Pd-catalyzed Desulfitative Coupling of Arylsulfinates with Arylboronic Acids

Kai Cheng,[a] Hai-Zhu Yu,[b] Baoli Zhao,[a] Sai Hu,[c] Xian-Man Zhang [a] and Chenze Qi*[a]

[a] Zhejiang Key Laboratory of Alternative Technologies for Fine Chemicals Process, Shaoxing University, Shaoxing, 312000, China. Tel: +86-575-88345681; Fax: +86-575-88345681.
[b] Department of Polymer Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China.
[c] College of Materials Science and Chemical Engineering, Ningbo University, Ningbo, 310014, China.

qichenze@163.com.

Supporting Materials

Content

General ……S1

Typical procedure for the product……S1

Characterization data of the product……S2

References……S16

General

All solvents were purified and dried according to standard methods prior to use. 1H NMR spectra were recorded on a Bruker AVANCE III 400 M Hz spectrometer using TMS as internal standard. Proton chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) with the residual solvent peak as the internal reference. Multiplicities are reported as: singlet (s), doublet (d), triplet (t) and multiplet (m). GC Mass spectroscopy data were collected on an Agilent 6890/5975 GC/MS instrument with a programmable split/splitless injector. HRMS (EI) data were collected on High Resolution mass spectrometer (ion trap). Arylsulfinate salts were obtained from the corresponding arylsulfonyl chlorides. Other substrates and catalysts were commercially available and used without additional purification.

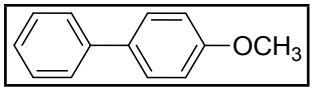
Typical procedure for the products:

A mixture of arylsulfinate salt (0.50 mmol), $PdCl_2$ (5 mol%) $Cu(OTf)_2$ (10 mol%) and arylboronic acid (0.60 mmol) was stirred in the mixture solvent of DMSO (1.0 ml) and acetonitrile (1.0 ml) at 90^{o}C for 2.0 hours. After cooling down to room temperature, the insoluble was first removed by filtration and then the reaction mixture was extracted with diethyl ether (Et_2O) (2 ml) for three times. The combined organic layer was washed with water, saturated brine, and then dried over anhydrous sodium sulfate. Solvent was removed under a reduced pressure. The cross-coupling products were purified by silica gel chromatography with a mixture of petroleum ether and ethyl acetate. The cross-coupling products were confirmed by melting point and spectroscopic (^{1}H NMR, ^{13}C NMR and HRMS-EI) analysis, which were all consistent with the literature results.

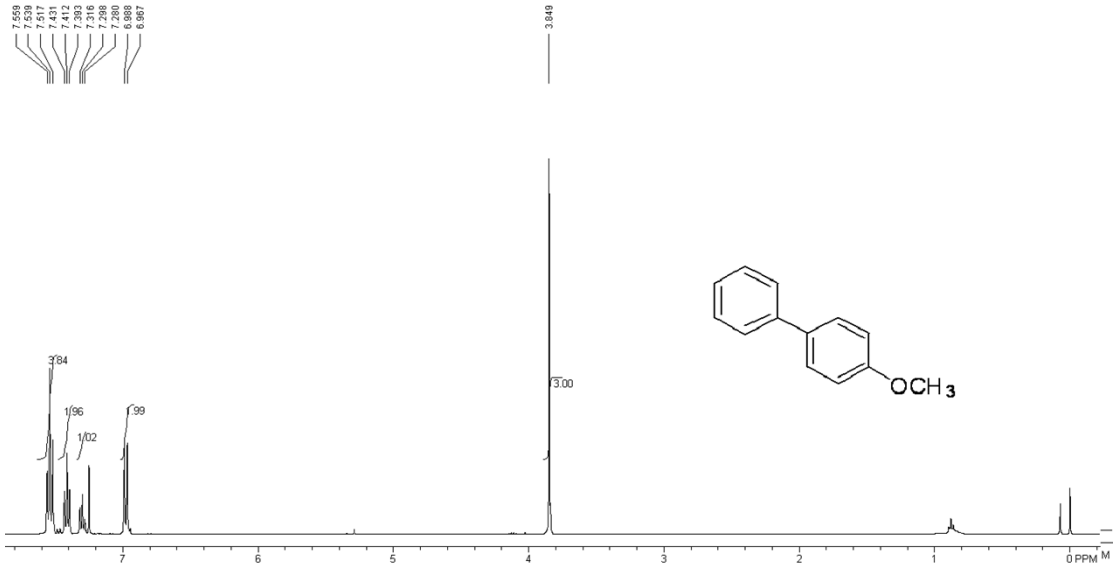
.

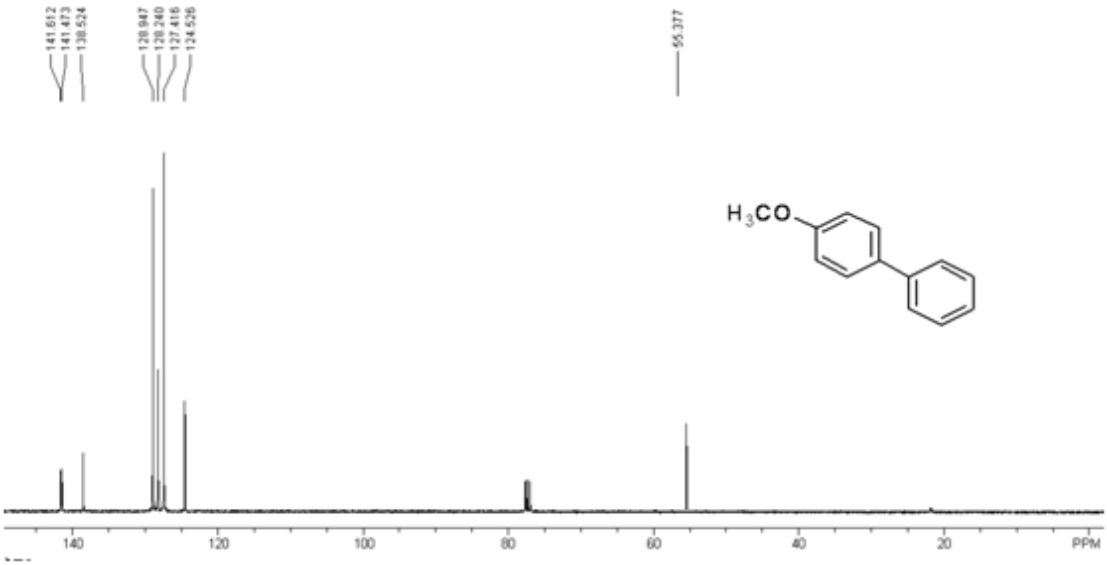
Characterization data of the product

4-methoxy-1,1'-biphenyl (T 4−1, CAS no. 613-37-6)

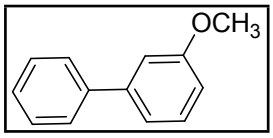


White solid, m.p. 88-90°C(lit.[1] mp 88-89°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.54 (t, *J* = 8.8 Hz, 4 H), 7.39 (t, *J* = 7.6 Hz, 2 H), 7.30 (t, *J* = 7.6 Hz, 1 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 3.81 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.6, 141.5, 138.5, 128.9, 128.2, 127.4, 124.5, 55.4. HRMS (EI) Calcd for $C_{13}H_{12}O$ (M^+) 184.0888, Found 184.0884.

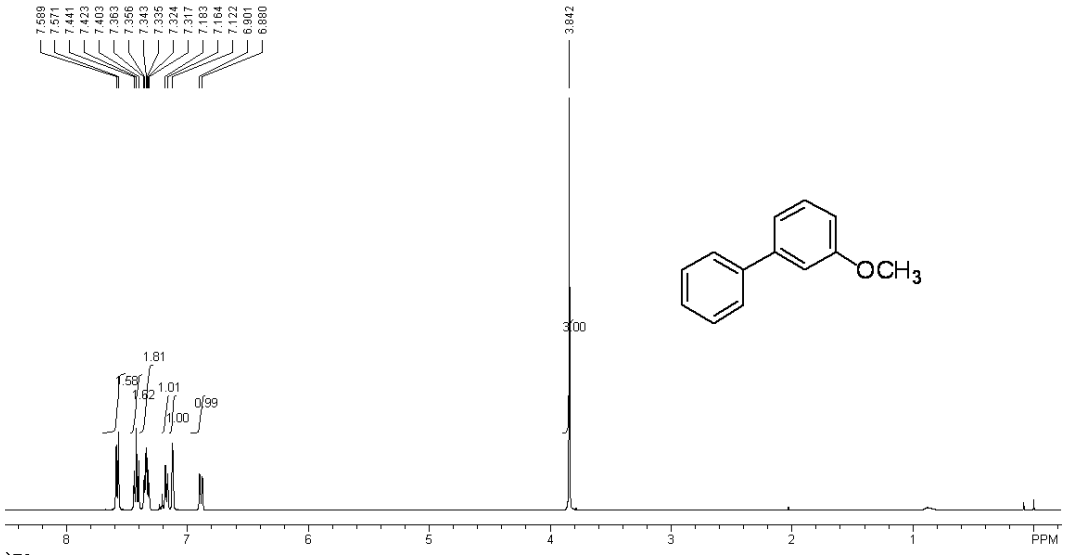


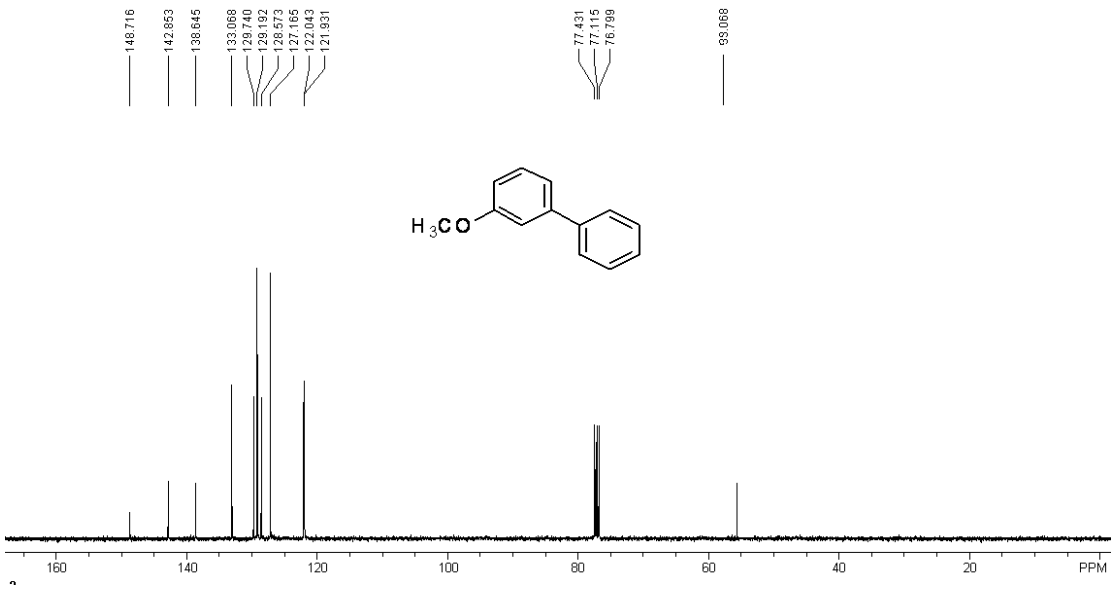


3-methoxy-1,1'-biphenyl (T 4−2, CAS no. 2113-56-6)

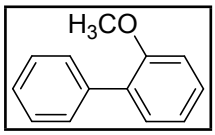


White solid, m.p. 83-84°C(lit.[1] mp 82-83°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, *J* = 7.2 Hz, 2 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.32-7.36 (m, 2 H), 7.17 (d, *J* = 7.6 Hz, 1 H), 7.12 (s, 1 H), 6.89 (d, *J* = 8.4 Hz, 1 H), 3.84 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 148.7, 142.9, 138.6, 133.0, 129.7, 129.2, 128.5, 127.2, 122.0, 121.8, 55.0. HRMS (EI) Calcd for $C_{13}H_{12}O$ (M^+) 184.0888, Found 184.0881.

