Electronic Supplementary Material (ESI) for RSC Advances.

Pd-catalyzed Desulfitative and Denitrogenative Suzuki-type Reaction of Arylsulfonyl Hydrazides

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Supporting Materials

Content

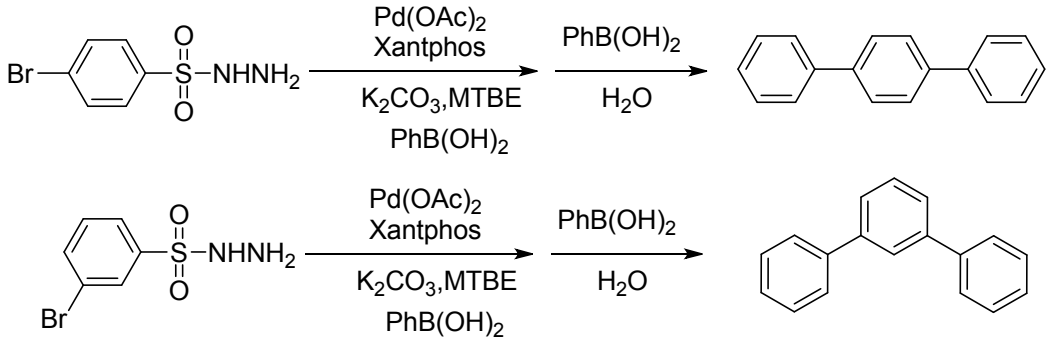
General

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 arylboronic acids (0.50 mmol), arylsulfonyl hydrazides (0.50 mmol), $Pd(OAc)_2$ (5 mol%), Xantphos (10 mol%) and K_2CO_3 (0.50 mmol) was stirred in the solvent of MTBE (1.0 ml) at 60^{o}C for 6.0 hours under air. After cooling down to room temperature, the insoluble was first removed by filtration and then the 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.

Typical procedure for “One-pot” synthesis of terphenyl



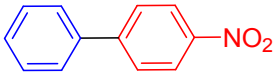
A mixture of bromo-phenylsulfonohydrazide (0.5 mmol), phenylboronic acid (0.5 mmol), $Pd(OAc)_2$ (5 mol%), Xantphos (10 mol%) and K_2CO_3 (0.50 mmol) was stirred in the solvent of MTBE (1.0 ml) at 60^{o}C for 6 h under air. Then phenylboronic acid (0.5 mmol) and water (0.5 mL) were added to the mixture for 3h. Afterward, the mixture was filtered through a pad of celite and the solution was extracted by Et_2O (2 mL) for three times. The organic phase was evaporated under reduced pressure, and the residue was subjected to flash column chromatography to obtain the desired product.

Typical procedure for Gram-scale synthesis of OTBN

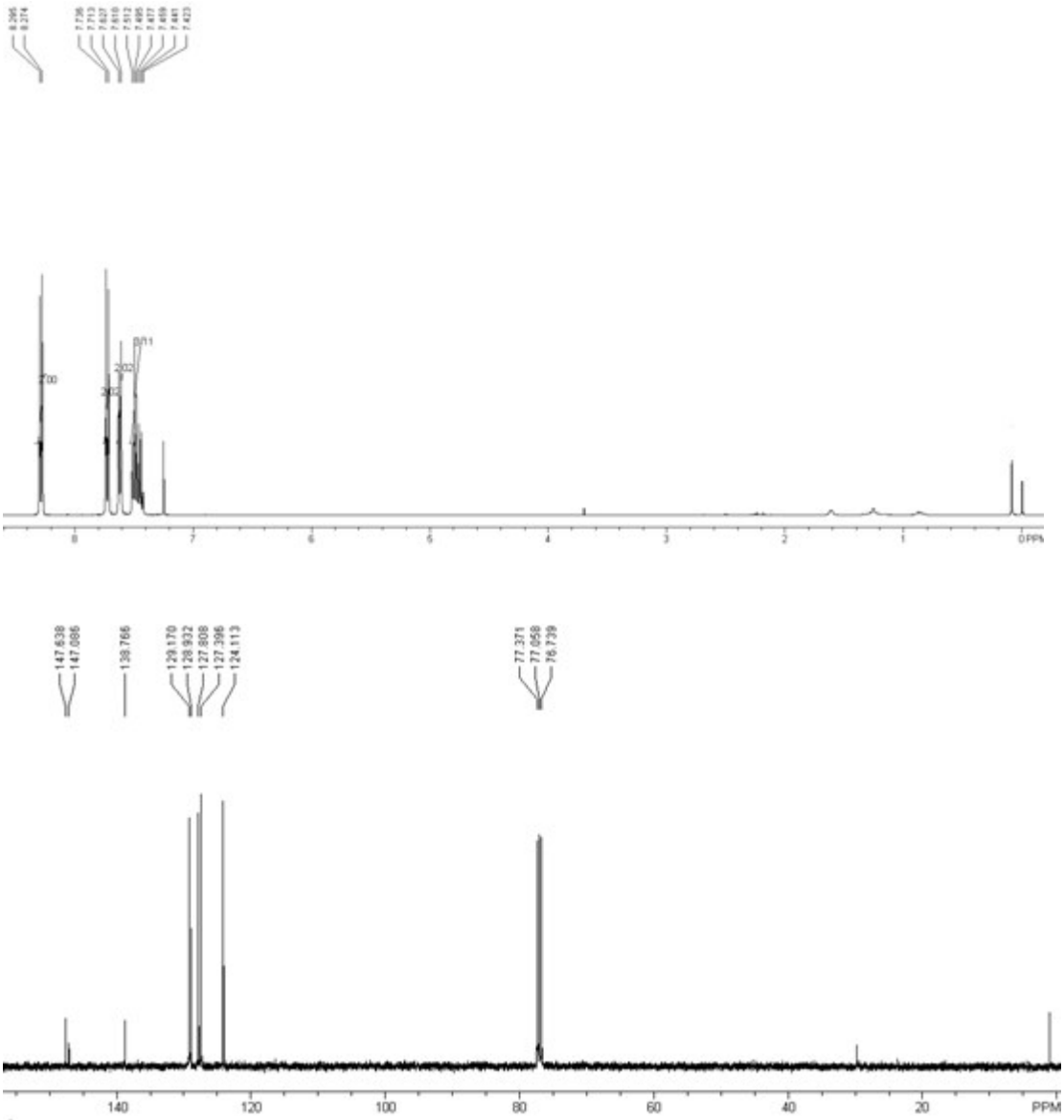
A mixture of 4-methyl-phenylsulfonohydrazide (5.25 mmol, 977mg), (2-cyanophenyl)boronic acid (5 mmol, 735 mg), $Pd(OAc)_2$ (2 mol%, 22.4 mg), Xantphos(3 mol%, 86.8 mg), K_2CO_3 (5 mmol, 690mg) was stirred at 60^{o}C for 6h in MTBE (5 mL). Afterward, the mixture was filtered through a pad of celite and the solution was evaporated under reduced pressure, and the residue was subjected to flash column chromatography to obtain 2-cyano-4-methylbiphenyl.

Characterization data of the product

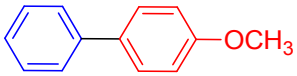
4-nitro-1,1'-biphenyl (3a, CAS#92-93-3)



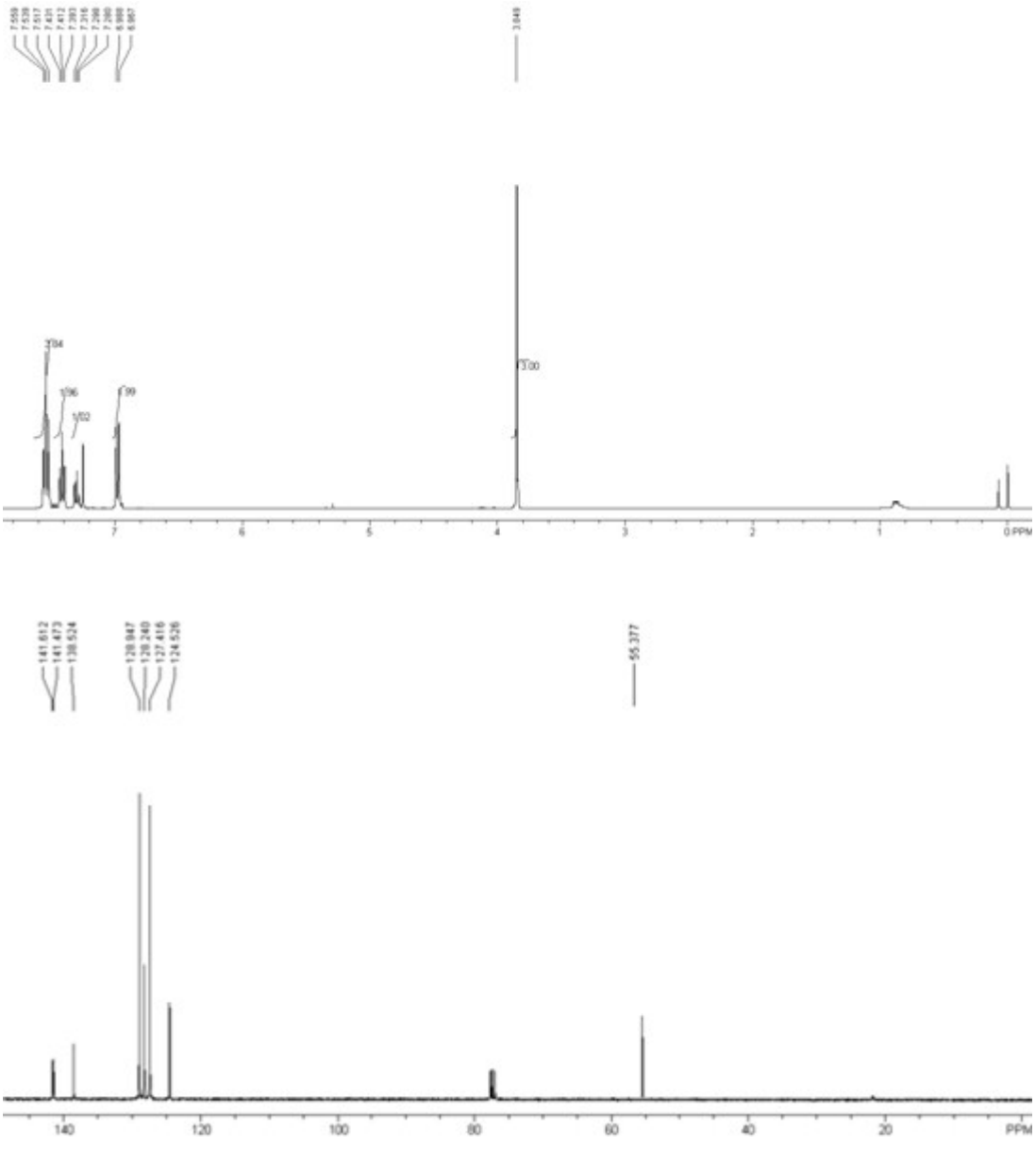
White solid, m.p. 114-115°C(lit.[1] mp 115-116°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.27 (d, *J* = 8.4 Hz, 2 H), 7.73 (d, *J* = 8.8 Hz, 2 H), 7.63 (d, *J* = 7.2 Hz, 2 H), 7.42-7.50 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 147.5, 147.1, 138.9, 129.2, 128.8, 127.9, 127.4, 124.2. HRMS (EI) Calcd for $C_{12}H_9NO_2$ (M^+) 199.0633, Found 199.0637.



