Palladium-Catalyzed Hiyama Coupling Reaction of Arylsulfonyl Hydrazides under Oxygen

Hui Miao, Fenhua Wang, Shuangliu Zhou,* Guangchao Zhang and Yang Li

The Key Laboratory of Functional Molecular Solids, Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, P. R. China
shuangliu_zhou@126.com

Supporting Materials

Content

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). HRMS (EI) data were collected on High Resolution mass spectrometer (ion trap). Arylsulfonyl hydrazide compounds were synthesized by corresponding arylsulfonyl chloride. Other materials were purchased from common commercial sources and used without additional purification.

Typical procedure for the products:

A mixture of arylsulfonyl hydrazides (0.50 mmol), aryl silanes (0.60 mmol), $Pd(TFA)_2$ (5 mol%) and TBAT(0.6 mmol) was stirred in the solvent of DMI (1.0 ml) at 60^{o}C for 12 hours. Afterwards, the mixture was filtered through a pad of celite and the solution was extracted by Et_2O (2 mL) for three times. the reaction solution was evaporated under reduced pressure. The combined organic phase was purified on a SiO_2 column to afford the desired product 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.

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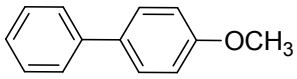
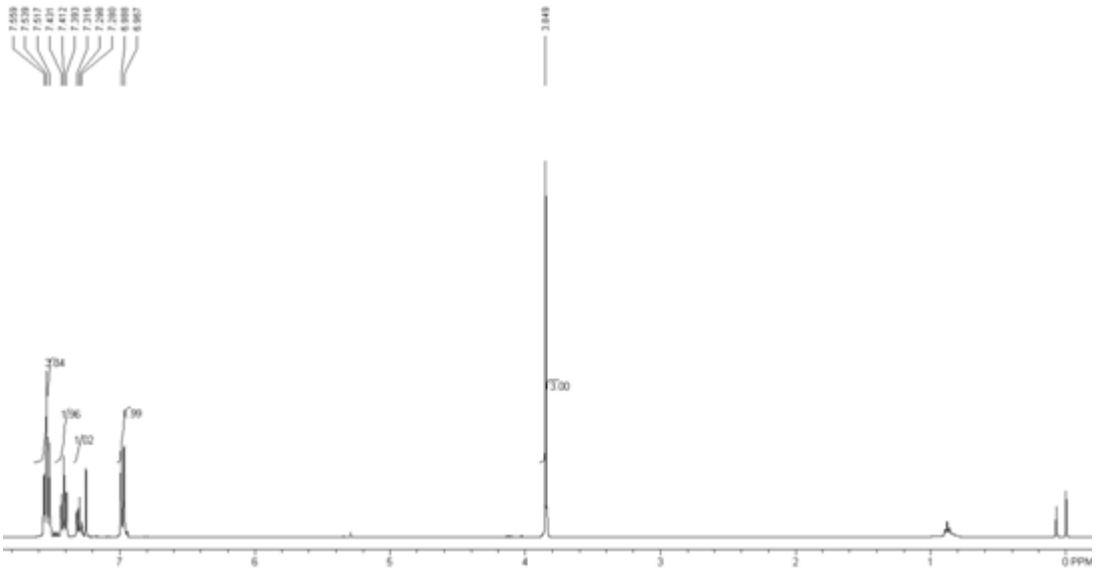
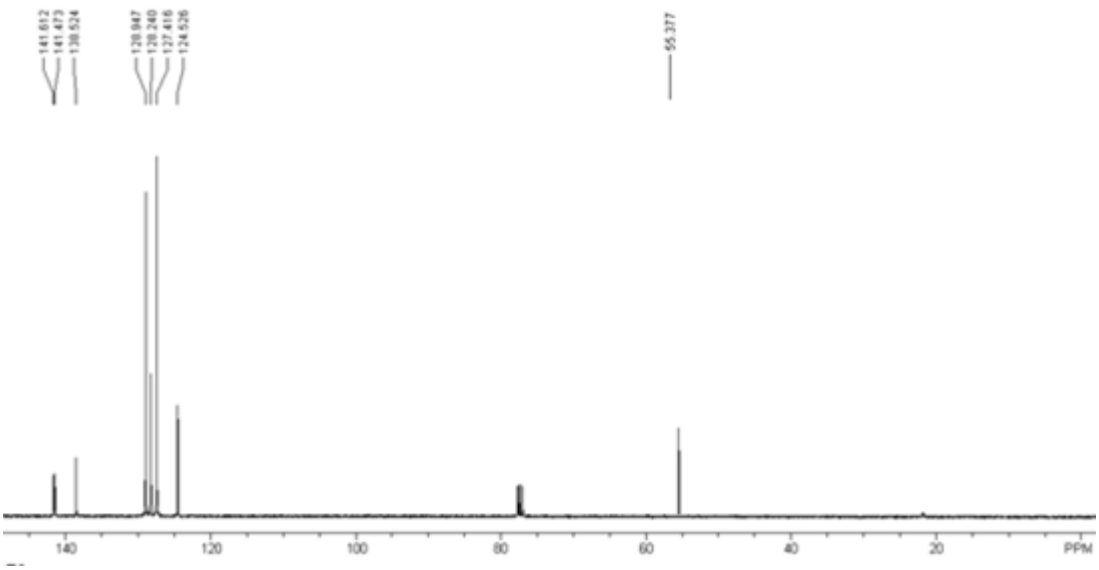
Characterization data of the product

4-methoxy-1,1'-biphenyl (T 3−1, CAS no.613-37-6)

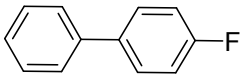


White solid, m.p. 89-91°C(lit.[1] mp 88-89°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.54 (t, *J* = 8.4 Hz, 4 H), 7.39 (t, *J* = 7.6 Hz, 2 H), 7.31 (t, *J* = 7.6 Hz, 1 H), 6.94 (d, *J* = 8.4 Hz, 2 H), 3.80 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.7, 141.4, 138.4, 128.9, 128.1, 127.3, 124.5, 55.3. HRMS (EI) Calcd for $C_{13}H_{12}O$ (M^+) 184.0888, Found 184.0887.

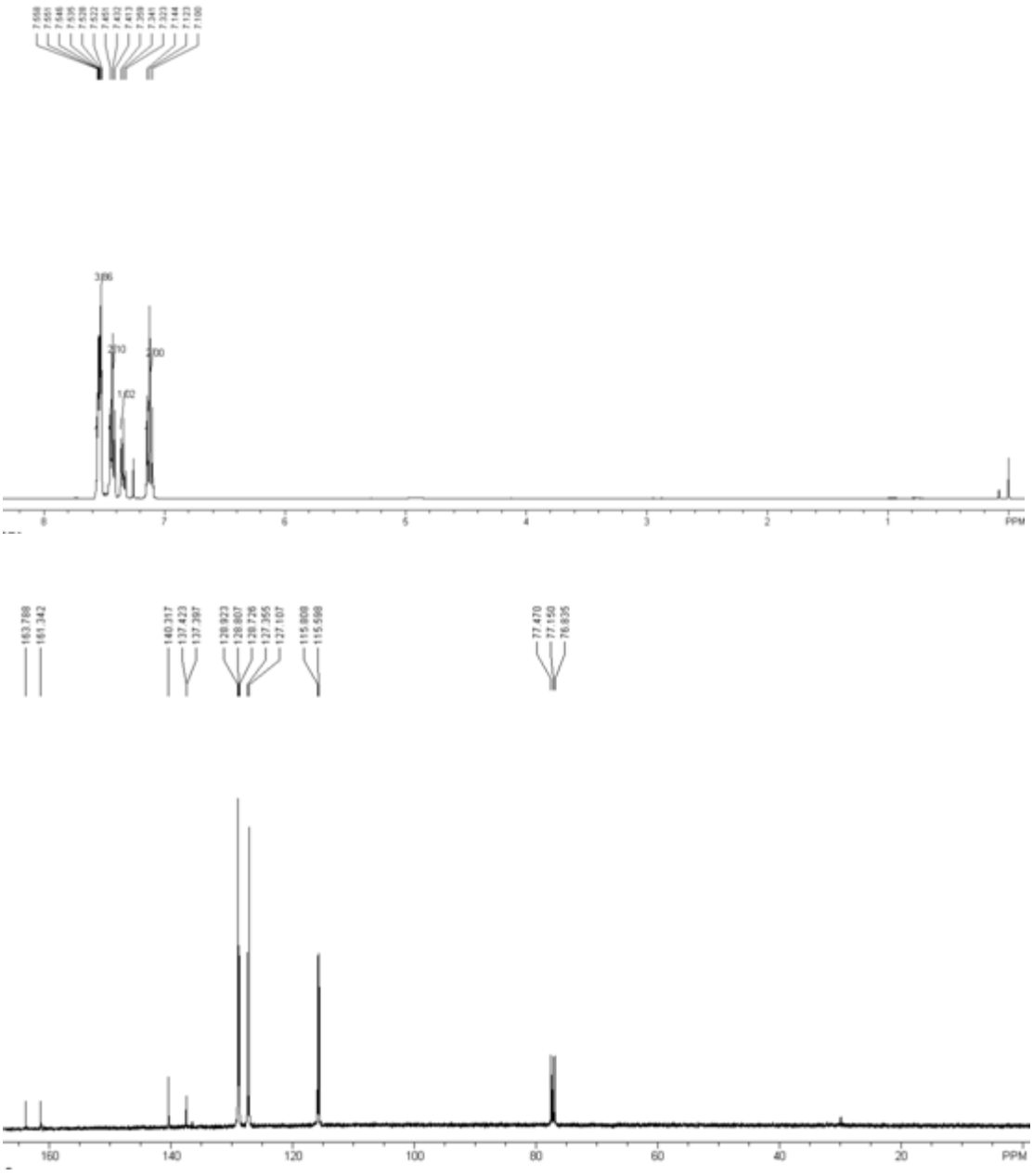




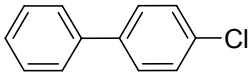
4-fluoro-1,1'-biphenyl (T 3−2, CAS no.324-74-3)



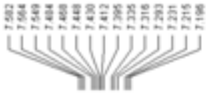
White solid, m.p. 73-75°C(lit.[2] mp 73-74°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52-7.57 (m, 4 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.12 (t, *J* = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 163.5 (d, *J* = 245 Hz), 140.3, 137.43, 137.40, 128.9, 128.6 (d, *J* = 8.2 Hz), 127.3, 127.1, 115.6 (d, *J* = 21 Hz). HRMS (EI) Calcd for $C_{12}H_9F$ (M^+) 172.0688, Found 172.0684.