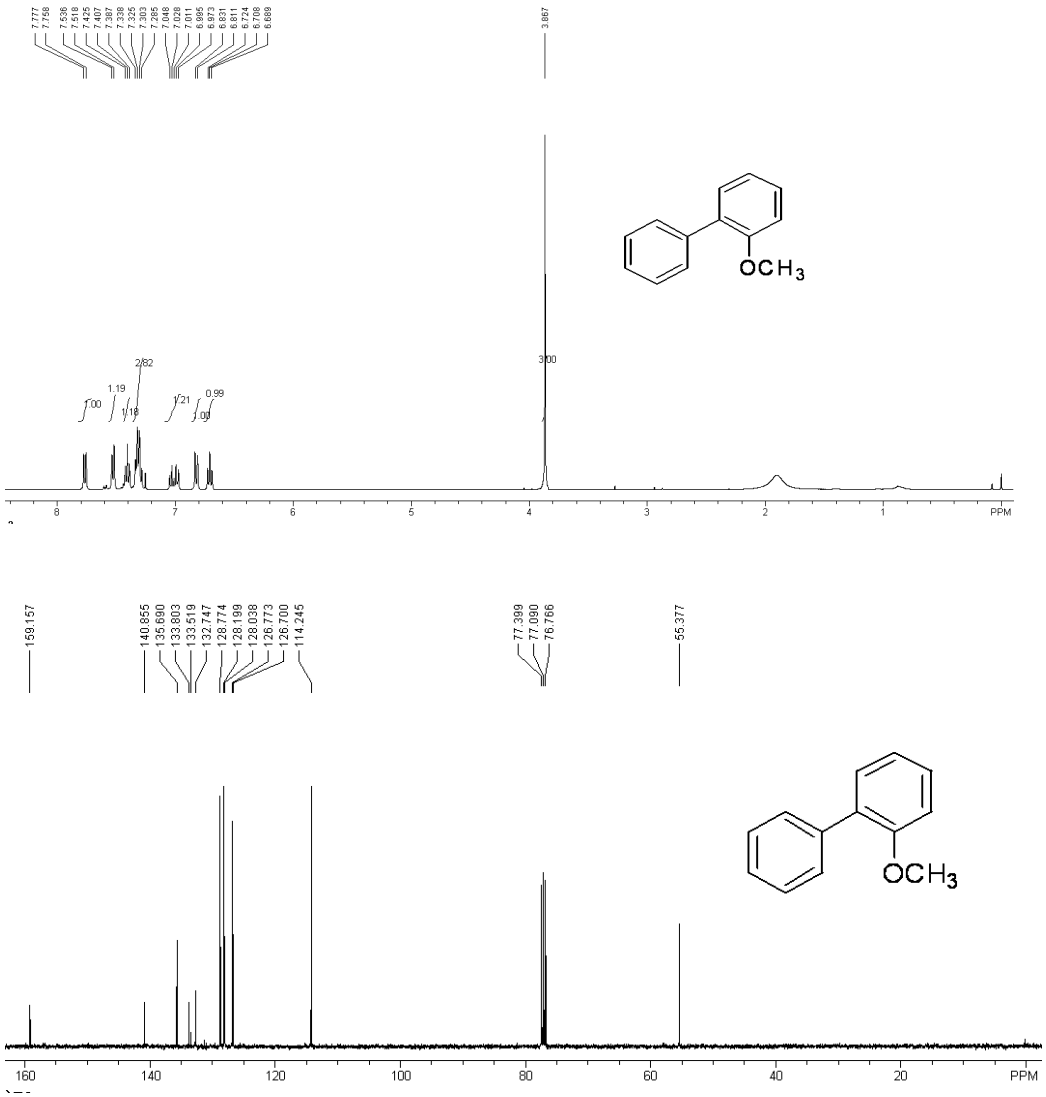




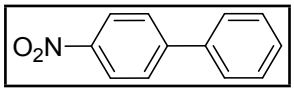
2-methoxy-1,1'-biphenyl (T 4−3, CAS no. 86-26-0)



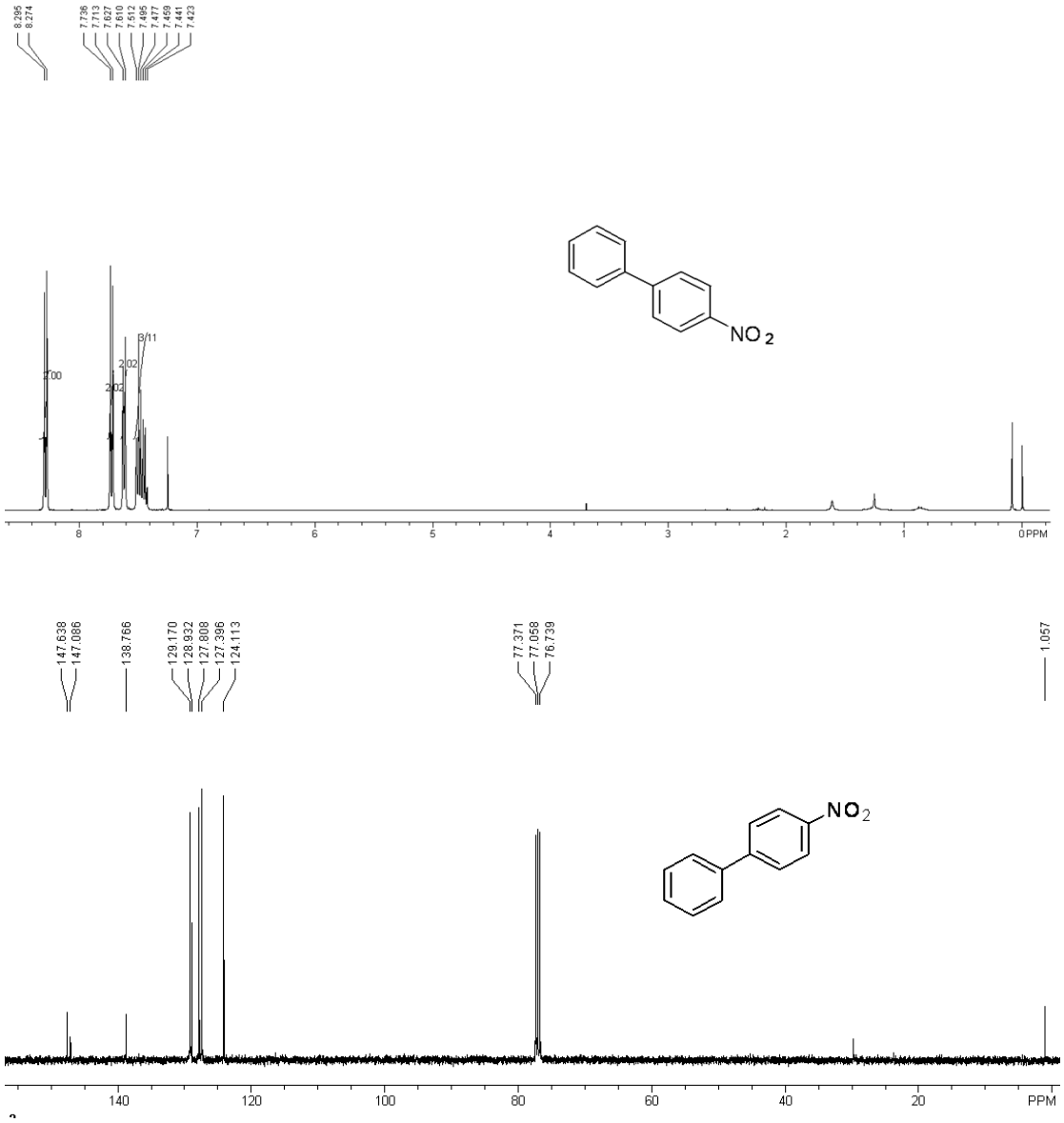
White solid, m.p. 31-32°C(lit.[1] mp 31-32°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.77 (d, *J* = 7.6 Hz, 1 H), 7.53 (d, *J* = 7.2 Hz, 1 H), 7.41 (t, *J* = 7.6 Hz, 1 H), 7.29-7.34 (m, 3 H), 6.97-7.05 (m, 1 H), 6.82 (d, *J* = 8.0 Hz, 1 H), 6.71 (t, *J* = 7.2 Hz, 1 H), 3.87 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 159.2, 140.9, 135.7, 133.8, 133.5, 132.7, 128.8, 128.2, 128.0, 126.8, 126.7, 114.2, 55.4. HRMS (EI) Calcd for $C_{13}H_{12}O$ (M^+) 184.0888, Found 184.0891.



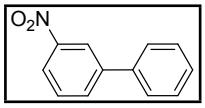
4-nitro-1,1'-biphenyl (T 4−4, CAS no. 92-93-3)



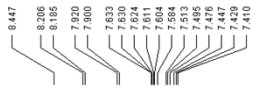
White solid, m.p. 115-117°C(lit.[1] mp 115-116°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.28 (d, *J* = 8.4 Hz, 2 H), 7.72 (d, *J* = 9.2 Hz, 2 H), 7.62 (d, *J* = 6.8 Hz, 2 H), 7.42-7.51 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 147.6, 147.1, 138.8, 129.2, 128.9, 127.8, 127.4, 124.1. HRMS (EI) Calcd for $C_{12}H_9NO_2$ (M^+) 199.0633, Found 199.0634.

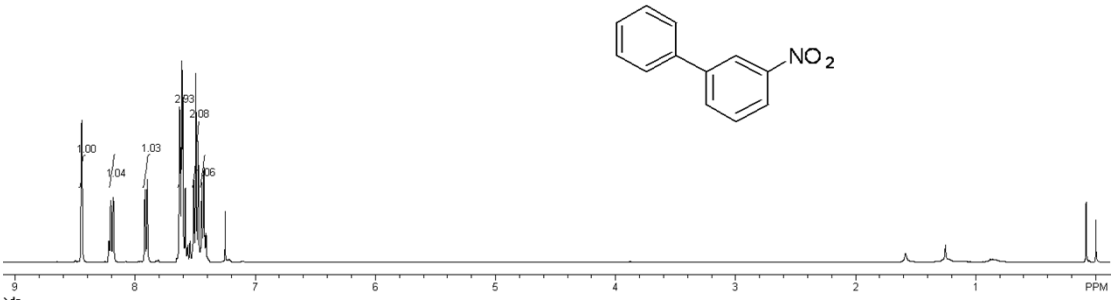


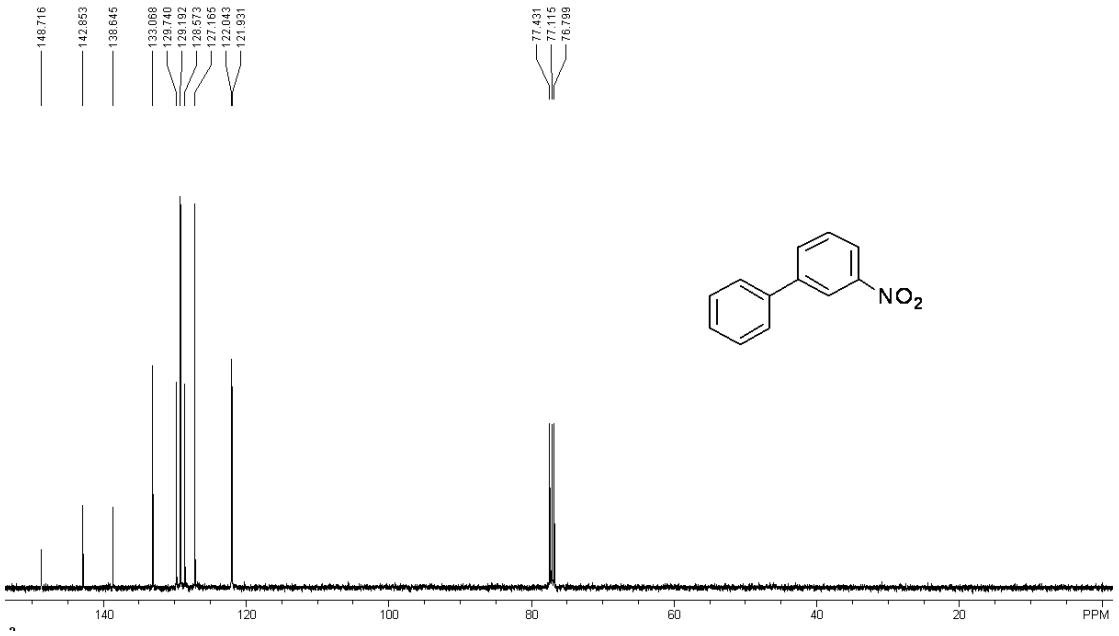
3-nitro-1,1'-biphenyl (T 4−5, CAS no.2113-58-8)



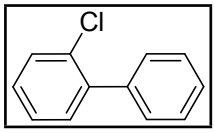
White solid, m.p. 59-60°C(lit.[1] mp 59-60°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.45 (s, 1 H), 8.19 (d, *J* = 8.4 Hz, 1 H), 7.91 (t, *J* = 8.0 Hz, 1 H), 7.58-7.63 (m, 3 H), 7.50 (t, *J* = 7.2 Hz, 2 H), 7.43 (t, *J* = 7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 148.7, 142.9, 138.6, 133.0, 129.7, 129.2, 128.6, 127.2, 122.0, 121.9. HRMS (EI) Calcd for $C_{12}H_9NO_2$ (M^+) 199.0633, Found 199.0631.