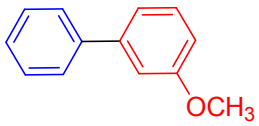
4-methoxy-1,1'-biphenyl (3b, CAS#613-37-6)



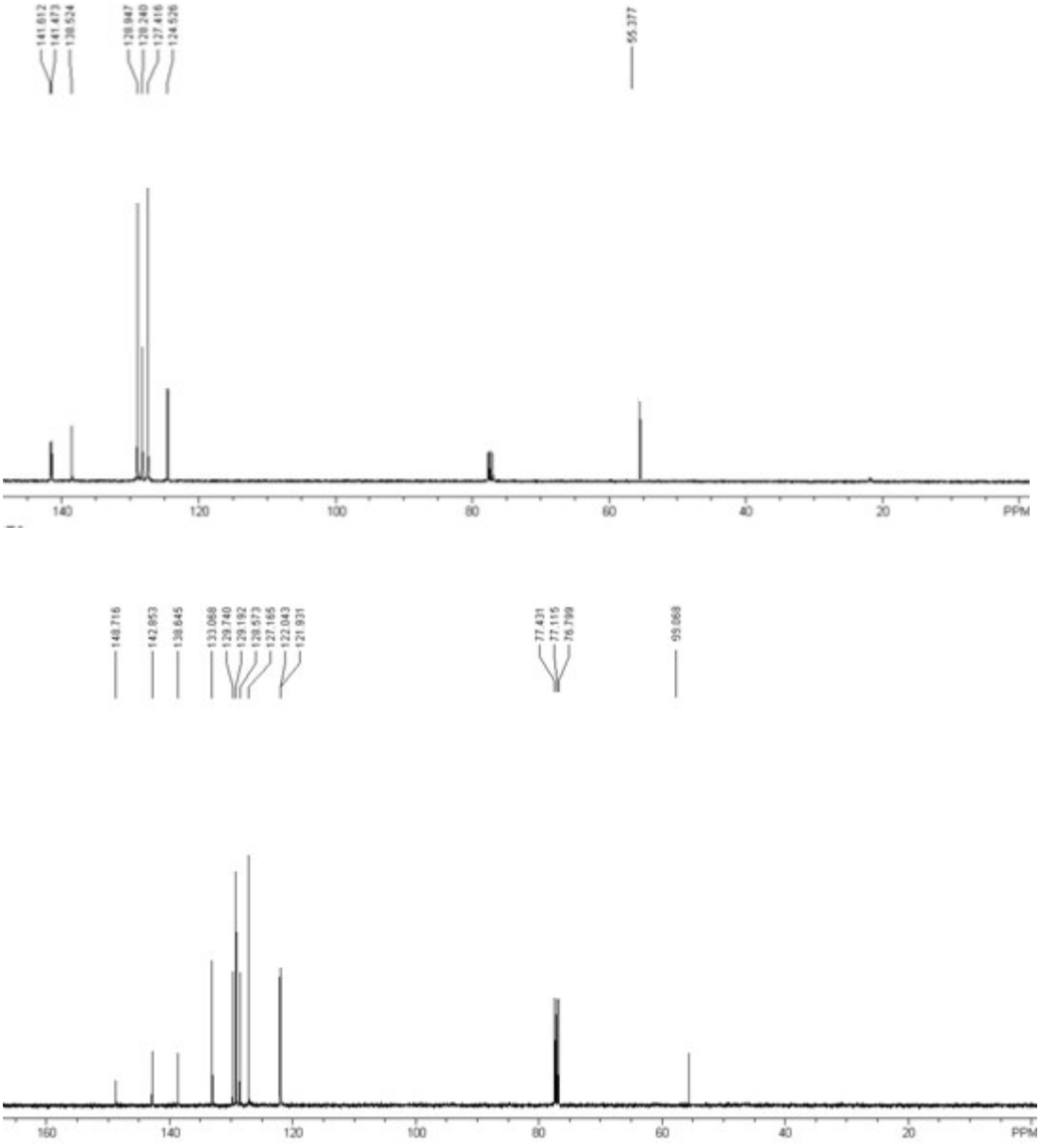
White solid, m.p. 90°C(lit.[1] mp 88-89°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53 (t, *J* = 8.6 Hz, 4 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 7.31 (t, *J* = 7.6 Hz, 1 H), 6.96 (d, *J* = 8.6 Hz, 2 H), 3.81 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.6, 141.4, 138.4, 128.8, 128.2, 127.3, 124.6, 55.3. HRMS (EI) Calcd for $C_{13}H_{12}O$ (M^+) 184.0888, Found 184.0889.



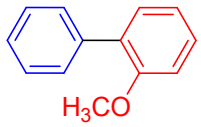
3-methoxy-1,1'-biphenyl (3c, CAS #2113-56-6)



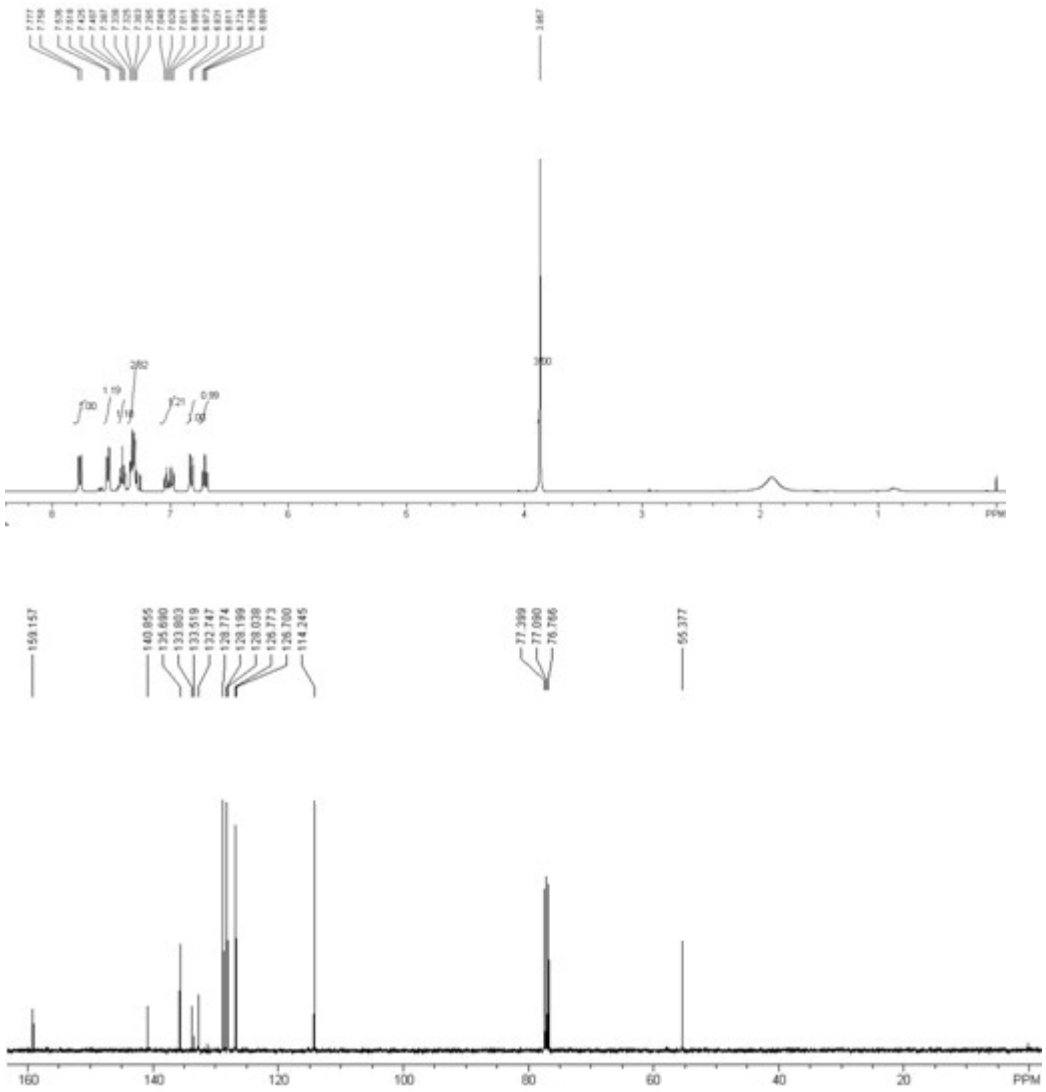
White solid, m.p. 82-84°C(lit.[1] mp 82-83°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.57 (d, *J* = 7.2 Hz, 2 H), 7.43 (t, *J* = 7.4 Hz, 2 H), 7.31-7.36 (m, 2 H), 7.18 (d, *J* = 7.4 Hz, 1 H), 7.13 (s, 1 H), 6.88 (d, *J* = 8.0 Hz, 1 H), 3.83 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 148.6, 142.8, 138.7, 133.1, 129.6, 129.3, 128.5, 127.1, 122.0, 121.9, 55.2. HRMS (EI) Calcd for $C_{13}H_{12}O$ (M^+) 184.0888, Found 184.0886.



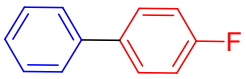
2-methoxy-1,1'-biphenyl (3d, CAS#86-26-0)



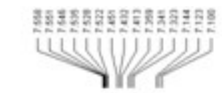
White solid, m.p. 32-33°C(lit.[1] mp 31-32°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.75 (d, *J* = 7.6 Hz, 1 H), 7.53 (d, *J* = 7.4 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 1 H), 7.29-7.33 (m, 3 H), 6.98-7.05 (m, 1 H), 6.82 (d, *J* = 8.0 Hz, 1 H), 6.71 (t, *J* = 7.4 Hz, 1 H), 3.86 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 159.3, 140.8, 135.6, 133.7, 133.4, 132.6, 128.7, 128.2, 127.9, 126.7, 126.6, 114.3, 55.3. HRMS (EI) Calcd for $C_{13}H_{12}O$ (M^+) 184.0888, Found 184.0893.

