Supplementary Material (ESI) for Chemical Communications

Supporting Information

Nickel-Catalyzed Reductive Cleavage of Aryl–Oxygen Bonds in Alkoxy- and Pivaloxyarenes Using Hydrosilane as a Mild Reducing Agent

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CONTENTS

I. General Information.

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-270 spectrometer or JEOL ECS-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained on a Horiba FT-700 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 or GCMS-QP 2010 instrument with ionization voltages of 70 eV. Elemental analyses and high resolution mass spectra (HRMS) were performed by the Elemental Analysis Section of Osaka University. Column chromatography was performed with SiO_2 (Merck SilicaGel 60 (230-400 mesh)). All catalytic reactions were carried out in 10-mL sample vials with a teflon-sealed screwcap in a glovebox filled with nitrogen.

II. Materials.

$Ni(cod)_2$ and PCy_3 were purchased from Strem Chemicals and Aldrich, respectively, and used as received. Hydrosilanes **2a**-**e** were purchased from TCI or Aldrich and used after distillation over CaH_2. Triethylsilane-*d* was purchased from Aldrich and used as received. Toluene was purchased from Wako Chemicals and used as received. Alkoxyarenes **1a**, **1b**, **4**, **7**, **8**, and **9** were commercially available and used as received. Alkoxyarenes **1c** (CAS [15052-09-2]),[1] **1d** (CAS [613-62-7]),[2] **5** (CAS [5043-02-7]),[3] **6** (CAS [5085-74-5]),[4] **10** (CAS 2150-40-5]),[5] **11** (CAS [5857-89-1])[6] and **12** (CAS [1002908-37-2])[7] were prepared by following literature procedures. Aryl pivalates **13** (CAS [188114-77-4]), **14**, **15**, **16**, **17**, **18** (CAS [1228374-05-7]), **19** (CAS [106290-83-9]), **20** (CAS [1503-86-2]), **21** (CAS [1072840-84-6]), **22** (CAS [38453-16-6]) and **23** (CAS [97483-86-8]) were prepared from the corresponding phenols by the treatment with pivaloyl chloride, NEt_3 and DMAP in CH_2Cl_2.[8] The spectroscopic data for newly synthesized aryl pivalates are as follows.

3-(Dimethylamino)phenyl pivalate (14).

Colorless oil. *Rf* = 0.40 (hexane/EtOAc = 8/1).

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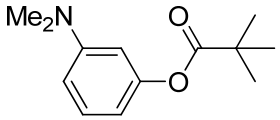
^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 1.35 (9H, s), 2.94 (s, 6H), 6.32-6.42 (m, 2H), 6.57 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 8.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 27.2, 39.0, 40.5, 105.4, 109.2, 109.7, 129.5, 151.7, 152.2, 177.2.

IR (neat): 2974 m, 2933 m, 2906 m, 2873 m, 2808 m, 1751 s, 1614 s, 1576 m, 1502 s, 1479 m, 1458 m, 1442 m, 1396 m, 1358 m, 1279 m, 1230 s, 1201 m, 1169 m, 1146 s, 1120 s, 1063 w, 1030 w, 1001 s, 974 w, 941 w, 904 w, 879 w, 833 w, 758 m, 685 m, 567 w, 507 w, 455 w.

MS, *m/z* (relative intensity, %): 221 (M^+, 45), 137 (100), 136 (68), 108 (13), 65 (10), 57 (72).

HRMS Calcd for $C_{13}H_{19}NO_2$: 221.1416. Found: 221.1417.



3,5-Dimethoxyphenyl pivalate (15).

Colorless oil. *Rf* = 0.31 (hexane/EtOAc = 10/1).

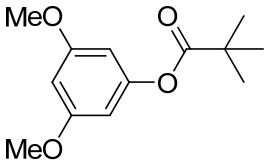
^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 1.35 (s, 9H), 3.77 (s, 6H), 6.22 (d, *J* = 2.3 Hz, 2H), 6.33 (t, *J* = 2.3 Hz, 1H).

^{13}C NMR ($CDCl_3$,67.80 MHz) δ: 27.1, 39.1, 55.5, 98.1, 100.1, 152.7, 161.1, 176.9.

IR (neat): 2972 s, 2939 s, 2908 m, 2875 m, 2839 m, 1753 s, 1620 s, 1599 s, 1477 s, 1429 s, 1396 m, 1367 m, 1348 m, 1327 m, 1275 s, 1205 s, 1157 s, 1134 s, 1113 s, 1063 s, 1032 m, 995 m, 976 w, 941 m, 930 m, 895 m, 837 s, 791 w, 760 w, 683 m, 625 w, 569 w, 538 w, 501 w.

MS, *m/z* (relative intensity, %): 238 (M^+, 21), 154 (52), 125 (42), 57 (100).

HRMS Calcd for $C_{13}H_{18}O_4$: 238.1205. Found: 238.1202.



Dimethyl 5-pivaloxyisophthalate (16).

White solid. *Rf* = 0.40 (hexane/EtOAc = 5/1). mp = 78-79 °C.

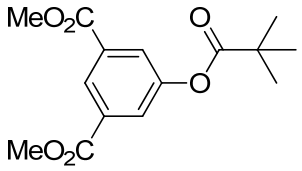
^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 1.38 (s, 9H), 3.95 (s, 6H), 7.92 (s, 2H), 8.56 (s, 1H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 27.1, 39.2, 52.5, 127.2, 127.8, 131.9, 151.1, 165.4, 176.6.

IR (KBr): 3141 w, 3093 w, 2981 m, 2958 m, 2875 w, 1745 s, 1732 s, 1614 w, 1587 m, 1481 m, 1433 s, 1398 w, 1367 w, 1327 m, 1281 s, 1254 s, 1240 s, 1180 m, 1130 s, 1032 w, 1011 s, 945 w, 903 w, 862 w, 809 w, 787 w, 754 s, 719 w, 665 w, 580 w, 544 w, 490 w, 444 w.

MS, *m/z* (relative intensity, %): 294 (M^+, 0.2), 210 (21), 179 (18), 85 (26), 57 (100).

HRMS Calcd for $C_{15}H_{18}O_6$: 294.1103. Found: 294.1102.



4-(*N*-Methylacetamido)phenyl pivalate (17).

White solid. *Rf* = 0.30 (hexane/EtOAc = 1/1). mp = 62-63 °C.

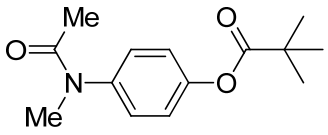
^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 1.37 (s, 9H), 1.88 (s, 3H), 3.26 (s, 3H), 7.11 (d, *J* = 8.9 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 22.4, 27.0, 37.2, 39.1, 122.8, 128.0, 141.8, 150.2, 170.5, 176.9.

IR (KBr): 3058 w, 3041 w, 2981 m, 2937 m, 2912 w, 2875 w, 1743 s, 1655 s, 1595 w, 1504 s, 1477 m, 1427 m, 1381 s, 1354 m, 1300 m, 1277 m, 1230 m, 1198 s, 1159 m, 1115 s, 1084 s, 1022 m, 976 w, 899 m, 860 w, 822 w, 798 w, 760 w, 729 w, 625 w, 600 w, 563 m, 476 w.

MS, *m/z* (relative intensity, %): 249 (M^+, 18), 165 (18), 123 (94), 122 (28), 57 (100), 56 (45).

HRMS Calcd for $C_{14}H_{19}NO_3$: 249.1365. Found: 249.1362.



(*S*)-4-(2-Acetamido-3-ethoxy-3-oxopropyl)phenyl pivalate (22).

White powder. *Rf* = 0.26 (hexane/EtOAc = 1/2).

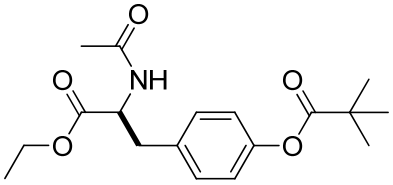
^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 1.25 (t, *J* = 7.0 Hz, 3H), 1.99 (s, 3H), 3.12 (d, *J* = 5.7 Hz, 1H), 4.17 (q, *J* = 7. 0Hz), 4.86 (dd, *J* = 13.4 and 5.7 Hz, 1H), 5.93 (d, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 14.1, 23.0, 27.0, 37.2, 39.0, 53.1, 61.5, 121.5, 130.2, 133.2, 150.1, 169.7, 171.5, 177.1.

IR (KBr): 3373 s, 3064 m, 2978 s, 2935 s, 2908 s, 2873 m, 1749 s, 1734 s, 1678 s, 1552 s, 1508 s, 1481 m, 1446 m, 1396 m, 1373 s, 1346 m, 1279 s, 1167 s, 1118 s, 1030 s, 939 w, 899 m, 858 w.

MS, *m/z* (relative intensity, %): 335 (M^+, 0.2), 276 (16), 192 (25), 107 (46), 85 (34), 57 (100).

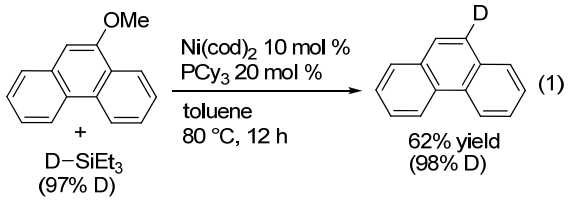
HRMS Calcd for $C_{18}H_{25}NO_5$: 335.1732. Found: 335.1725.



III. General Procedure for Reductive Deoxygenation of Alkoxyarenes (entry 5 in Table 2).

An oven-dried 5 mL screw-capped vial was charged with 9-methoxyphenanthrene (105 mg, 0.5 mmol), $HSiMe(OMe)_2$ (**2e**, 106 mg, 1 mmol), $Ni(cod)_2$ (7 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) and toluene (1.5 mL) in a glovebox filled with nitrogen. After the cap was closed, the vessel was heated in an oil bath at 80 °C for 12 h followed by cooling. The contents were subjected to flash chromatography (hexane/CH_2Cl_2 = 100/1) to furnish phenanthrene (89 mg, 99%) as a white powder.

IV. Labelling Experiment (Eq. 1)



To confirm that the introduced hydrogen atom is derived from the hydrosilane used, a labelling experiment was conducted (Eq. 1). 9-Methoxyphenanthrene was employed as a substrate since all aromatic hydrogen atoms resolve by ^1H NMR. Commercially available $DSiEt_3$ (Aldrich, 97%D) was employed as a reducing agent.

An oven-dried 5 mL screw-capped vial was charged with 9-methoxyphenanthrene (105 mg, 0.5 mmol), $DSiEt_3$ (106 mg, 1 mmol), $Ni(cod)_2$ (14 mg, 0.05 mmol), PCy_3 (28 mg, 0.10 mmol) and toluene (1.5 mL) in a glovebox filled with nitrogen. After the cap was closed, the vessel was heated in an oil bath at 80 °C for 12 h followed by cooling. The contents were subjected to flash chromatography (hexane/CH_2Cl_2 = 100/1) to furnish phenanthrene (56 mg, 62%) as a white powder. The content of a deuterium atom was determined to be 98% based on the integration value of the singlet resonance appeared at 7.76 ppm (1.02H when normalized by the integration value of non-deuterated phenanthrene.

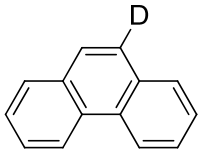
9-Deuteriophenanthrene (CAS [4819-99-2])

White solid. *Rf* = 0.34 (hexane).

^1H NMR ($CDCl_3$, 599.85 MHz) δ: 7.60-7.64 (m, 2H), 7.66-7.70 (m, 2H), 7.76 (s, 1H), 7.92 (dd, *J* = 1.3 and 7.9 Hz, 2H), 8.71 (d, *J* = 8.1 Hz, 2H).

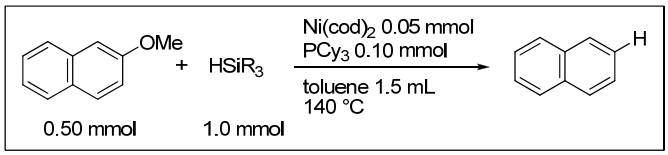
^{13}C NMR ($CDCl_3$, 150.84 MHz) δ: 122.6 (2C), 126.53, 126.53 (*J* = 14.6 Hz), 126.6 (2C), 126.8 (2C), 128.49, 128.55, 130.26, 130.27, 131.95, 132.02.

HRMS Calcd for $C_{14}H_9D$: 179.0845. Found: 179.0847.