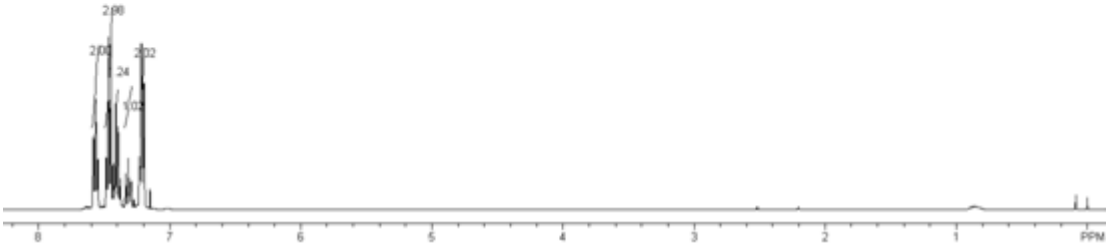


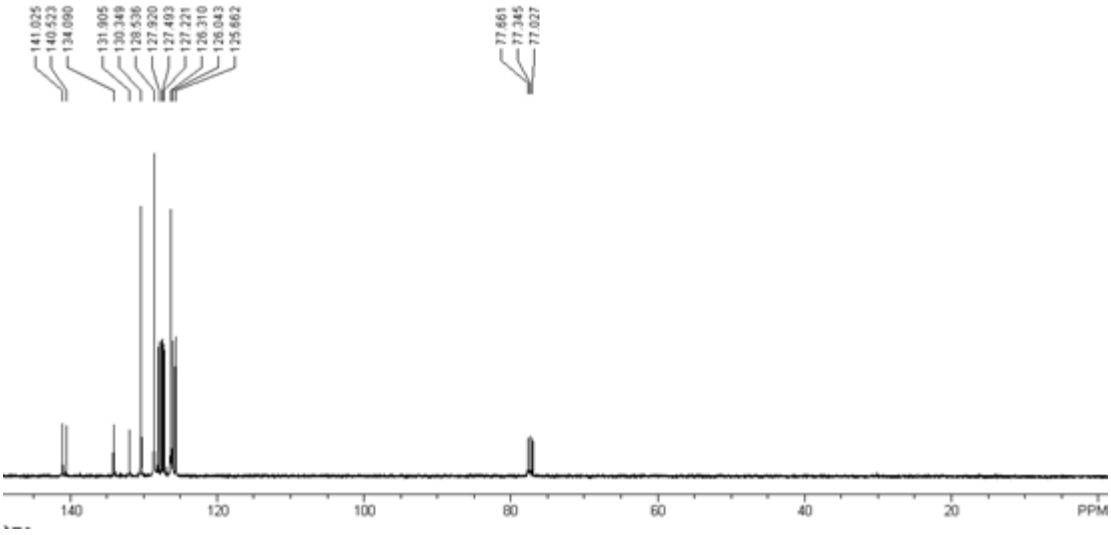
4-cholro-1,1'-biphenyl (T 3−3, CAS no.2051-62-9)



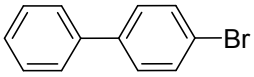
White solid, m.p. 47-48°C(lit.[1] mp 47-48°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.55 (t, *J* = 7.2 Hz, 2 H), 7.39-7.48 (m, 4 H), 7.31 (t, *J* = 7.2 Hz, 1 H), 7.21 (d, *J* = 7.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.0, 140.6, 134.2, 131.8, 130.4, 128.4, 127.9, 127.4, 127.2, 126.2, 126.0, 125.6. HRMS (EI) Calcd for $C_{12}H_9Cl$ (M^+) 188.0393, Found 188.0395.



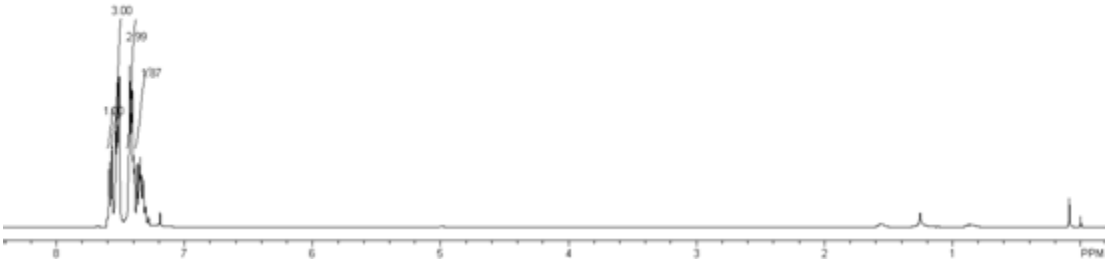


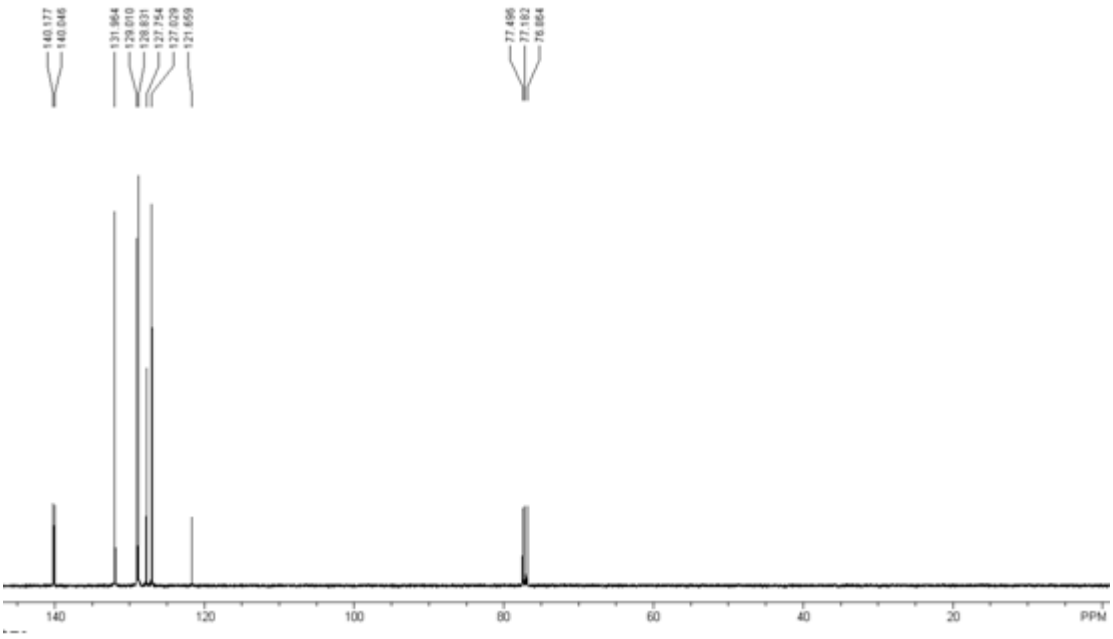


4-bromo-1,1'-biphenyl (T 3−4, CAS no.92-66-0)

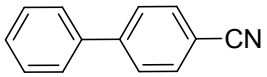


White solid, m.p. 90-91°C(lit.[1] mp 91-92°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 (d, *J* = 7.2 Hz, 1 H), 7.51-7.55 (m, 3 H), 7.39-7.44 (m, 3 H), 7.30-7.36 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 140.2, 139.9, 132.0, 129.1, 128.7, 127.8, 127.0, 121.6. HRMS (EI) Calcd for $C_{12}H_9Br$ (M^+) 231.9888, Found 231.9892.

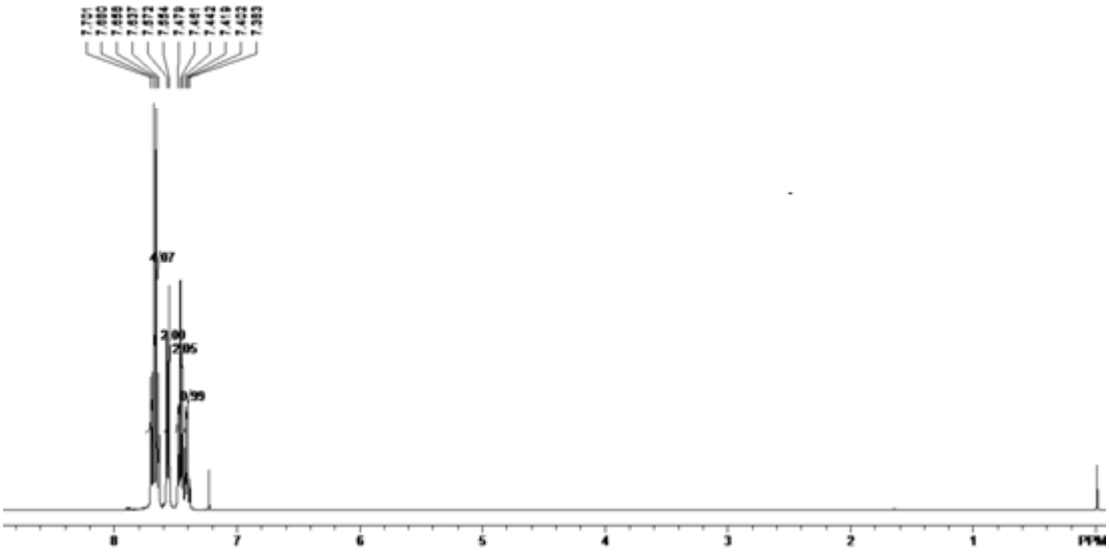


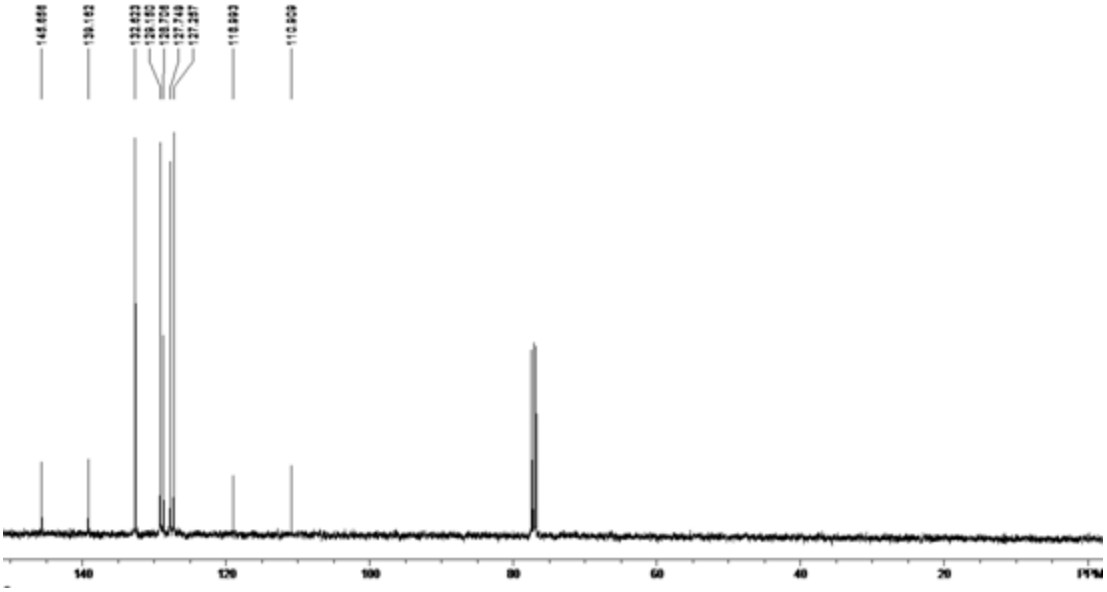


4-cyanobiphenyl (T 3−5, CAS no. 2920-38-9)

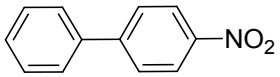


White solid, m.p. 74-76°C(lit.[2] mp 73-74°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.67 (q, *J* = 7.6 Hz, 4 H), 7.55 (d, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* = 7.2 Hz, 2 H), 7.39 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 145.6, 139.1, 132.5, 129.3, 128.7, 127.6, 127.2, 119.1, 110.8. HRMS (EI) Calcd for $C_{13}H_9N$ (M^+) 179.0735, Found 179.0732.