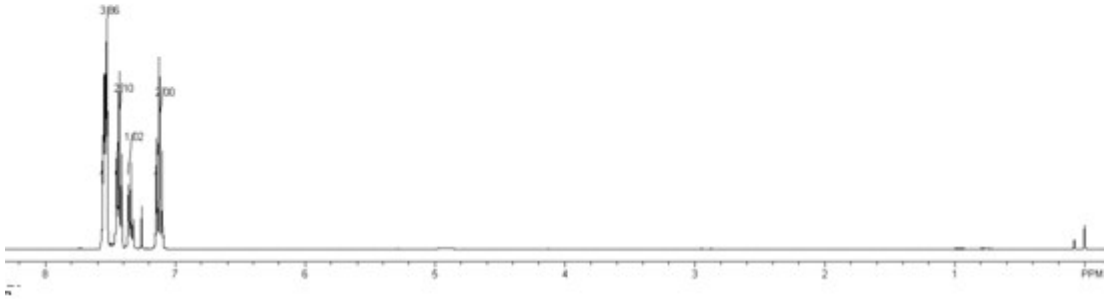


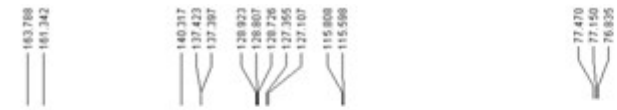
4-fluoro-1,1'-biphenyl (3e, CAS#324-74-3)

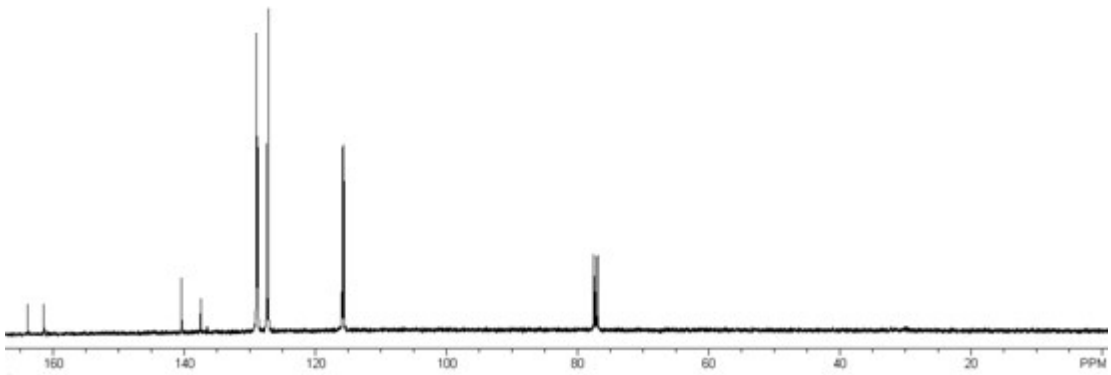


White solid, m.p. 72-74°C(lit.[2] mp 73-74°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52-7.57 (m, 4 H), 7.42 (t, *J* = 7.4 Hz, 2 H), 7.34 (t, *J* = 7.2 Hz, 1 H), 7.12 (t, *J* = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 163.4 (d, *J* = 244 Hz), 140.3, 137.5, 137.4, 128.8, 128.6 (d, *J* = 8.2 Hz), 127.4, 127.2, 115.8 (d, *J* = 21.2 Hz). HRMS (EI) Calcd for $C_{12}H_9F$ (M^+) 172.0688, Found 172.0691.

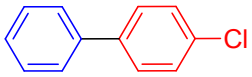




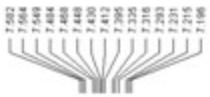


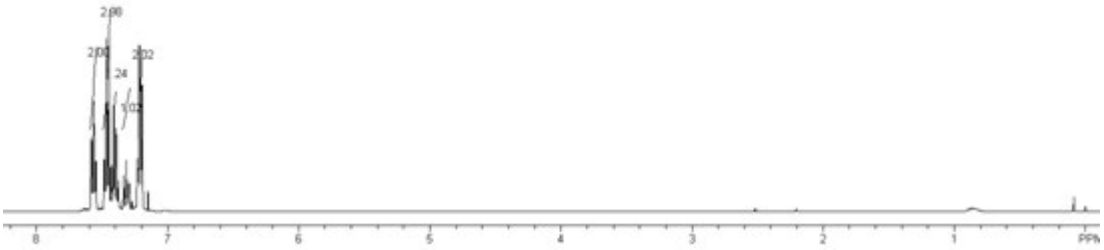


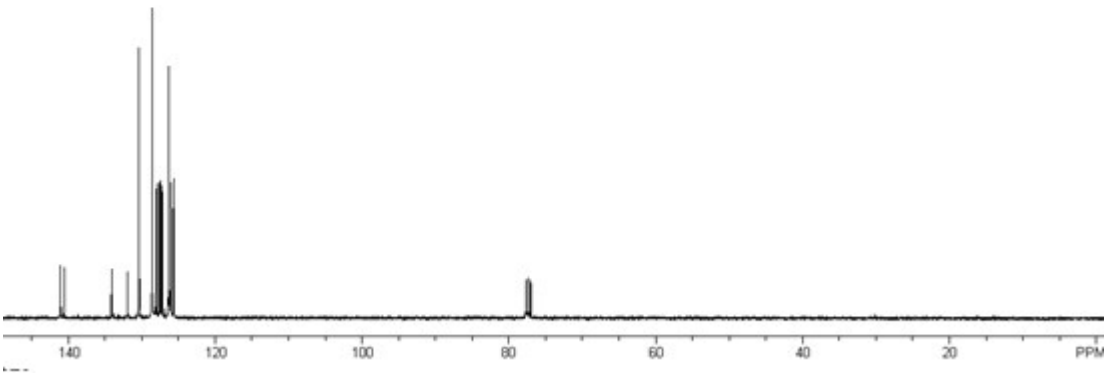
4-Cholro-1,1'-biphenyl (3f, CAS#2051-62-9)



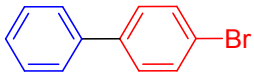
White solid, m.p. 46-47°C(lit.[1] mp 47-48°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.56 (t, J = 7.0 Hz, 2 H), 7.40-7.47 (m, 4 H), 7.33 (t, J = 7.2 Hz, 1 H), 7.23 (d, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.2, 140.6, 134.0, 131.8, 130.4, 128.4, 127.9, 127.6, 127.3, 126.2, 126.0, 125.6. HRMS (EI) Calcd for $C_{12}H_9Cl$ (M^+) 188.0393, Found 188.0390.



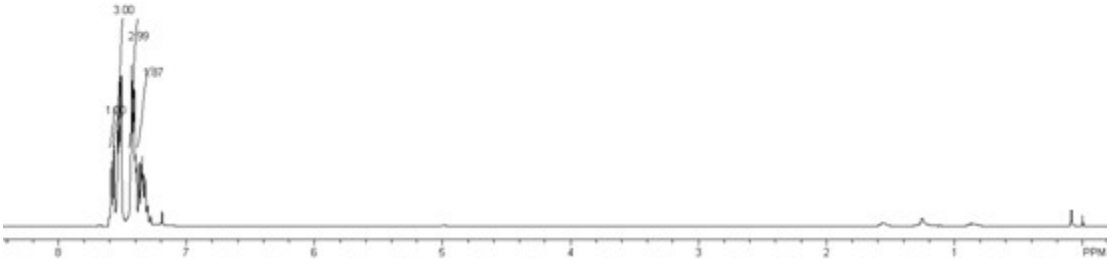


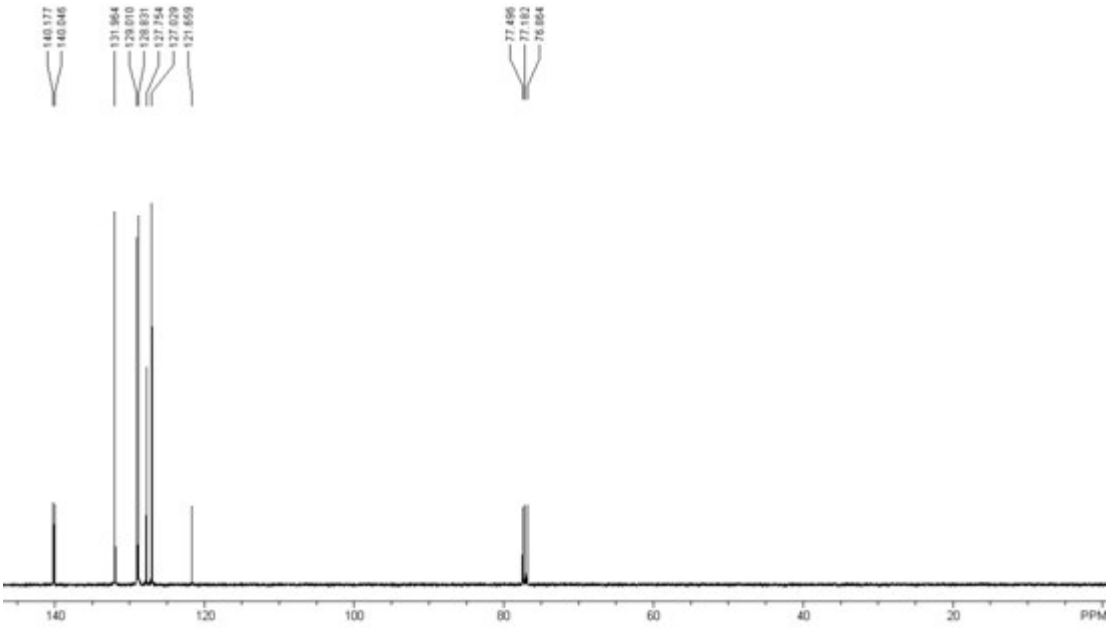


4-bromo-1,1'-biphenyl (3g, CAS#92-66-0)

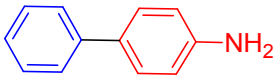


White solid, m.p. 90-91°C(lit.[1] mp 91-92°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.57 (d, *J* = 7.2 Hz, 1 H), 7.50-7.54 (m, 3 H), 7.39-7.44 (m, 3 H), 7.30-7.36 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 140.3, 140.0, 132.0, 129.1, 128.7, 127.8, 127.1, 121.8. HRMS (EI) Calcd for $C_{12}H_9Br$ (M^+) 231.9888, Found 231.9885.