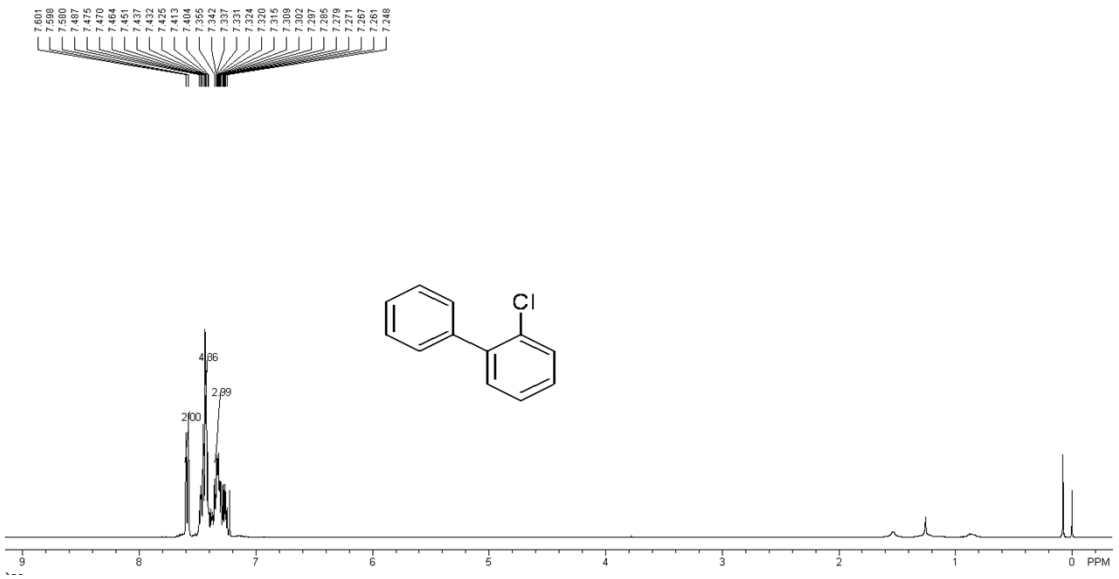


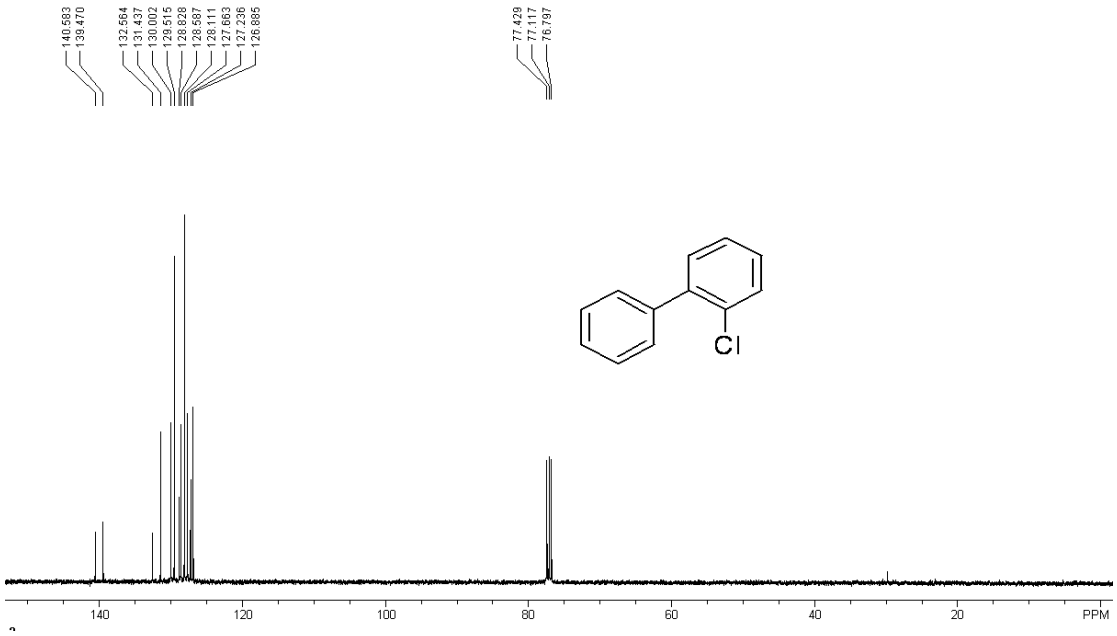


2-chloro-1,1'-biphenyl (T 4−6, CAS no.2051-60-7)

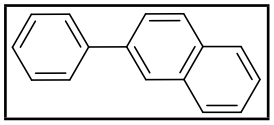


White solid, m.p. 33-34°C(lit.[2] mp 34°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 (d, *J* = 8.4 Hz, 2 H), 7.40-7.49 (m, 4 H), 7.25-7.36 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 140.6, 139.5, 132.6, 131.4, 130.0, 129.5, 128.8, 128.6, 128.1, 127.7, 127.2, 126.9. HRMS (EI) Calcd for $C_{12}H_9Cl$ (M^+) 188.0393, Found 188.0391.

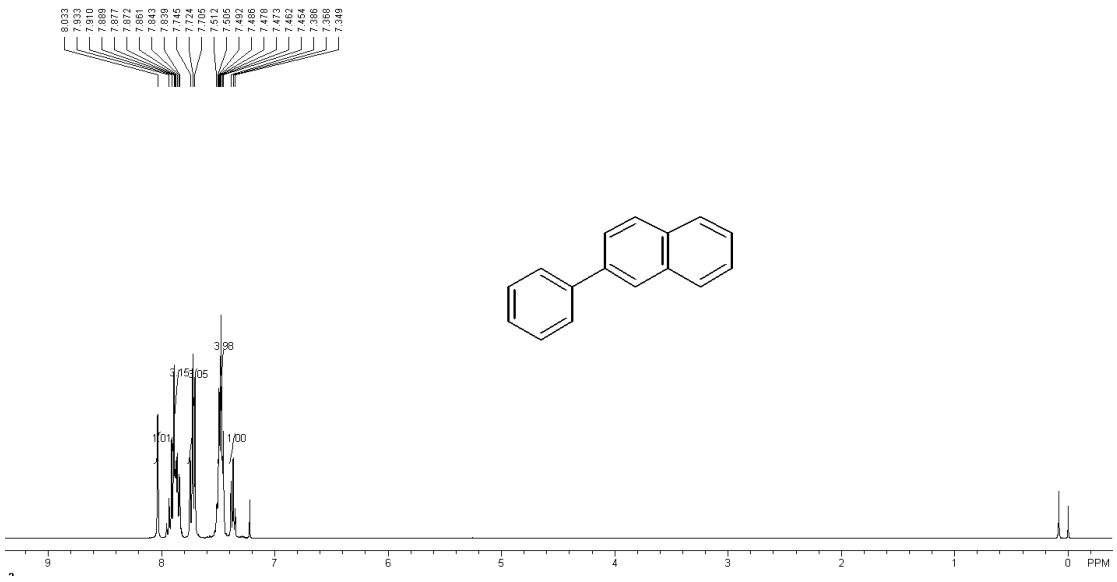




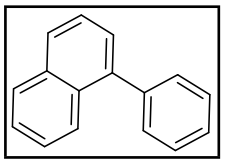
2-phenylnaphthalene (T 4−7, CAS no.612-94-2)



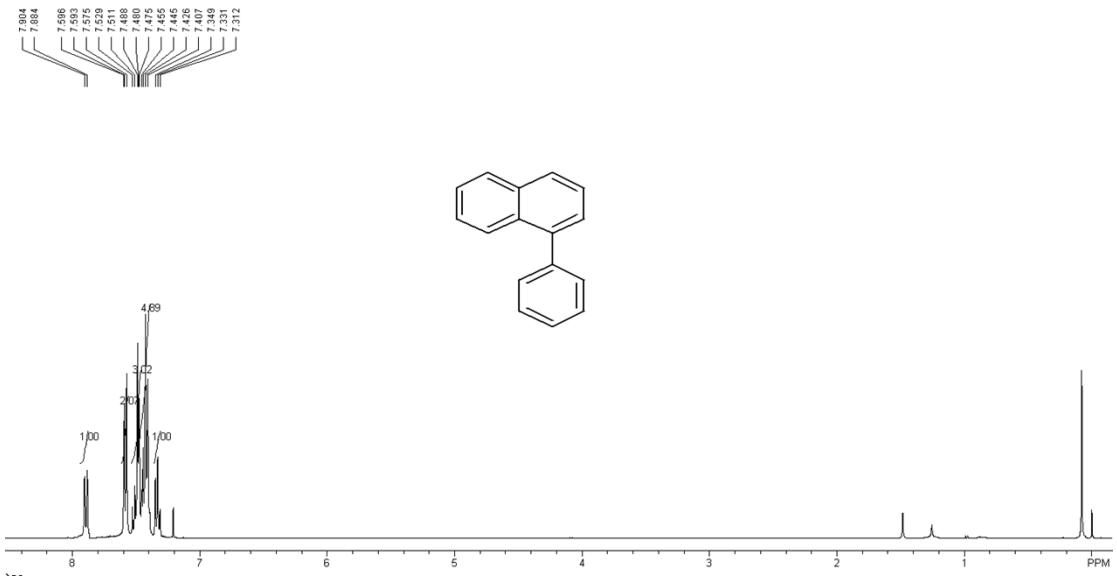
White solid, m.p. 96-97°C(lit.[2] mp 96-97°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.03 (s, 1 H), 7.84-7.93 (m, 3 H), 7.72 (t, J = 8.0 Hz, 3 H), 7.45-7.51 (m, 4 H), 7.37 (t, J = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ141.4, 138.9, 134.1, 133.8, 133.0, 129.2, 128.8, 128.6, 128.3, 128.0, 127.8, 127.7, 126.6, 126.3, 126.2, 125.9. HRMS (EI) Calcd for $C_{16}H_{12}$ (M^+) 204.0939, Found 204.0936.

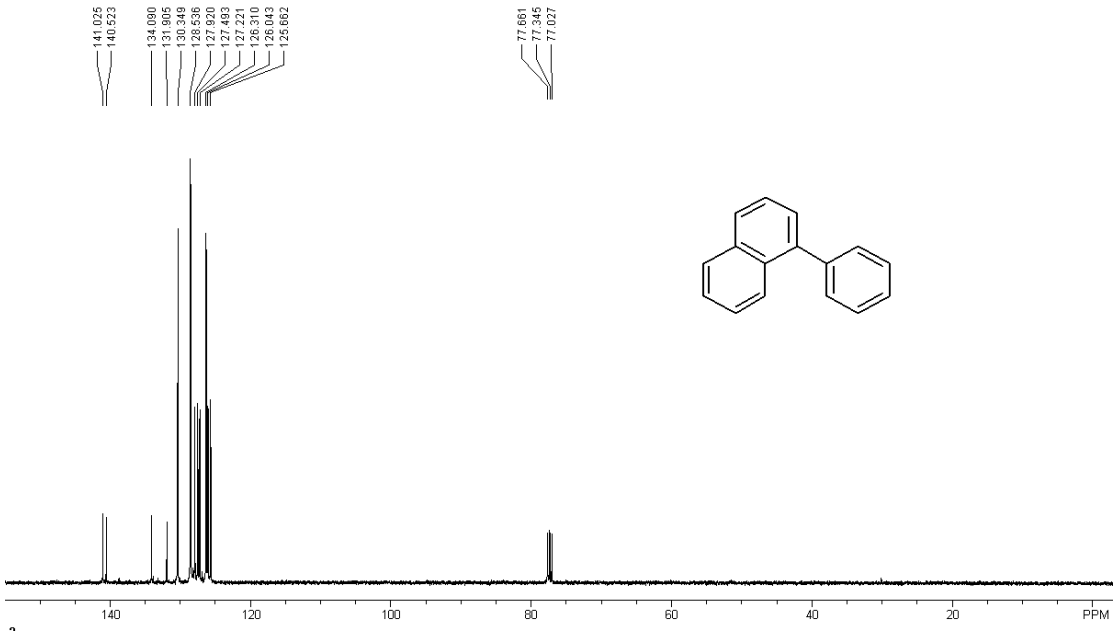


1-phenylnaphthalene (T 4−8, CAS no. 605-02-7)

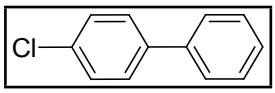


White solid, m.p. 42-43°C(lit.[2] mp 41-43°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.90 (t, *J* = 8.0 Hz, 1 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.48-7.53 (m, 3 H), 7.41-7.47 (m, 5 H), 7.33 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.0, 140.5, 134.1, 131.9, 130.3, 128.5, 127.9, 127.5, 127.2, 126.3, 126.0, 125.7. HRMS (EI) Calcd for $C_{16}H_{12}$ (M^+) 204.0939, Found 204.0937.