V. Effect of Hydrosilanes

At 140 °C, $HSi(OEt)_3$ and $HSiMe(OMe)_2$ afforded the product in much higher yields (91 and 96%, respectively) than trialkylsilanes bearing similar sterics, such as $HSiEt_3$ (67%), $HSiMeEt_2$ (67%), and $HSiMe_2Et$ (60%). This can be well-rationalized by higher Lewis acidity of alkoxysilanes, which should facilitate the key σ-bond metathesis step [Eq.(2)]. The different reactivity of $HSi(OEt)_3$ and $HSiMe(OMe)_2$ at 80 °C should be attributed to the sterics: smaller $HSiMe(OMe)_2$ afforded the product in better yield.



entry	$HSiR_3$	time	product[a]	SM[a]	note
1	$HSiEt_3$	12 h	67%	34%	
2	$HSiEt_3$	20 h	88%	16%	
3	$HSiEt_3$	12 h	2%	96%	CsF(1.00 mmol) was added.
4	$HSiMeEt_2$	12 h	67%	24%	
5	$HSiMe_2Et$	12 h	60%	39%	
6	HSi^iPr_3	12 h	27%	76%	
7	$HSiBu_3$	12 h	66%	39%	
8	$HSiPh_3$	12 h	3%	99%	
9	$HSiMe_2Ph$	12 h	46%	49%	
10	$HSiMe_2{}^tBu$	12 h	12%	82%	
11	PMHS[b]	20 h	6%	91%	
12	$HSi(OEt)_3$	12 h	91%	10%	
13	$HSiMe_2(OEt)$	12 h	74%	22%	
14	$HSiMe(OMe)_2$	12 h	96%	0	
15	$HSiMe(OMe)_2$	12 h	96%	0	80 °C
16	$HSiMe(OMe)_2$	12 h	95%	0	80 °C $Ni(cod)_2$ 0.025 mmol PCy_3 0.05 mmol
17	$HSiMe(OMe)_2$	12 h	51%	56%	80 °C $Ni(cod)_2$ 0.0125 mmol PCy_3 0.025 mmol

[a] GC yield
[b] PMHS = polymethylhydrosiloxane

VI. Spectroscopic Data of Products

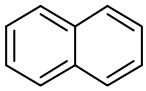
Naphthalene (CAS [91-20-3], entries 1-5 in Table 2, entry 8 in Table 3). The general procedure was followed. Yield was determined by GC using eicosane as an internal standard due to the volatility of this compound.

White solid. *Rf* = 0.55 (hexane).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 7.42-7.52 (m, 4H), 7.80-7.88 (m, 4H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 125.8, 127.9, 133.4.

HRMS Calcd for $C_{10}H_8$: 128.0626. Found: 128.0617.



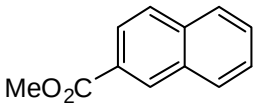
Methyl 2-naphthoate (CAS [2459-25-8], entry 6 in Table 2).

White solid. *Rf* = 0.36 (hexane/EtOAc = 10/1).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 3.98 (s, 3H), 7.48-7.68 (m, 2H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.95 (d, *J* = 8.9 Hz, 1H), 8.06 (dd, J = 1.8 and 8.7 Hz), 8.61 (s, 1H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 52.2, 125.2, 126.6, 127.4, 127.7, 128.1, 128.2, 129.3, 131.0, 132.5, 135.5, 167.3.

HRMS Calcd for $C_{12}H_{10}O_2$: 186.0681. Found: 186.0683.



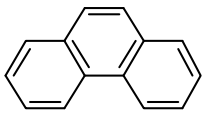
Phenanthrene (CAS [85-01-8], entry 7 in Table 2).

White solid. *Rf* = 0.44 (hexane).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 7.55-7.70 (m, 4H), 7.74 (s, 2H), 7.89 (dd, *J* = 1.8 and 7.9 Hz, 2H), 8.69 (d, *J* = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 122.6, 126.5 (2C), 126.9, 128.6, 130.3, 132.0.

HRMS Calcd for $C_{14}H_{10}$: 178.0783. Found: 178.0785.



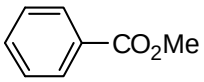
Methyl benzoate (CAS [93-58-3], entries 9 and 10 in Table 2). The general procedure was followed. Yield was determined by GC using eicosane as an internal standard due to the volatility of this compound.

Colorless oil. *Rf* = 0.47 (hexane/EtOAc = 10/1).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 3.92 (s, 3H), 7.44 (dd, *J* = 7.7 and 7.7 Hz, 2H), 7.56 (dd, *J* = 7.6 and 7.6 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 52.1, 128.3, 129.5, 130.1, 132.9, 167.1.

HRMS Calcd for $C_8H_8O_2$: 136.0524. Found: 136.0525.



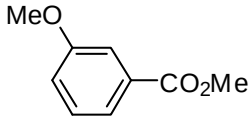
Methyl 3-methoxybenzoate (CAS [5368-81-0], entry 11 in Table 2).

Colorless oil. *Rf* = 0.51 (hexane/EtOAc = 5/1).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 3.80 (s, 3H), 3.92 (s, 3H), 7.11 (dd, *J* = 8.4 and 2.7 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.56-7.57 (m, 1H), 7.64 (d, *J* = 7.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 52.2, 55.4, 113.9, 119.5, 122.0, 129.4, 131.4, 159.5, 167.0.

HRMS Calcd for $C_9H_{10}O_3$: 166.0630. Found: 166.0629.



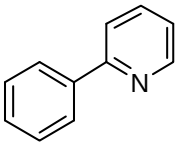
2-Phenylpyridine (CAS [1008-89-5], entry 12 in Table 2).

Colorless oil. *Rf* = 0.31 (hexane/EtOAc = 10/1).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 7.20-7.26 (m, 1H), 7.38-7.53 (m, 3H), 7.70-7.80 (m, 2H), 7.95-8.04 (m, 2H), 8.7 (d, *J* = 4.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 120.6, 122.1, 126.9, 128.7, 128.9, 136.8, 139.3, 149.6, 157.4.

HRMS Calcd for $C_{11}H_9N$: 155.0735. Found: 155.0732.



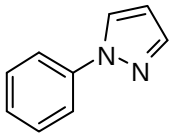
1-Phenyl-1*H*-pyrazole (CAS [1126-00-7], entry 13 in Table 2).

Colorless oil. *Rf* = 0.37 (hexane/EtOAc = 5/1).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 6.47 (s, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.69-7.74 (m, 3H), 7.93 (d, *J* = 2.4 Hz, 1H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 107.5, 119.1, 126.4, 126.7, 129.4, 140.1, 141.0.

HRMS Calcd for $C_9H_8N_2$: 144.0688. Found: 144.0685.



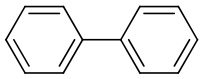
Biphenyl (CAS [92-52-4], entries 1 and 7 in Table 3).

White solid. *Rf* = 0.5 (hexane).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 7.30-7.38 (m, 2H), 7.39-7.7.48 (m, 4H), 7.56-7.63 (m, 4H).

^{13}C NMR ($CDCl_3$,67.80 MHz) δ: 127.1, 127.2, 128.7, 141.2.

HRMS Calcd for $C_{12}H_{10}$: 154.0783. Found: 154.0783.

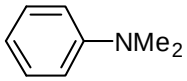


***N*,*N*-Dimethylaniline (CAS [121-69-7], entry 2 in Table 3).** The general procedure was followed. Yield was determined by GC using eicosanes as an internal standard due to the volatility of this compound.

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 2.94 (s, 6H), 6.68-6.78 (m, 3H), 7.19-7.7.28 (m, 3H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 40.6, 112.6, 116.6, 129.0, 150.6.

HRMS Calcd for $C_8H_{11}N$: 121.0891. Found: 121.0886.



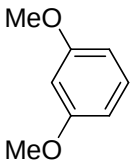
1,3-Dimethoxybenzene (CAS [151-10-0], entry 3 in Table 3).

Colorless oil. *Rf* = 0.37 (hexane/EtOAc = 10/1).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 3.79 (s, 6H), 6.42-6.57 (m, 3H), 7.19 (dd, *J* = 8.1 and 8.1 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 55.3, 100.4, 106.1, 129.9, 160.8.

HRMS Calcd for $C_8H_{10}O_2$: 138.0681. Found: 138.0679.



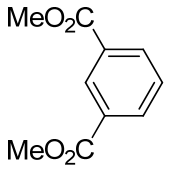
Dimethyl isophthalate (CAS [1459-93-4], entry 4 in Table 3).

White solid. *Rf* = 0.19 (hexane/EtOAc = 10/1).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 3.95 (s, 6H), 7.54 (dd, *J* = 8.1 and 8.1 Hz, 1H), 8.23 (dd, *J* = 0.8 and 8.1 Hz), 8.69 (dd, *J* = 0.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 52.4, 128.6, 130.6, 130.7, 133.8, 166.3.

HRMS Calcd for $C_{10}H_{10}O_4$: 194.0579. Found: 194.0583.



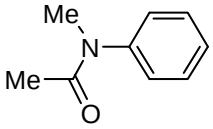
***N*-Methyl-*N*-phenylacetamide (CAS [579-10-2], entry 5 in Table 3).**

White solid. R*f* = 0.27 (hexane/EtOAc = 1/1).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 1.88 (s, 3H), 3.27 (s, 3H), 7.15-7.23 (m, 2H), 7.28-7.47 (m, 3H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 22.4, 37.1, 127.1, 127.7, 129.7, 144.6, 170.6.

HRMS Calcd for $C_9H_{11}NO$: 149.0841. Found: 149.0835.



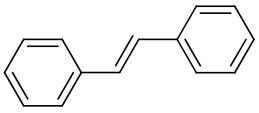
(*E*)-1,2-Diphenylethene (CAS [103-30-0], entry 6 in Table 3).

White solid. *Rf* = 0.34 (hexane).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 7.12 (s, 2H), 7.27-7.32 (m, 2H), 7.37 (dd, *J* = 7.4 and 7.4 Hz, 4H), 7.53 (d, *J* = 7.3 Hz, 4H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 126.5, 127.6, 128.7 (2C), 137.3.

HRMS Calcd for $C_{14}H_{12}$: 180.0939. Found: 180.0942.



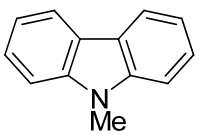
9-Methyl-9*H*-carbazole (CAS [1484-12-4], entry 9 in Table 3).

White solid. *Rf* = 0.34 (hexane/EtOAc = 10/1).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 3.87 (s, 3H), 7.23 (d, *J* = 6.9 Hz, 2H), 7.37-7.53 (m, 4H), 8.11 (d, *J* = 7.9 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 29.1, 108.4, 118.8, 120.3, 122.7, 125.6, 141.0.

HRMS Calcd for $C_{13}H_{11}N$: 181.0891. Found: 181.0891.



Ethyl 2-acetamido-3-phenylpropanoate (CAS [2361-96-8], entry 10 in Table 3). The general procedure was followed, and an analytically pure sample was obtained by the purification by GPC.

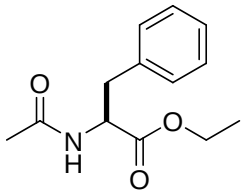
White solid. *Rf* = 0.17 (hexane/EtOAc = 1/1).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 1.25 (t, *J* = 7.3 Hz, 3H), 1.99 (s, 3H), 3.11 (dd, *J* = 14.3 and 5.9 Hz, 2H), 4.17 (q, *J* = 7.3 Hz, 2H), 4.87 (dd, *J* = 13.5 and 5.9 Hz, 1H), 5.91 (d, *J* = 6.5 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.22-7.31 (m, 3H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 14.1, 23.2, 37.9, 53.1, 61.5, 127.1, 128.5, 129.3, 135.9, 169.6, 171.6.

HRMS Calcd for $C_{13}H_{17}NO_3$: 235.1208. Found: 235.1208.

Enantiomeric excess of the product was determined to be > 99% ee by HPLC analysis (chiracel IB, hexane:IPA = 90:10, 1 mL/min, S-isomer: t = 10.03 min; R-isomer: t = 9.42 min).



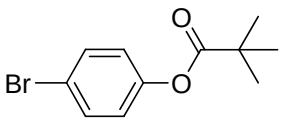
V. Experiment for Regioselective Functionalization of Arene 23 (Scheme 2)

4-Bromophenyl pivalate (24, CAS [63549-55-3]).[9] To a 10 mL two necked flask was sequentially added phenyl pivalate (**23**, 357 mg, 2.0 mmol), NBS (377, 2.1 mmol), $FeCl_3$ (30 mg, 0.20 mmol) and CH_3CN (2 mL). The vial was stirred at 60 °C for 5 h. The mixture was purified by flash chromatography (hexane/EtOAc = 20/1) to give **24** (371 mg, 72%).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 1.35 (s, 9H), 6.95 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 27.1, 39.1, 118.6, 123.3, 132.3, 150.1, 176.8.

HRMS Calcd for $C_{11}H_{13}BrO_2$: 256.0098. Found: 256.0103.



24

4'-Methoxybiphenyl-4-yl pivalate (25, CAS [917375-65-6]). A 20 mL two-necked flask with a reflux condenser was charged with **24** (257 mg, 1.0 mmol), 4-methoxyphenyl boronic acid (228 mg, 1.5 mmol), $PdCl_2(PPh_3)_2$ (44 mg, 0.10 mmol), K_3PO_4 (1.27 mg, 6.0 mmol), toluene (3 mL), and H_2O (3 mL) under a gentle stream of nitrogen. The vessel was heated in an oil bath under nitrogen atmosphere at 90 °C for 15 h followed by cooling. The contents were subjected to flash chromatography (hexane/EtOAc = 20/1) to

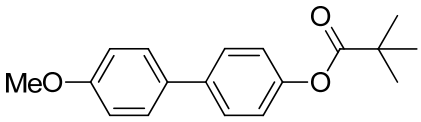
[9] Tonemura, K.; Suzuki, T.; Nishida, Y.; Satsumabayashi, K.; Horaguchi, T. *Chem. Lett.* **2003**, *32*, 932.

furnish **25** (234 mg, 82%) as a white powder.

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 1.38 (s, 9H), 3.85 (s, 3H), 6.97 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.48-7.55 (m, 4H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 27.1, 39.1, 55.3, 114.2, 121.7, 127.6, 128.1, 133.0, 138.3, 150.0, 159.1, 177.2.

HRMS Calcd for $C_{18}H_{20}O_3$: 284.1412. Found: 284.1414.