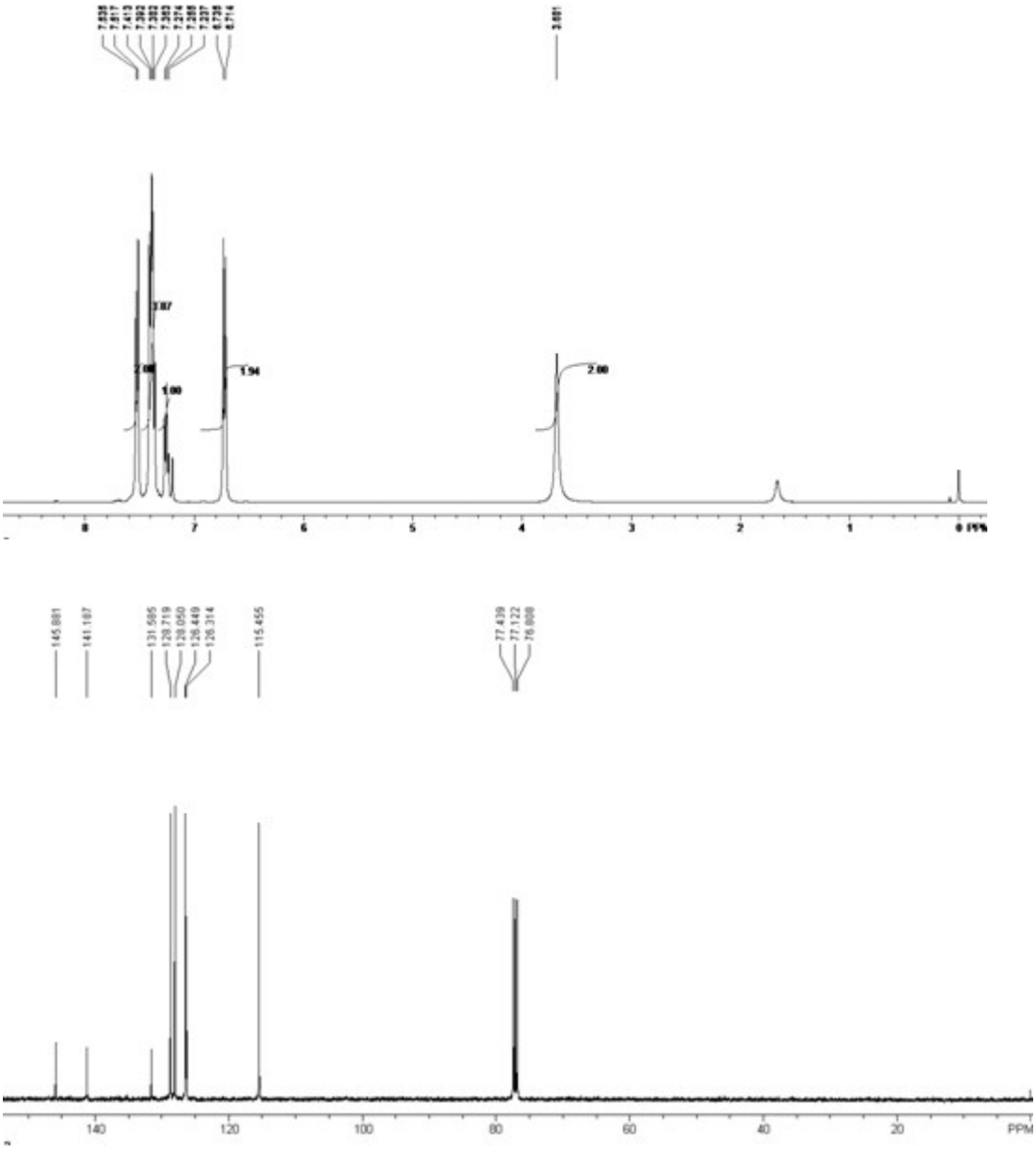




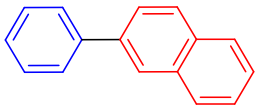
4-amine-1,1'-biphenyl (3h, CAS#92-67-1)



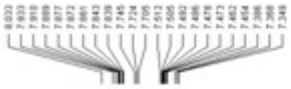
White solid, m.p. 73-75°C(lit.[2] mp 73-74°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.54 (d, *J* = 7.2 Hz, 2 H), 7.36-7.40 (m, 4 H), 7.24 (t, *J* = 7.2 Hz, 1 H), 6.71 (d, *J* = 8.0 Hz, 2 H), 3.69 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 145.8, 141.3, 131.6, 128.6, 128.1, 126.4, 126.2, 115.6. HRMS (EI) Calcd for $C_{12}H_{11}N$ (M^+) 169.0891, Found 169.0889.

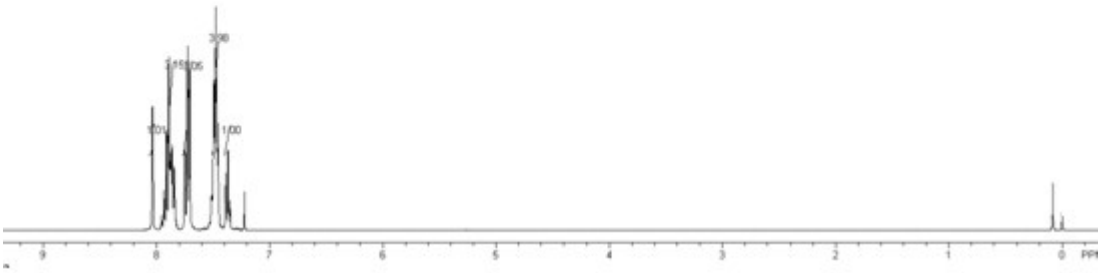


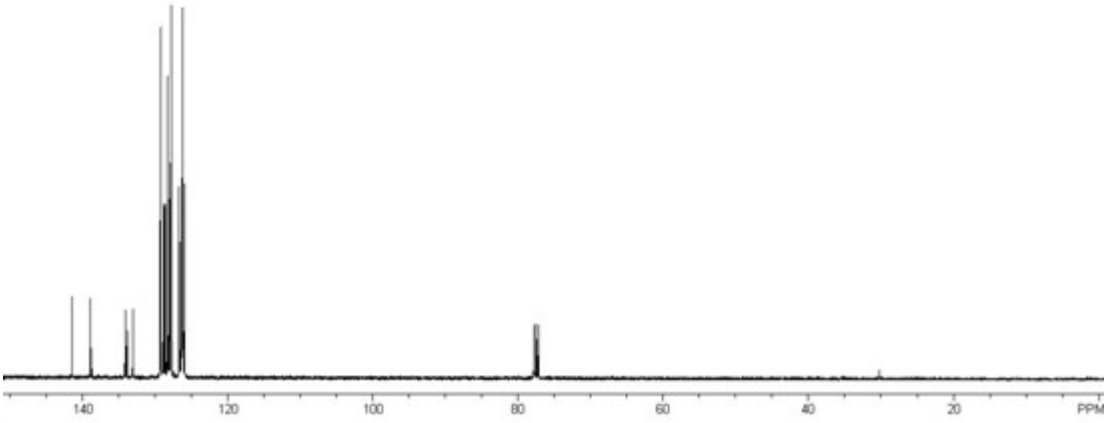
2-phenylnaphthalene (3i, CAS#612-94-2)



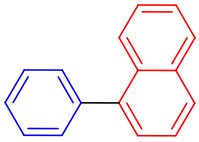
White solid, m.p. 97-98°C(lit.[2] mp 96-97°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02 (s, 1 H), 7.84-7.92 (m, 3 H), 7.73 (t, J = 7.6 Hz, 3 H), 7.46-7.51 (m, 4 H), 7.37 (t, J = 7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.3, 138.8, 134.2, 133.8, 133.1, 129.3, 128.8, 128.5, 128.3, 127.9, 127.7, 127.6, 126.7, 126.3, 126.1, 125.8. HRMS (EI) Calcd for $C_{16}H_{12}$ (M^+) 204.0939, Found 204.0942.



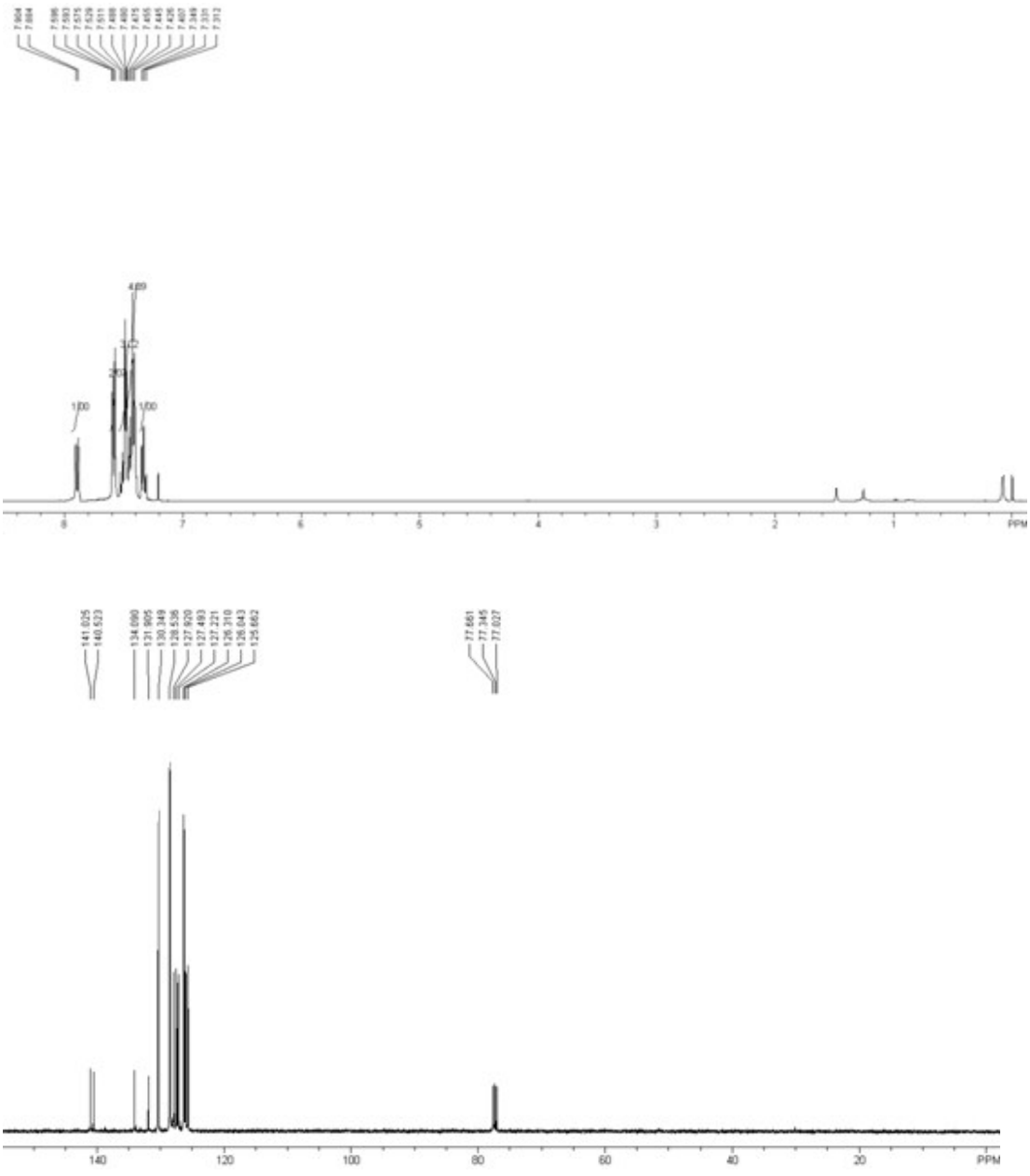




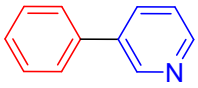
1-phenylnaphthalene (3j, CAS#605-02-7)



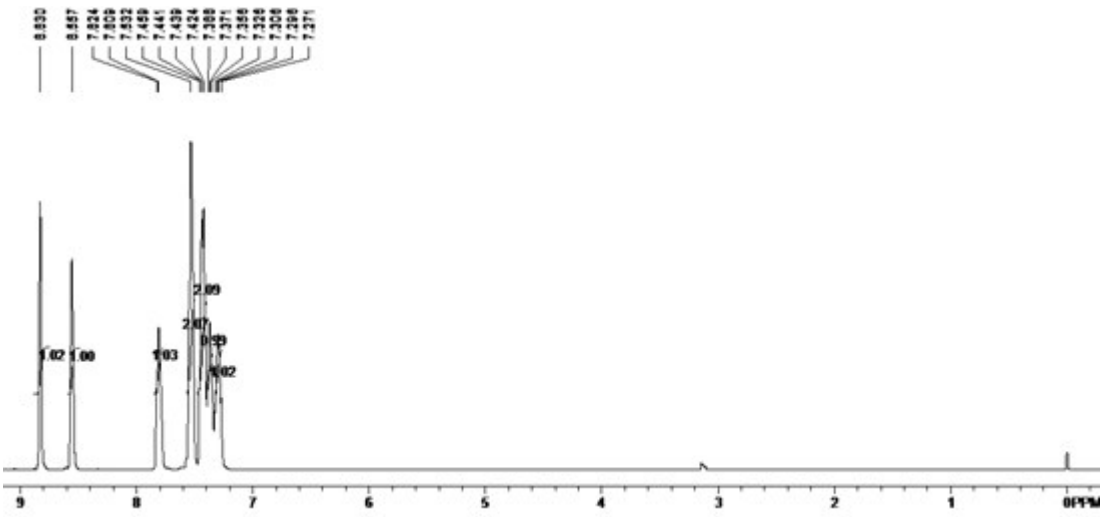
White solid, m.p. 43-44°C(lit.[2] mp 41-43°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.89 (t, *J* = 8.4 Hz, 1 H), 7.58 (d, *J* = 8.4 Hz, 2 H), 7.47-7.53 (m, 3 H), 7.41-7.46 (m, 5 H), 7.32 (t, *J* = 7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.0, 140.4, 134.0, 132.0, 130.3, 128.6, 127.9, 127.6, 127.1, 126.4, 126.1, 125.6. HRMS (EI) Calcd for $C_{16}H_{12}$ (M^+) 204.0939, Found 204.0935.