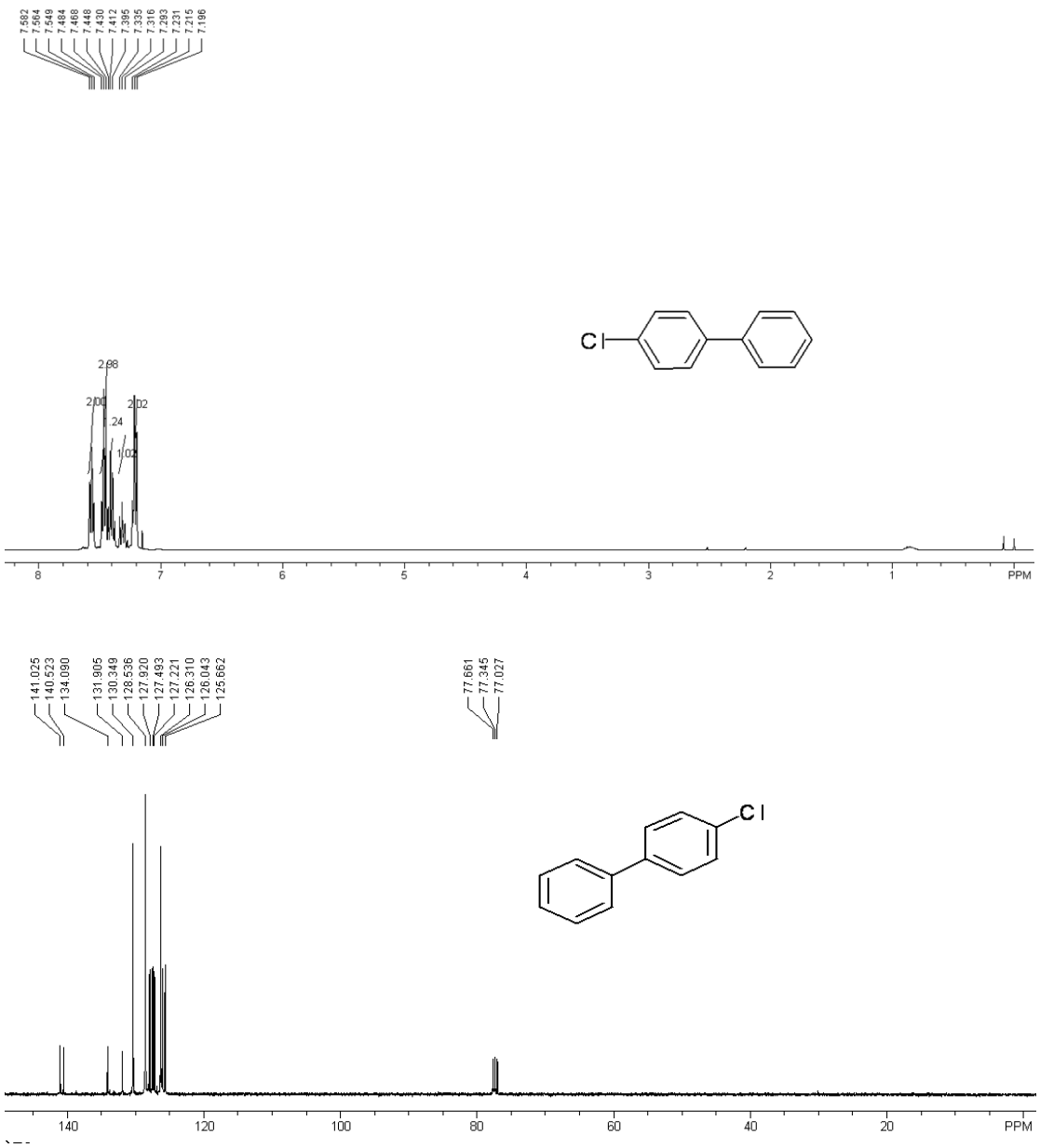




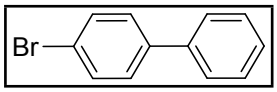
4-Cholro-1,1'-biphenyl (T 4−9, CAS no.2051-62-9)



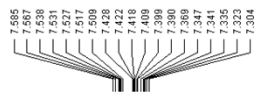
White solid, m.p. 48-49°C(lit.[1] mp 47-48°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.56 (t, *J* = 6.8 Hz, 2 H), 7.40-7.48 (m, 4 H), 7.32 (t, *J* = 7.2 Hz, 1 H), 7.22 (d, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.1, 140.5, 134.1, 131.9, 130.3, 128.5, 127.9, 127.5, 127.2, 126.3, 126.0, 125.7. HRMS (EI) Calcd for $C_{12}H_9Cl$ (M^+) 188.0393, Found 188.0396.

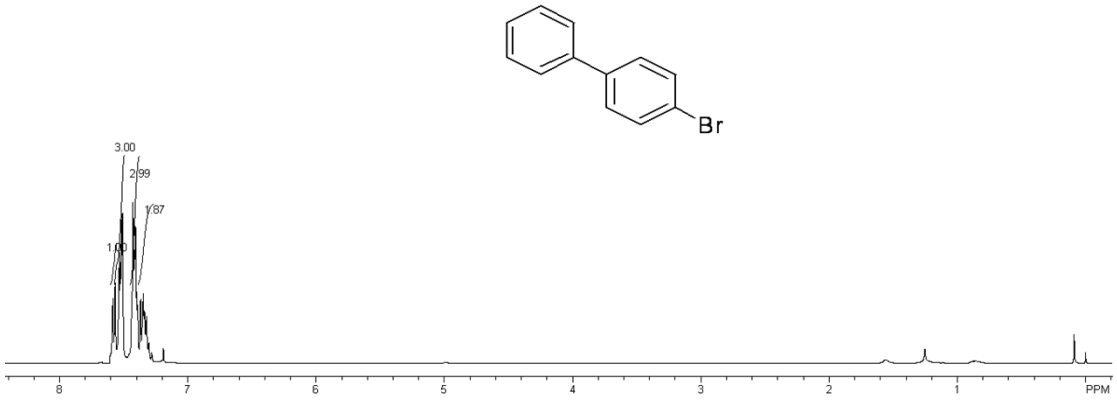


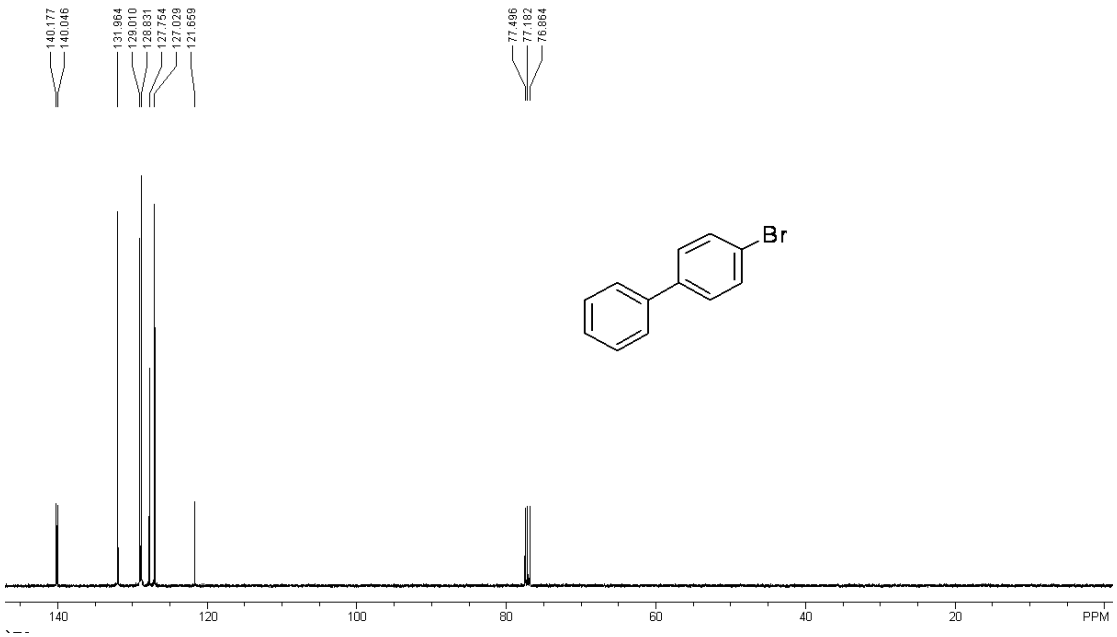
4-bromo-1,1'-biphenyl (T 4−10, CAS no.92-66-0)



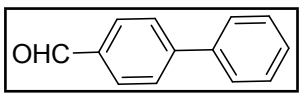
White solid, m.p. 90-92°C(lit.[1] mp 91-92°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, *J* = 7.2 Hz, 1 H), 7.51-7.54 (m, 3 H), 7.39-7.43 (m, 3 H), 7.30-7.37 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 140.2, 140.0, 132.0, 129.0, 128.8, 127.8, 127.0, 121.7. HRMS (EI) Calcd for $C_{12}H_9Br$ (M^+) 231.9888, Found 231.9887.





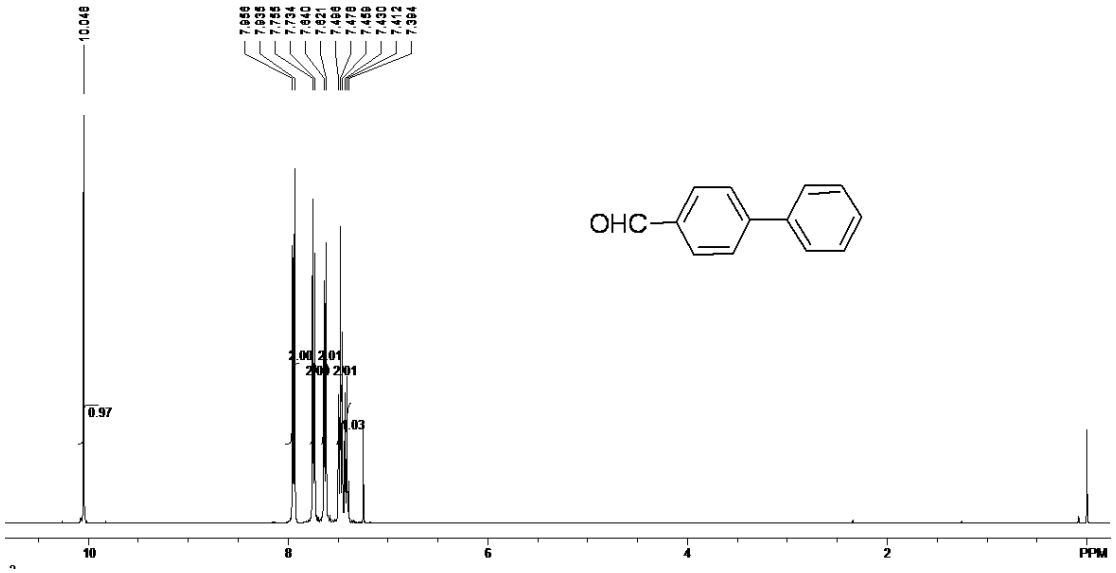


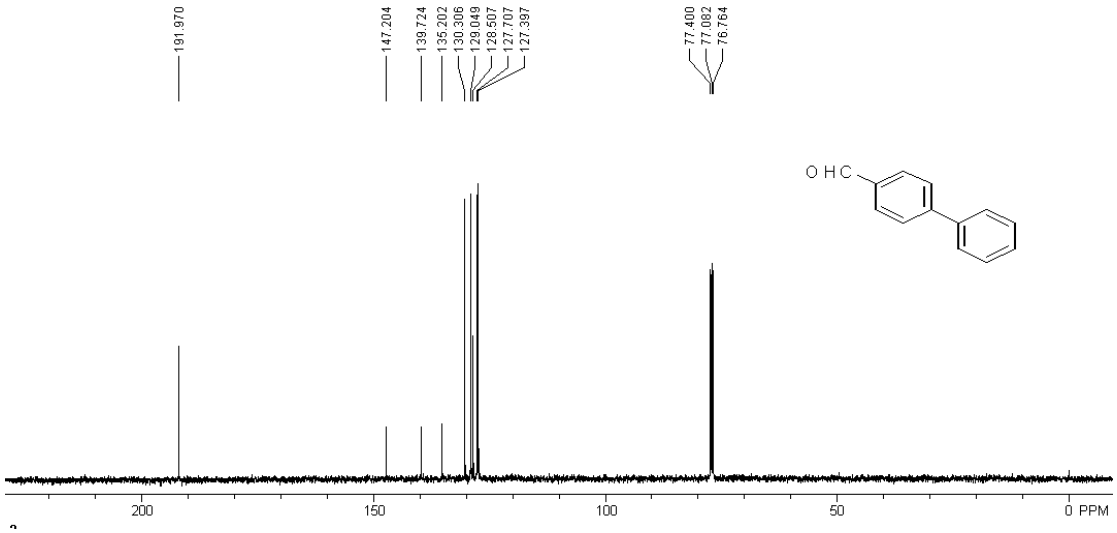
[1,1'-biphenyl]-4-carbaldehyde (T 4−11, CAS no. 3218-36-8)



