Extension studies on iron(III)-promoted free radical oxidation of anilines: self-coupling and self-bridged assembling reactions

Jing Pan, Jiaqiang Li, Ruofeng Huang, Xiaohui Zhang, Hang Shen, Yan Xiong, Xiangming Zhu

PII: S0040-4020(15)00873-X
DOI: 10.1016/j.tet.2015.06.018
Reference: TET 26853

To appear in: *Tetrahedron*

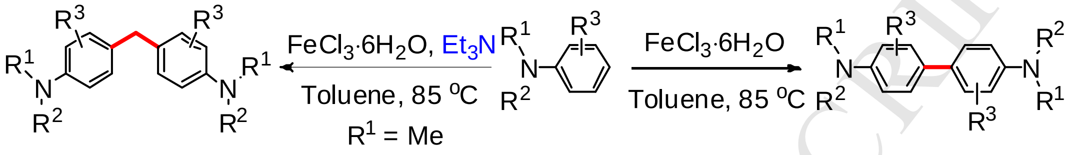
Received Date: 23 January 2015
Revised Date: 2 June 2015
Accepted Date: 3 June 2015

Please cite this article as: Pan J, Li J, Huang R, Zhang X, Shen H, Xiong Y, Zhu X, Extension studies on iron(III)-promoted free radical oxidation of anilines: self-coupling and self-bridged assembling reactions, *Tetrahedron* (2015), doi: 10.1016/j.tet.2015.06.018.

Graphical Abstract

Extension studies on iron(III)-promoted free radical oxidation of anilines: self-coupling and self-bridged assembling reactions

Jing Pan[a], Jiaqiang Li[a], Ruofeng Huang[a], Xiaohui Zhang[a], Hang Shen[a], Yan Xiong[a,]* and Xiangming Zhu[b]
[a] *School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400030, China.*
[b]*UCD School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland.*



Tetrahedron
journal homepage: www.elsevier.com

Extension studies on iron(III)-promoted free radical oxidation of anilines: self-coupling and self-bridged assembling reactions

Jing Pan[a] , Jiaqiang Li[a] , Ruofeng Huang[a] , Xiaohui Zhang[a] , Hang Shen[a] , Yan Xiong[a,]∗ and Xiangming Zhu[b]

[a] *School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400030, China.*
[b] *UCD School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland.*

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Anilines
FeCl$_3$·6H$_2$O
Oxidation
Self-bridged
Self-coupling

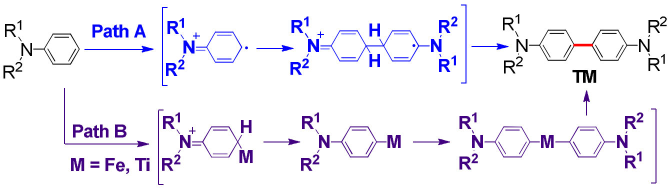
ABSTRACT

The iron(III)-promoted free radical oxidation of anilines has been further developed. Anilines including those bearing strong electron-withdrawing groups on benzene ring were readily converted into corresponding self-coupling benzidines. With addition of base, the methyl on nitrogen was activated and the free radical oxidations tended to furnish the corresponding self-bridged assembling diaminodiarylmethanes.

∗ Corresponding author. Tel.: +86-15086903431; fax: +86-023 65112134; e-mail: xiong@cqu.edu.cn