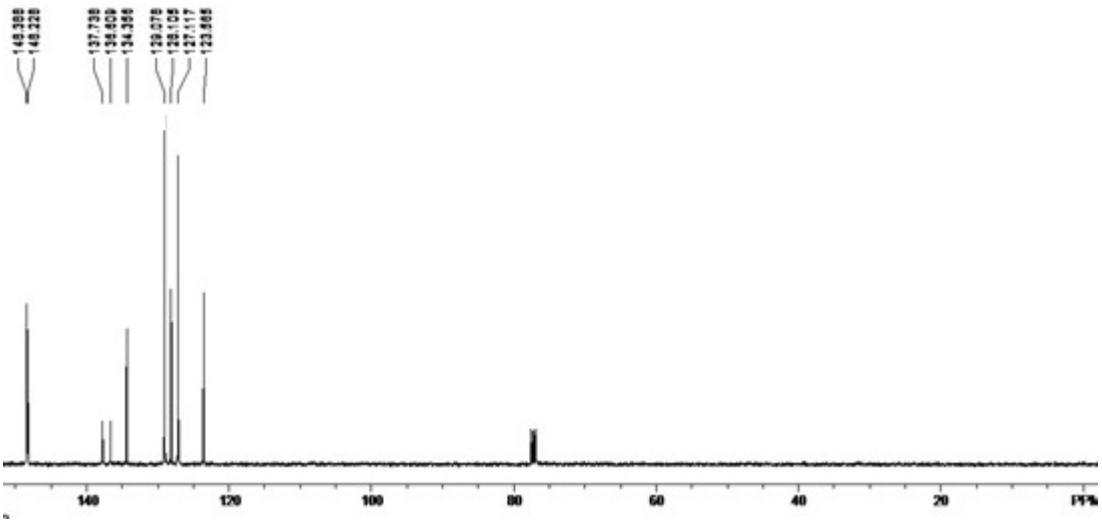


3-phenylpyridine (3k, CAS# 1008-88-4)

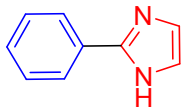


Colorless oil;^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.83 (s, 1 H), 8.56 (s, 1 H), 7.82 (d, J = 6.0 Hz, 1 H), 7.53 (s, 2 H), 7.43 (d, J = 6.8 Hz, 2 H), 7.37 (t, J = 6.8 Hz, 1 H), 7.27-7.33 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ148.4, 148.2, 137.7, 136.6, 134.4, 129.1, 128.1, 127.1, 123.6. HRMS (EI) Calcd for $C_{11}H_9N$ (M^+) 155.0735, Found 155.0739.

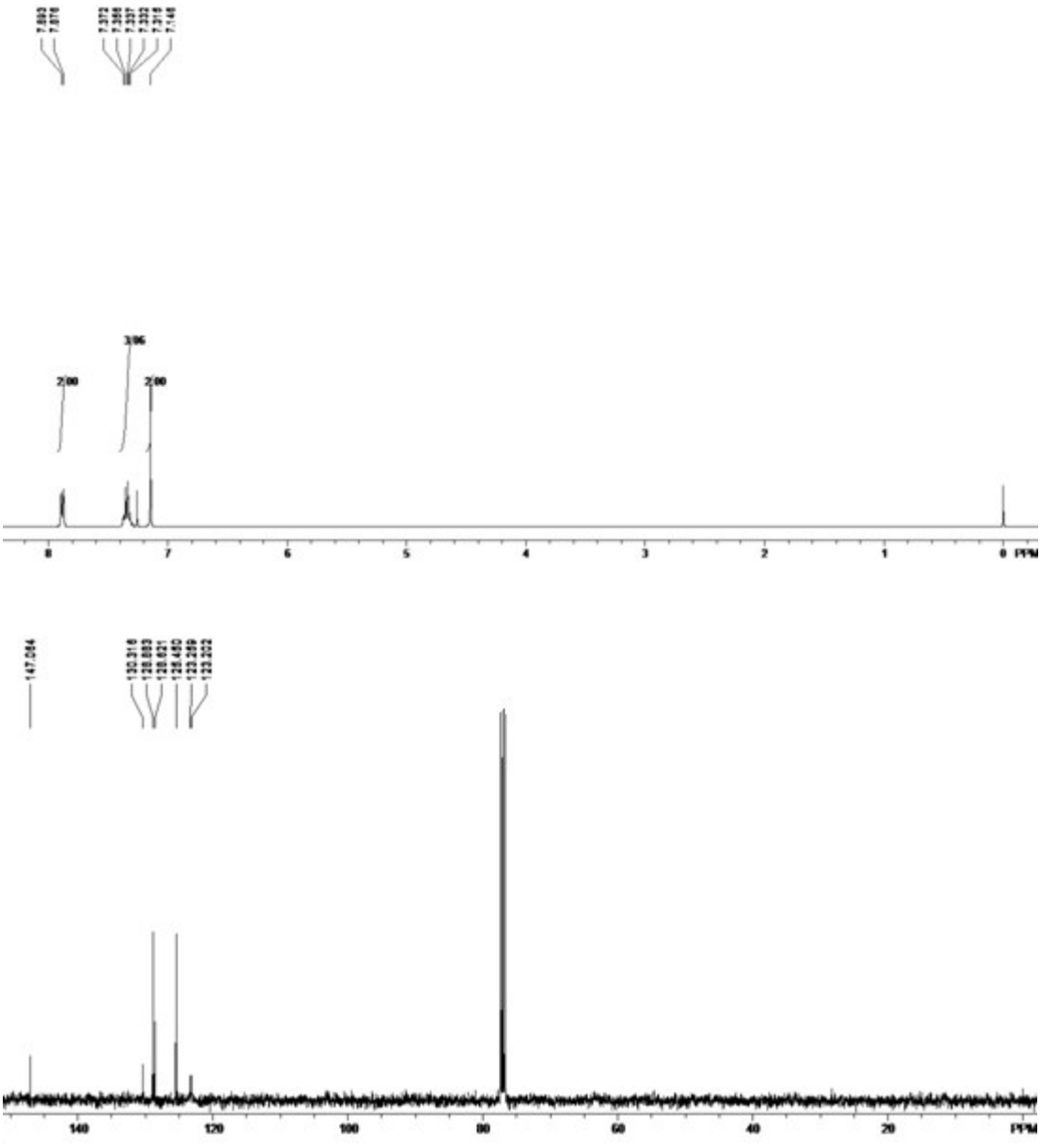




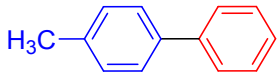
2-phenyl-1H-tetrazole (3l, CAS#670-96-2)



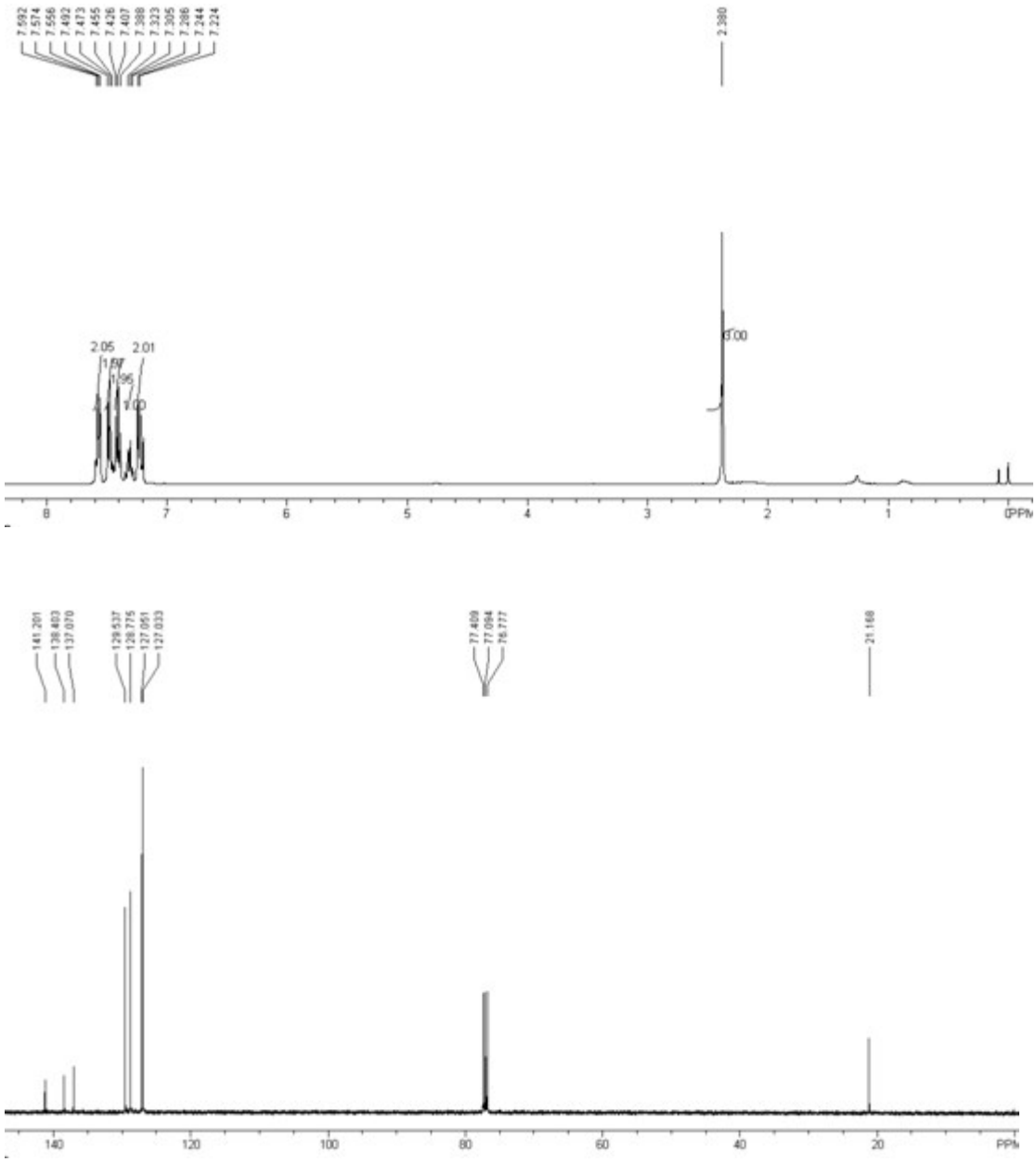
White solid, m.p. 149-150°C(lit.[3] mp 144-146°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.88 (d, J = 6.8 Hz, 2 H), 7.31-7.37 (m, 3 H), 7.15 (s, 2 H). ^{13}C NMR (100 MHz, d^6-DMSO, TMS) δ147.1, 130.3, 128.9, 128.6, 125.5, 123.26, 123.20. HRMS (EI) Calcd for $C_9H_8N_2$ (M^+) 144.0687, Found 144.0685.