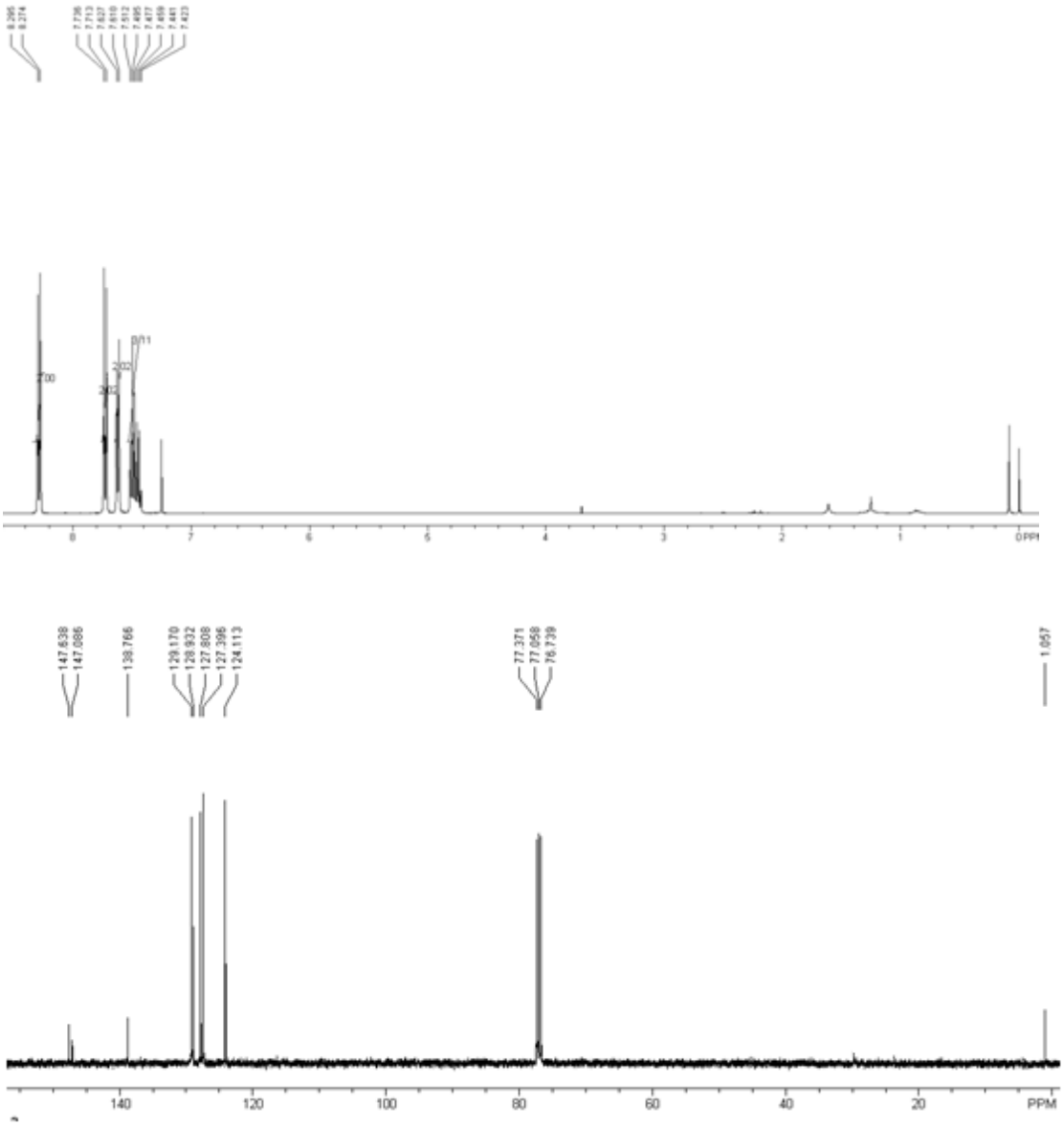




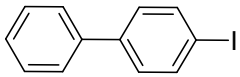
4-nitro-1,1'-biphenyl (T 3−6, CAS no. 92-93-3)



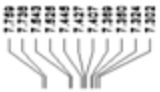
White solid, m.p. 116-117°C(lit.[1] mp 115-116°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.29 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 8.8 Hz, 2 H), 7.62 (d, *J* = 7.2 Hz, 2 H), 7.42-7.52 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 147.6, 147.0, 138.7, 129.2, 128.8, 127.7, 127.3, 124.0. HRMS (EI) Calcd for $C_{12}H_9NO_2$ (M^+) 199.0633, Found 199.0637.

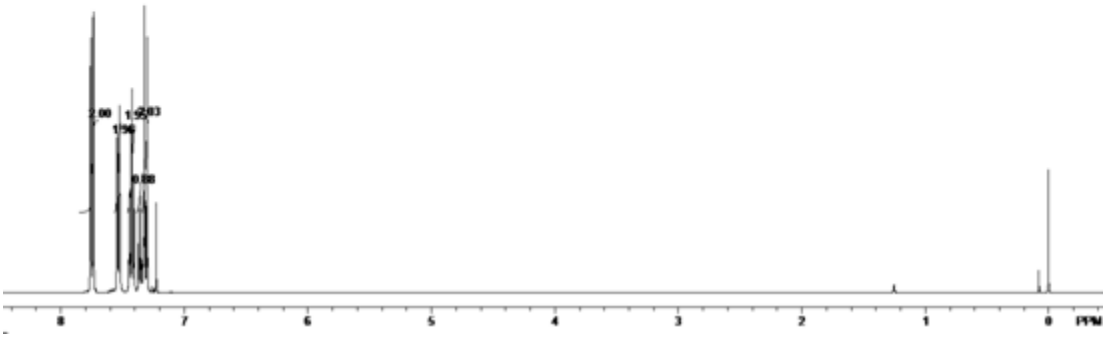


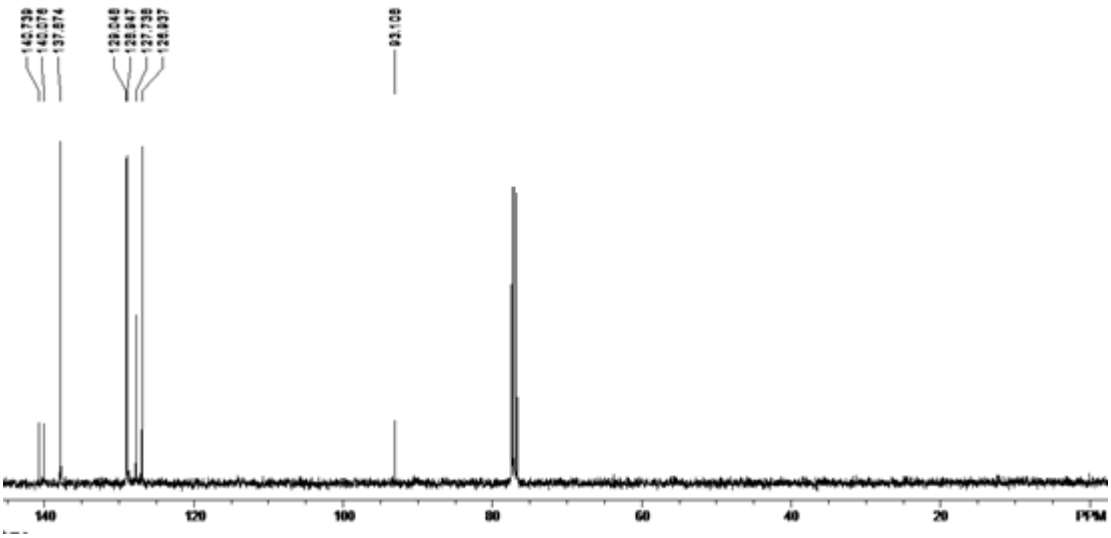
4-iodo-1,1'-biphenyl (T 3−7, CAS no. 1591-31-7)



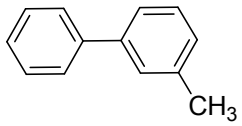
White solid, m.p. 73-75°C(lit.[2] mp 73-74°C);[1]H NMR (400 MHz, $CDCl_3$, TMS) δ7.76 (d, *J* = 8.0 Hz, 2 H), 7.54 (d, *J* = 7.2 Hz, 2 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.37 (d, *J* = 7.6 Hz, 1 H), 7.32 (t, *J* = 8.4 Hz, 2 H). [13]C NMR (100 MHz, $CDCl_3$, TMS) δ 140.6, 140.2, 137.8, 129.0, 128.8, 127.8, 126.7, 93.2. HRMS (EI) Calcd for $C_{12}H_9I$ (M^+) 297.9749, Found 297.9755.



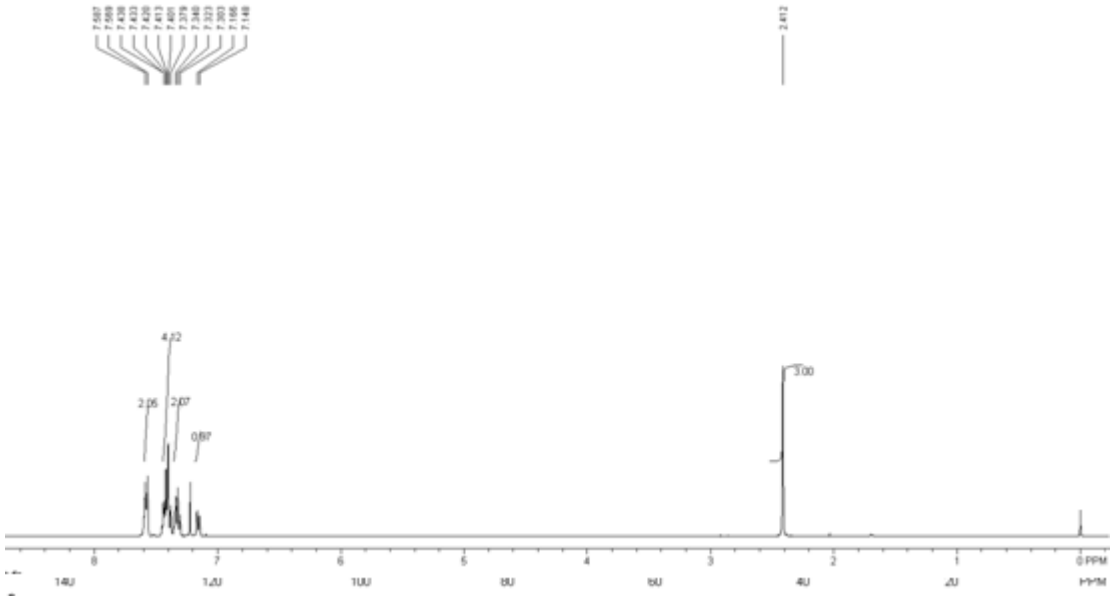


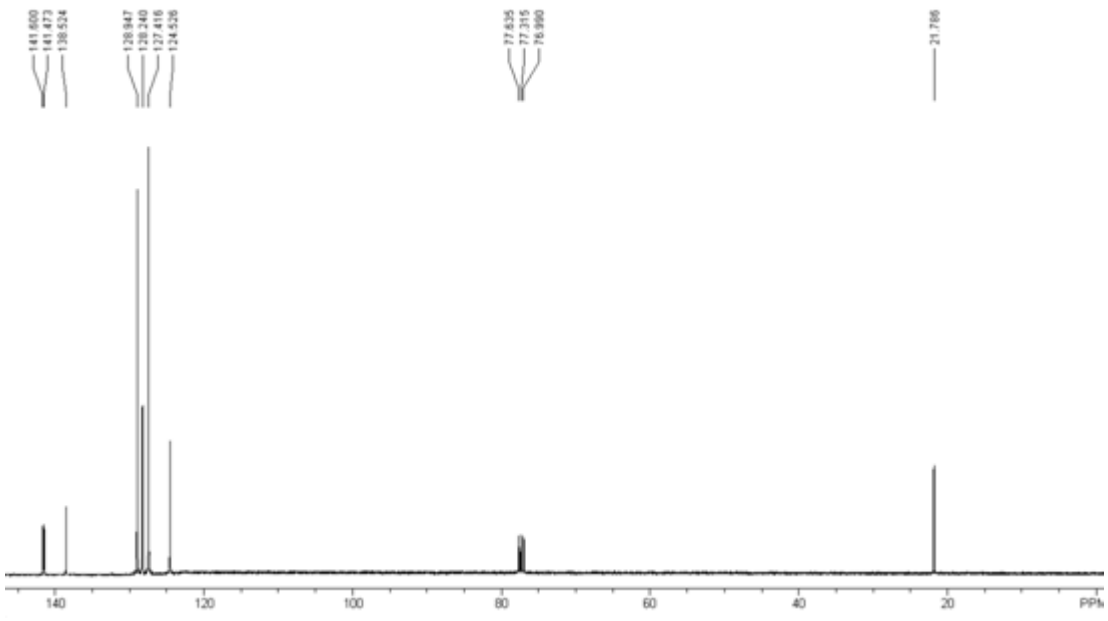


3-methyl-1,1'-biphenyl (T 3−8, CAS no. 643-93-6)

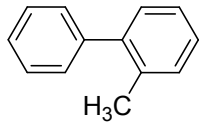


White solid, m.p. 41-43°C(lit.[2] mp 42-44°C);[1]H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59(d, *J* = 7.2 Hz, 2 H), 7.38-7.45 (m, 4 H), 7.32 (t, *J* = 7.2 Hz, 2 H), 7.17 (d, *J* = 7.2 Hz, 1 H), 2.41 (s, 3 H). [13]C NMR (100 MHz, $CDCl_3$, TMS) δ 141.6, 141.4, 128.9, 128.1, 127.4, 124.6, 21.7. HRMS (EI) Calcd for $C_{13}H_{12}$ (M^+) 168.0939, Found 168.0941.