1. Introduction

As a consequence of the versatile application of benzidines in functional material[1,2] and immunohistochemistry,[3] for instance, the hole-transport material *N*,*N′*-bis(3-methylphenyl)-*N*,*N′*-diphenylbenzidine (TPD) and *N*,*N′*-bis(1-naphthyl)-*N*,*N′*-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB),[4] and safe staining reagents 3,3',5,5'-tetramethylbenzidine (TMB),[3] numerous strategies have been exploited to synthesize these benzidines and derivatives in the past decades.[5-13] Traditionally, the acid catalyzed rearrangement of hydrazobenzenes has been thought to be the main protocol for the synthesis of several benzidines, but inevitable byproducts in this reaction and the multi-step synthetic routes of hydrazobenzenes limit its scope of usage.[6] In order to obtain diversely functionalized benzidines effectively, the direct self-coupling of anilines employing $TiCl_4$,[7] cerium(IV) ammonium nitrate (CAN),[8] $CuBr/H_2O_2$,[9] $Cu(ClO_4)_2$,[10] anhydrous $FeCl_3$,[11] $FeCl_3\cdot 6H_2O$[12a] and organic 1,8-bis(diphenylmethylium)-naphthalenediyl dications[13] as oxidants have been developed, in which self-coupling reactions involved either free radical cation (Path A) or aryl-metal intermediate (Path B) (Fig. 1).



TM = target molecule

Fig. 1. Free radical (path A) and aryl-metal (Path B) involved self-coupling of anilines

In $FeCl_3\cdot 6H_2O$ mediated free radical oxidative self-coupling of anilines, we found that the different substituents at nitrogen atom affected both reactivity and selectivity largely (Fig. 2).[12] For example, unprotected aniline (**i**) coordinated with $FeCl_3\cdot 6H_2O$ exhibit no reactivity, and the increased basicity of *N*,*N*-dimethyl substituted aniline (**ii**) providing desired *N*,*N*,*N′*,*N′*-tetramethylbenzidines results in 88% yield. *N*,*N*-dibenzylanilines (**iii**) improves the selectivity without the loss of reactivity. However, the *ortho*-substituents inhibit the self-coupling reactions due to steric repulsions with dibenzyl substitution. Monobenzyl substitution (**iv**) overcomes the steric shielding, whereas, compared with **ii**, the decreased basicity of nitrogen in **iii** as well as **iv** are disadvantage for the substitutions such as fluoro, acetyl, ester and nitro, even no reactivity. As a promising expectation, different substituents at nitrogen atom would expand the substrate scope of iron(III)-promoted free radical oxidative self-coupling reaction. Hence, we turn our attention to methyl substitution on nitrogen, a stronger electron-donating group, and wish to enlarge the substrate scope bearing the electron-deficient benzene ring.

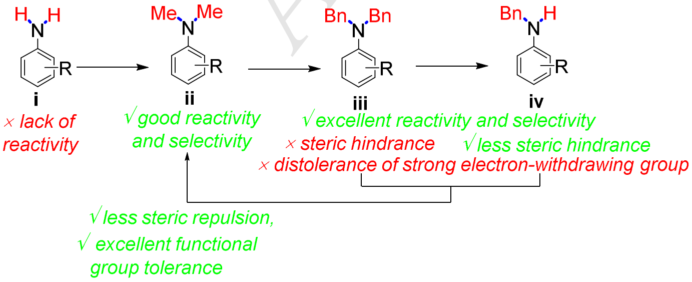
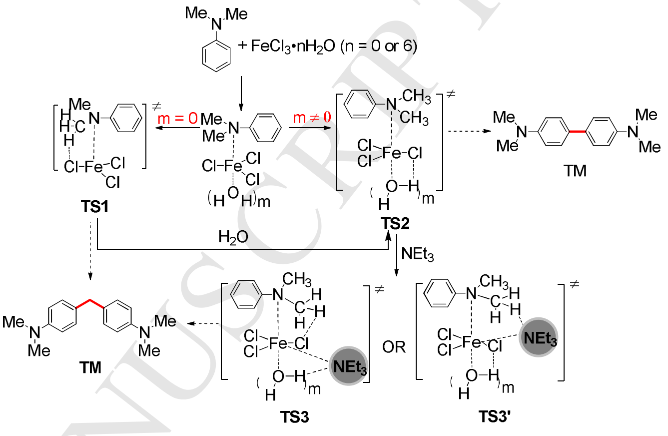