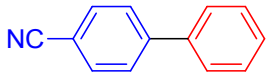
4-methyl-1,1'-biphenyl (3m, CAS#644-08-6)



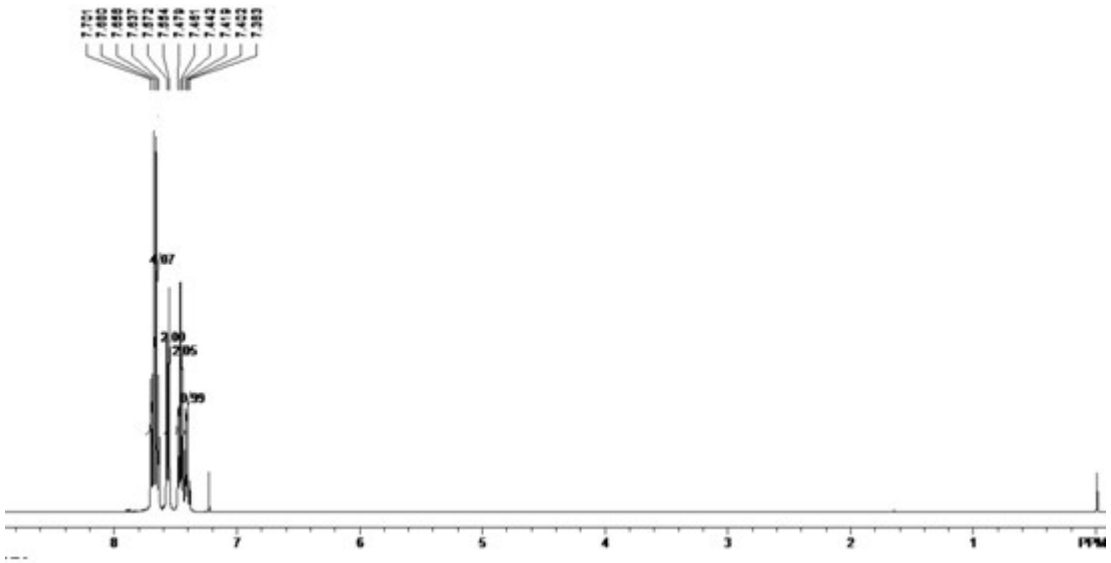
White solid, m.p. 46-47°C(lit.[1] mp 47-48°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.57 (t, *J* = 7.2 Hz, 2 H), 7.46 (t, *J* = 7.2 Hz, 2 H), 7.40 (t, *J* = 7.4 Hz, 2 H), 7.32 (t, *J* = 7.2 Hz, 2 H), 7.23 (d, *J* = 7.6 Hz, 2 H), 2.39 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.1, 138.5, 137.2, 129.5, 128.9, 127.1, 126.9, 21.3. HRMS (EI) Calcd for $C_{13}H_{12}$ (M^+) 168.0939, Found 168.0935.

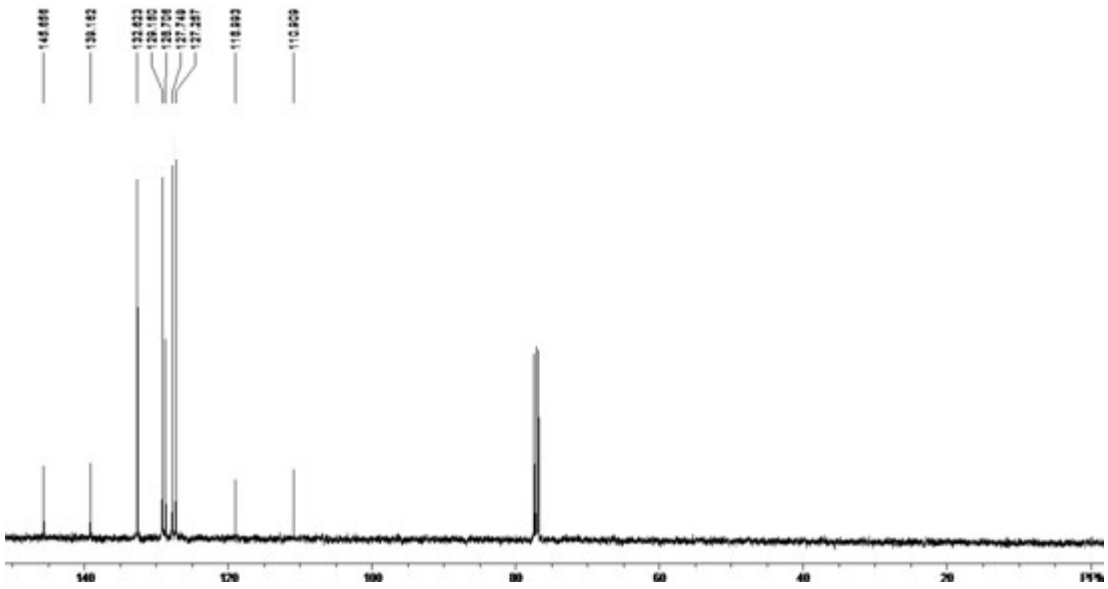


4-Cyanobiphenyl (3s, CAS#2920-38-9)

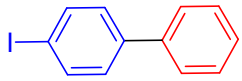


White solid, m.p. 72-73°C(lit.[2] mp 73-74°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.67 (q, *J* = 8.0 Hz, 4 H), 7.57 (d, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* = 7.2 Hz, 2 H), 7.40 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 145.6, 139.1, 132.7, 129.3, 128.7, 127.8, 127.4, 119.0, 110.8. HRMS (EI) Calcd for $C_{13}H_9N$ (M^+) 179.0735, Found 179.0739.

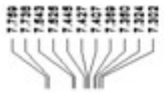


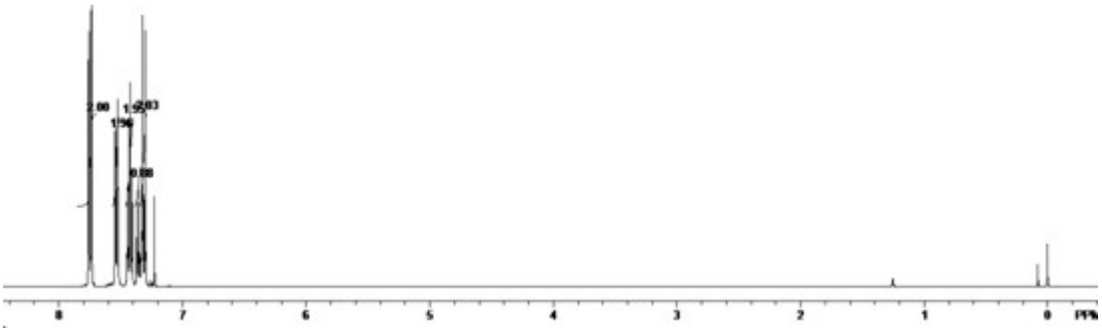


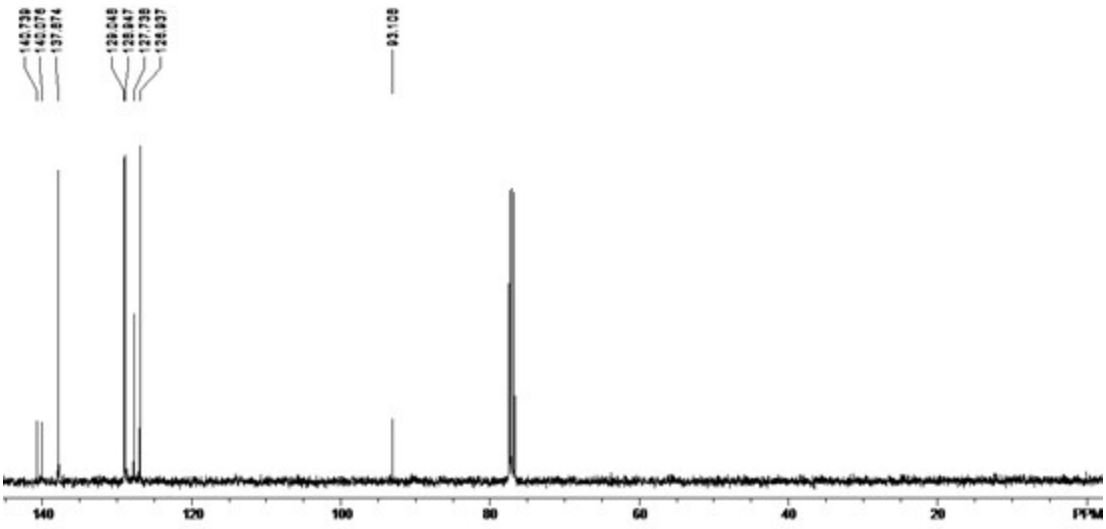
4-iodo-1,1'-biphenyl (3v, CAS#1591-31-7)



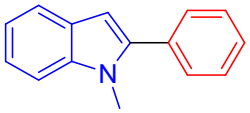
White solid, m.p. 73-75°C(lit.[2] mp 73-74°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.74 (d, *J* = 8.0 Hz, 2 H), 7.54 (d, *J* = 7.6 Hz, 2 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.35 (d, *J* = 7.6 Hz, 1 H), 7.30 (t, *J* = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 140.6, 140.1, 137.8, 129.1, 128.8, 127.6, 126.9, 93.2. HRMS (EI) Calcd for $C_{12}H_9I$ (M^+) 297.9749, Found 297.9747.