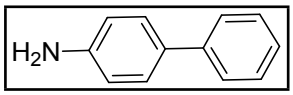
White solid, m.p. 73-74^{o}C(lit.[2] mp 73-74°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ10.05 (s, 1 H), 7.95 (d, *J* = 8.4 Hz, 2 H), 7.74 (d, *J* = 8.4 Hz, 2 H), 7.63 (d, *J* = 7.6 Hz, 2 H), 7.48 (t, *J* = 7.2 Hz, 2 H), 7.41 (d, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 191.9, 147.2, 139.7, 135.3, 130.3, 129.1, 128.5, 127.7, 127.3,

20.7. HRMS (EI) Calcd for $C_{13}H_{10}O$ (M^+) 182.0732, Found 182.0735.



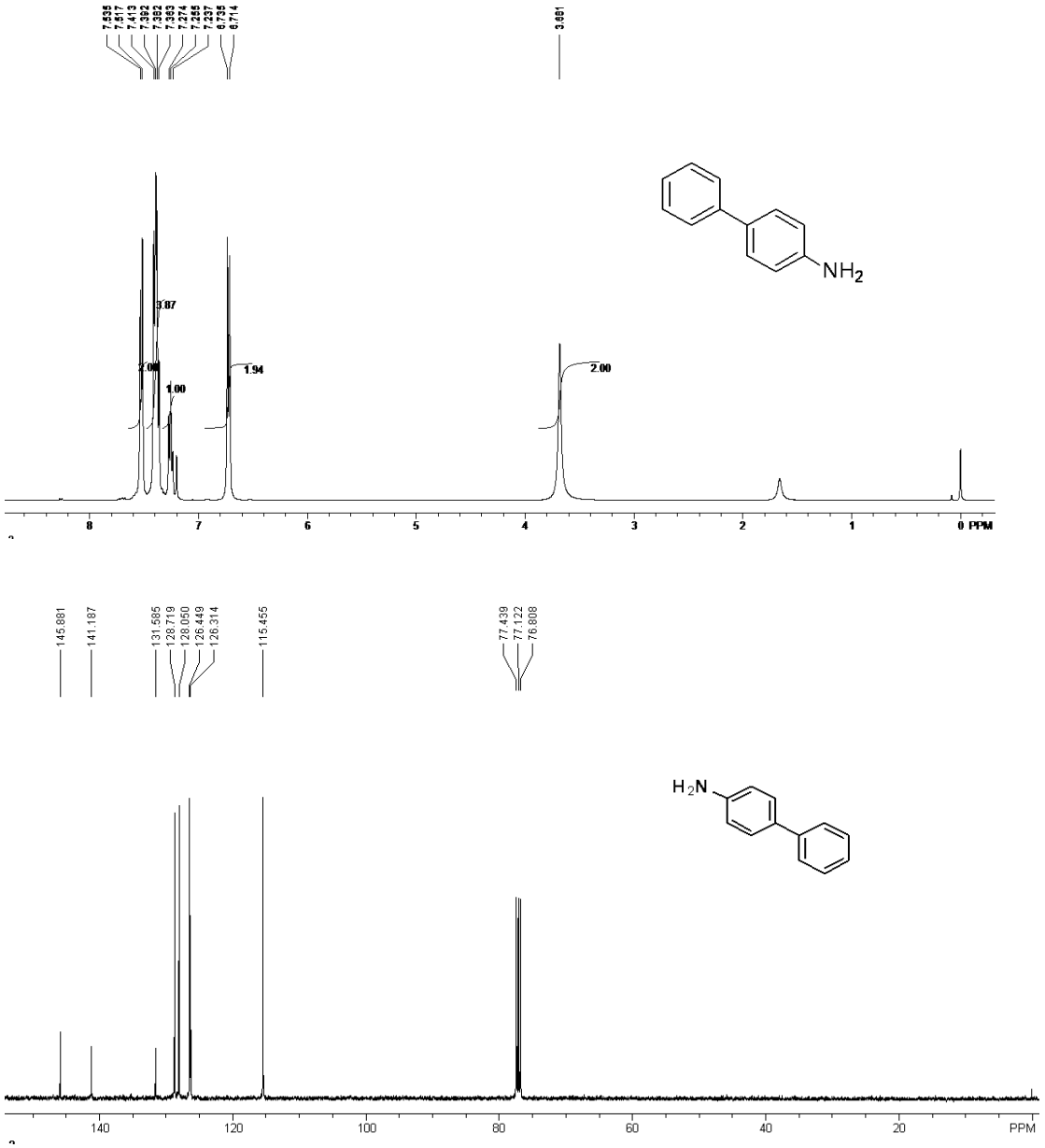


4-amine-1,1'-biphenyl (T 4−12, CAS no. 92-67-1)

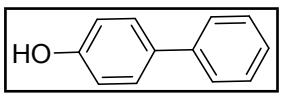


White solid, m.p. 73-74°C(lit.[2] mp 73-74°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.53 (d, *J* = 7.2 Hz, 2 H), 7.36-7.41 (m, 4 H), 7.25 (t, *J* = 7.2 Hz, 1 H), 6.72 (d, *J* = 8.4 Hz, 2 H), 3.68 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 145.9, 141.2,

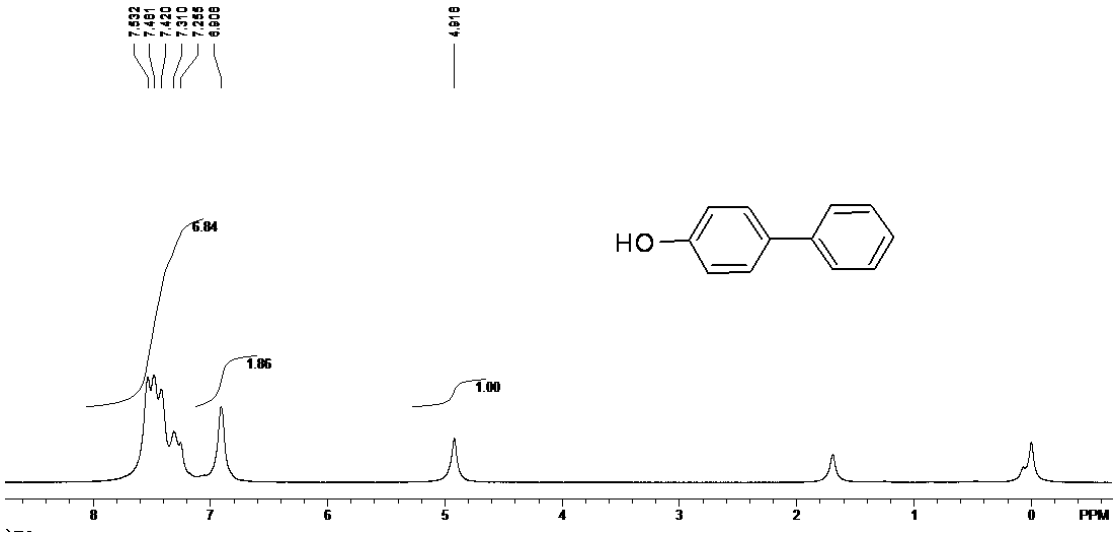
131.6, 128.7, 128.1, 126.4, 126.3, 115.5. HRMS (EI) Calcd for $C_{12}H_{11}N$ (M^+) 169.0891, Found 169.0888.



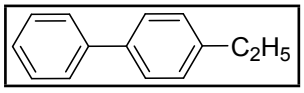
4-hydroxyl-1,1'-biphenyl (T 4−13, CAS no. 92-69-3)



White solid, m.p. 73-74°C(lit.[2] mp 73-74°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.25-7.53 (m, 7 H), 6.91 (s, 2 H), 4.92 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 155.0, 140.8, 134.1, 128.7, 128.4, 126.7. HRMS (EI) Calcd for $C_{12}H_{10}O$ (M^+) 170.0732, Found 170.0730.

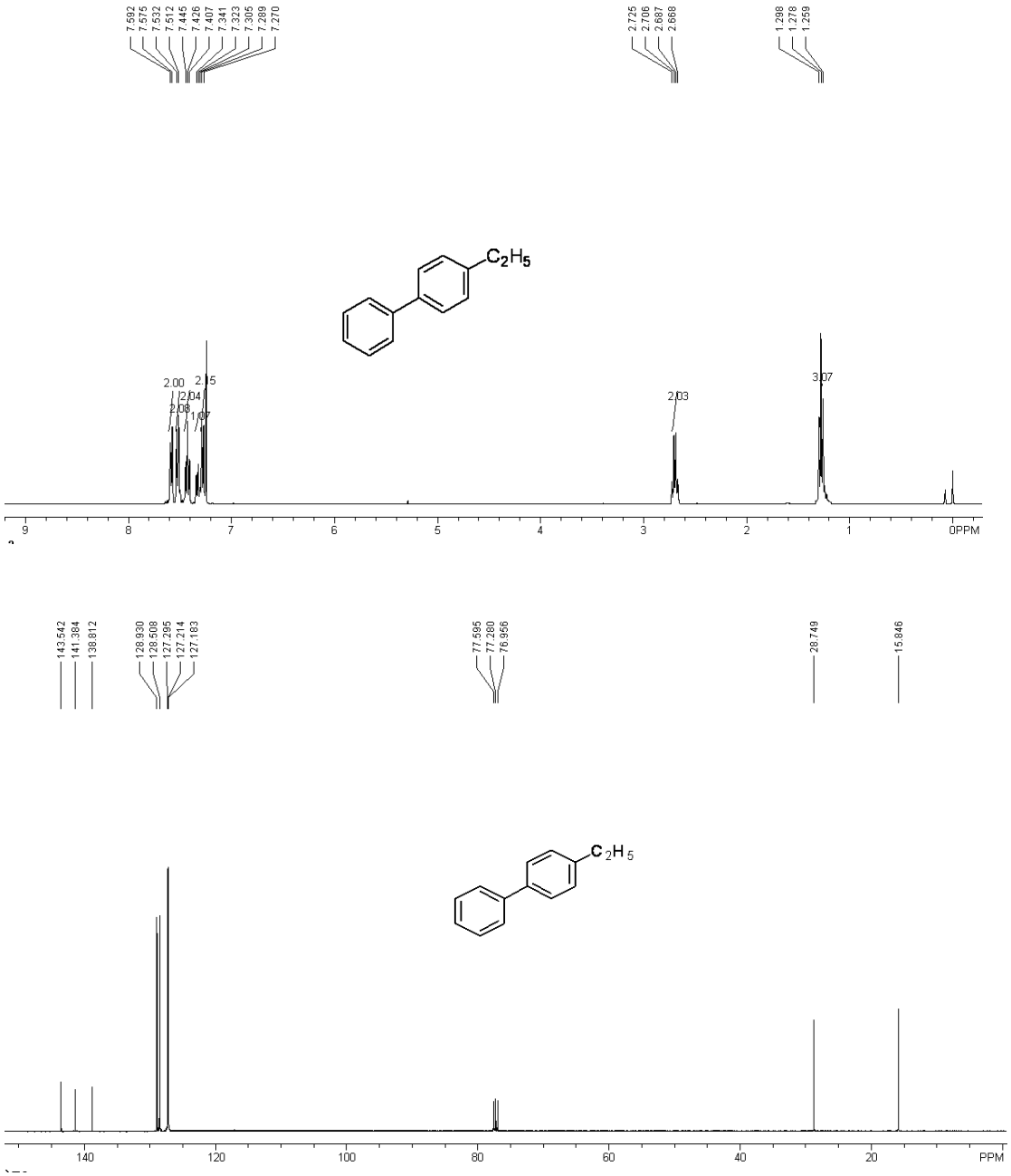


4-ethyl-1,1'-biphenyl (T 4–15, CAS no. 5707-44-8)

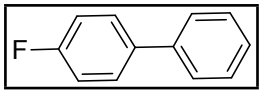


White solid, m.p. 37-38°C(lit.[3] mp 36-37°C);[1]H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, *J* = 6.8 Hz, 2 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.32 (t, *J* = 7.2 Hz, 1 H), 7.28 (d, *J* = 7.6 Hz, 2 H), 2.70 (q, *J* = 7.6 Hz, 2 H), 1.28 (t, *J* = 7.6 Hz, 3 H). [13]C NMR (100 MHz, $CDCl_3$, TMS) δ 143.5, 141.4, 138.8, 128.9,

128.5, 127.3, 127.21, 127.18, 28.7, 15.8. HRMS (EI) Calcd for $C_{14}H_{14}$ (M^+) 182.1096, Found 182.1093.