Fig. 2. Influence of substituents at nitrogen atom

In $FeCl_3$-mediated methylene-bridged assembling,[12a] the basicity of Cl^- activates the methyl group directly to form iminium intermediate through Cl···H (-CH_3) hydrogen bonding as in **TS1** (Fig. 3). In the presence of crystal water or additional water, Cl^- is bonded by water as in **TS2**, and the former hydrogen bond is broken. Therefore no iminium intermediate is formed and give rise to only self-coupling product. When extra NEt_3 was added, either the hydrogen of methyl group is activated by H···N (NEt_3) hydrogen bond as in **TS3′** or the Cl···H (H_2O) hydrogen bond is broken to release Cl, which is capable of connecting and activating the methyl group, through interaction of water and NEt_3 as in **TS3**. On the basis of above principle, we have gotten methylene-bridged product in yield of 68%. Here we wish to obtain the methylene-bridged products in better yield and enlarge the scope of substrate.



TM = target molecule

Fig. 3. Self-coupling reaction and self-bridged assembling activation model of methyl protected anilines

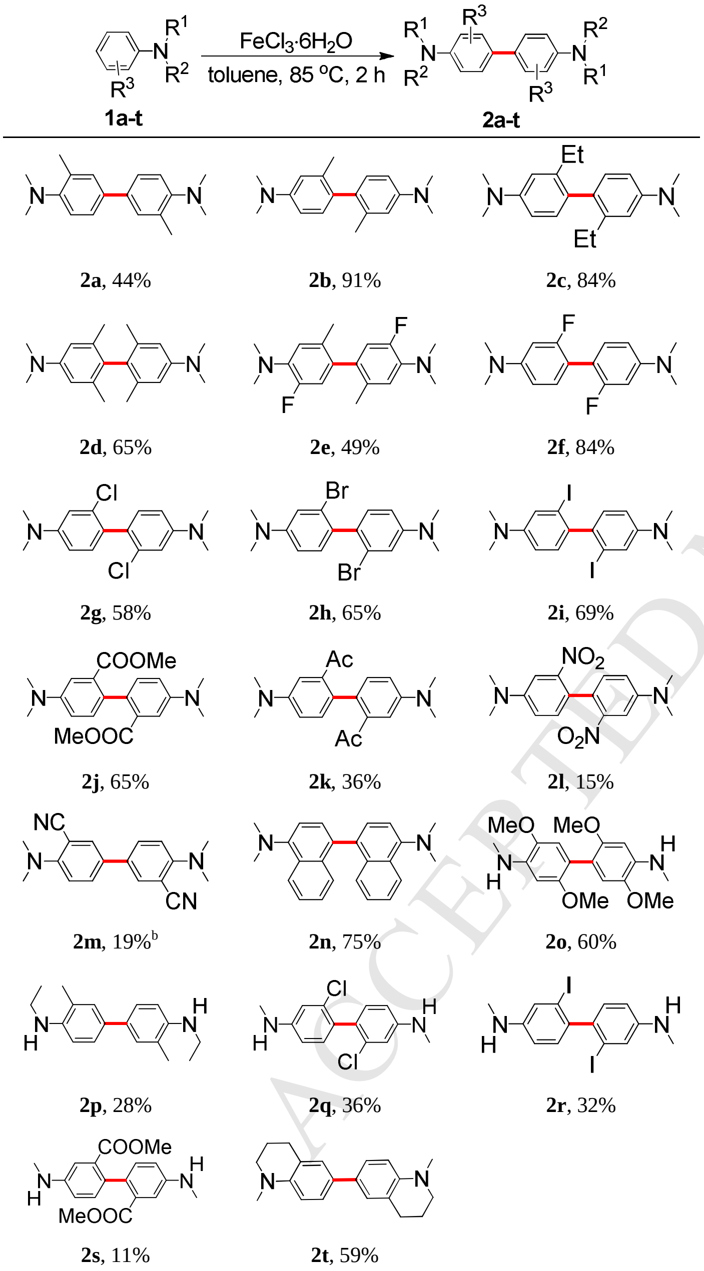
2. Results and discussion

The oxidative self-coupling reaction of N-substituted anilines was utilized to test the substrate scope (Table 1). Basically, *N*,*N*-dimethylaniline gave the coupling product in yield of 88%.[12a] It is noteworthy that the yield was directly depended on steric hindrance. As a result, *N*,*N*,2-trimethylaniline gave desired coupling product **2a** in 44% yield, and no coupling benzidines were obtained by employing 2-isopropyl-*N*,*N*-dimethylaniline, and 2-(tert-butyl)-*N*,*N*-dimethylaniline as substrates. Similiarly, the remote methyl group substituted at *meta*-position (**1b**) resulted in the yield of 91%, the ethyl group at *meta*-position afforded self-coupling product **2c** in yield of 84%, and a further decreased yield of 65% was obtained employing dimethyl substituted aniline (**1d**) as substrate.