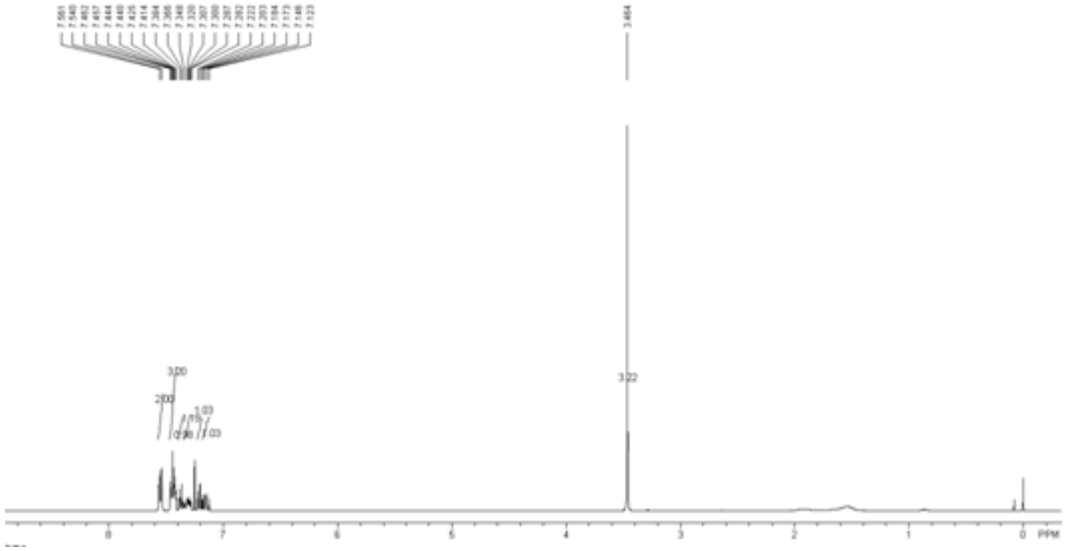


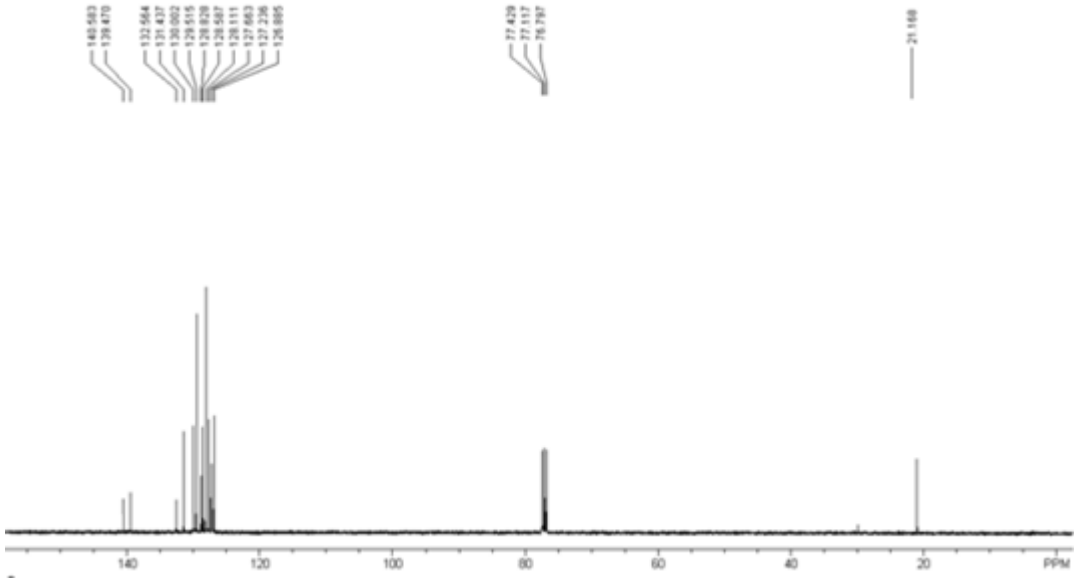


2-methyl-1,1'-biphenyl (T 3−9, CAS no. 643-58-3)

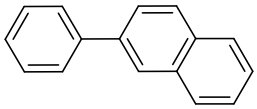


Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.54 (d, *J* = 8.0 Hz, 2 H), 7.41-7.46 (m, 3 H), 7.37 (d, *J* = 7.2 Hz, 1 H), 7.28-7.33 (m, 1 H), 7.19 (t, *J* = 7.6 Hz, 1 H), 7.16 (t, *J* = 8.8 Hz, 1 H), 3.47 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 140.6, 139.5, 132.7, 131.5, 130.0, 129.4, 128.9, 128.5, 128.0, 127.7, 127.1, 126.8, 21.0. HRMS (EI) Calcd for $C_{13}H_{12}$ (M^+) 168.0939, Found 168.0937.

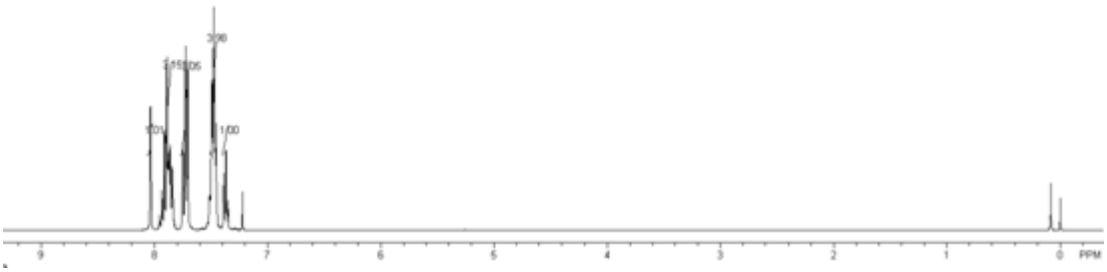


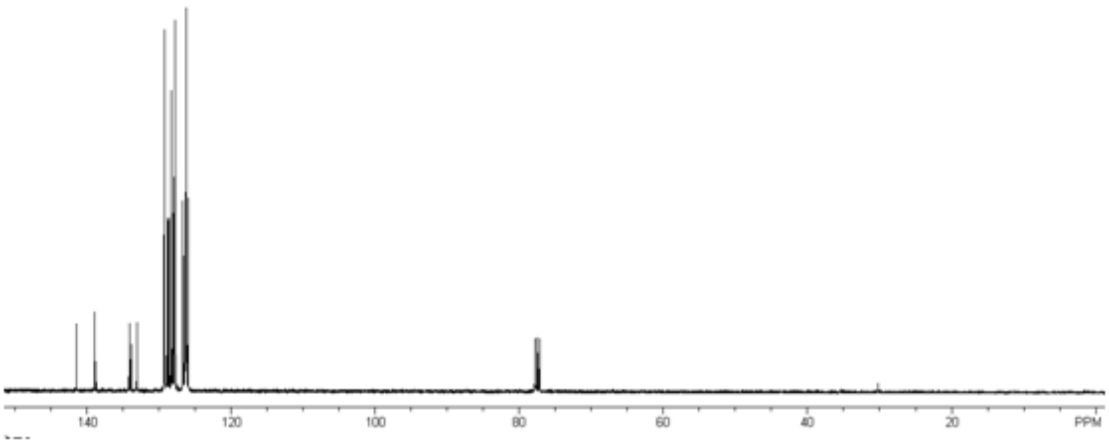


2-phenylnaphthalene (T 3−10, CAS no.612-94-2)

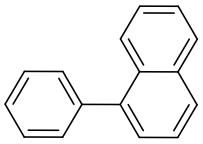


White solid, m.p. 96-98°C(lit.[2] mp 96-97°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.04 (s, 1 H), 7.84-7.94 (m, 3 H), 7.71 (t, *J* = 8.0 Hz, 3 H), 7.45-7.52 (m, 4 H), 7.36 (t, *J* = 7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.5, 138.8, 134.2, 133.7, 133.1, 129.1, 128.8, 128.7, 128.4, 128.0, 127.9, 127.7, 126.5, 126.3, 126.1, 125.8. HRMS (EI) Calcd for $C_{16}H_{12}$ (M^+) 204.0939, Found 204.0937.

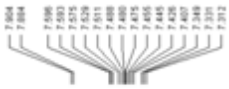


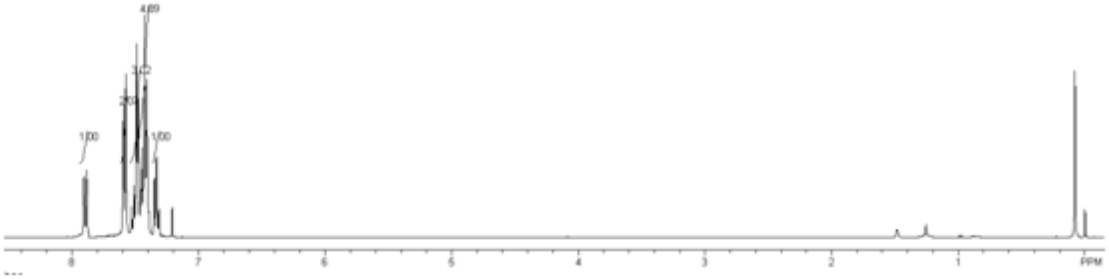


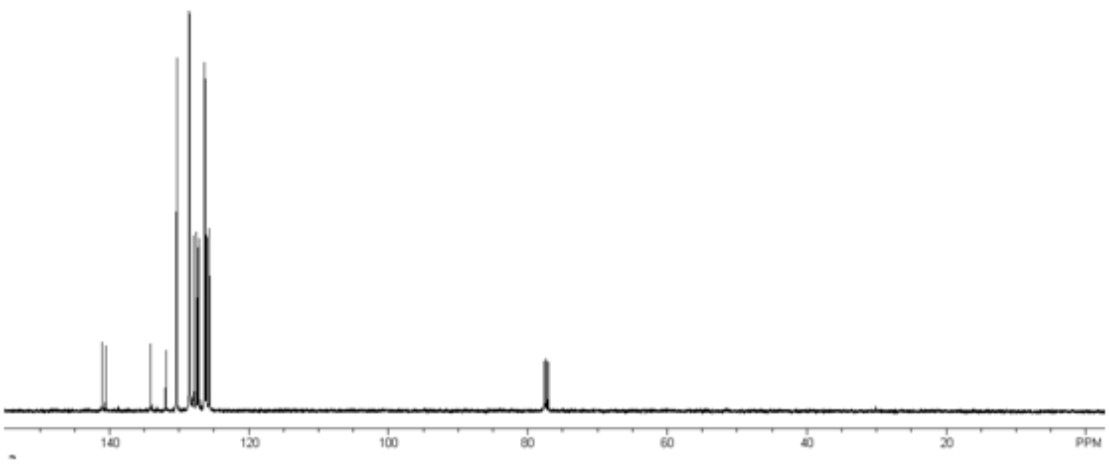
1-phenylnaphthalene (T 3−11, CAS no. 605-02-7)



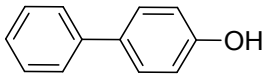
White solid, m.p. 42-43°C(lit.[2] mp 41-43°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.89 (t, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 2 H), 7.49-7.53 (m, 3 H), 7.42-7.47 (m, 5 H), 7.34 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.1, 140.4, 134.2, 131.8, 130.3, 128.6, 127.9, 127.6, 127.2, 126.4, 126.1, 125.6. HRMS (EI) Calcd for $C_{16}H_{12}$ (M^+) 204.0939, Found 204.0932.