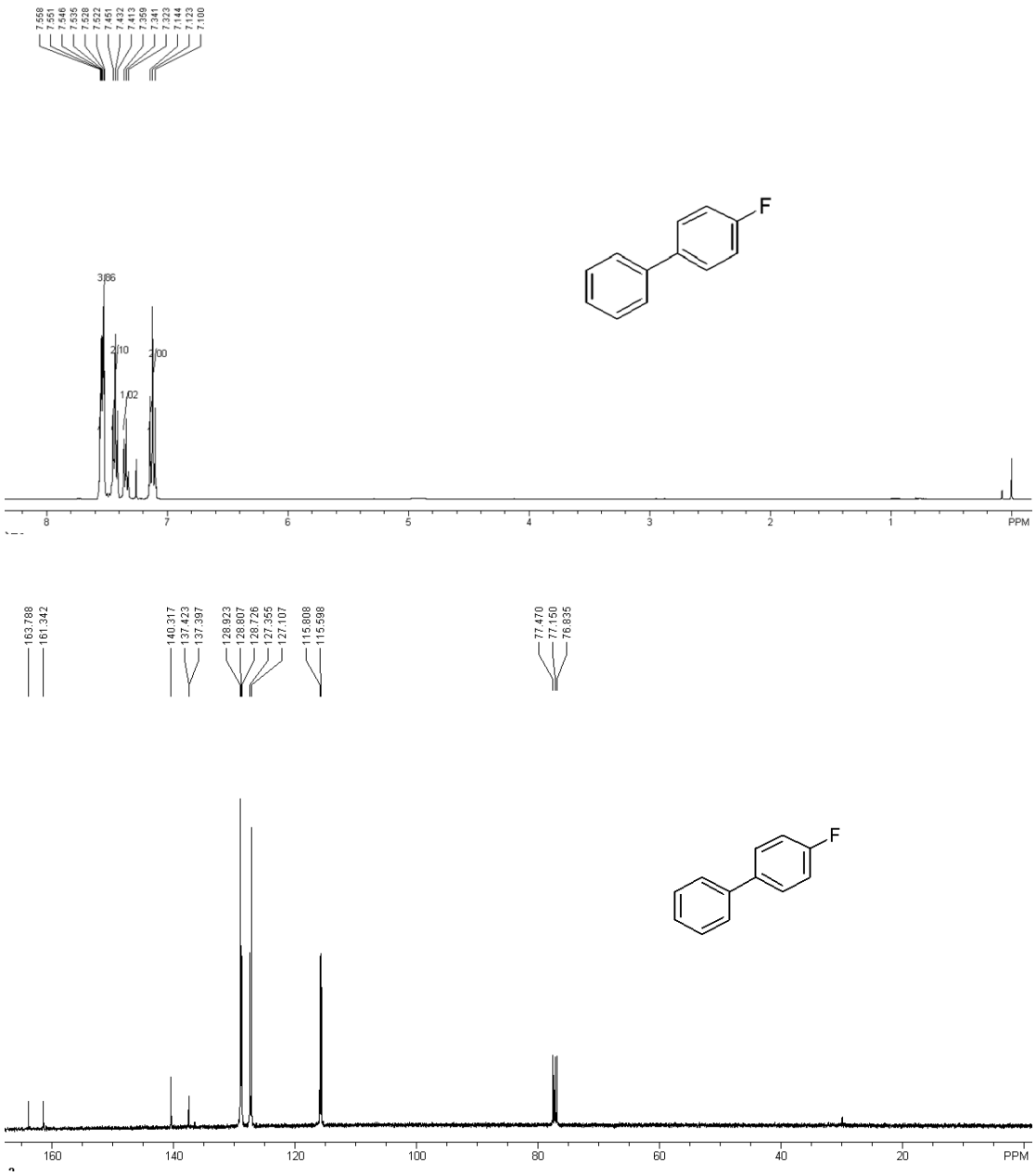


4-fluoro-1,1'-biphenyl (T 4−18, CAS no. 324-74-3)

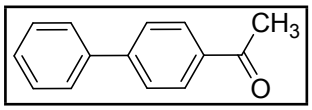


White solid, m.p. 73-74°C(lit.[2] mp 73-74°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52-7.56 (m, 4 H), 7.42 (t, J = 7.6 Hz, 2 H), 7.33 (t, J = 7.2 Hz, 1 H), 7.11 (t, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 163.5 (d, J = 247 Hz), 140.3, 137.42, 137.40, 128.9, 128.7 (d, J = 8.1 Hz), 127.4, 127.1, 115.7 (d, J = 21 Hz).

HRMS (EI) Calcd for $C_{12}H_9F$ (M^+) 172.0688, Found 172.0686.

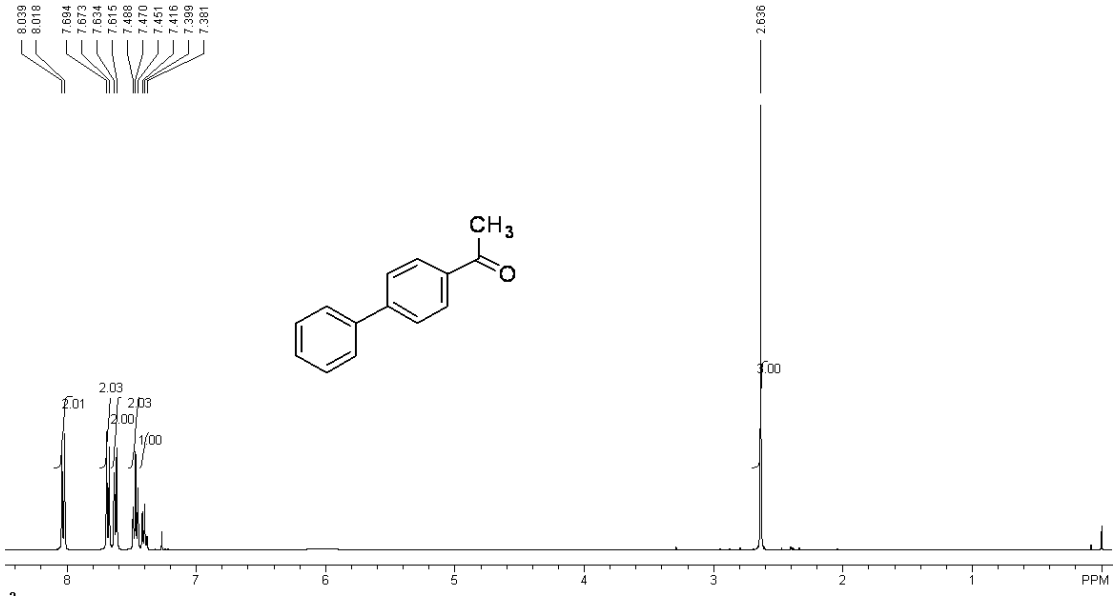


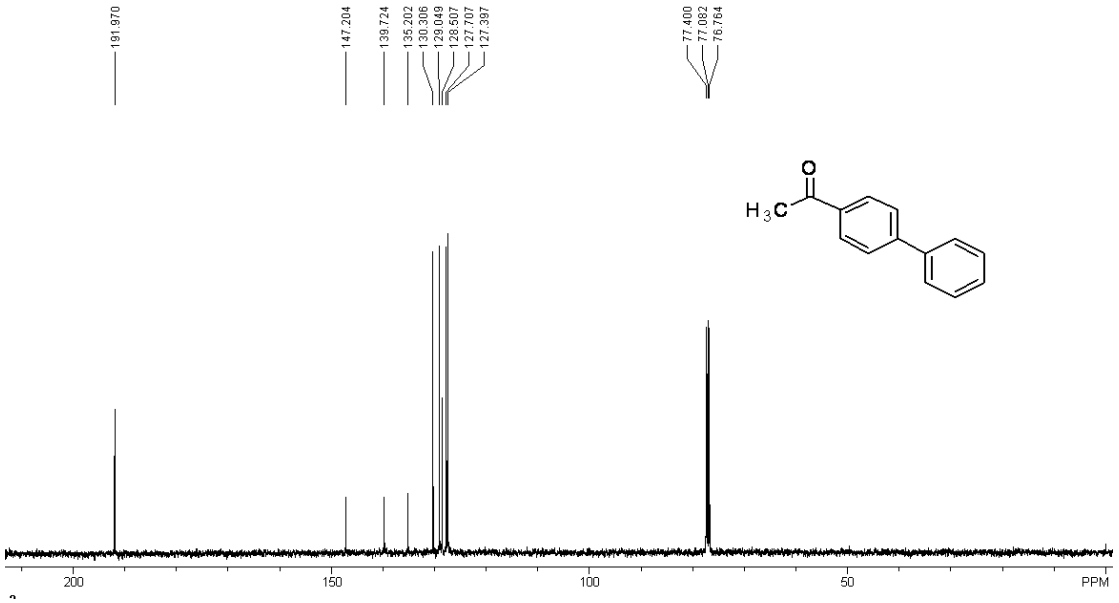
1-([1,1'-biphenyl]-4-yl)ethanone (T 4−20, CAS no.92-91-1)



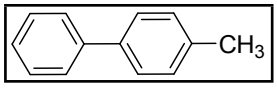
White solid, m.p. 118-120°C(lit.[3] mp 119-120°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.05 (d, *J* = 8.4 Hz, 2 H), 7.68 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 7.6 Hz, 2 H), 7.47 (d, *J* = 7.2 Hz, 2 H), 7.40 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$,

TMS) δ192.0, 147.2, 139.7, 135.2, 130.3, 129.0, 128.5, 127.7, 127.4. HRMS (EI) Calcd for $C_{14}H_{12}O$ (M^+) 196.0888, Found 196.0893.



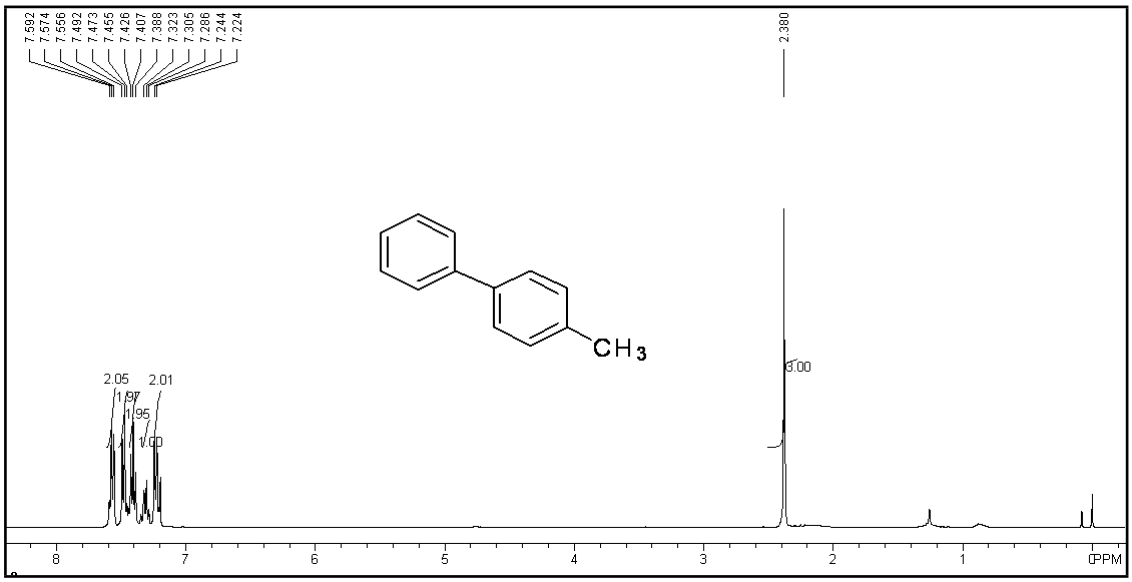


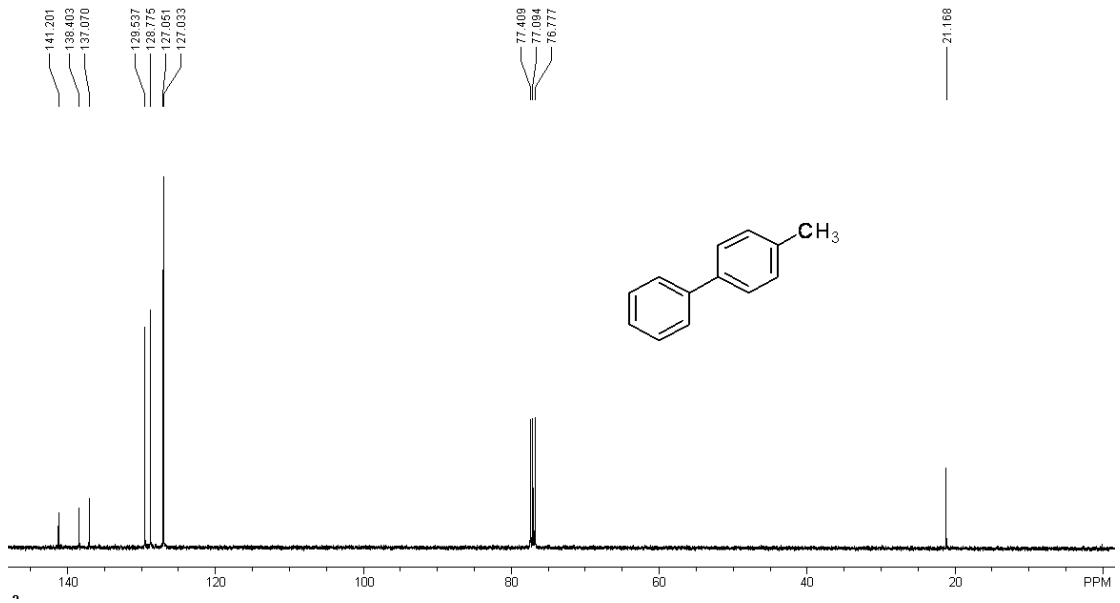
4-methyl-1,1'-biphenyl (T 4–21, CAS no.644-08-6)



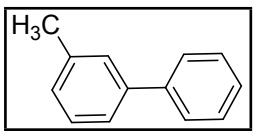
White solid, m.p. 46-47°C(lit.[1] mp 47-48°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.57 (t, *J* = 7.2 Hz, 2 H), 7.47 (t, *J* = 7.2 Hz, 2 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 7.31 (t, *J* = 7.2 Hz, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 2.38 (s, 3 H). ^{13}C NMR (100 MHz,

$CDCl_3$, TMS) δ 141.2, 138. 4, 137.1, 129.5, 128.8, 127.1, 127.0, 21.2. HRMS (EI) Calcd for $C_{13}H_{12}$ (M^+) 168.0939, Found 168.0936.



