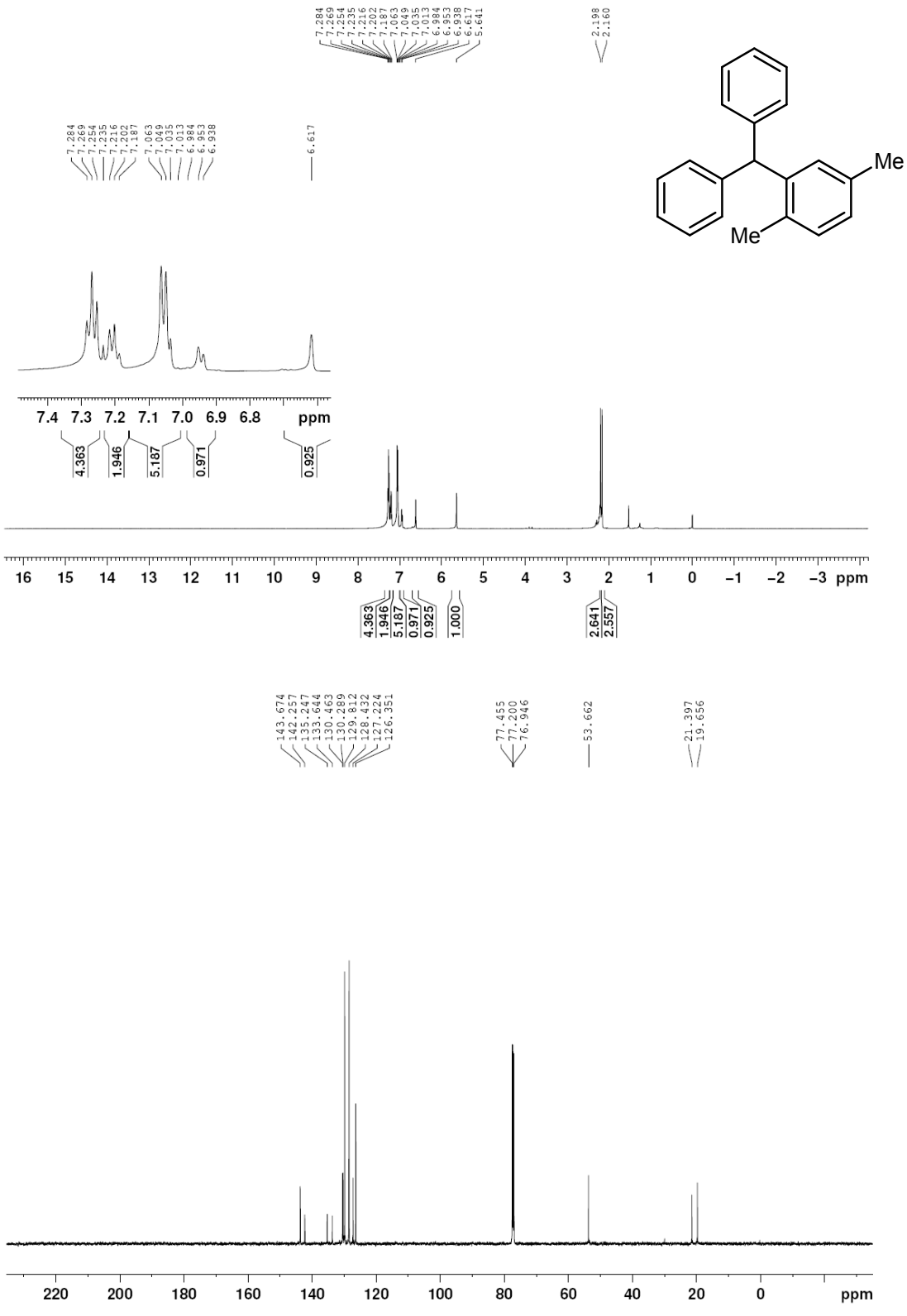
(mesitylmethylene)dibenzene (**5j**)