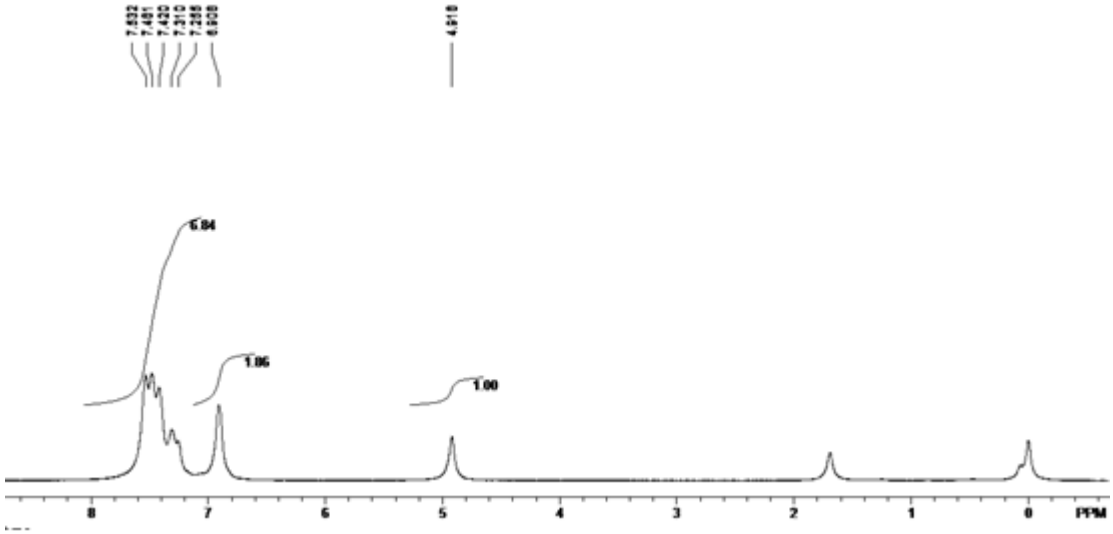


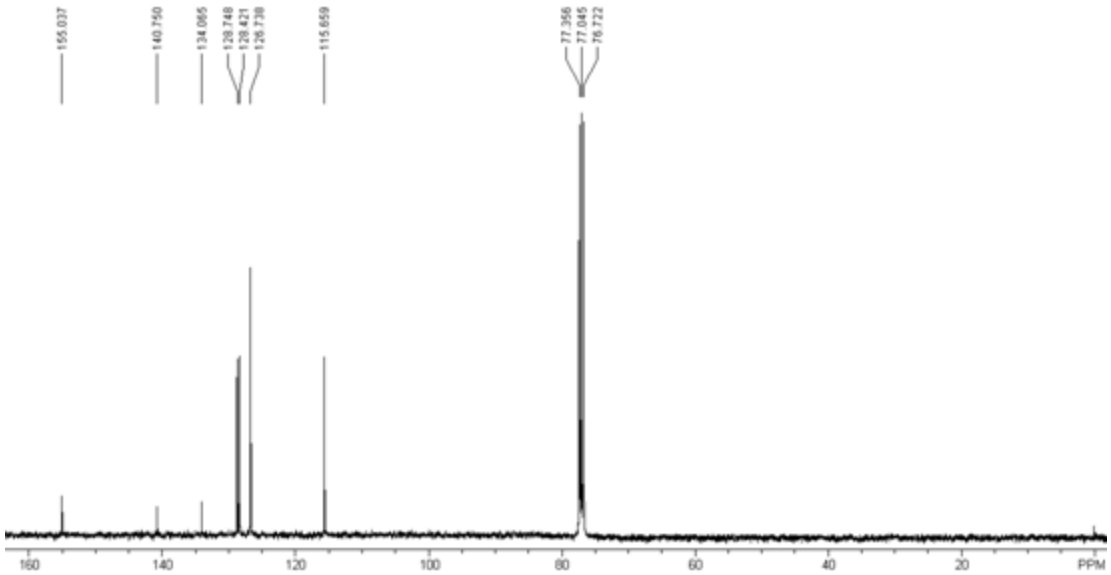


4-hydroxyl-1,1'-biphenyl (T 3−12, CAS no. 92-69-3)

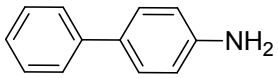


White solid, m.p. 73-75°C(lit.[2] mp 73-74°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.25-7.54 (m, 7 H), 6.90 (s, 2 H), 4.91 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 154.9, 140.7, 134.2, 128.7, 128.3, 126.7. HRMS (EI) Calcd for $C_{12}H_{10}O$ (M^+) 170.0732, Found 170.0735.

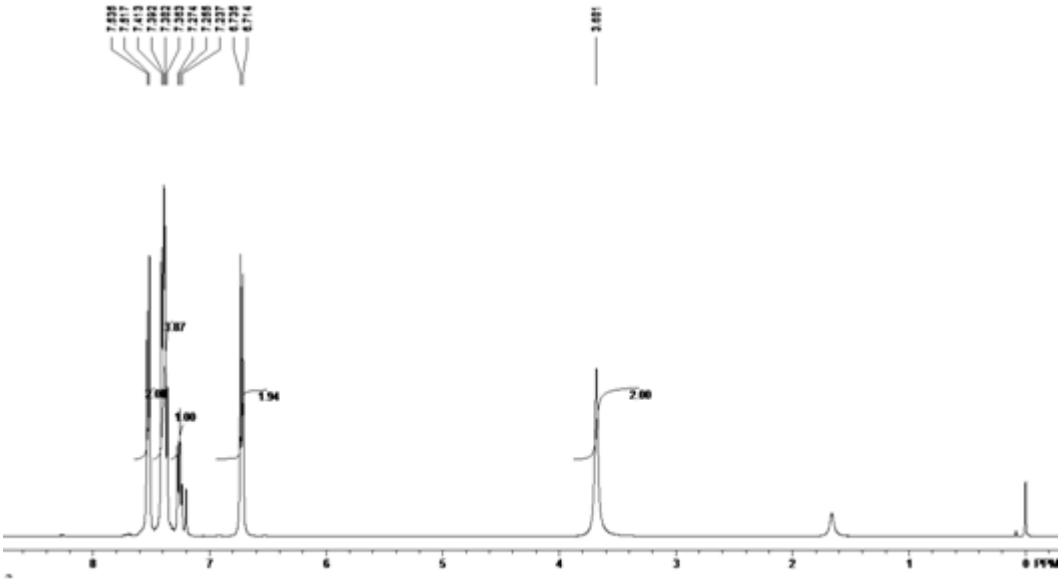


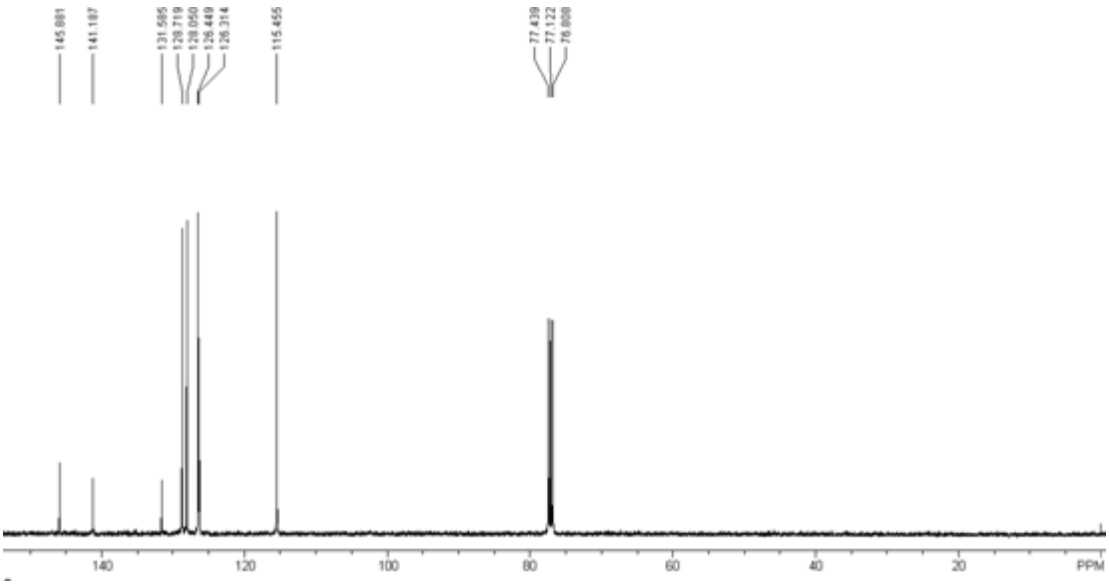


4-amine-1,1'-biphenyl (T 3−13, CAS no. 92-67-1)

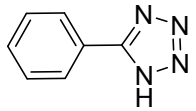


White solid, m.p. 72-74°C(lit.[2] mp 73-74°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.54 (d, *J* = 7.2 Hz, 2 H), 7.35-7.41 (m, 4 H), 7.26 (t, *J* = 7.2 Hz, 1 H), 6.73 (d, *J* = 8.4 Hz, 2 H), 3.69 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 145.8, 141.1, 131.5, 128.8, 128.1, 126.5, 126.3, 115.4. HRMS (EI) Calcd for $C_{12}H_{11}N$ (M^+) 169.0891, Found 169.0889.