ortho-Fluro substituted *N*,*N*-dimethylaniline generated product **2e** in yield of 49%, whereas 2,3,5,6-tetrafluro *N*,*N*-dimethylaniline gave no desired product, remote *meta*-fluoro substituted aniline was effective for this coupling process obtaining **2f** in 84% isolated yield. Rationally, anilines bearing bulky halo (Cl, Br and I)-substitutions presented slightly lower reactivity giving corresponding coupling products in 58%, 65% and 69% yields, respectively (**2g**-**2i**). Interestingly, anilines bearing a strong electron-withdrawing group are tolerated under present conditions. The ester group provided corresponding coupling product **2j** in 65% yield, and acetyl and nitro group afforded corresponding **2k** and **2l** in acceptable yields (36% and 15%). Abided by steric effect, *ortho*-nitro substituted aniline gave no coupling product, while *ortho*-cyano substituted aniline proceeded readily to achieve coupling benzidine **2m** in 19% yield. Naphthylamine was also suitable for this coupling reaction and furnished the desired coupling product **2n** in yield of 75%. Heteroaromatic *N*,*N*-dimethylpyridin-2-amine was investigated but no corresponding product was obtained.

Mono-protected anilines were likewise investigated and the decreased basicity of nitrogen lowered the reactivity of anilines. *ortho*-Alkoxy aniline performed a good reactivity affording the coupling product **2o** in 60% yield, *N*-ethylaniline bearing an *ortho*-methyl group underwent the coupling reaction to provide corresponding product **2p** in 28% yield, and *N*-methyl anilines bearing halo-substituents such as chlorine and iodine were tolerated and generated corresponding benzidine **2q** and **2r** in 36% and 32% yields, respectively. Bearing ester group, the correspondingly self-coupling product **2s** was obtained in 11% yield. *N*-methyl tetrahydroquinoline was also suitable for this coupling procedure and corresponding **2t** was obtained in 59% yield.

Table 1. Self-coupling reactions of functionalized anilines[a]

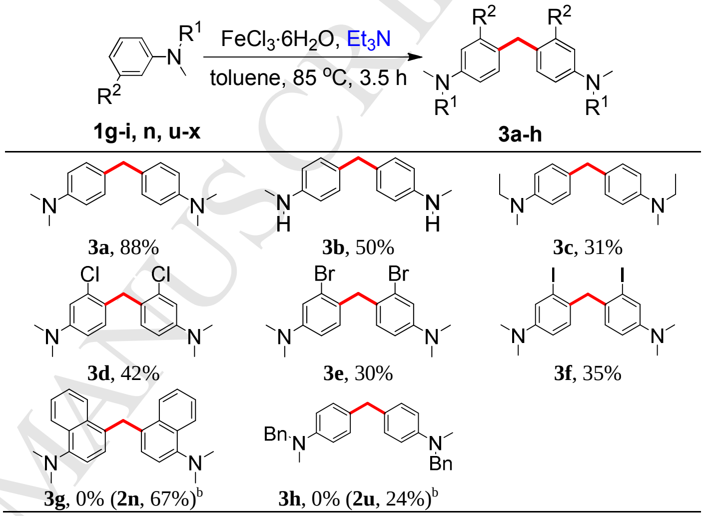


[a] Reaction conditions: anilines (0.4 mmol), $FeCl_3\cdot6H_2O$ (1.0 mmol), toluene (2.0 mL), 85 °C, 2 h; isolated yields.