25

4-Methoxy-1,1':3',1''-terphenyl-4'-yl pivalate (26). The literature procedure was followed.[10] To a 10 mL two necked flask was sequentially added $Pd(OAc)_2$ (11 mg, 0.05 mmol), $Ph_2I^+OTf^-$ (323 mg, 0.75 mmol), **25** (142 mg, 0.5 mmol), Piv_2O (51 μL, 0.25 mmol), and DCE (2 mL). The vial was stirred at room temperature for 5 minutes and then TfOH (22 μL, 0.25 mL) was added. The flask was stirred at 25 °C for 20 h under air. The mixture was purified by flash chromatography (hexane/EtOAc = 10/1) to give **26** (112 mg, 62%) as a viscous colorless oil.

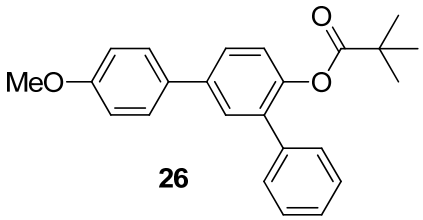
^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 1.14 (s, 9H), 3.85 (s, 3H), 6.98 (d, *J* = 8.9 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 1H), 7.34-7.45 (m, 5H), 7.52-7.55 (m, 4H).

^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 27.0, 38.9, 55.3, 114.2, 122.9, 126.6, 127.4, 128.0, 128.2, 129.1, 129.2, 132.8, 135.4, 137.6, 138.7, 147.1, 159.2, 176.9.

IR (neat): 3033 w, 2971 m, 1749 s, 1610 m, 1517 m, 1502 m, 1479 s, 1444 w, 1394 w, 1367 w, 1288 m, 1251 m, 1198 s, 1182 m, 1114 s, 1045 w, 1027 m, 896 w.

MS, *m/z* (relative intensity, %): 360 (M^+, 29), 277 (21), 276 (100), 261 (26), 57 (90).

HRMS Calcd for $C_{24}H_{24}O_3$: 360.1725. Found: 360.1716.



26

4-Methoxy-1,1':3',1''-terphenyl (27, CAS [1060666-61-6]). An oven-dried 5 mL screw-capped vial was charged with **26** (52 mg, 0.14 mmol), $HSiMe(OMe)_2$ (**2e**, 35 mg, 0.33 mmol), $Ni(cod)_2$ (4.4 mg, 0.016

[10] B. Xiao, Y. Fu, J. Xu, T.-J. Gong, J.-J. Dai, J. Yi, L. Liu, *J. Am. Chem Soc.* **2010**, *132*, 468.

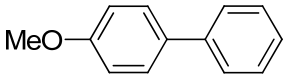
mmol), PCy_3 (9.0 mg, 0.032 mmol) and toluene (1.0 mL) in a glovebox. After the cap was closed, the vessel was heated in an oil bath at 80 °C for 12 h followed by cooling. The contents were subjected to flash chromatography (hexane/EtOAc = 10/1) to furnish **27** (33.2 mg, 91%) as a white powder.

White solid. *Rf* = 0.54 (hexane/EtOAc = 10/1).

^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 3.87 (s, 3H), 6.99-7.03 (m, 2H), 7.34-7.40 (m, 1H), 7.44-7.67 (m, 9H), 7.76-7.77 (m, 1H).

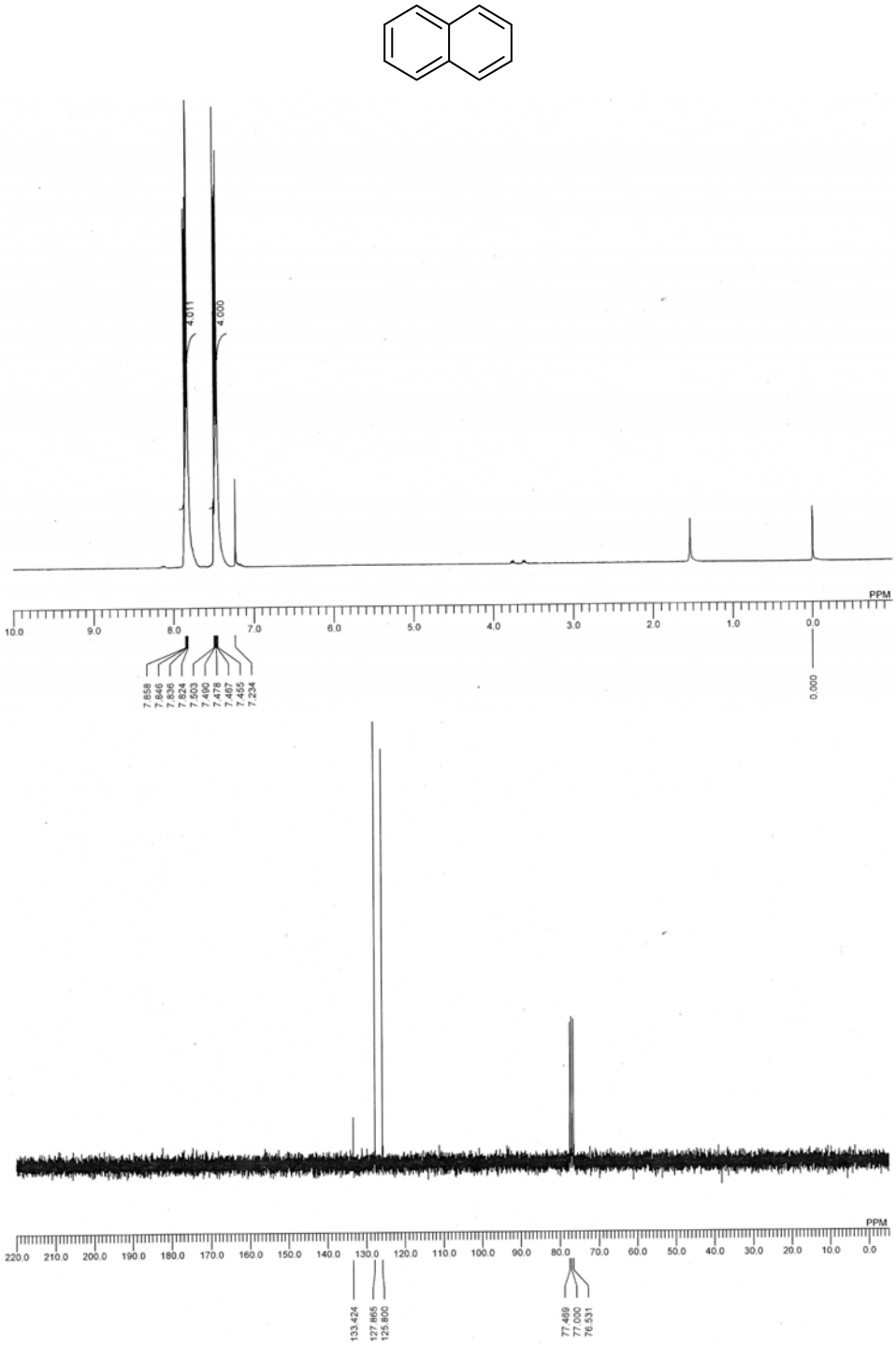
^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 55.3, 114.2, 125.5, 125.69, 125.73, 127.2, 127.3, 128.3, 128.8, 129.1, 133.7, 141.25, 141.33, 141.7, 159.2.

HRMS Calcd for $C_{19}H_{16}O$: 260.1201. Found: 260.1197.

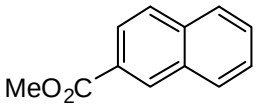


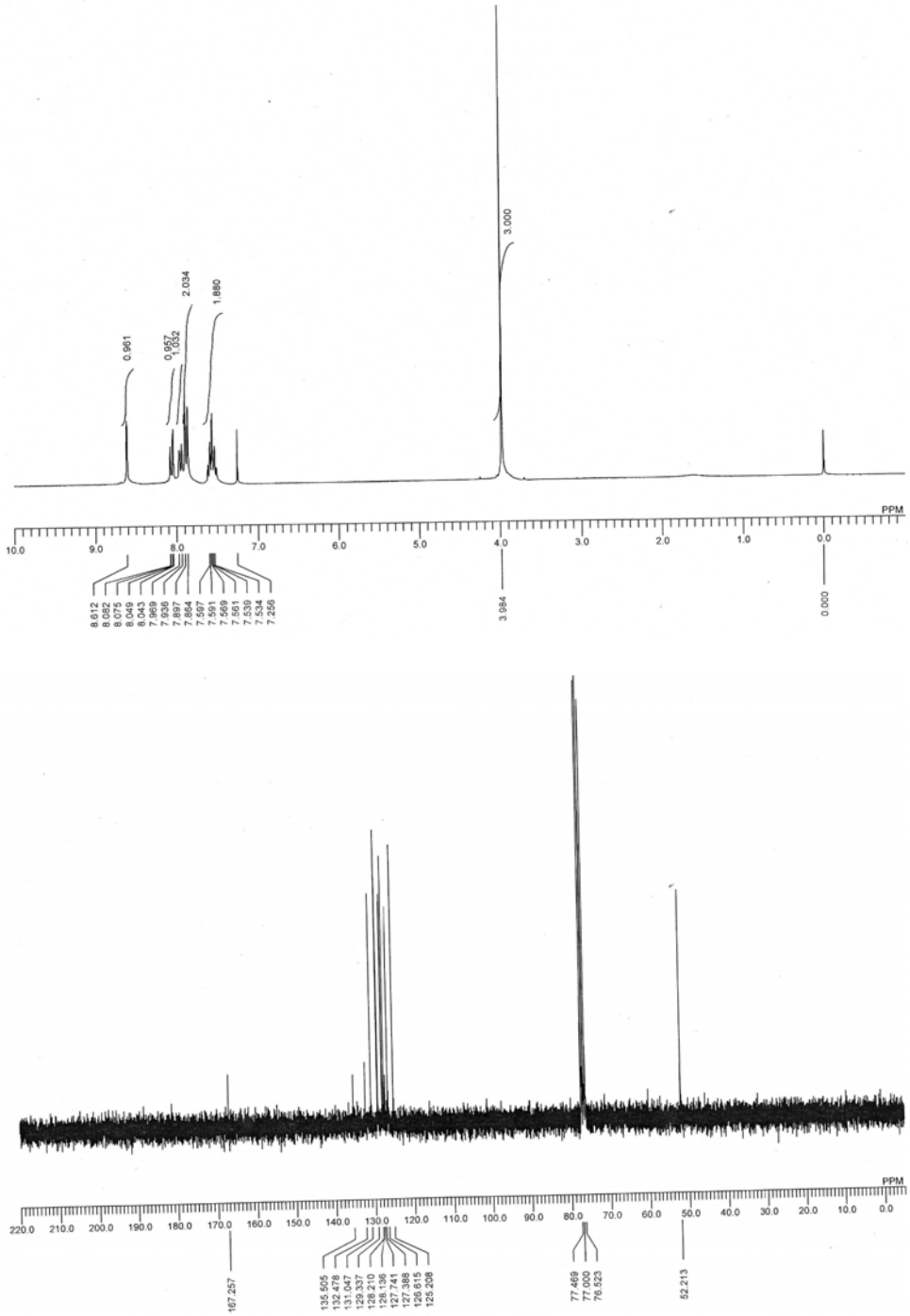
25

Naphthalene (entries 1-5 in Table 2, entry 8 in Table 3)

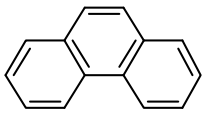


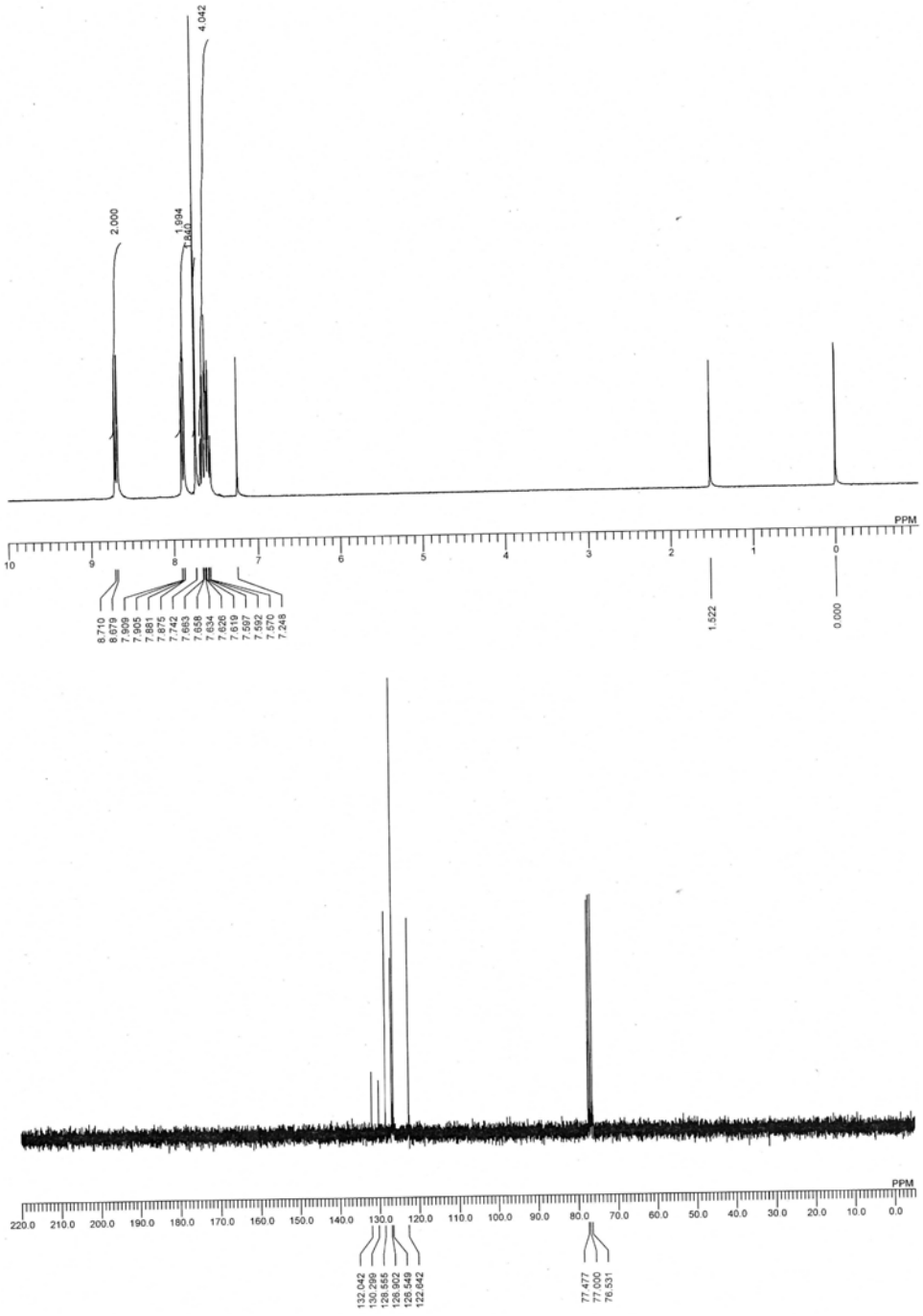
Methyl 2-naphthoate (entry 6 in Table 2)