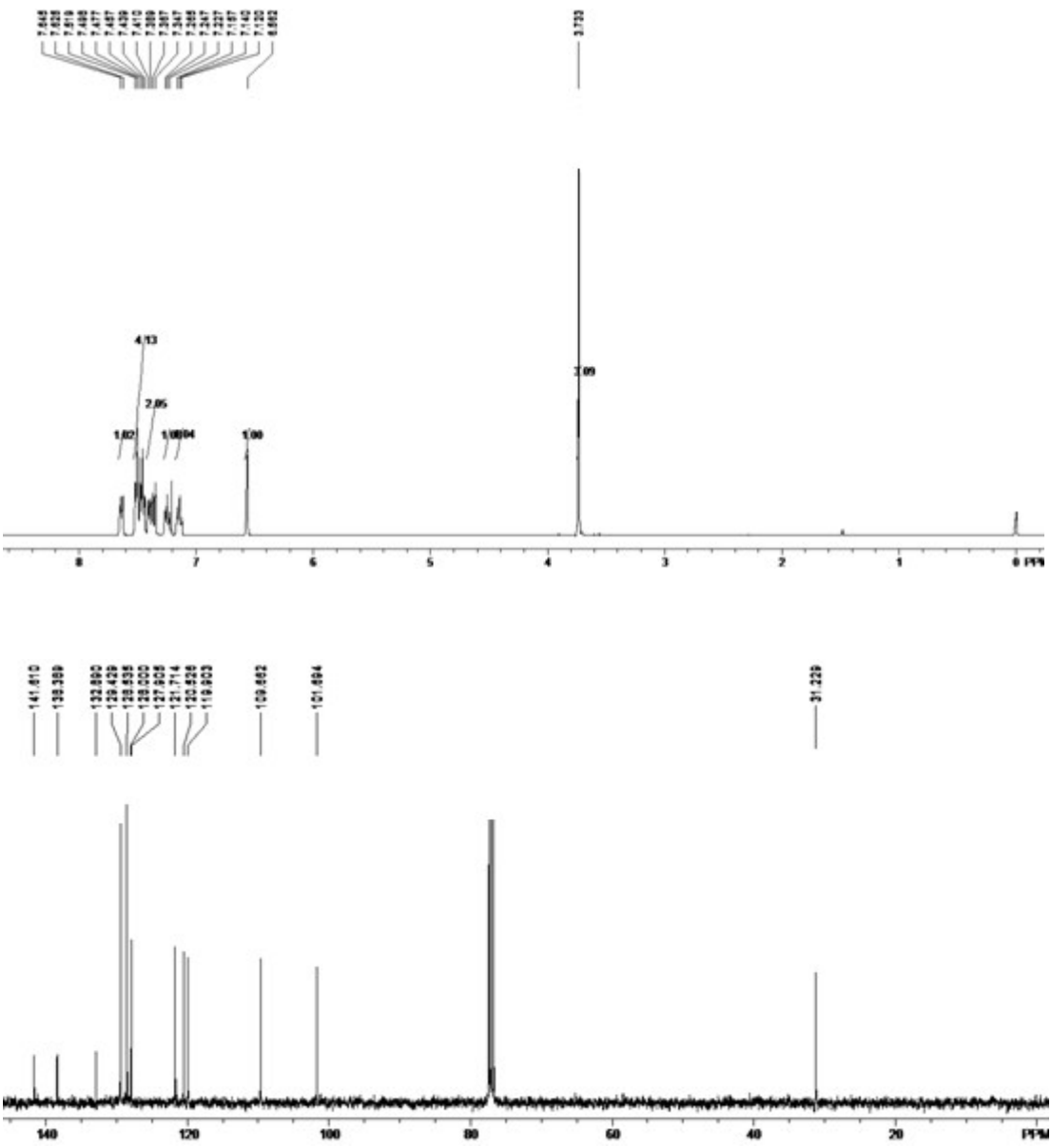




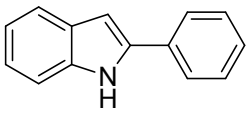
1-methyl-2-phenyl-indole (3w, CAS#3558-24-5)



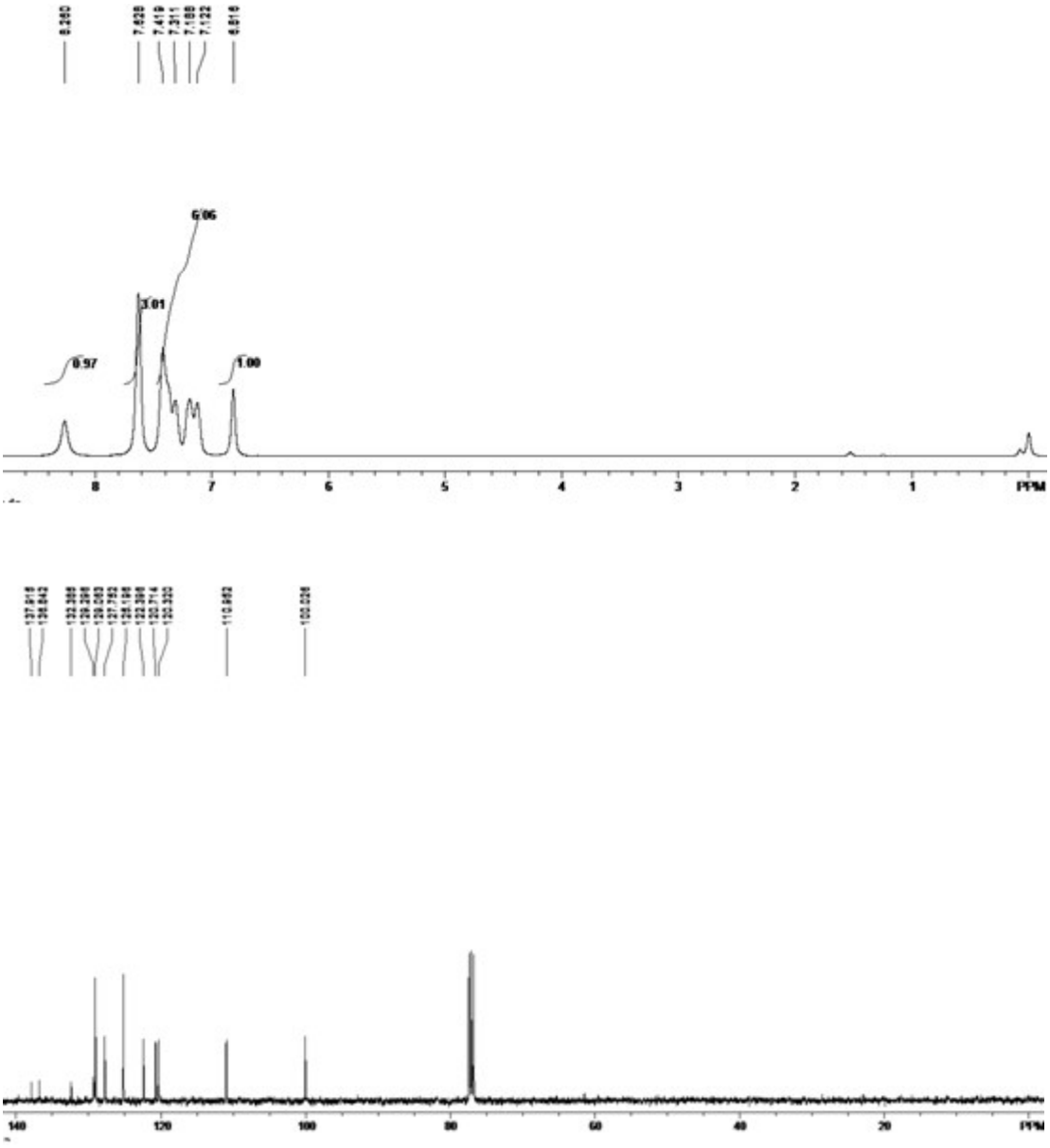
White solid, m.p. 100-101°C(lit.[4] mp 97-100°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.63 (d, *J* = 8.0 Hz, 1 H), 7.43-7.52 (m, 4 H), 7.34-7.41 (m, 2 H), 7.25 (t, *J* = 7.6 Hz, 1 H), 7.14 (t, *J* = 7.6 Hz, 1 H), 6.56 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ141.6, 138.4, 132.9, 129.4, 128.5, 128.0, 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.



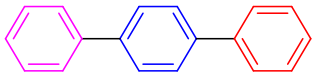
2-phenyl-indole (3x, CAS#948-65-2)



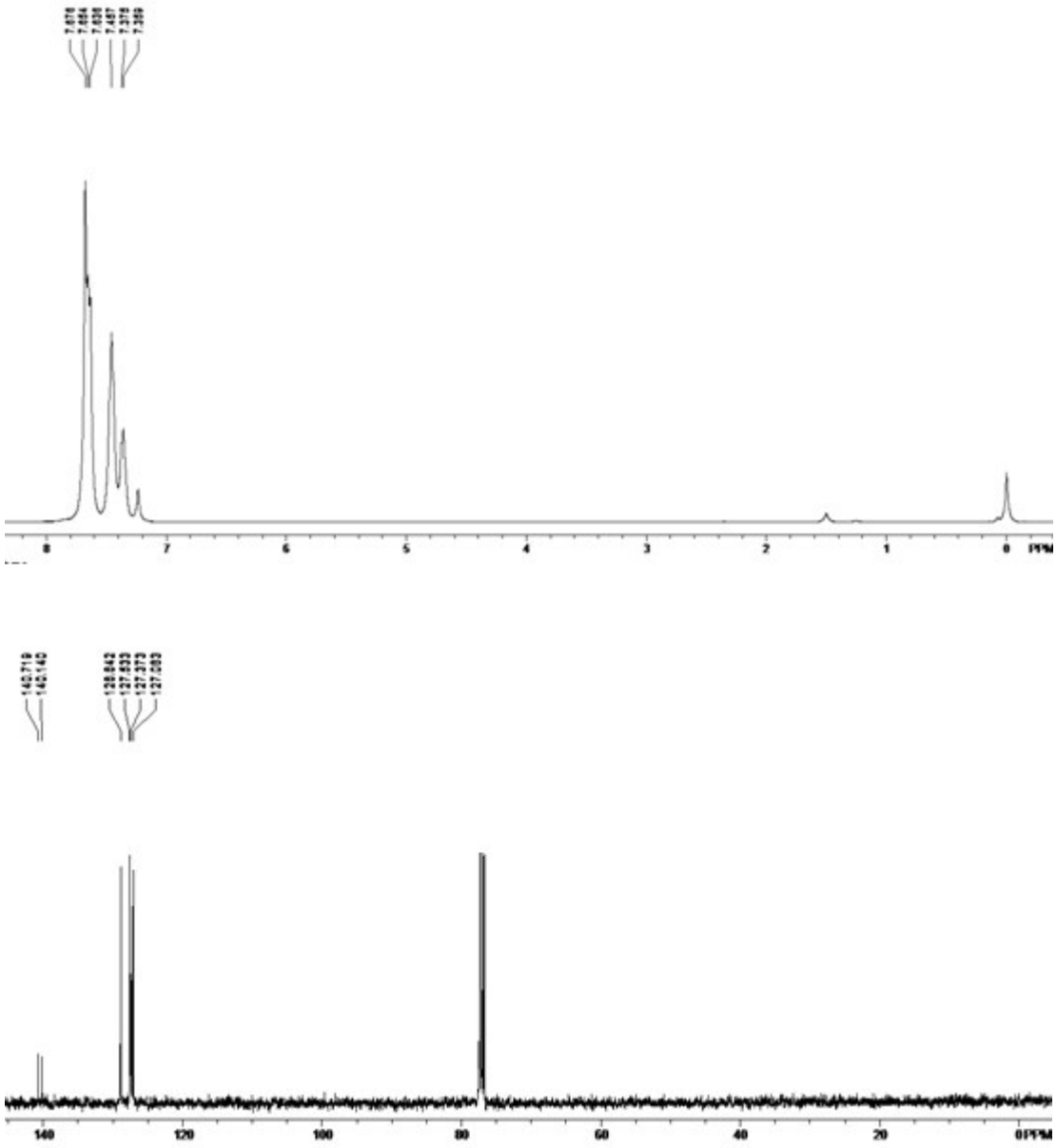
White solid, m.p. 185-187°C(lit.[5] mp 186-188°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.26 (s, 1 H), 7.63 (s, 3 H), 7.12-7.42 (m, 6 H), 6.82 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ137.9, 136.8, 132.4, 129.3, 129.1, 127.8, 125.2, 122.4, 120.7, 120.3, 111.0, 100.0. HRMS (EI) Calcd for $C_{14}H_{11}N$ (M^+) 193.0891, Found 193.0893.