[b] Reaction time 12 h.

Diarylalkane fragments exhibit in pharmacologically active compounds and act as key subunits of functional materials. The self-bridged assembling reactions of anilines were further examined,[14] and the reaction provided the best results in the presence of 1.0 equiv of additional triethylamine under standard conditions for 3.5 h, assembling diphenylmethane **3a** in 88% yield (Table 2).[15] Under the same conditions, monomethyl protected aniline was a suitable substrate to furnish desired self-bridged assembling product **3b** in 50% isolated yield. *N*-ethyl-*N*-methylaniline exhibited a moderate reactivity giving the diphenylmethane product **3c** with 31% yield. *N*,*N*-dimethylanilines bearing halo-substitutions at the *meta*-position on benzene ring afforded methylene-bridged products **3d-3f** in yields of 42%, 30% and 35%, respectively. However, the self-bridged assembling reaction did not proceed with naphthylamine and *N*-benzyl-*N*-methylaniline, only corresponding self-coupling product **2n** and **2u** were obtained in 67% and 24% yields, respectively.

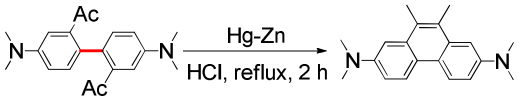
Table 2. Self-bridged assembling reaction of functionalized methyl protected anilines[a]



[a] Reaction conditions: anilines (0.4 mmol), $FeCl_3\cdot6H_2O$ (1.0 mmol), Et_3N (0.4 mmol), toluene (2.0 mL), 85 °C, 3.5 h; isolated yields.

[b] Isolated yields of coupling products **2** in parentheses.

To demonstrate the potential application of our synthesized benzidines in functional materials, 2,2'-diacetyl benzidine **2k** was considered to construct larger conjugated system. As a consequence, polysubstituted 9,10-dimethyl-2,7-bisdimethaminophenanthrene **4** was assembled through a Clemmensen reduction in the presence of amalgamated zinc,[16] and gratifyingly, an acceptable yield of 26% was afforded.



2k

4, 26% yield

Scheme 1. Synthesis of 9,10-dimethyl-2,7-bisdimethaminophenanthrene **4**.

3. Conclusion

In conclusion, we have further developed the effective $FeCl_3\cdot6H_2O$-promoted free radical oxidation of anilines for preparing benzidine derivatives and diaminodiarylmethanes with wider substrate scope. The substrate scope of the self-coupling reaction was largely expanded to anilines bearing strong electronic withdrawing groups. The role of extra organic base triethylamine orientated the coupling reaction and self-bridged assembling reaction to some extent.

4. Experimental section

4.1. General Information

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at a Bruker Avance 500/125 MHz spectrometer at 20-25 °C. ^{1}H NMR chemical shifts were reported in ppm using tetramethylsilane (TMS, δ = 0.00 ppm) as the internal standard. The data of ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (J values) in Hz and integration. ^{13}C NMR spectra were reported in parts per million using solvent $CDCl_3$ (δ = 77.2 ppm) as an internal standard. All the reagents used were of analytical grade, purchased locally and used without any purification unless otherwise specified. Column chromatographys were performed using silica gel, and analytical thin-layer chromatography (TLC) which was used to monitor the reactions was performed on silica gel plates. IR spectra were recorded on a Nicolet 550II spectrophotometer. HRMS (ESI) data were measured on a Agilent 6510 Q-TOF mass spectrometer.