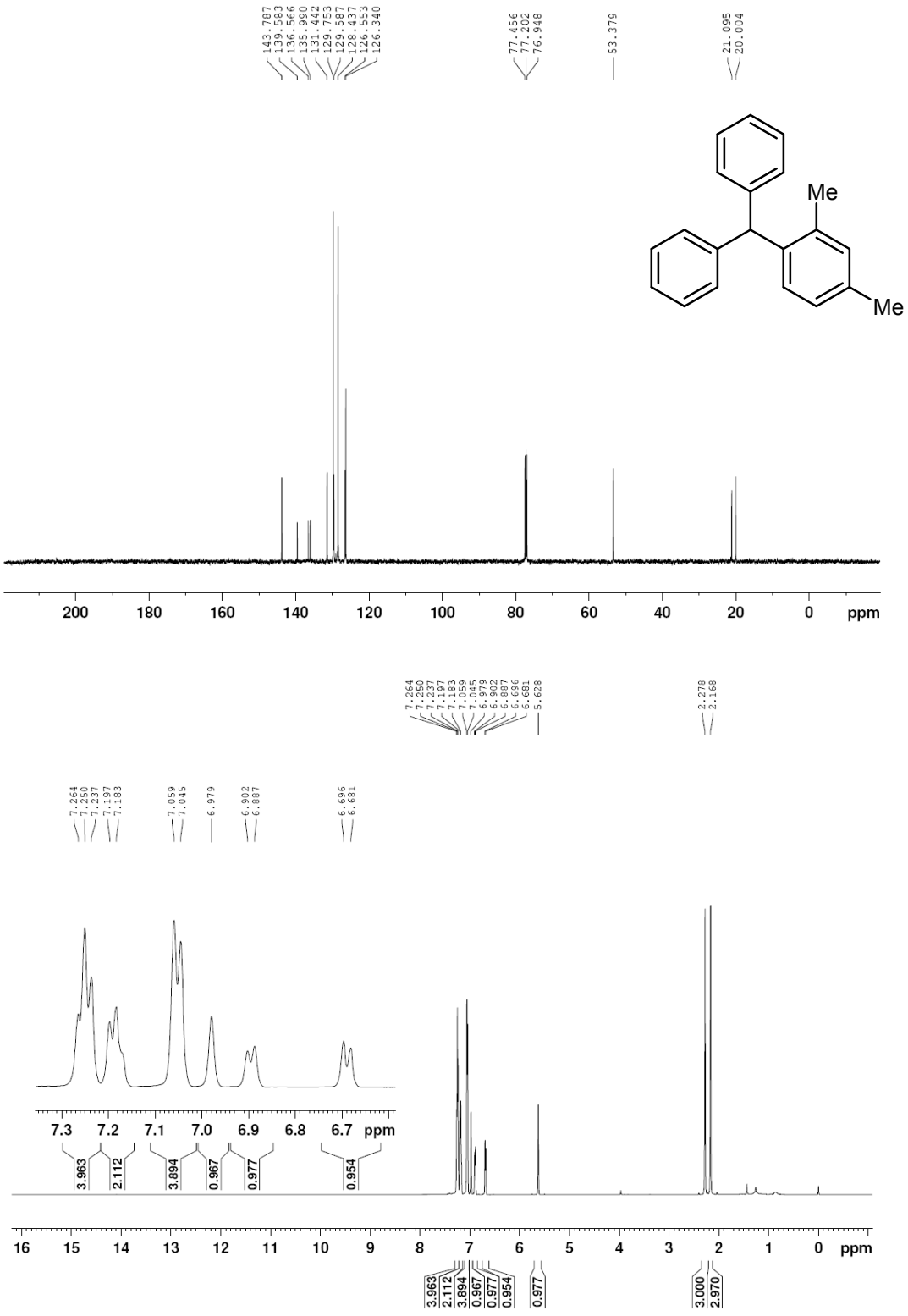
((3, 4-Dimethylphenyl)methylene)dibenzene (**5k**)