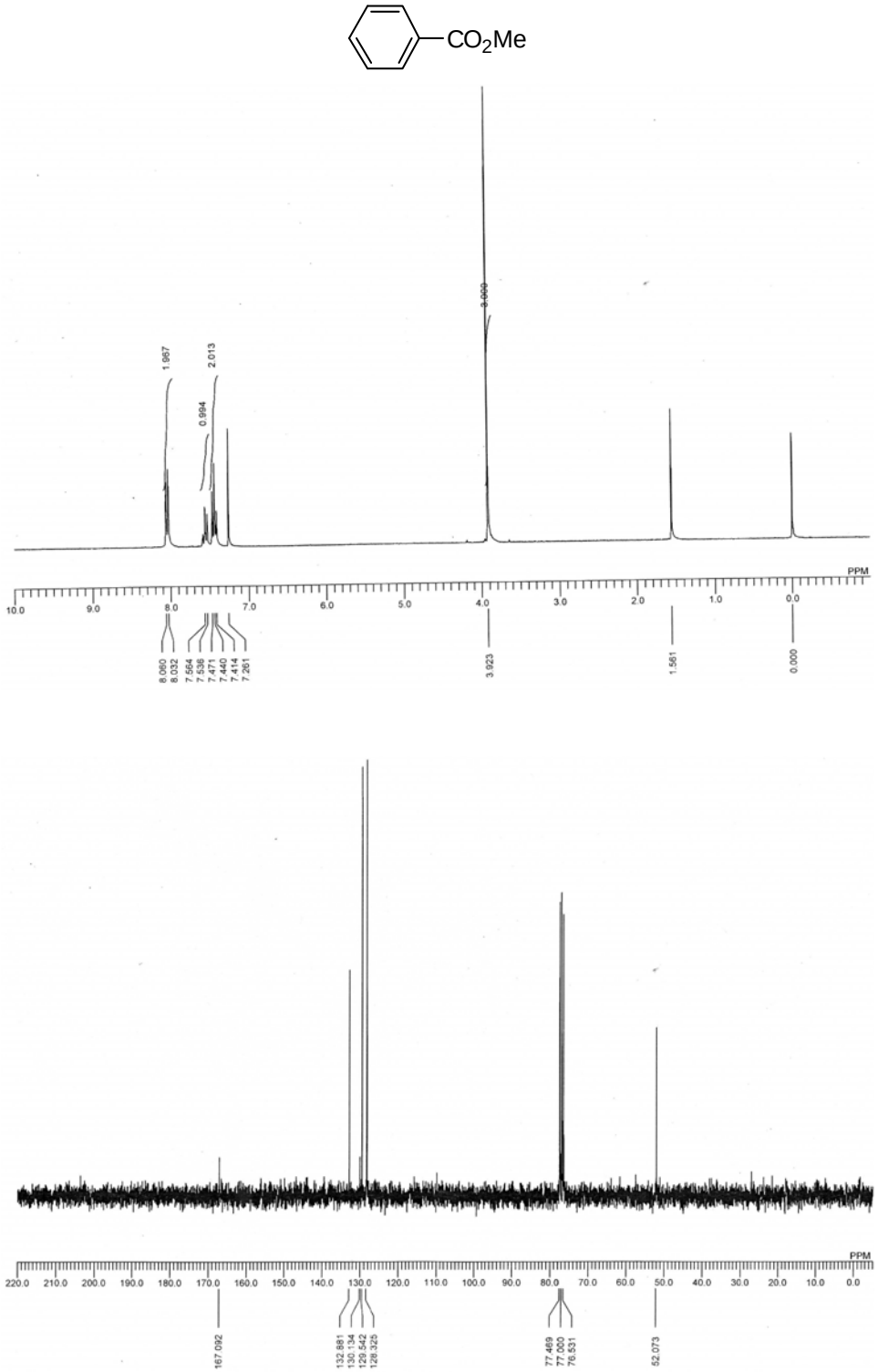


Phenanthrene (entry 7 in Table 2)

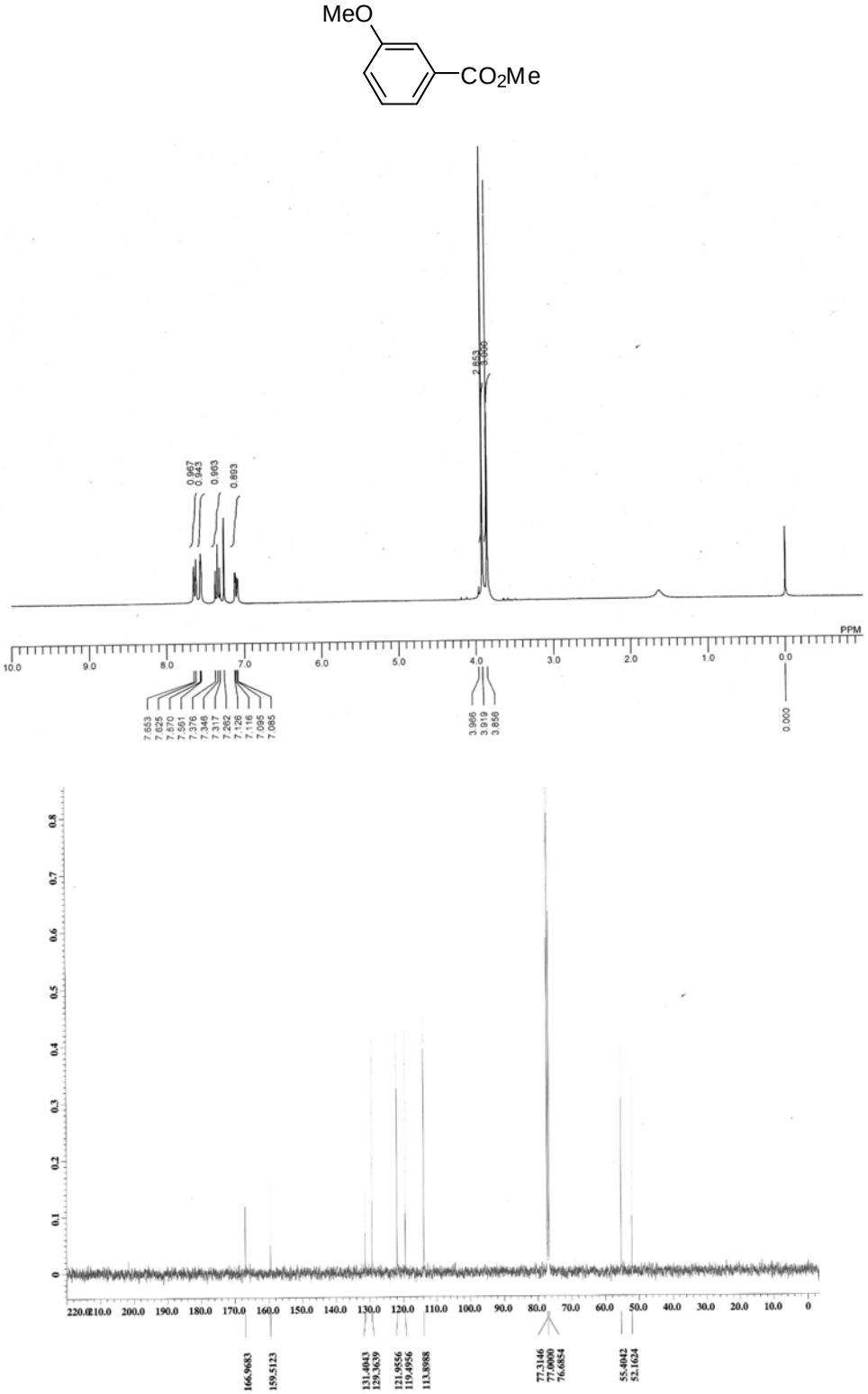




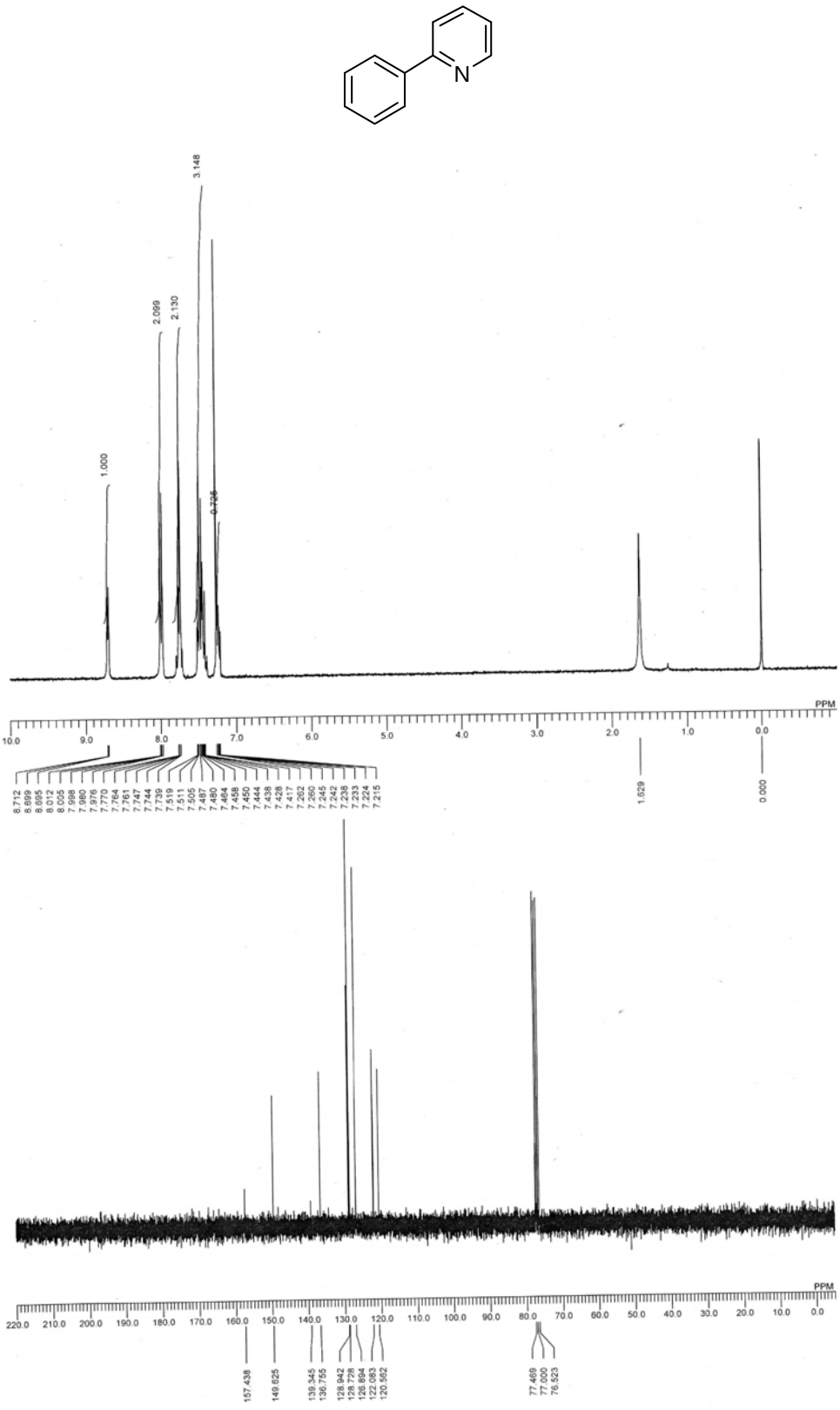
Methyl benzoate (entries 9 and 10 in Table 2)