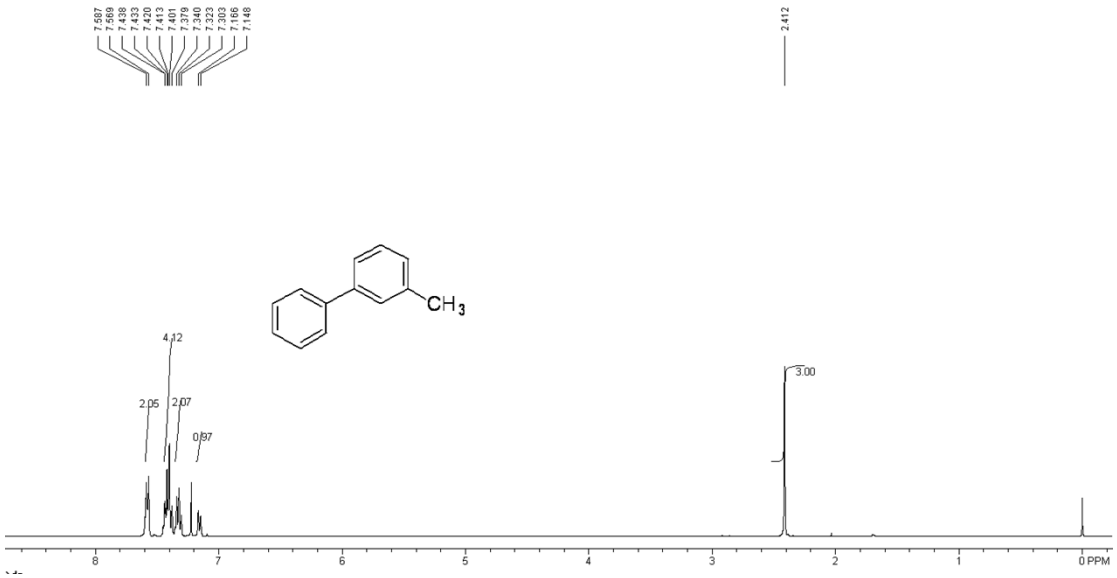


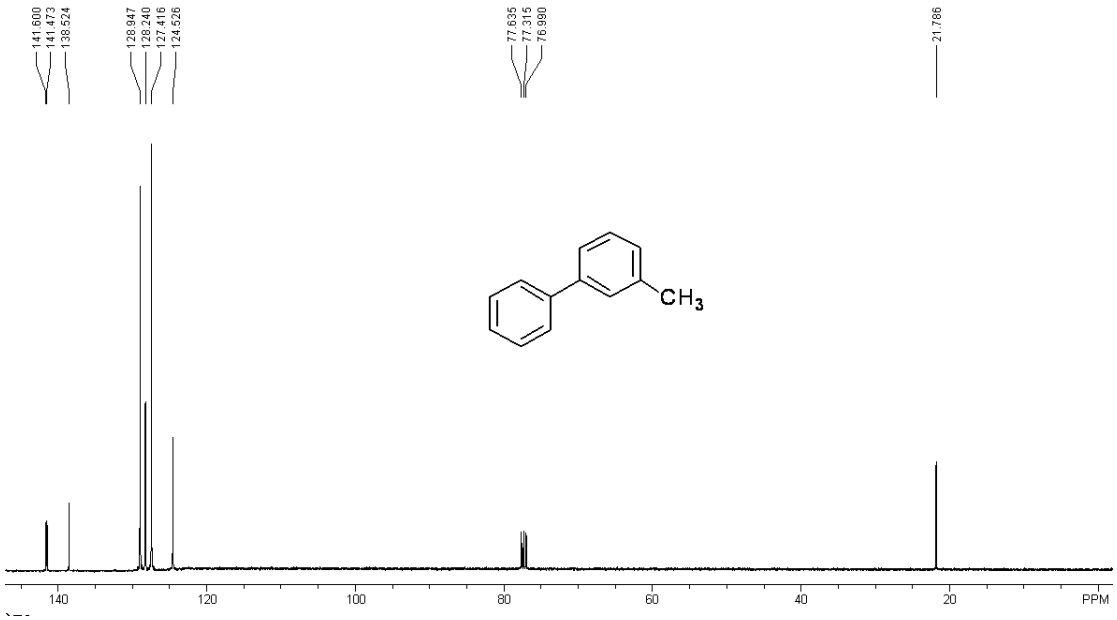
3-methyl-1,1'-biphenyl (T 4−22, CAS no. 643-93-6)



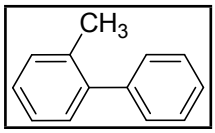
White solid, m.p. 42-43°C(lit.[2] mp 42-44°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58(d, *J* = 7.2 Hz, 2 H), 7.38-7.44 (m, 4 H), 7.31 (t, *J* = 7.2 Hz, 2 H), 7.16 (d, *J* =

7.2 Hz, 1 H), 2.42 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.6, 141.5, 128.9, 128.2, 127.4, 124.5, 21.8. HRMS (EI) Calcd for $C_{13}H_{12}$ (M^+) 168.0939, Found 168.0940.



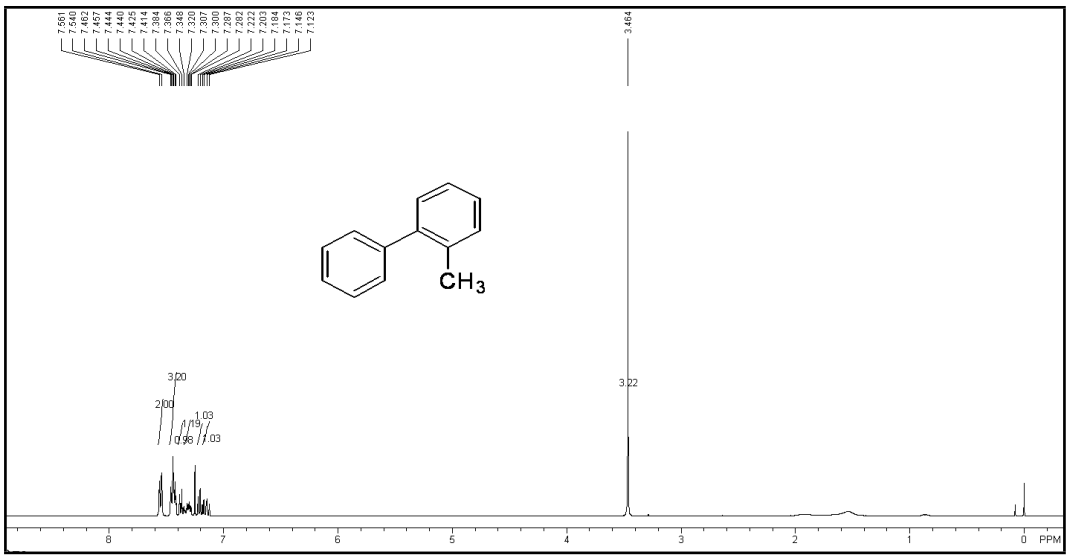


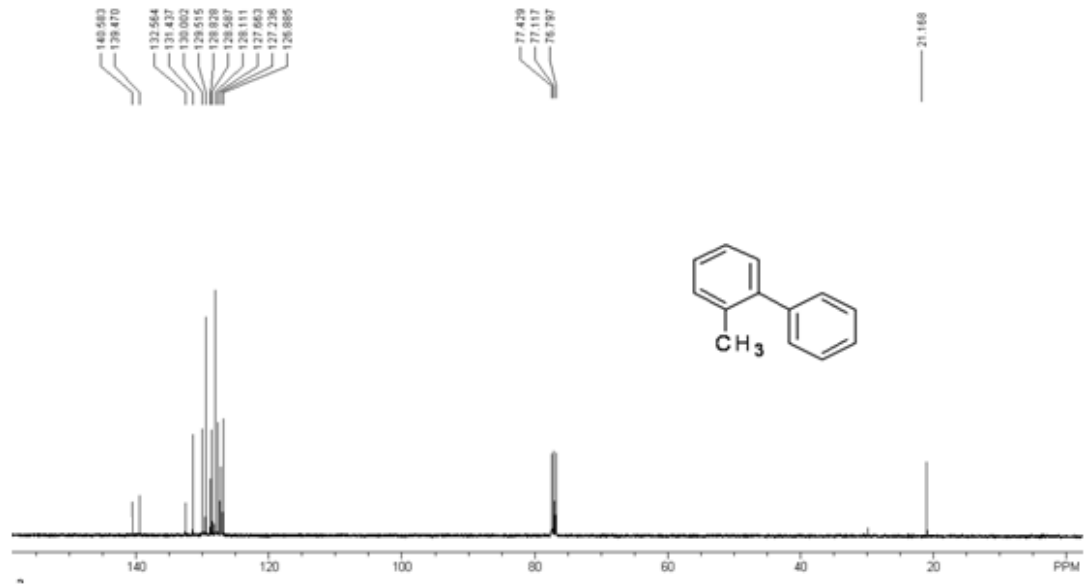
2-methyl-1,1'-biphenyl (T 4−23, CAS no. 643-58-3)



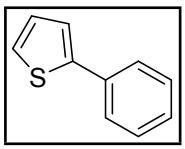
Colorless oil;^1H NMR (400 MHz, $CDCl_3$, TMS) δ7.55 (d, *J* = 8.4 Hz, 2 H), 7.41-7.46 (m, 3 H), 7.38 (d, *J* = 7.2 Hz, 1 H), 7.28-7.32 (m, 1 H), 7.20 (t, *J* = 7.6 Hz, 1

H), 7.16 (t, *J* = 9.2 Hz, 1 H), 3.46 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ140.5, 139.5, 132.6, 131.4, 130.0, 129.5, 128.8, 128.5, 128.1, 127.8, 127.2, 126.8, 21.1. HRMS (EI) Calcd for $C_{13}H_{12}$ (M^+) 168.0939, Found 168.0936.