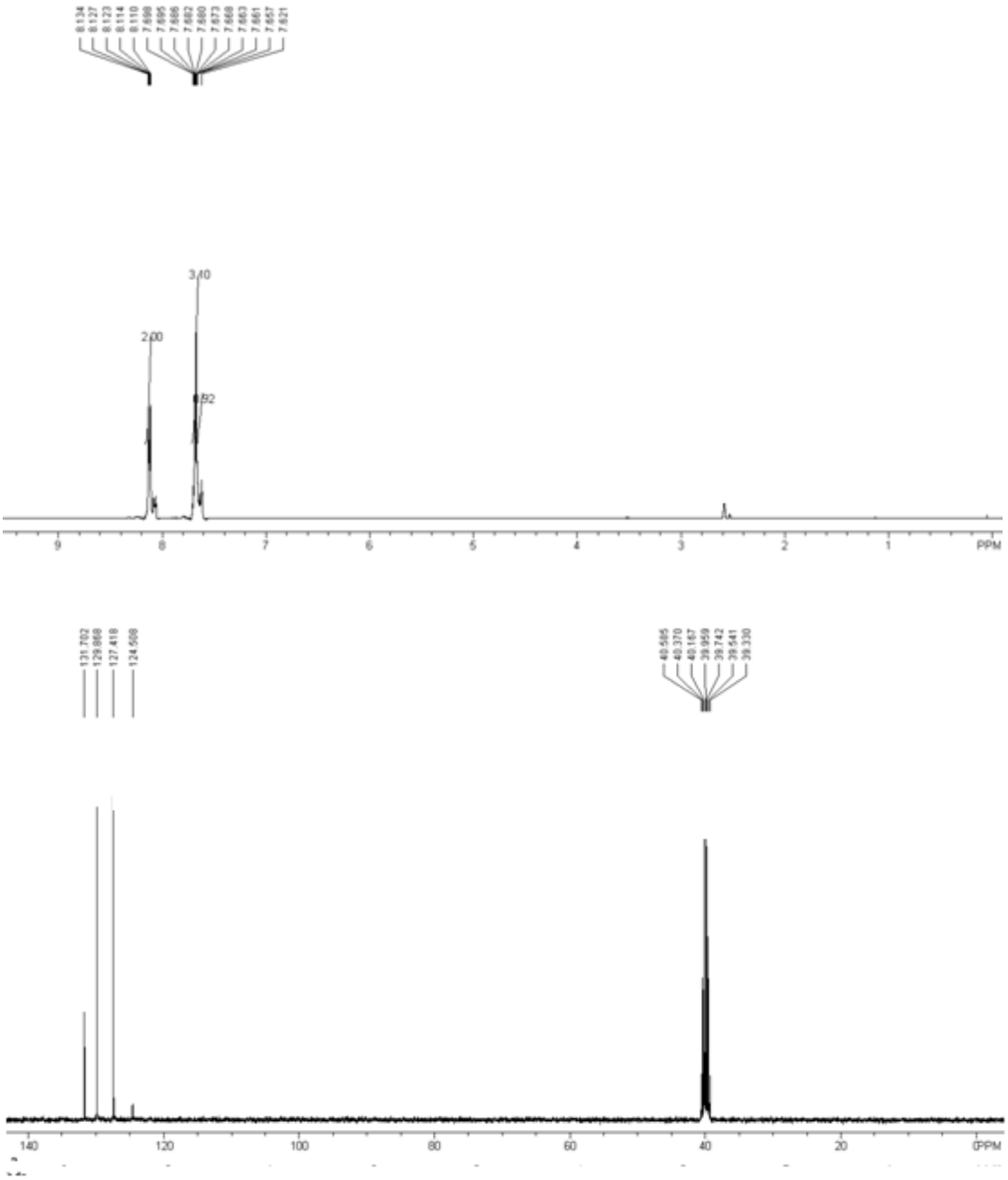




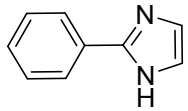
5-phenyl-1H-tetrazole (T 3−14, CAS no. 18039-42-4)



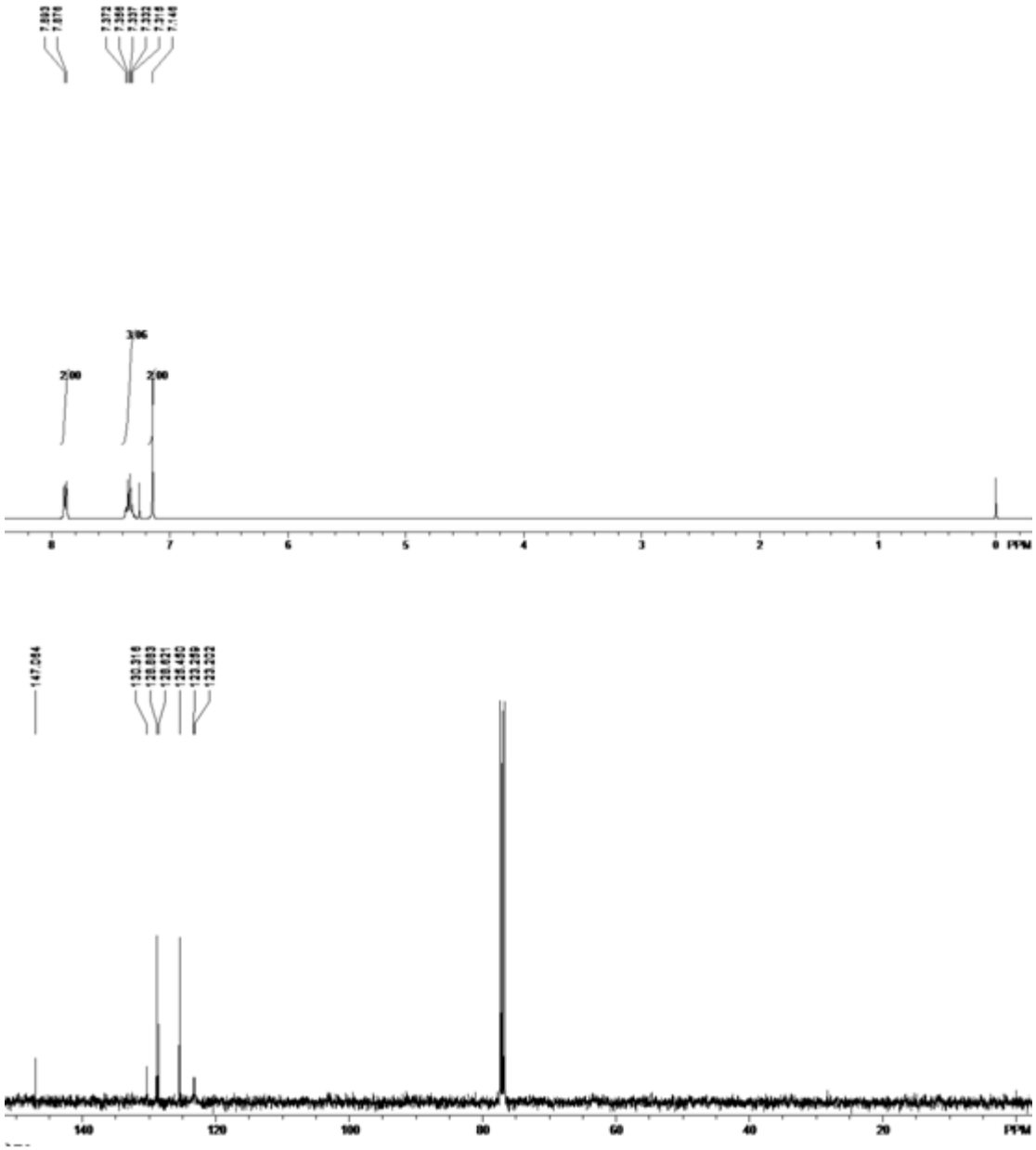
White solid, m.p. 214°C(dec.); ^{1}H NMR (400 MHz, d^{6}-DMSO, TMS) δ 8.11-8.14 (m, 2 H), 7.65-7.71 (m, 3 H), 7.61 (s, 2 H). ^{13}C NMR (100 MHz, d^{6}-DMSO, TMS) δ 131.8, 129.9, 127.4, 124.4. HRMS (EI) Calcd for $C_7H_6N_4$ (M^+) 146.0592, Found 146.0591.



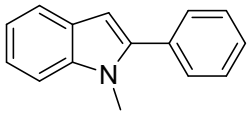
2-phenyl-1H-tetrazole (T 3−15, CAS no. 670-96-2)



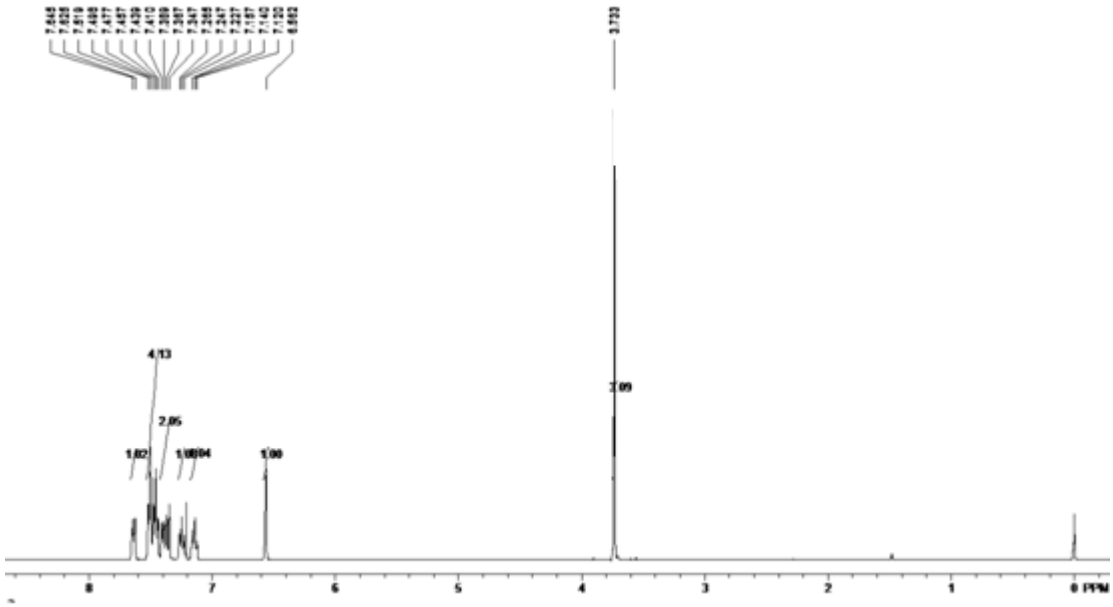
White solid, m.p. 146-147°C(lit.[3] mp 144-146°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.88 (d, J = 6.8 Hz, 2 H), 7.31-7.37 (m, 3 H), 7.15 (s, 2 H). ^{13}C NMR (100 MHz, d^6-DMSO, TMS) δ147.1, 130.3, 128.9, 128.6, 125.5, 123.26, 123.20. HRMS (EI) Calcd for $C_9H_8N_2$ (M^+) 144.0687, Found 144.0685.

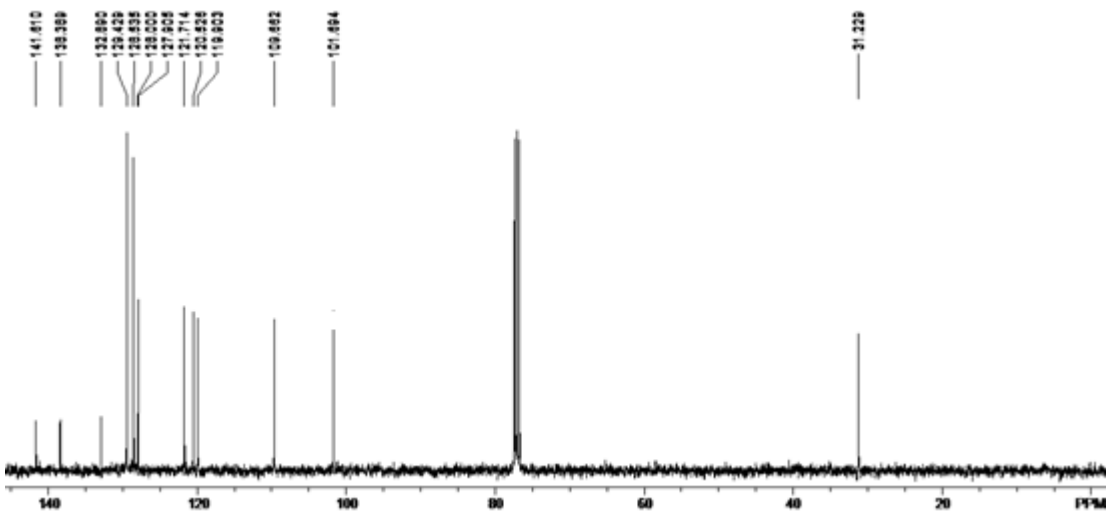


1-methyl-2-phenyl-indole (T 3−16, CAS no. 3558-24-5)

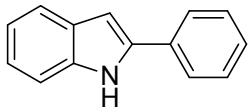


White solid, m.p. 98-99°C(lit.[4] mp 97-100°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (d, *J* = 8.0 Hz, 1 H), 7.43-7.52 (m, 4 H), 7.34-7.41 (m, 2 H), 7.25 (t, *J* = 7.6 Hz, 1 H), 7.14 (t, *J* = 7.6 Hz, 1 H), 6.56 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ141.6, 138.4, 132.9, 129.4, 128.5, 128.0, 127.9, 121.7, 120.5, 119.9, 109.7, 101.7, 31.2. HRMS (EI) Calcd for $C_{15}H_{13}N$ (M^+) 207.1048, Found 207.1047.