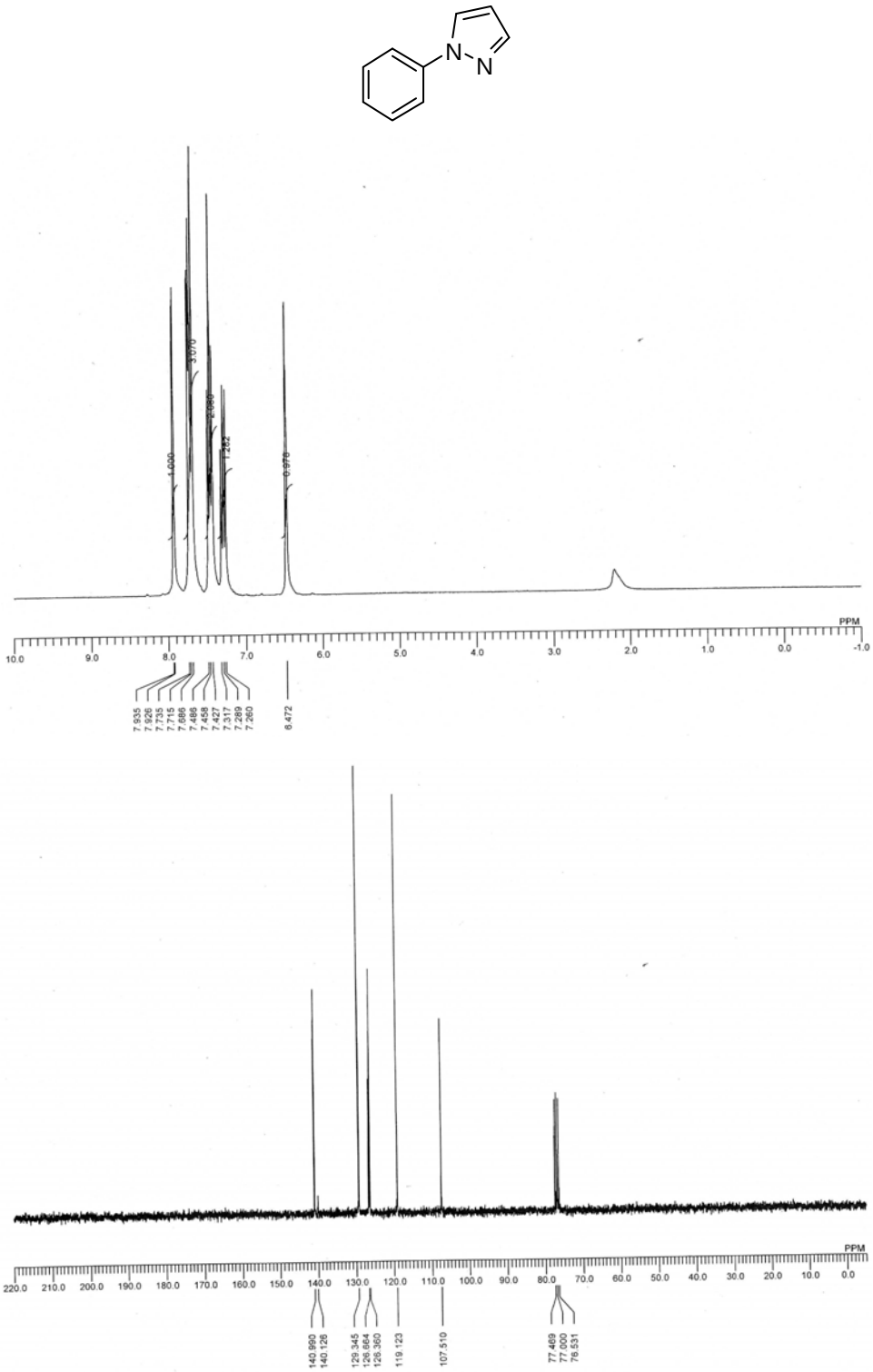
Methyl 3-methoxybenzoate (entry 11 in Table 2)



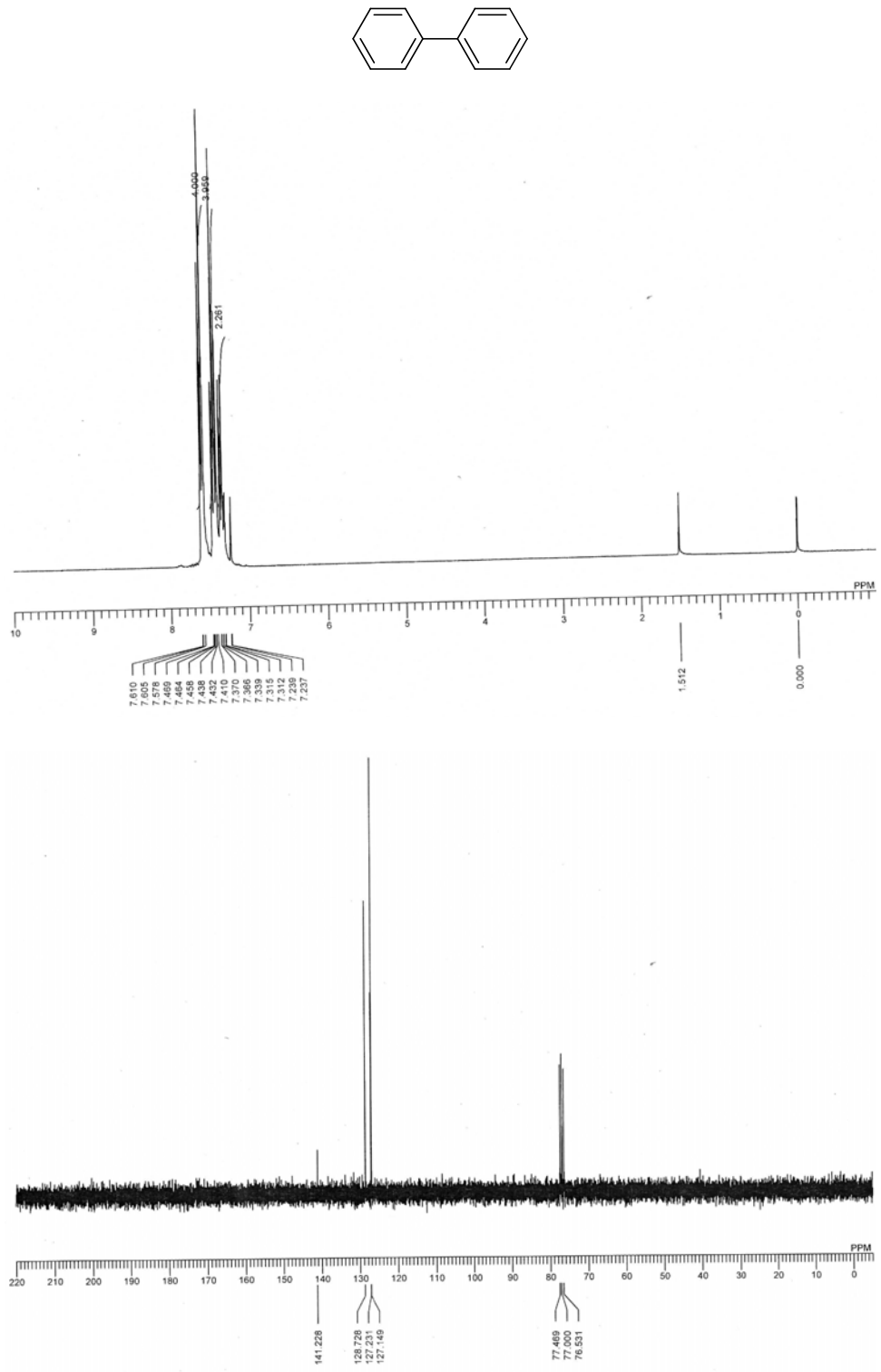
2-Phenylpyridine (entry 12 in Table 2)



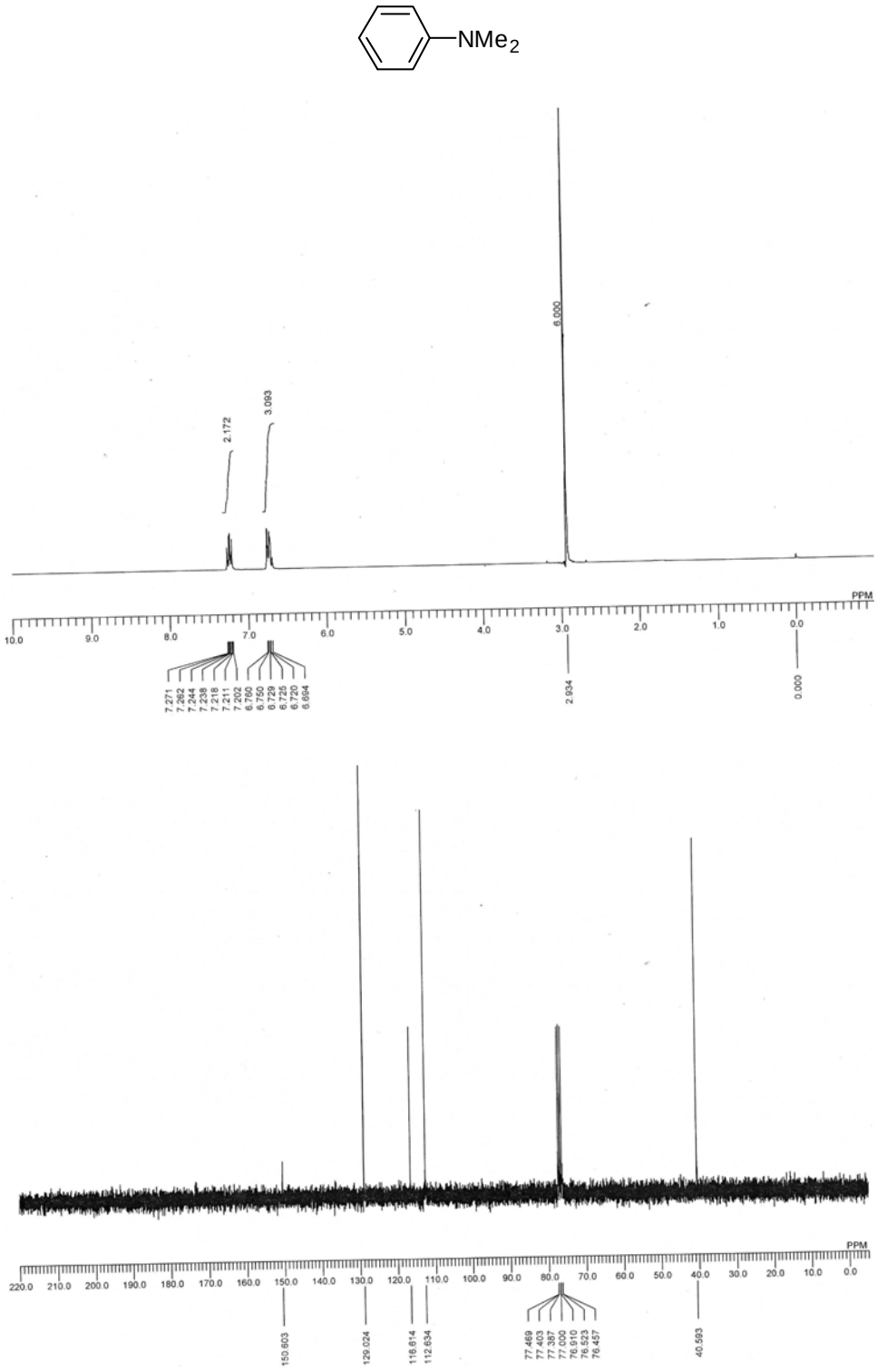
1-Phenyl-1*H*-pyrazole (entry 13 in Table 2)



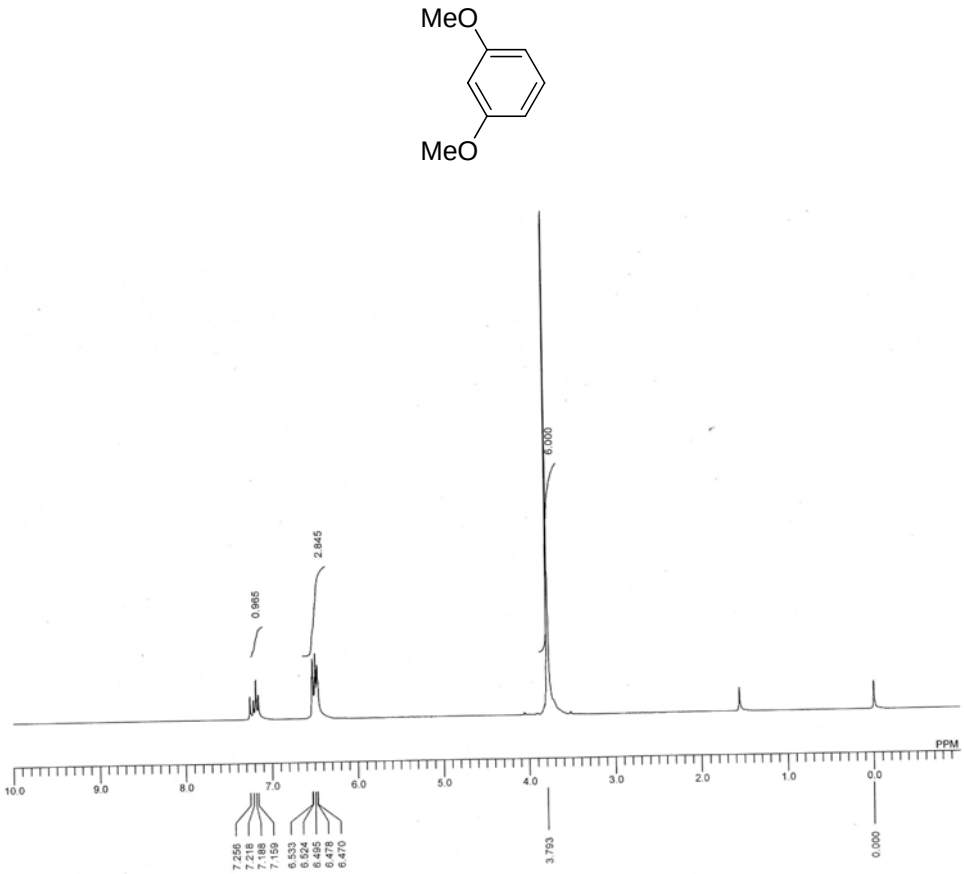
Biphenyl (CAS [92-52-4], entries 1 and 7 in Table 3)