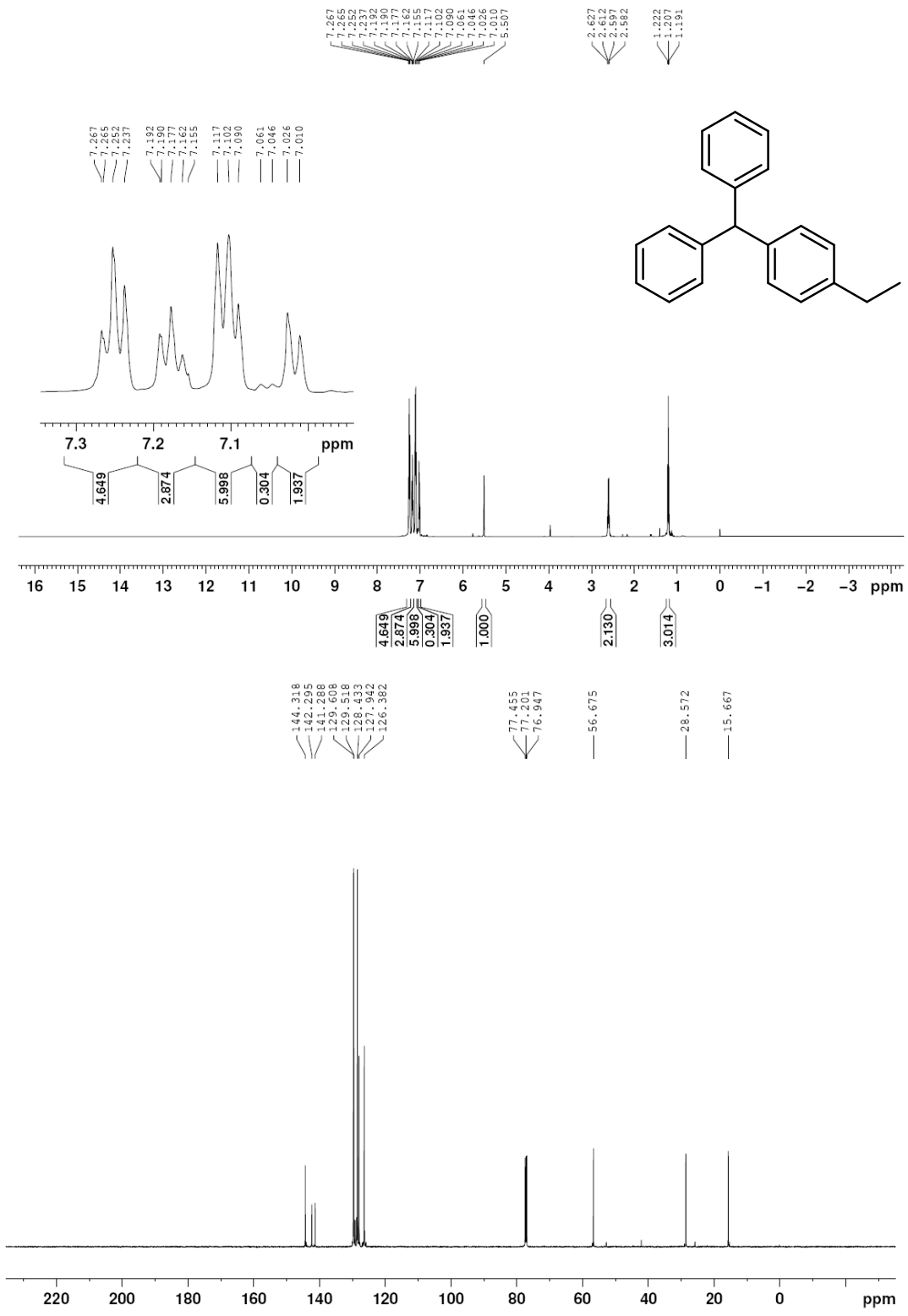
((2,5-Dimethylphenyl)methylene)dibenzene (**5l**)



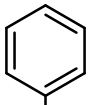
((2,4-Dimethylphenyl)methylene)dibenzene (**5m**)