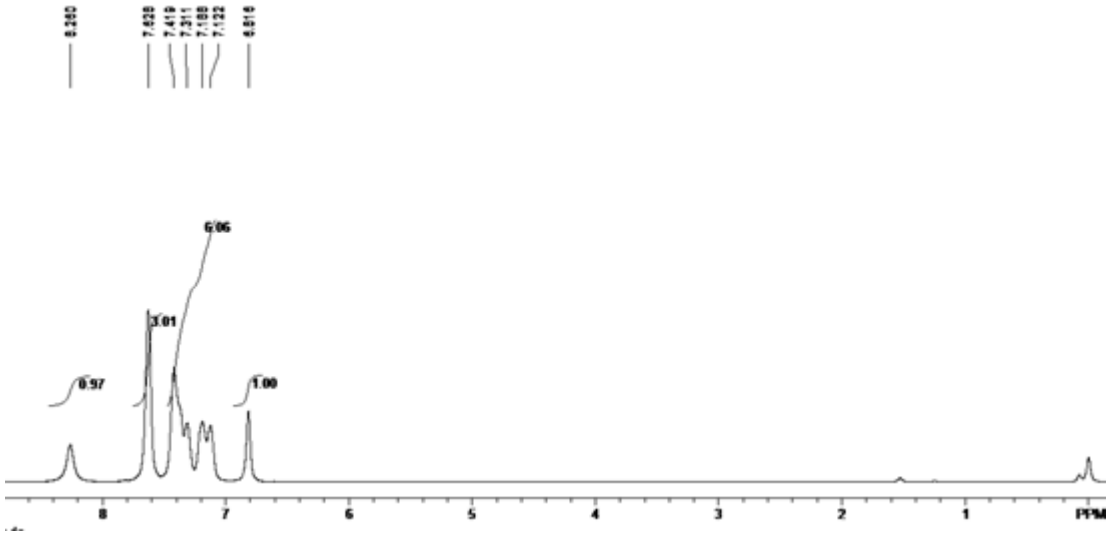


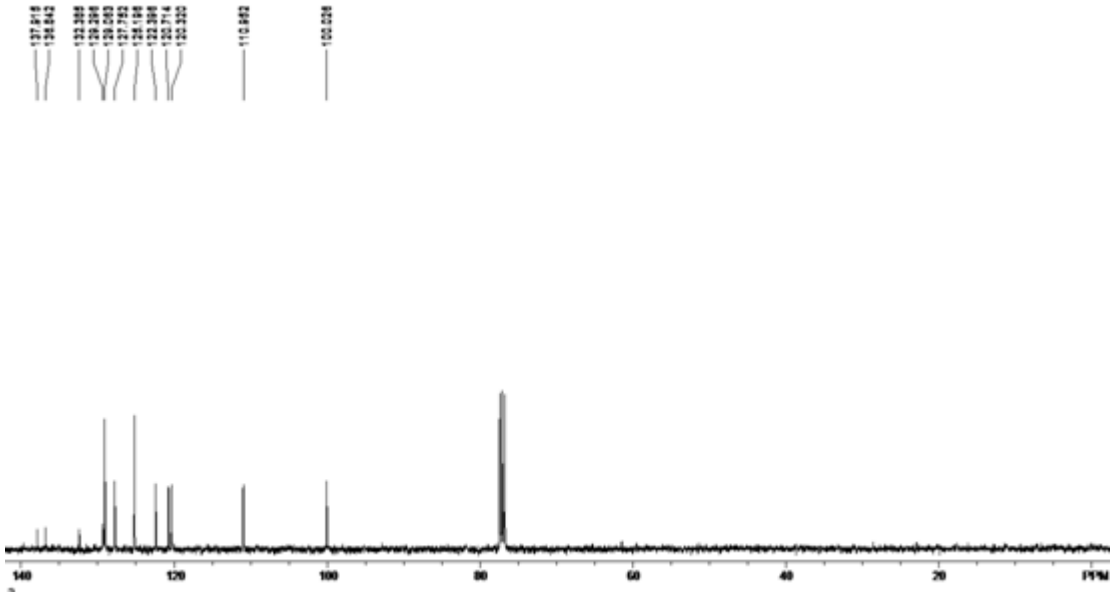


2-phenyl-indole (T 3−17, CAS no. 948-65-2)

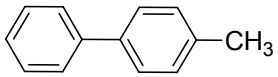


White solid, m.p. 187-189^{o}C(lit.[5] mp 186-188°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.26 (s, 1 H), 7.63 (s, 3 H), 7.12-7.42 (m, 6 H), 6.82 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ137.9, 136.8, 132.4, 129.3, 129.1, 127.8, 125.2, 122.4, 120.7, 120.3, 111.0, 100.0. HRMS (EI) Calcd for $C_{14}H_{11}N$ (M^+) 193.0891, Found 193.0893.

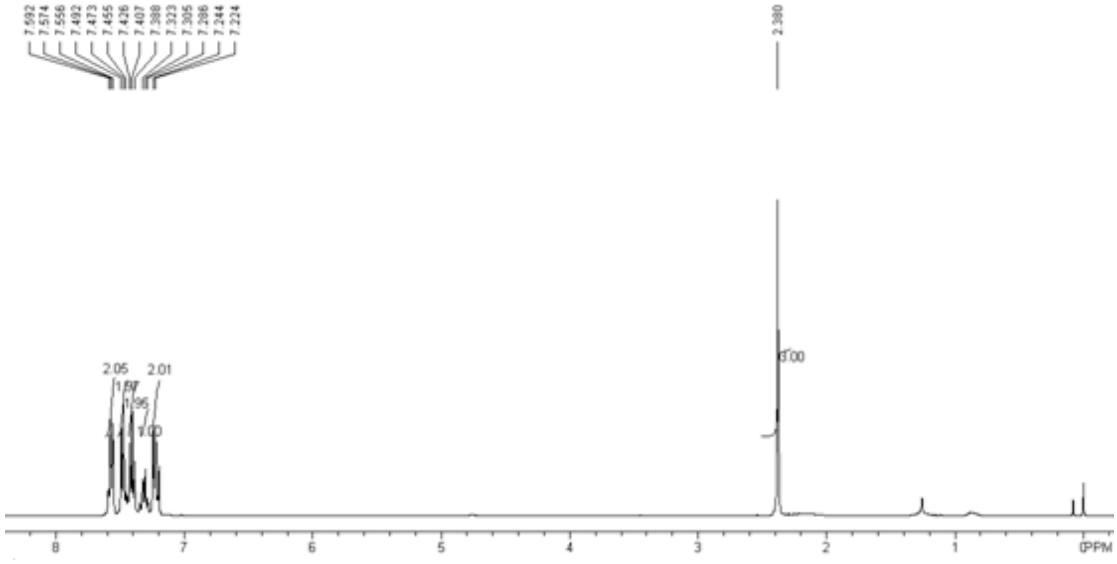


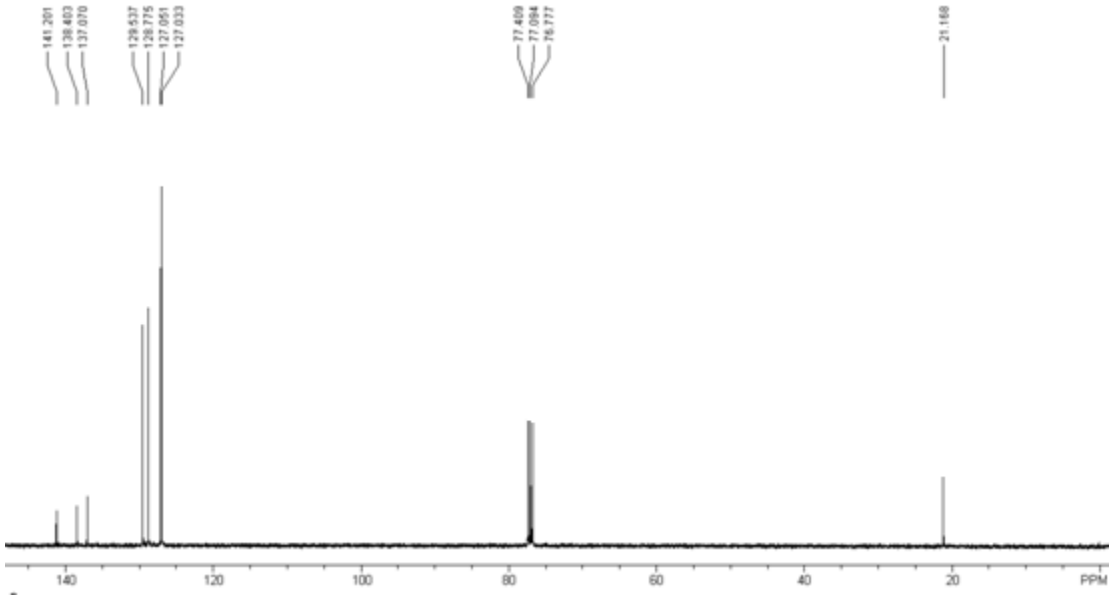


4-methyl-1,1'-biphenyl (T 4–5, CAS no.644-08-6)

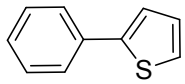


White solid, m.p. 47-48°C(lit.[1] mp 47-48°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (t, *J* = 7.2 Hz, 2 H), 7.47 (t, *J* = 7.2 Hz, 2 H), 7.40 (t, *J* = 7.2 Hz, 2 H), 7.30 (t, *J* = 7.2 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 2.37 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.1, 138.3, 137.2, 129.5, 128.9, 127.2, 127.0, 21.3. HRMS (EI) Calcd for $C_{13}H_{12}$ (M^+) 168.0939, Found 168.0938.