4.2. General Procedure for the oxidative self-coupling reactions

To a stirred mixture of $FeCl_3 \cdot 6H_2O$ (270.3 mg, 1.0 mmol) and 2.0 mL toluene was added aniline **1** (0.4 mmol) at room temperature. The reaction was stirred at 85 °C for 2 h in atmosphere. After it was cooled to room temperature, the reaction mixture was quenched by aqueous ammonia solution (mass fraction: 25%-28%, 10 mL) and extracted with dichloromethane (10 mL per time) until no product was observed in the extract, monitored by TLC. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give crude product, which was chromatographed on silica gel column using 1:100 to 1:70 (*v*/*v*) EtOAc-petroleum ether solutions as eluent to afford isolated product **2**.

*4.2.1. N^4,N^4,$N^{4'}$,$N^{4'}$,3,3'-hexamethyl-[1,1'-biphenyl]-4,4'-diamine (**2a**)*

White solid; 23.6 mg, 44% yield; mp: 73.2-74.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 2.77 (s, 12H), 2.42 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 135.5, 132.3, 129.9, 124.9, 118.7, 44.5, 18.8; IR (KBr): 3003, 2938, 2856, 1606, 1580, 1490, 1450, 1370, 819 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{24}N_2$ $(M+H)^+$: 269.2012; found: 269.2010.

*4.2.2. N^4,N^4,$N^{4'}$,$N^{4'}$,2,2'-hexamethyl-[1,1'-biphenyl]-4,4'-diamine (**2b**)*

White solid; 48.8 mg, 91% yield; mp: 79.7-80.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, J = 7.0 Hz, 2H), 6.64 (s, 2H), 6.62 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 2H), 2.96 (s, 12H), 2.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 137.3, 130.9, 130.6, 114.0, 110.1, 40.9, 20.7; IR (KBr): 3036, 2921, 2853, 1608, 1551, 1501, 1442, 1351, 834, 817 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{24}N_2$ $(M+H)^+$: 269.2012; found: 269.2000.

*4.2.3. 2,2'-diethyl-N^4,N^4,$N^{4'}$,$N^{4'}$-tetramethyl-[1,1'-biphenyl]-4,4'-diamine (**2c**)*

White solid; 49.8 mg, 84% yield; mp: 78.3-80.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 2.5 Hz, 2H), 6.61 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 2H), 2.97 (s, 12H), 2.48-2.32 (m, 4H), 1.05 (t, J = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 143.4, 131.3, 129.8, 112.4, 110.0, 40.9, 27.0, 15.6; IR (KBr): 3033, 2963, 2932, 2868, 1608, 1553, 1497, 810 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{28}N_2$ $(M+H)^+$: 297.2325; found: 297.2327.

*4.2.4. N^4,N^4,$N^{4'}$,$N^{4'}$,2,2',6,6'-octamethyl-[1,1'-biphenyl]-4,4'-diamine (**2d**)[13]*

White solid; 38.5 mg, 65% yield; mp: 170.5-171.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.52 (s, 4H), 2.95 (s, 12H), 1.88 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 137.2, 129.4, 111.9, 40.9, 20.7; IR (KBr): 2974, 2851, 1608, 1562, 1494, 1442, 1375, 826 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{28}N_2$ $(M+H)^+$: 297.2325; found: 297.2318.

*4.2.5. 5,5'-difluoro-N^4,N^4,$N^{4'}$,$N^{4'}$,2,2'-hexamethyl-[1,1'-biphenyl]-4,4'-diamine (**2e**)*

Yellow solid; 29.8 mg, 49% yield; mp: 150.4-151.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 (d, J = 4.5 Hz, 2H), 6.74 (s, 2H), 2.86 (s, 12H), 2.01 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9 (d, J = 242.3), 139.3 (d, J = 8.8 Hz), 133.2 (d, J = 7.5 Hz), 131.8 (d, J = 3.1 Hz), 119.4 (d, J = 3.5 Hz), 117.1 (d, J = 20.5 Hz), 42.9 (d, J = 4.0 Hz), 19.4; IR (KBr): 2948, 2877, 1618, 1555, 1503, 1457, 1388, 1222, 879 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{22}F_2N_2$ $(M+H)^+$: 305.1824; found: 305.1822.