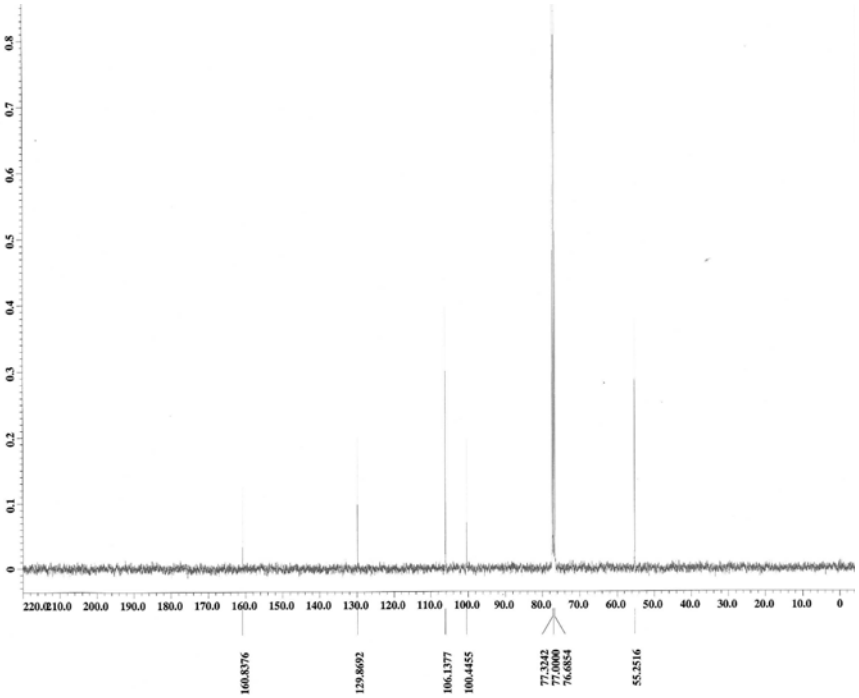


***N*,*N*-Dimethylaniline (CAS [121-69-7], entry 2 in Table 3)**

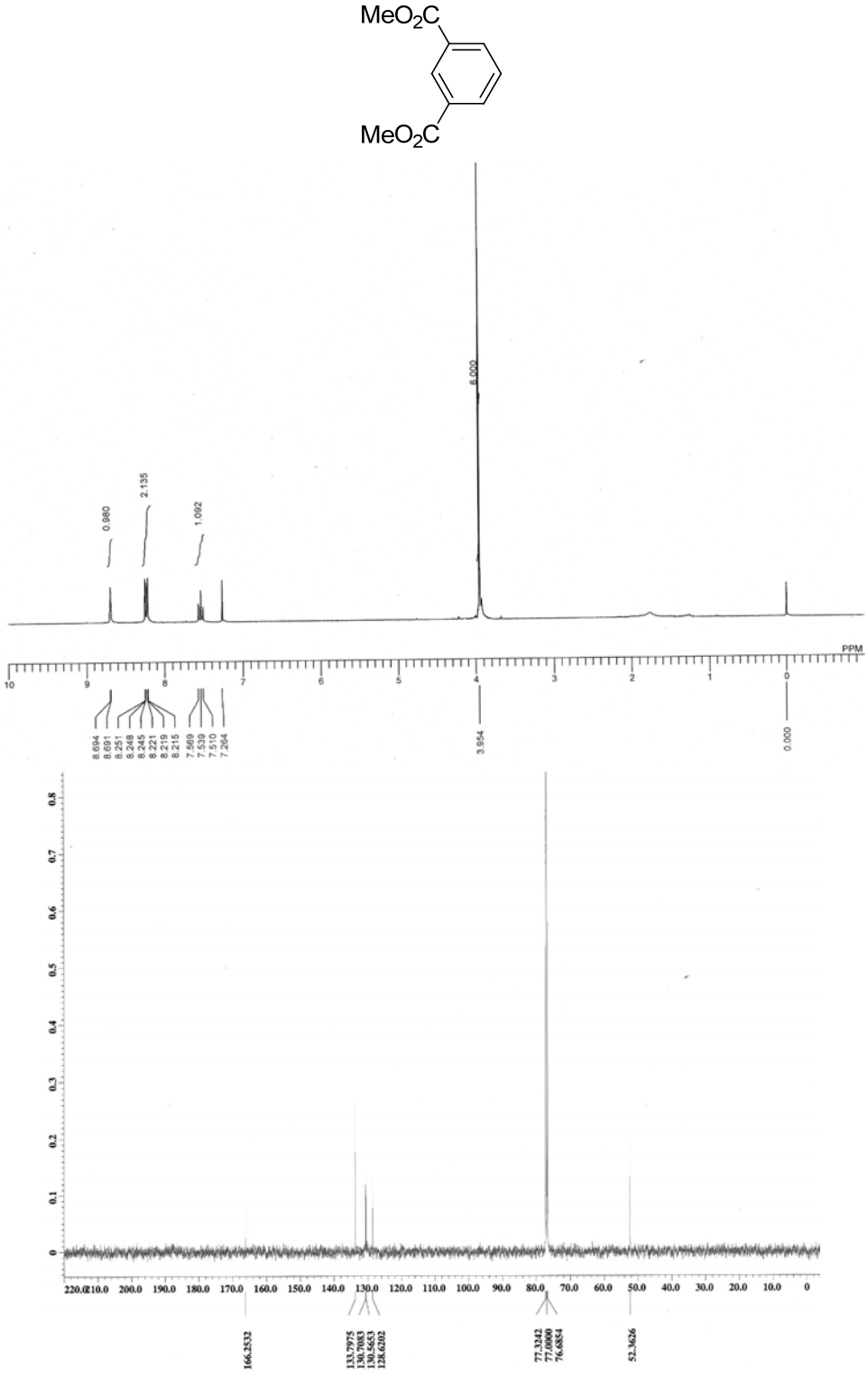


1,3-Dimethoxybenzene (entry 3 in Table 3)

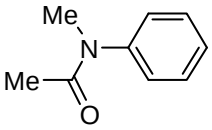


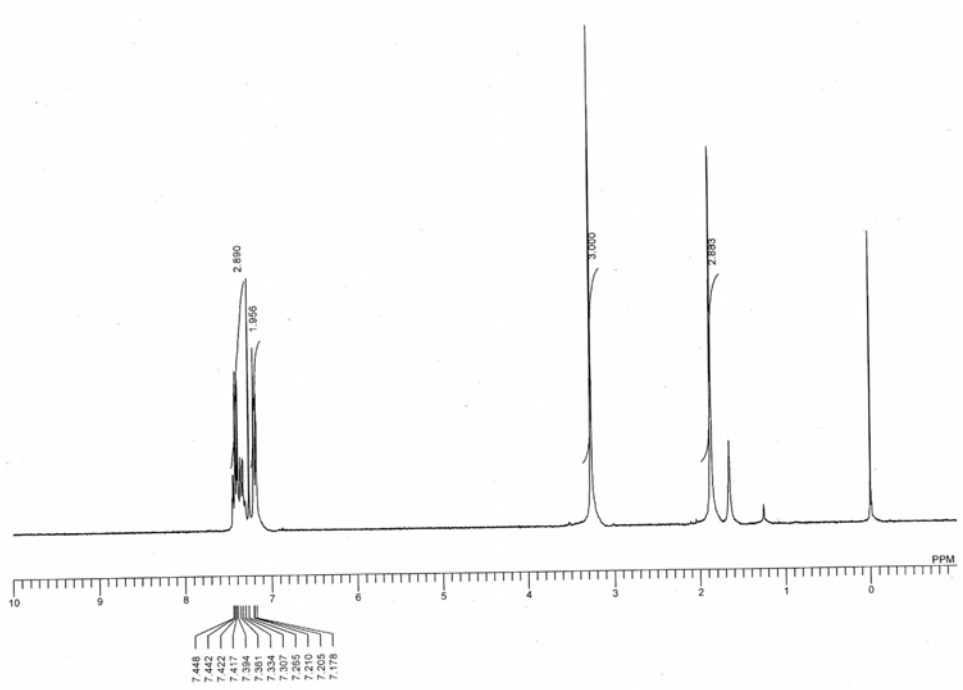


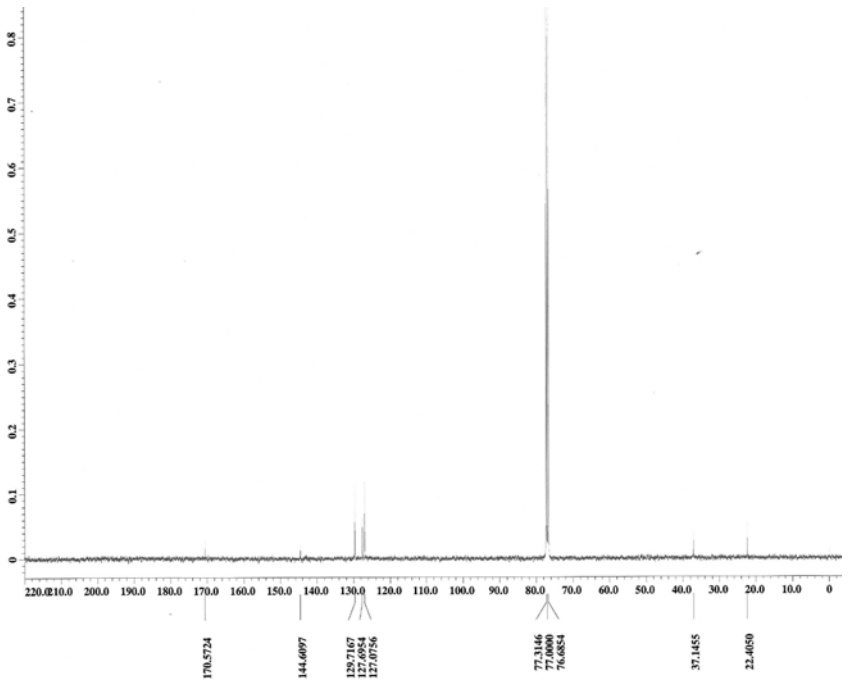
Dimethyl isophthalate (entry 4 in Table 3)



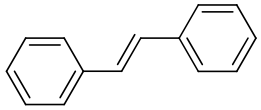
***N*-Methyl-*N*-phenylacetamide (entry 5 in Table 3)**