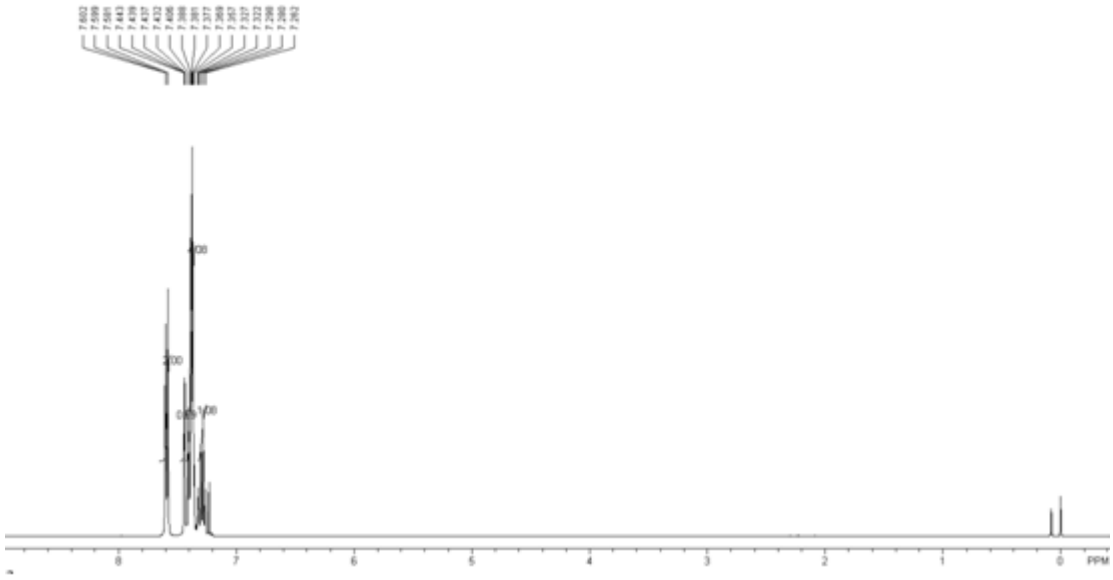


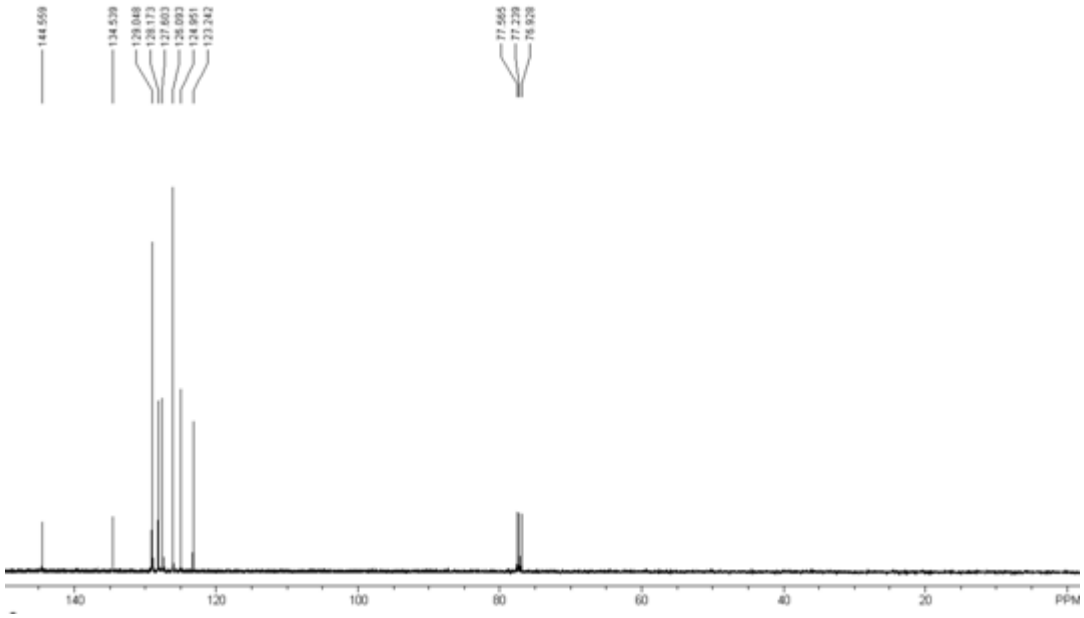


2-phenylthiophene (T 4−10, CAS no. 825-55-8)

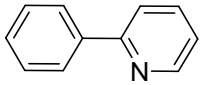


Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.25-7.33 (m, 1 H), 7.35-7.40 (m, 4 H), 7.43-7.46 (m, 1 H), 7.58-7.62 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.7, 134.4, 129.0, 128.2, 127.6, 126.0, 125.0, 123.2. HRMS (EI) Calcd for $C_{10}H_8S$ (M^+) 160.0347, Found 160.0349.

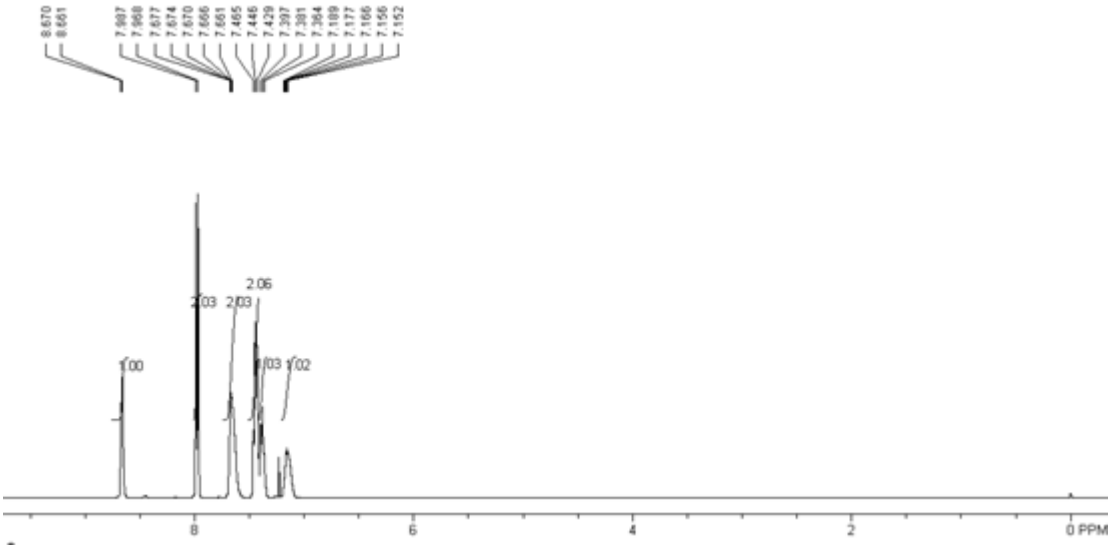


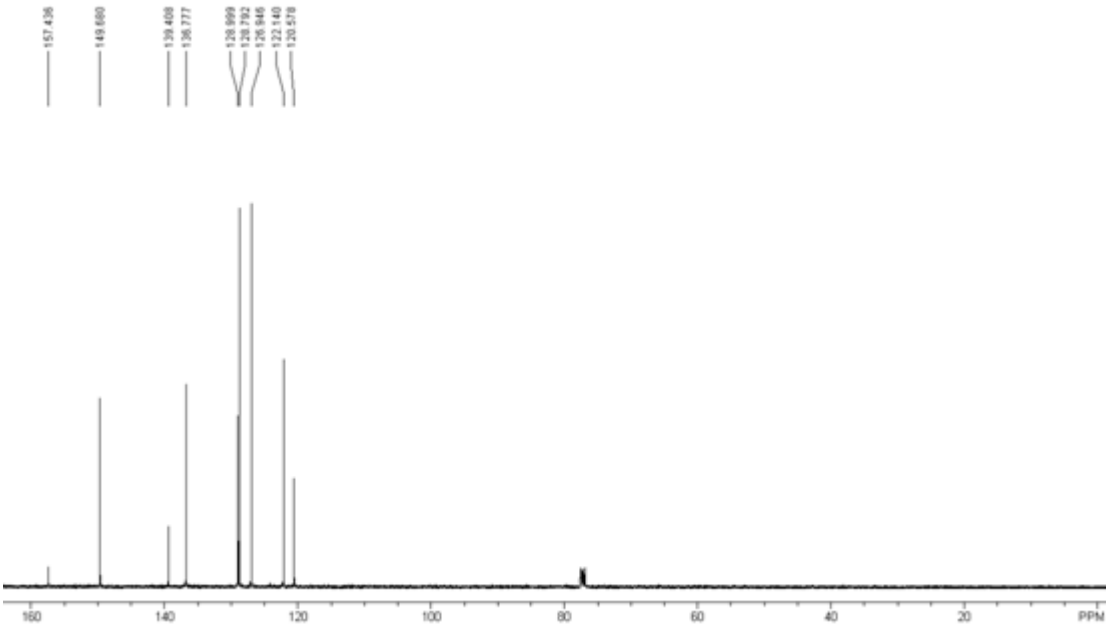


2-phenylpyridine(T 4−11, CAS no. 1008-89-5)

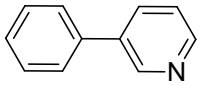


Colorless oil;^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.67 (d, *J* = 4.0 Hz, 1 H), 7.97 (d, *J* = 7.2 Hz, 2 H), 7.61-7.66 (m, 2 H), 7.46 (t, *J* = 7.2 Hz, 2 H), 7.39 (t, *J* = 7.2 Hz, 1 H), 7.11-7.18 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 157.3, 149.6, 139.3, 136.7, 129.0, 128.7, 126.8, 122.1, 120.5. HRMS (EI) Calcd for $C_{11}H_9N$ (M^+) 155.0735, Found 155.0737.

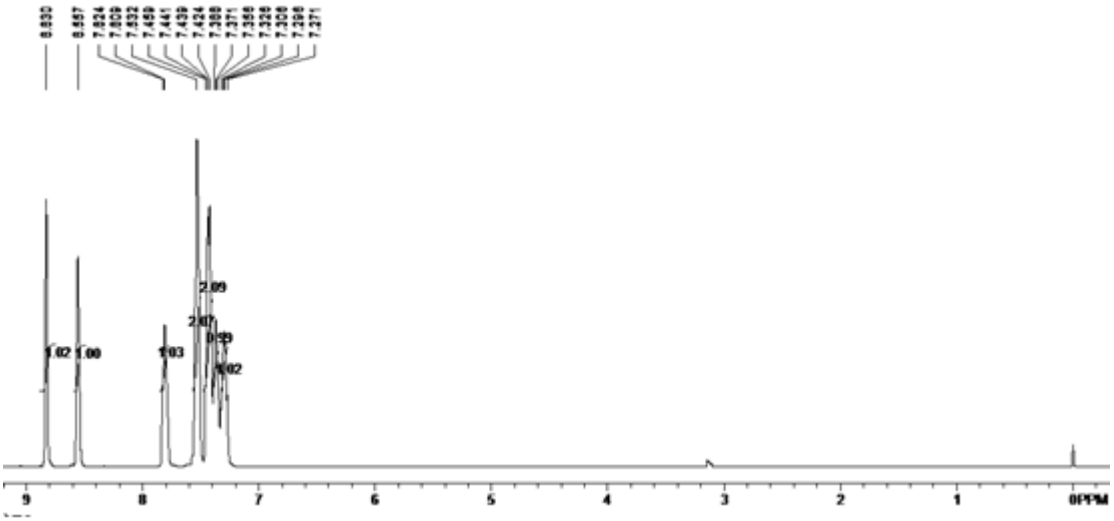


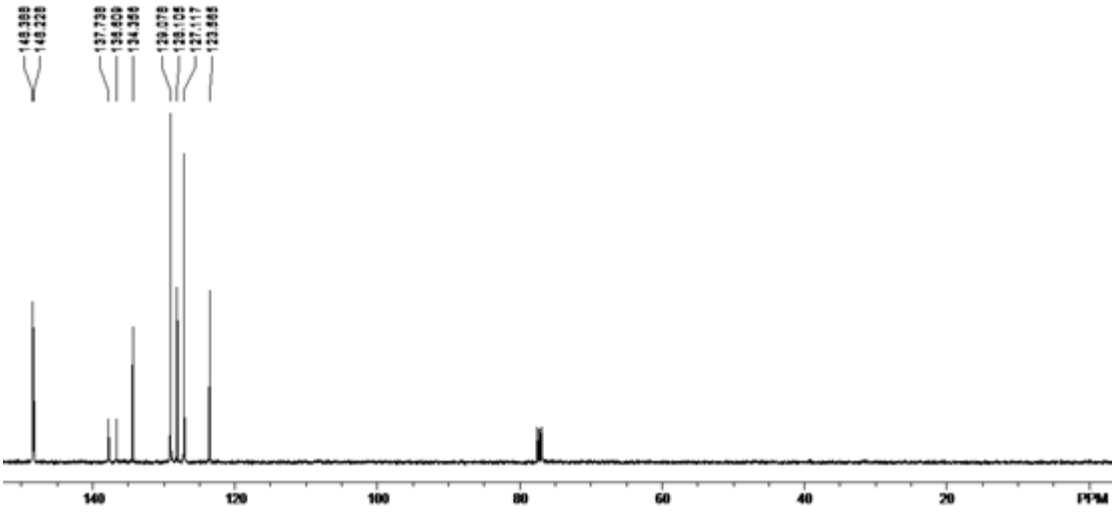


3-phenylpyridine(T 4−12, CAS no. 1008-88-4)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.82 (s, 1 H), 8.57 (s, 1 H), 7.81 (d, *J* = 6.4 Hz, 1 H), 7.52 (s, 2 H), 7.44 (d, *J* = 6.8 Hz, 2 H), 7.38 (t, *J* = 6.8 Hz, 1 H), 7.27-7.34 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 148.4, 148.1, 137.7, 136.5, 134.3, 129.1, 128.0, 127.1, 123.5. HRMS (EI) Calcd for $C_{11}H_9N$ (M^+) 155.0735, Found 155.0737.





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