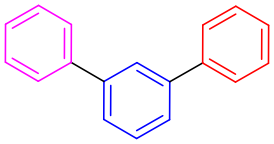
p-Terphenyl (Scheme 2, CAS#92-94-4)



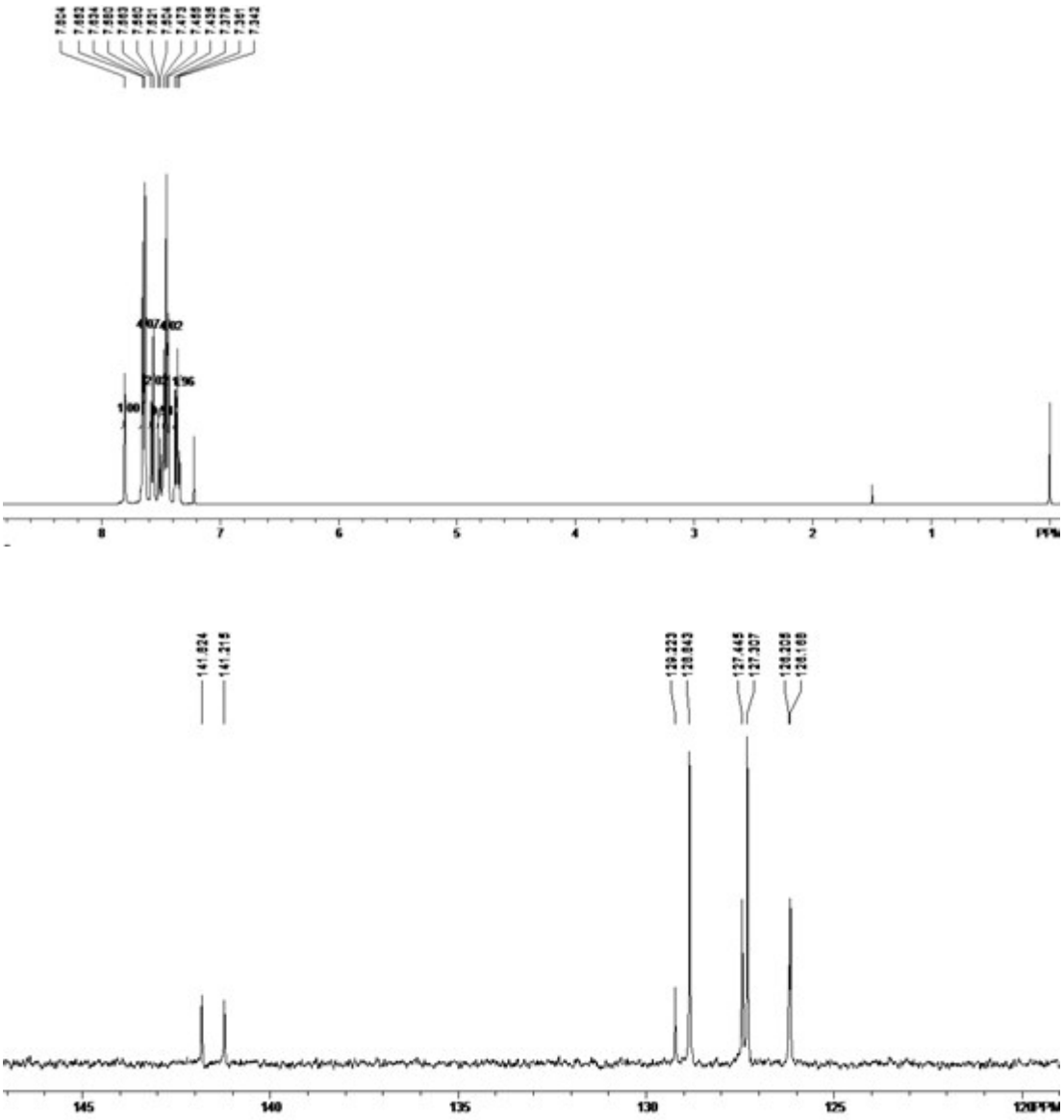
White solid, m.p. 210-212°C(lit.[6] mp 211-212°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.63-7.68 (m, 8 H), 7.46 (s, 4 H), 7.37 (d, J = 6.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 140.7, 140.1, 128.8, 127.5, 127.4, 127.1. HRMS (EI) Calcd for $C_{18}H_{14}$ (M^+) 230.1096, Found 230.1097.



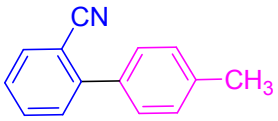
m-Terphenyl (Scheme 2, CAS#92-06-8)



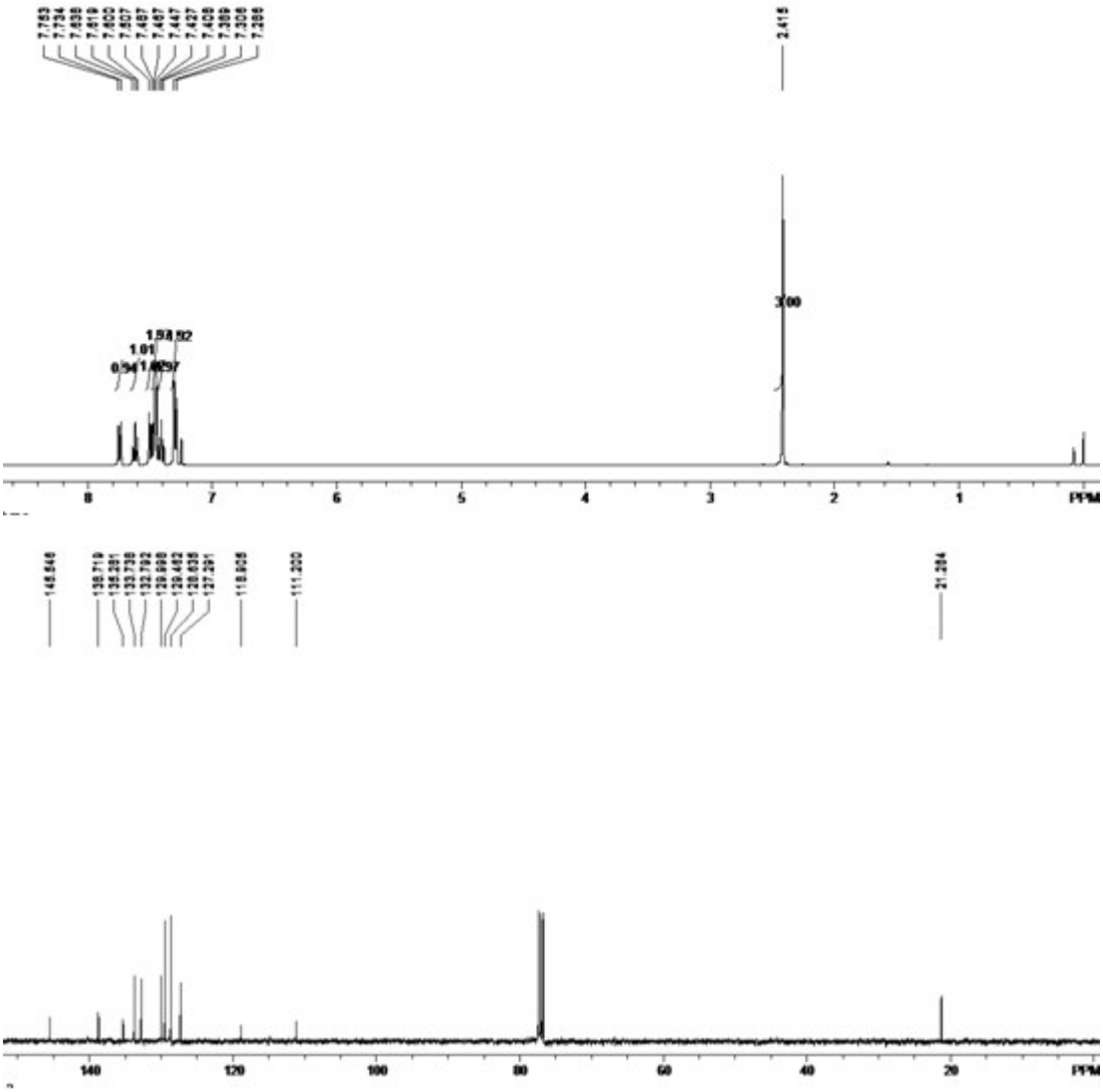
White solid, m.p. 85-87°C(lit.[6] mp 84-85°C);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.80 (s, 1 H), 7.64 (d, *J* = 7.2 Hz, 4 H), 7.57 (d, *J* = 6.8 Hz, 2 H), 7.51 (d, *J* = 6.8 Hz, 1 H), 7.44 (t, *J* = 7.6 Hz, 4 H), 7.36 (t, *J* = 7.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.8, 141.2, 129.2, 128.8, 127.4, 127.3, 126.2, 126.1. HRMS (EI) Calcd for $C_{18}H_{14}$ (M^+) 230.1096, Found 230.1091.



4'-Methyl-2-cyanobiphenyl (Scheme 3, CAS#114772−53−1)



White solid, m.p. 50-51°C(lit.[7] mp 49-51°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.74 (d, *J* = 7.6 Hz, 1 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.50 (d, *J* = 8.0 Hz, 1 H), 7.46 (t, *J* = 8.0 Hz, 2 H), 7.41 (t, *J* = 7.6 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 1 H), 2.415 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ145.5, 138.7, 135.3, 133.7, 132.8, 130.0, 129.5, 128.6, 127.3, 118.9, 111.2, 21.3. HRMS (EI) Calcd for $C_{14}H_{14}N$ (M^+) 193.0891, Found 193.0895.



References

1. Barbero, M. Cadamuro, S. Dughera, S and Giaveno, C. *Eur. J. Org. Chem*. **2006**, 4884.
2. Zhou, W.-J. Wang, K.-H. and Wang, J.-X. *Adv. Synth. Catal*. **2009**, 351, 1378.
3. Prokopcova, H. Kappe, C. O and Prokopcova, H. *J. Org. Chem*. **2007**, 72, 4440.
4. Denmark, S. E. and Baird, J. D. *Org. Lett*. **2004**, 6, 3649.
5. Ackermann, L. Barfuesser, S. and Potukuchi, H. K. *Adv. Synth. Catal*. **2009**, 351, 1064.
6. Fan, X.-H. and Yang, L.-M. *Eur. J. Org. Chem*. **2010**, 2457.
7. Lombardo, M. Chiarucci, M. and Trombini, C. *Green Chem*. **2009**, 11, 574.