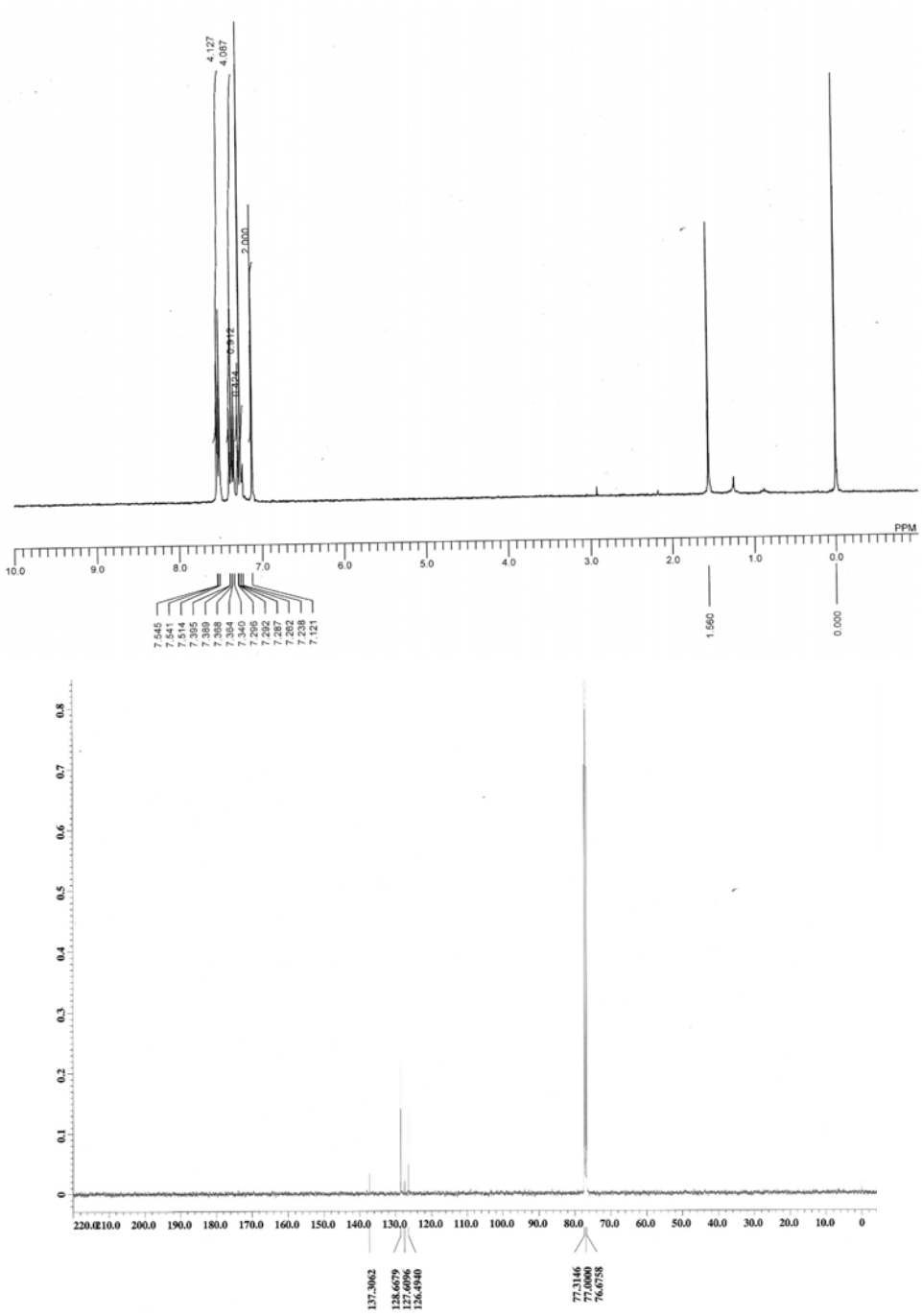




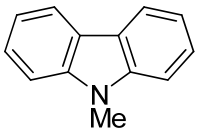


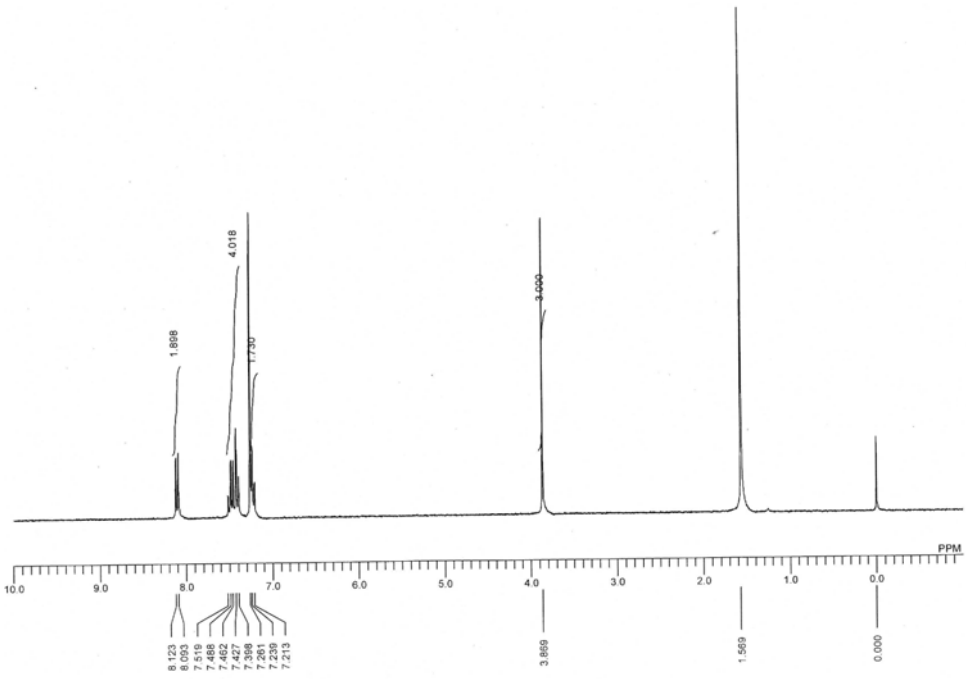
(*E*)-1,2-Diphenylethene (entry 6 in Table 3)

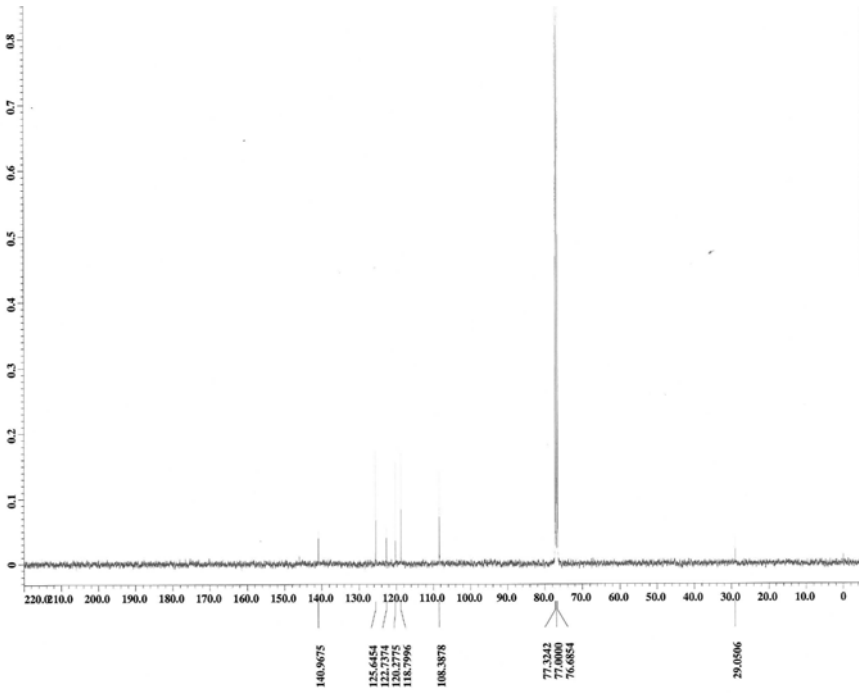




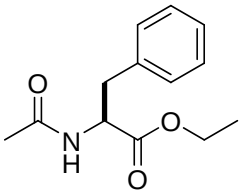
9-Methyl-9*H*-carbazole (entry 9 in Table 3)

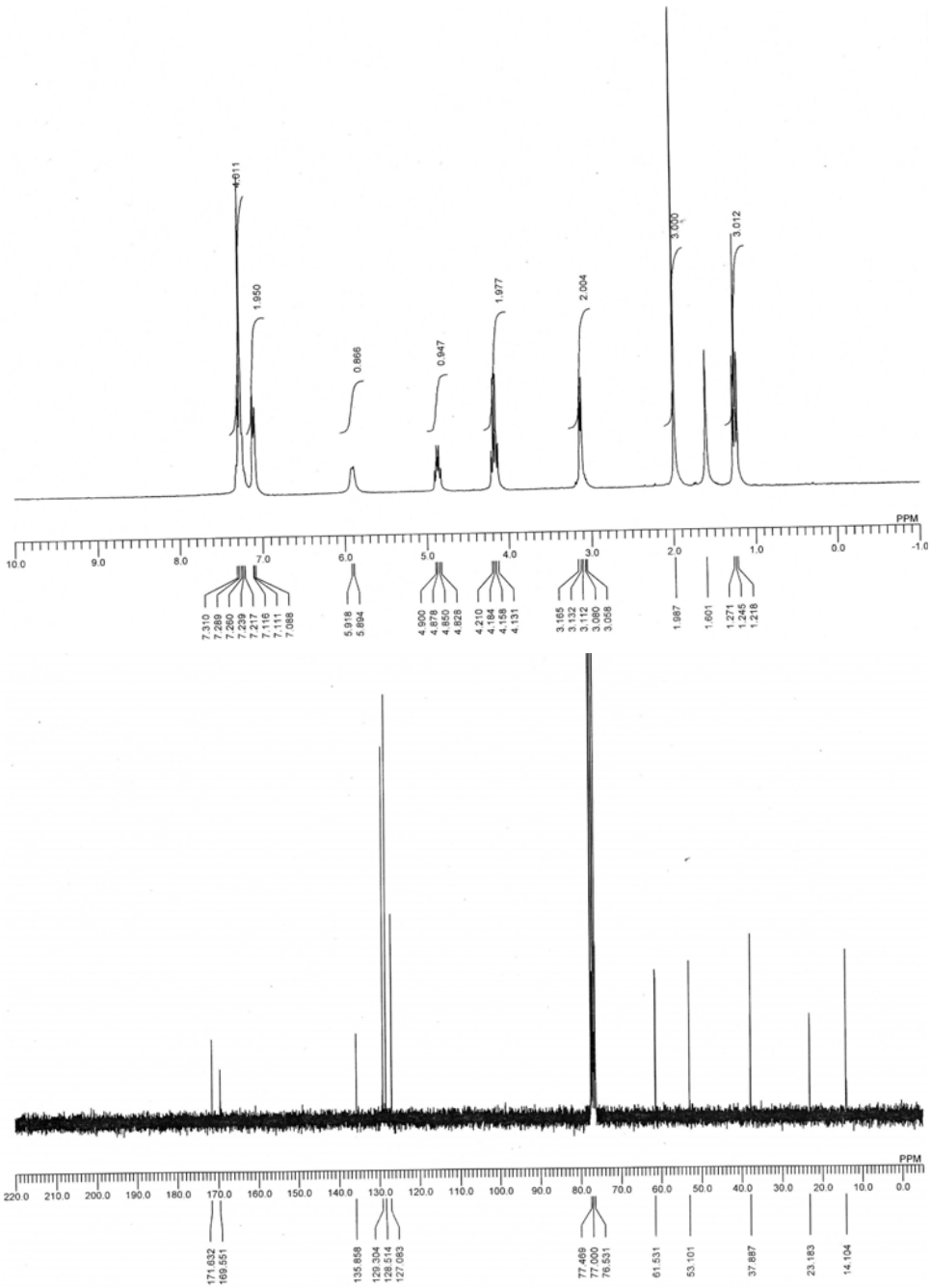




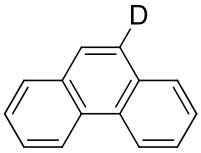


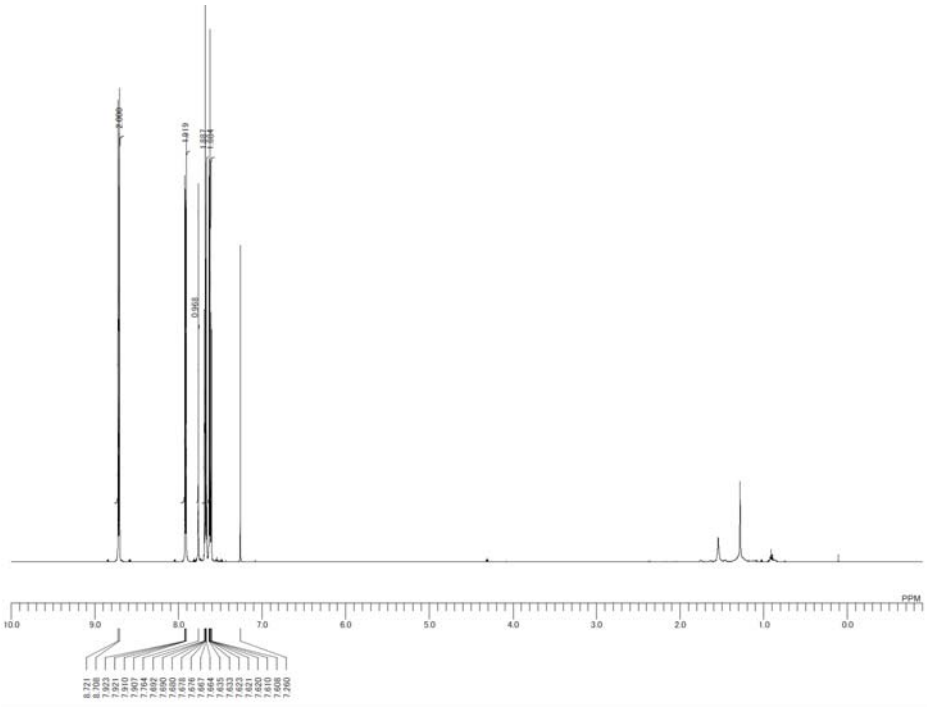
Ethyl 2-acetamido-3-phenylpropanoate (entry 10 in Table 3)

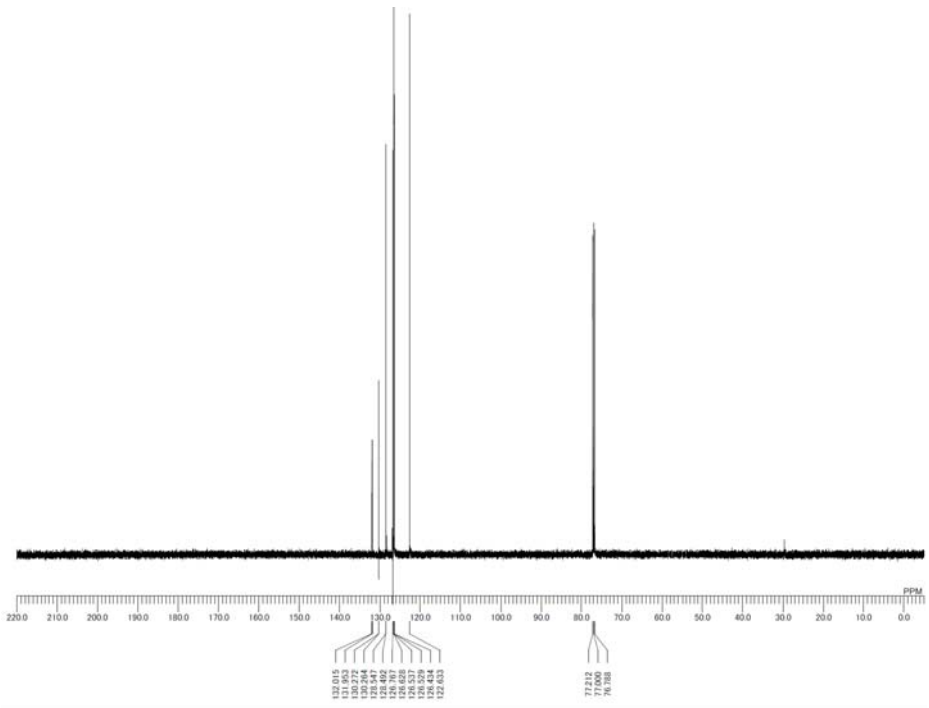




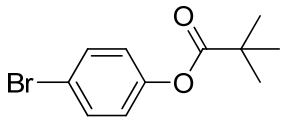
9-Deuteriophenanthrene (eqn(1))