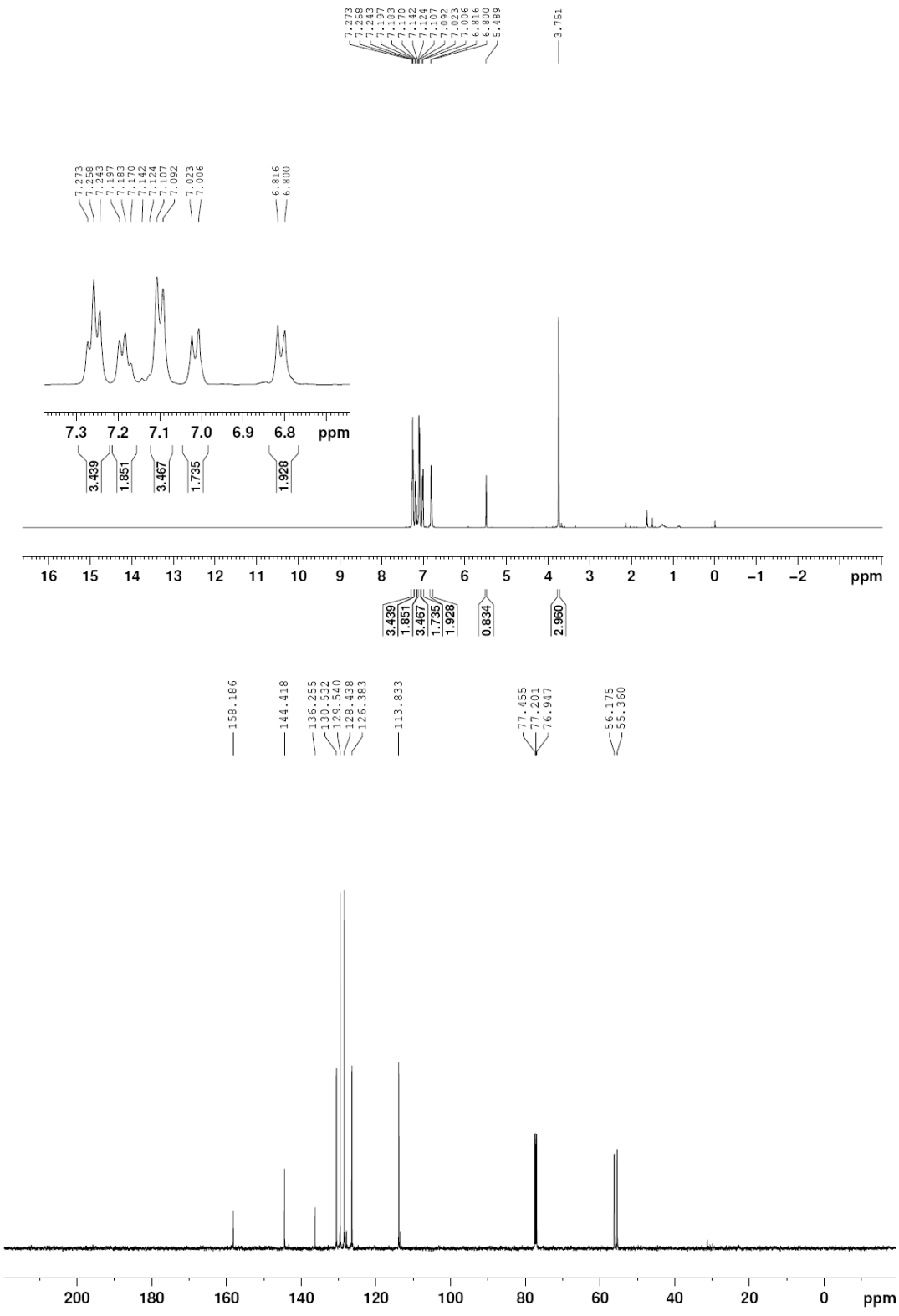


((4-Ethylphenyl)methylene)dibenzene (**5n**)