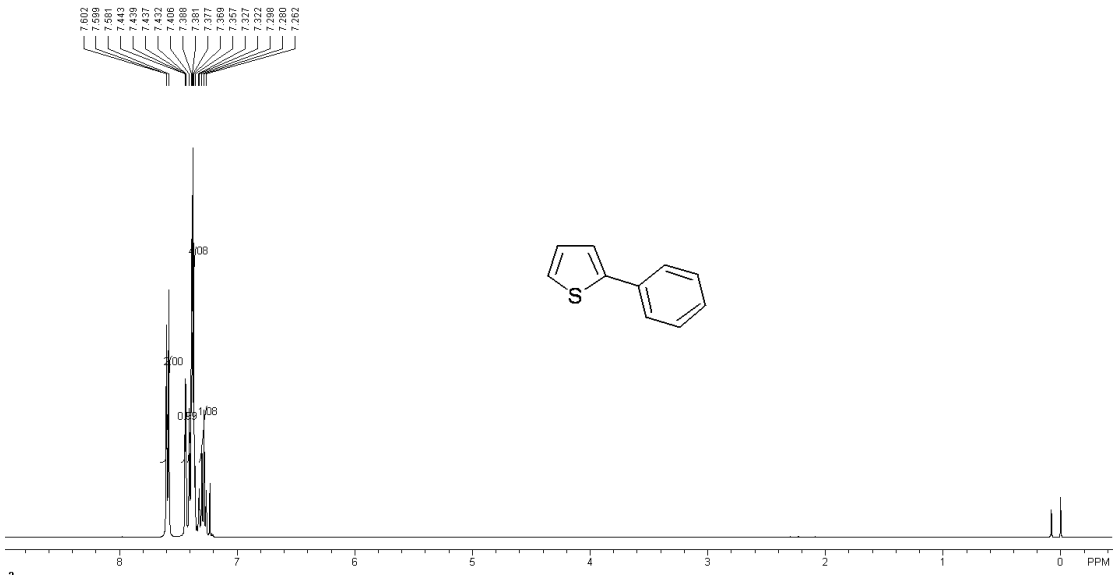


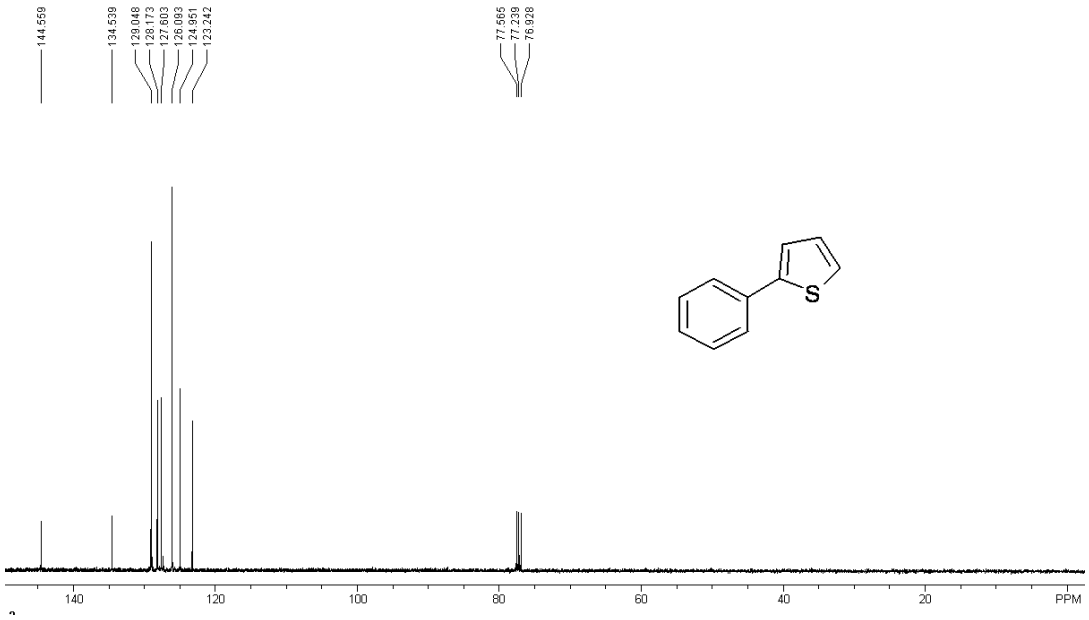
2-phenylthiophene (T 4−26, CAS no. 825-55-8)



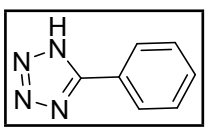
Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.26-7.33 (m, 1 H), 7.35-7.41 (m, 4 H), 7.43-7.45 (m, 1 H), 7.58-7.61 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS)

δ 144.6, 134.5, 129.0, 128.2, 127.6, 126.0, 125.0, 123.2. HRMS (EI) Calcd for $C_{10}H_8S$ (M^+) 160.0347, Found 160.0345.



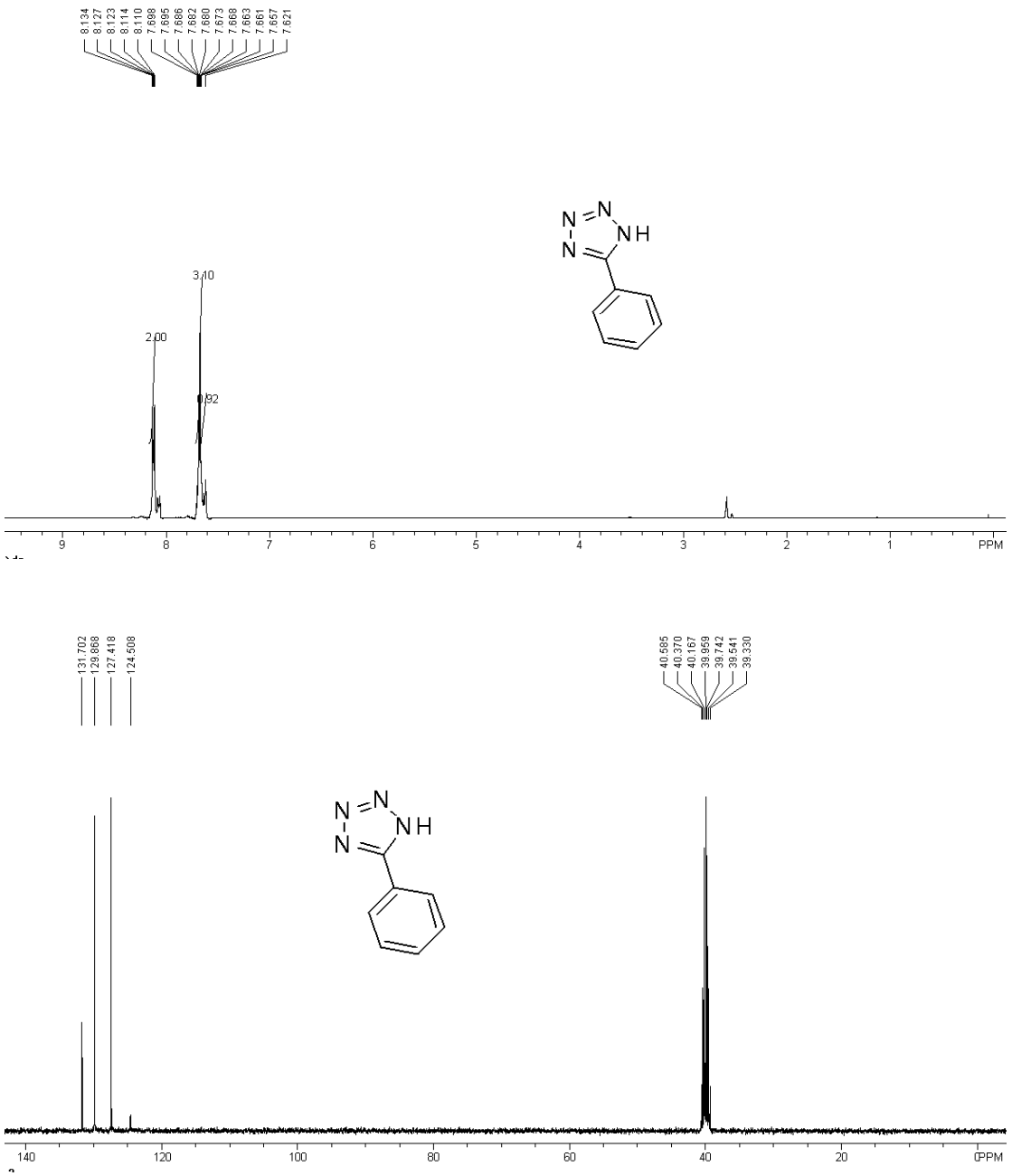


5-phenyl-1H-tetrazole(T 4−27, CAS no. 18039-42-4)

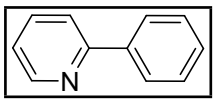


White solid, m.p. 216°C(dec.); ^{1}H NMR (400 MHz, d^6-DMSO, TMS) δ8.11-8.13 (m, 2 H), 7.65-7.70 (m, 3 H), 7.62 (s, 2 H). ^{13}C NMR (100 MHz, d^6-DMSO, TMS) δ 131.7, 129.9, 127.4, 124.5. HRMS (EI) Calcd for $C_7H_6N_4$ (M^+) 146.0592, Found

146.0595.

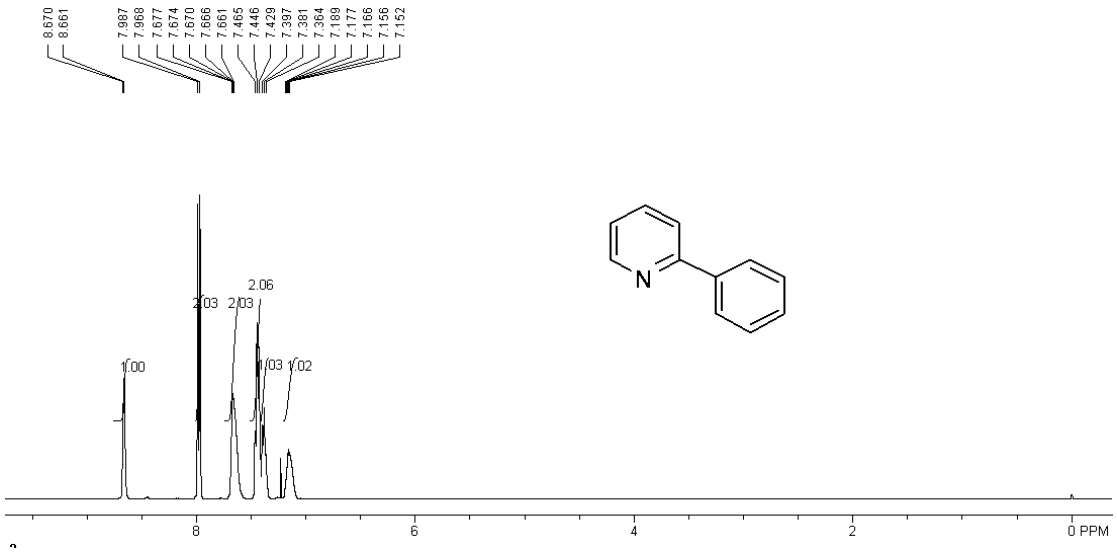


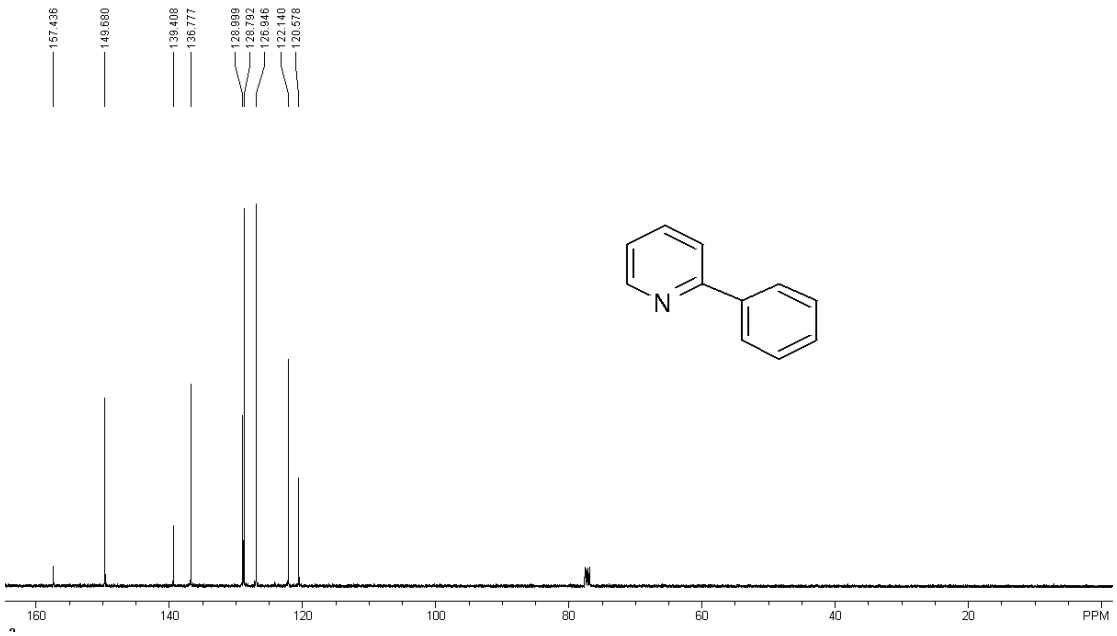
2-phenylpyridine(T 4−28, CAS no. 1008-89-5)



Colorless oil;^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.66 (d, *J* = 3.6 Hz, 1 H), 7.98 (d, *J* = 7.6 Hz, 2 H), 7.61-7.67 (m, 2 H), 7.45 (t, *J* = 7.2 Hz, 2 H), 7.38 (t, *J* = 6.8 Hz, 1 H), 7.11-7.19 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ157.4, 149.7,

139.4, 136.8, 129.0, 128.8, 126.9, 122.1, 120.6. HRMS (EI) Calcd for $C_{11}H_9N$ (M^+) 155.0735, Found 155.0736.





References

1. Barbero, M. et. al. *E. J. Org. Chem*. **2006**, 4884.

2. Zhou, W.-J. et. al. *Adv. Synth. Catal*. **2009**, 351, 1378.

3. Patrick, T. B. et. al. *J. Org. Chem*. **1985**, 50, 2232.