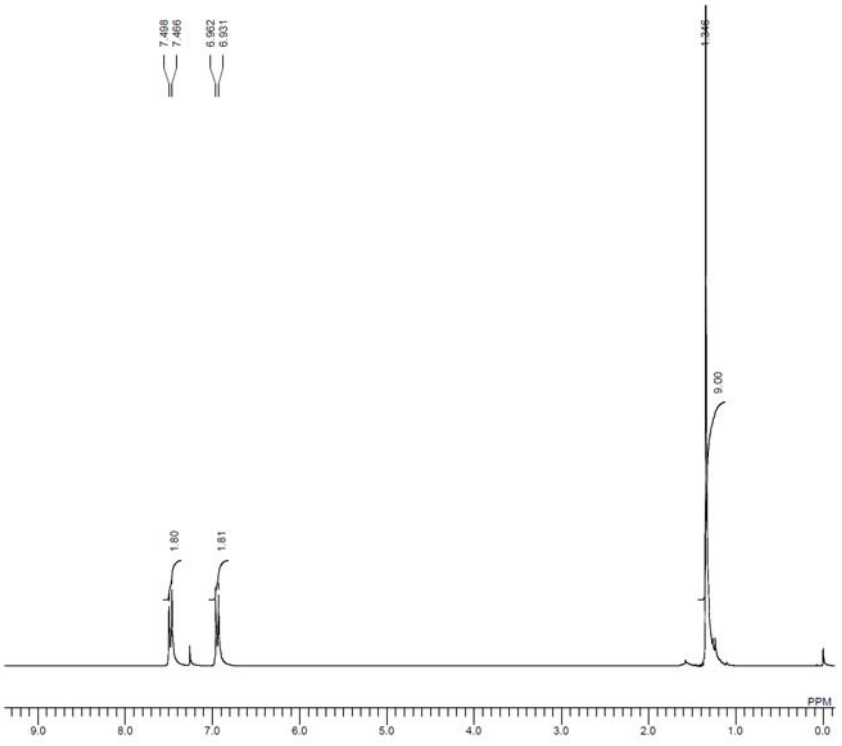


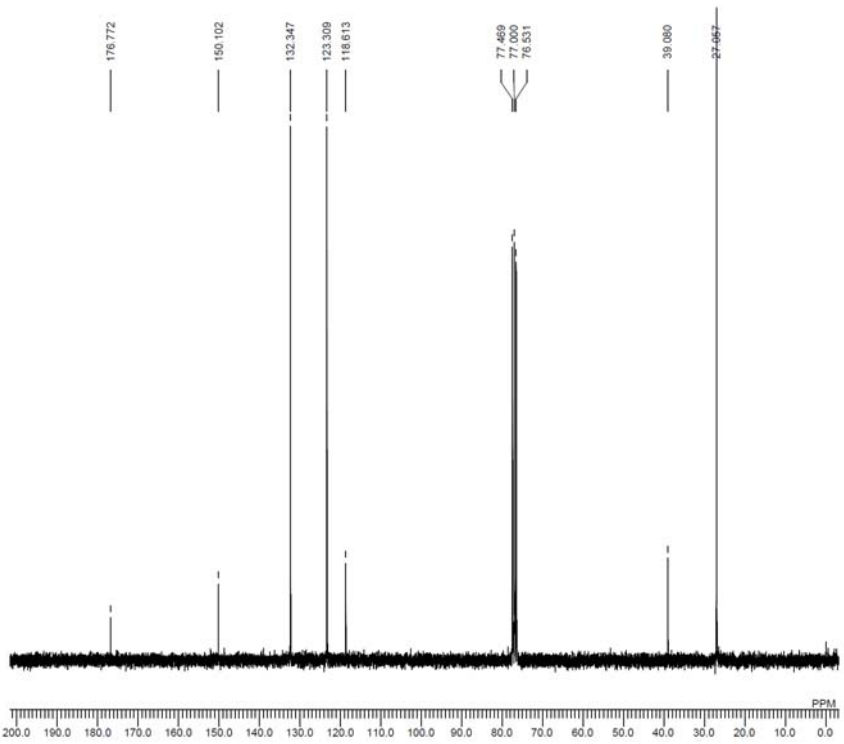




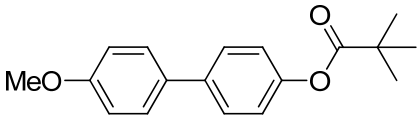
4-Bromophenyl pivalate (24)

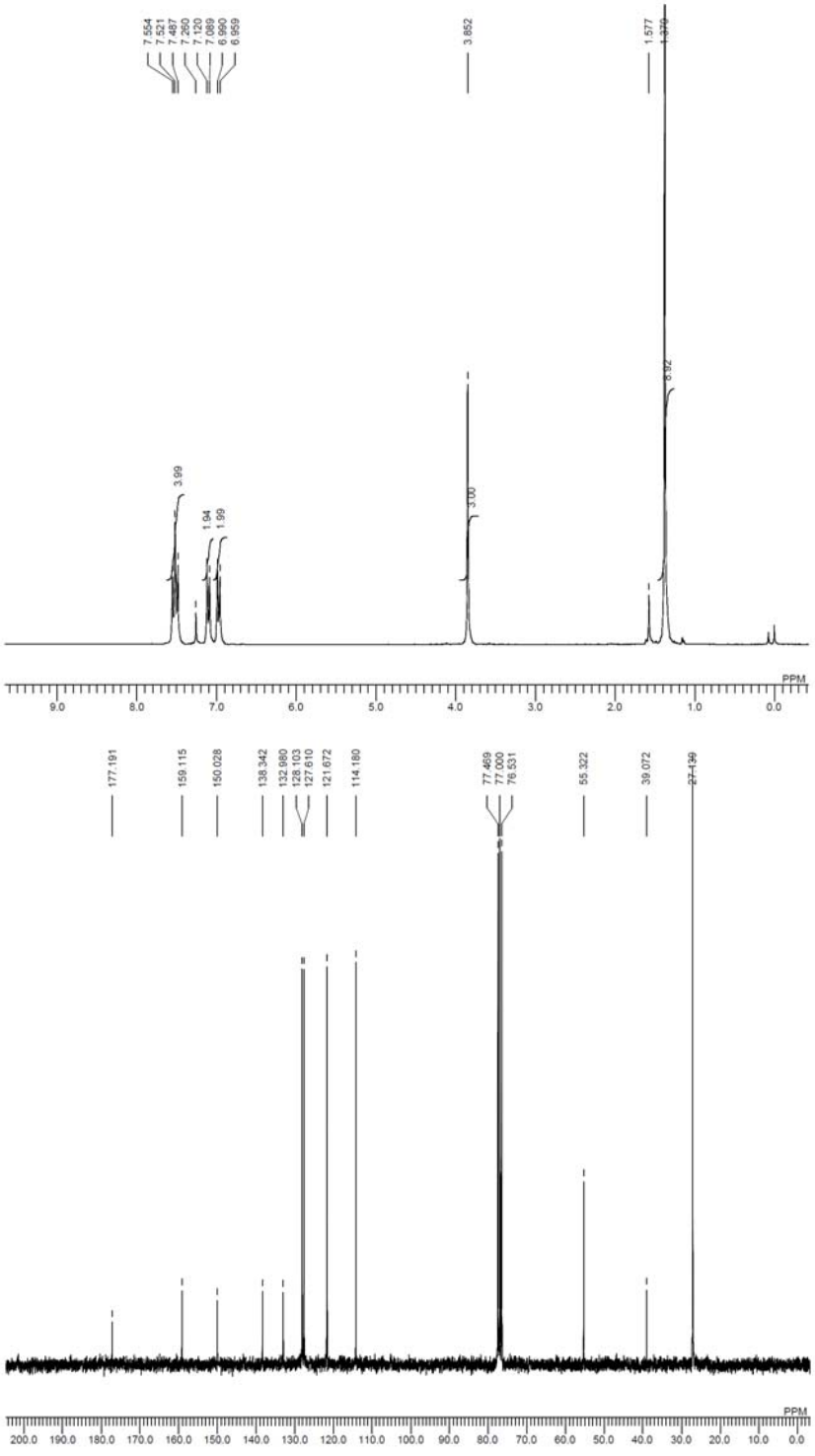




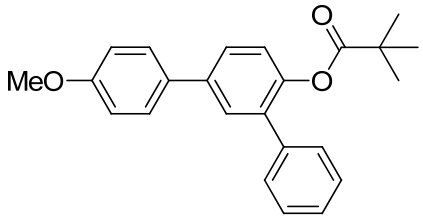


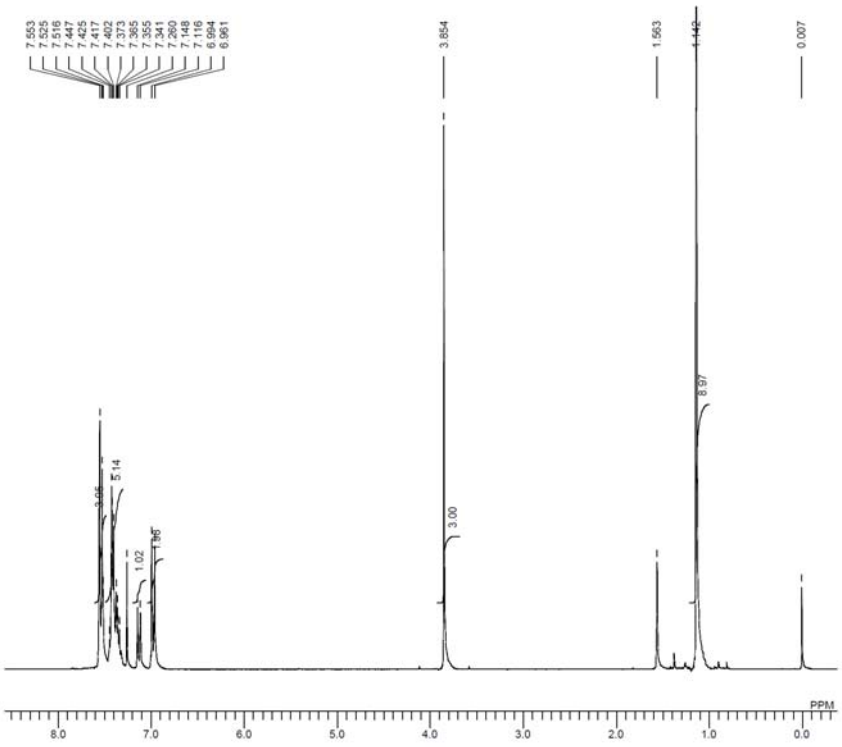
4-Methoxybiphenyl-4'-yl pivalate (25)

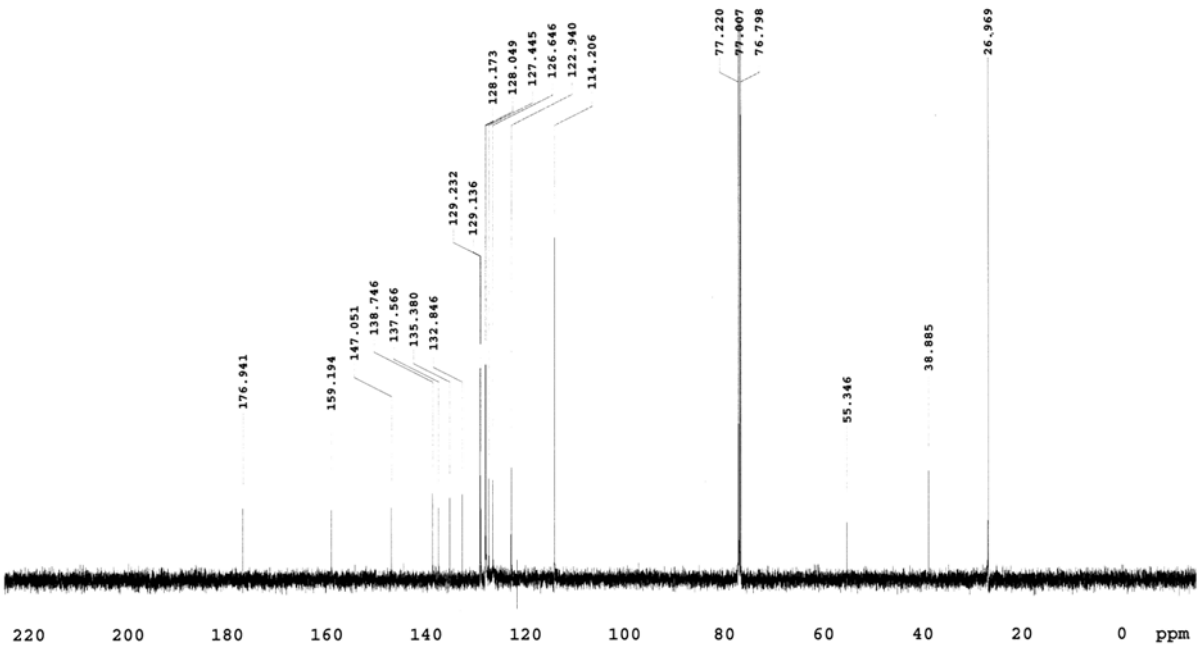




4-Methoxy-1,1';3',1"-terphenyl-4'-yl pivalate (26)







4-Methoxy-1,1';3',1"-terphenyl (27)