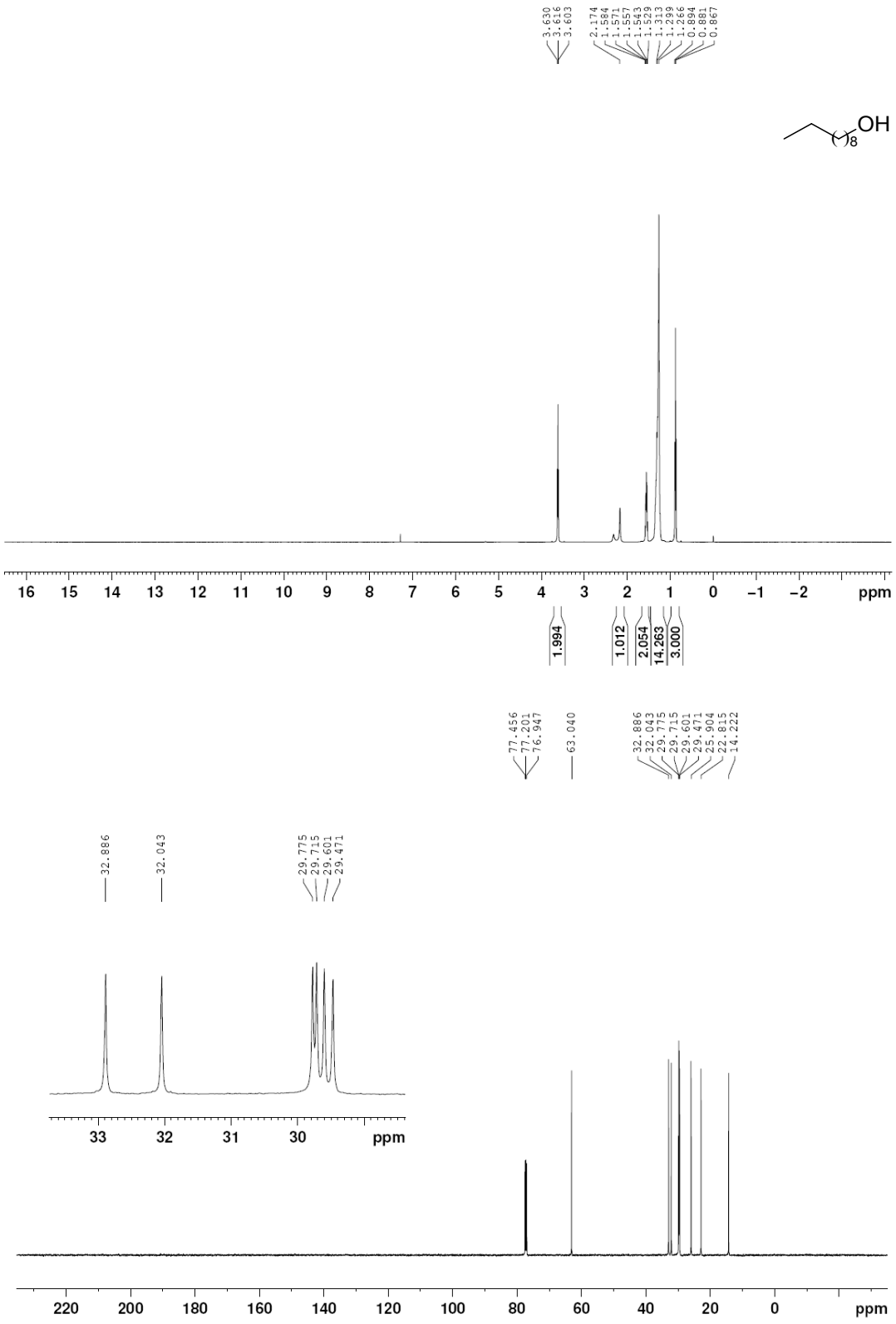


((4-Methoxyphenyl)methylene)dibenzene (**5o**)

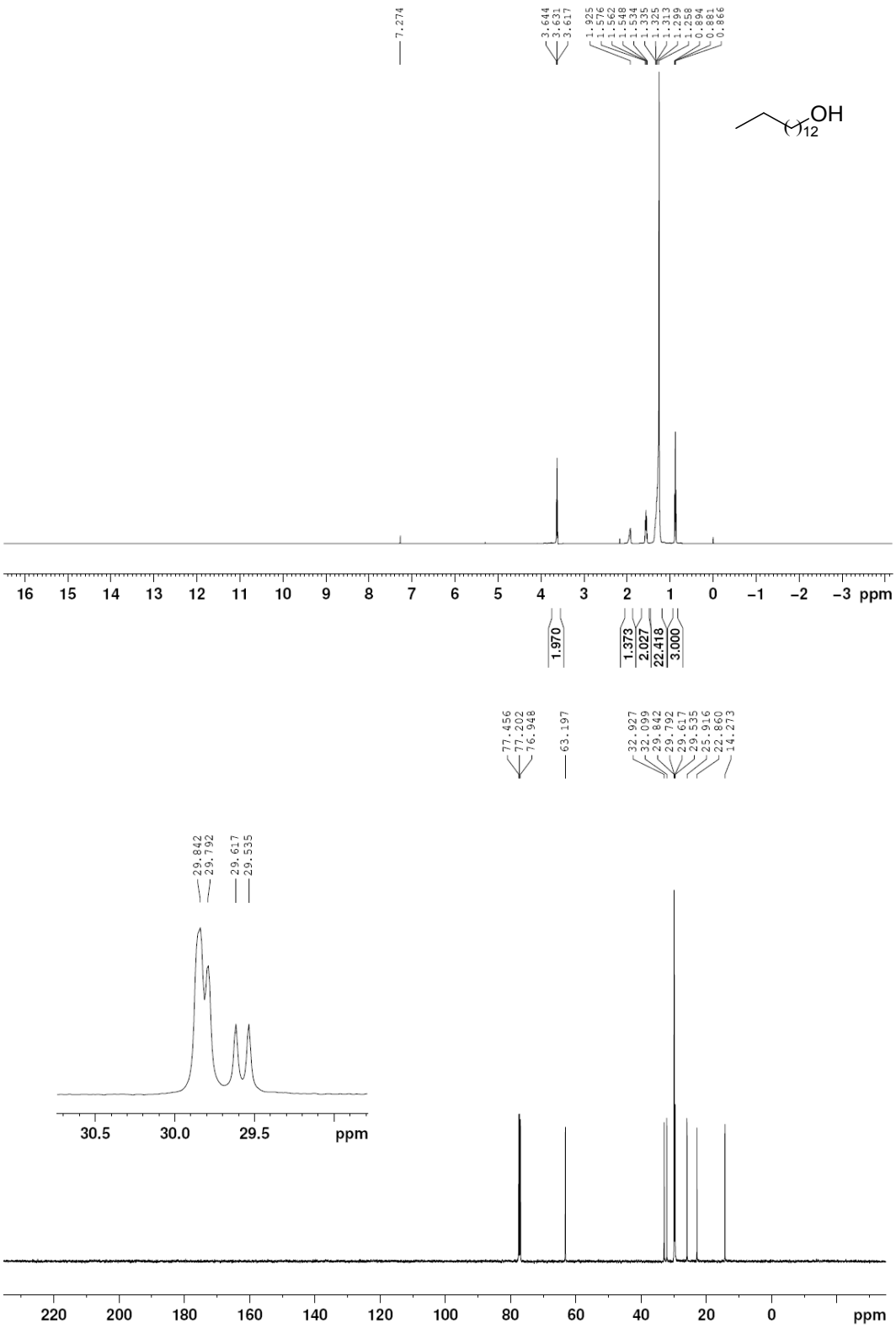



7.273
7.258
7.243
7.197
7.183
7.170
7.142
7.124
7.107
7.092
7.023
7.006
6.816
6.800
5.489
3.751
7.3
7.2
7.1
7.0
6.9
6.8
ppm
3.439
1.851
3.467
1.735
1.928
0.834
2.960
158.186
144.418
136.255
130.532
129.540
128.438
126.383
113.833
77.455
77.201
76.947
56.175
55.360
200
180
160
140
120
100
80
60
40
20
0
ppm

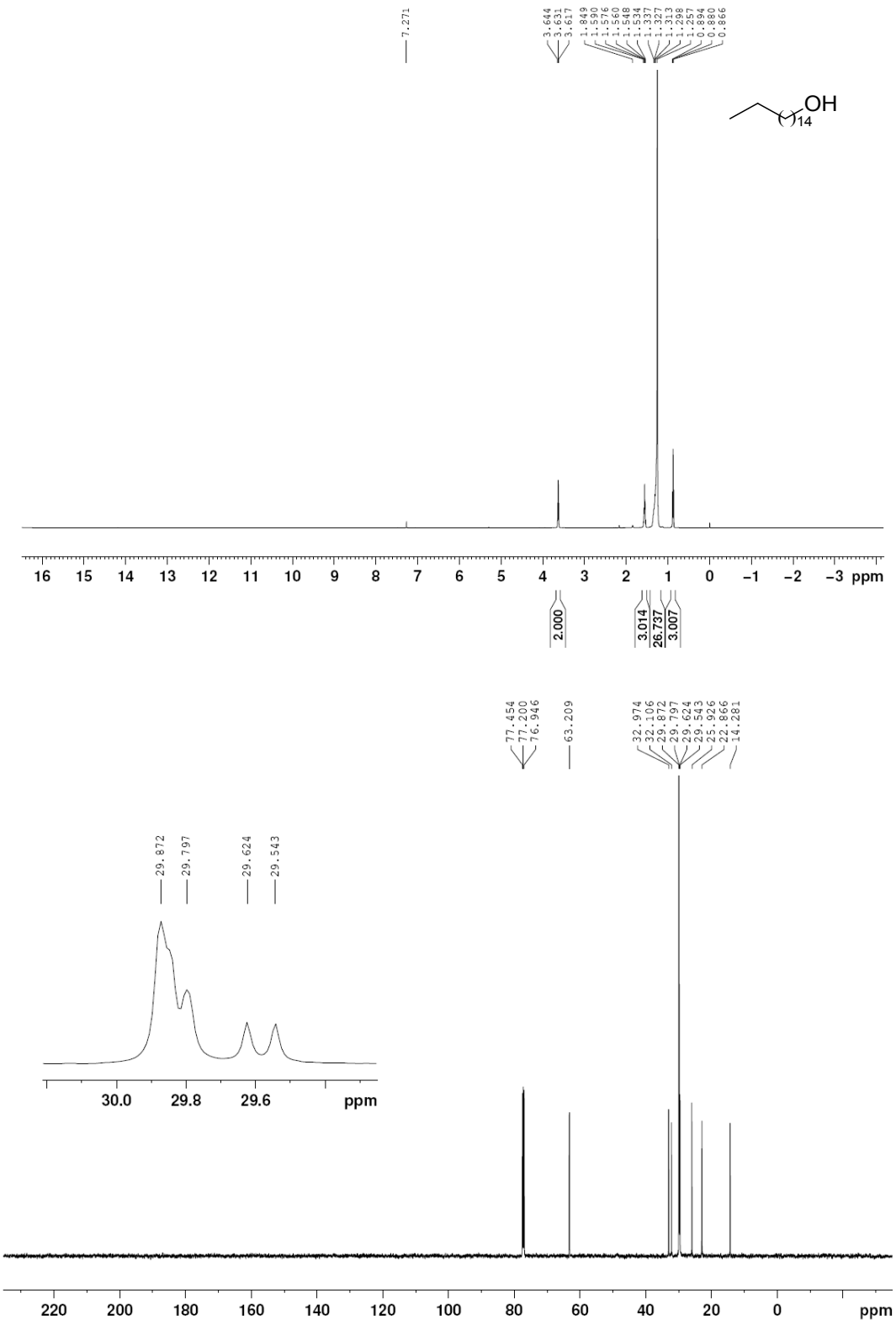
Decan-1-ol (**4j**)



Tetradecan-1-ol (**4k**)



Hexadecan-1-ol (**4l**)


7.271
3.644
3.631
3.617
1.849
1.590
1.576
1.560
1.548
1.534
1.337
1.327
1.313
1.298
1.257
0.894
0.880
0.866
OH
14
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 ppm
2.000
3.014
26.737
3.007
77.454
77.200
76.946
63.209
32.974
32.106
29.872
29.797
29.624
29.543
25.926
22.866
14.281
29.872
29.797
29.624
29.543
30.0 29.8 29.6 ppm
220 200 180 160 140 120 100 80 60 40 20 0 ppm