*4.2.6. 2,2'-difluoro-N^4,N^4,$N^{4'}$,$N^{4'}$-tetramethyl-[1,1'-biphenyl]-4,4'-diamine (**2f**)*

White solid; 46.4 mg, 84% yield; mp: 198.5-199.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.20 (m, 2H), 6.53 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 2H), 6.49-6.47 (m, 2H), 2.97 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0 (d, J = 243.8 Hz), 151.4 (t, J = 5.6 Hz), 131.9 (t, J = 4.0 Hz), 111.6 (d, J = 14.6 Hz), 108.2, 99.7 (dt, J_1 = 27.3 Hz, J_2 = 7.5 Hz), 40.6; IR (KBr): 3047, 2894, 1627, 1548, 1512, 1442, 1364, 1139, 798 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{18}F_2N_2$ $(M+H)^+$: 277.1511; found: 277.1507.

*4.2.7. 2,2'-dichloro-N^4,N^4,$N^{4'}$,$N^{4'}$-tetramethyl-[1,1'-biphenyl]-4,4'-diamine (**2g**)*

White solid; 35.9 mg, 58% yield; mp: 147.7-148.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 2.5 Hz, 2H), 6.64 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 2H), 2.97 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 134.9, 132.3, 126.3, 112.6, 110.6, 40.5; IR (KBr): 3036, 2988, 1609, 1504, 1443, 1358, 835, 801 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{18}Cl_2N_2$ $(M+H)^+$: 309.0920; found: 309.0923.

*4.2.8. 2,2'-dibromo-N^4,N^4,$N^{4'}$,$N^{4'}$-tetramethyl-[1,1'-biphenyl]-4,4'-diamine (**2h**)*

White solid; 51.8 mg, 65% yield; mp: 174.4-175.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 2.5 Hz, 2H), 6.68 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 2H), 2.97 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 132.0, 130.1, 125.5, 115.5, 111.0, 40.5; IR (KBr): 3034, 2896, 1605, 1498, 1441, 1350, 832, 602 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{18}Br_2N_2$ $(M+H)^+$: 396.9910; found: 396.9894.

*4.2.9. 2,2'-diiodo-N^4,N^4,$N^{4'}$,$N^{4'}$-tetramethyl-[1,1'-biphenyl]-4,4'-diamine (**2i**)*

White solid; 67.9 mg, 69% yield; mp: 201.1-203.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J = 2.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 6.73 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 2H), 2.97 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 137.4, 130.7, 121.7, 111.8, 102.7, 40.5; IR (KBr): 3033, 2962, 1596, 1497, 1441, 1357, 804, 538 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{18}I_2N_2$ $(M+H)^+$: 492.9632; found: 492.9633.

*4.2.10. dimethyl 4,4'-bis(dimethylamino)-[1,1'-biphenyl]-2,2'-dicarboxylate (**2j**)*

Green solid; 46.3 mg, 65% yield; mp: 144.2-145.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, J = 3.0 Hz, 2H), 7.07 (d, J = 8.5 Hz, 2H), 6.86 (dd, J_1 = 8.5 Hz, J_2 = 3.0 Hz, 2H), 3.62 (s, 6H), 3.01 (s, 12H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 168.9, 149.2, 131.8, 131.2, 130.7, 115.4, 113.5, 52.0, 40.7; IR (KBr): 2946, 1723, 1608, 1557, 1500, 1446, 1363,1230, 859 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{24}N_2O_4$ (M+H)$^+$: 357.1809; found: 357.1806.

*4.2.11. 1,1'-(4,4'-bis(dimethylamino)-[1,1'-biphenyl]-2,2'-diyl)bis(ethan-1-one) (**2k**)*

White solid; 23.4 mg, 36% yield; mp: 130.9-131.9 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.03 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 2.5 Hz, 2H), 6.80 (dd, J_1 = 8.5 Hz, J_2 = 3.0 Hz, 2H), 3.01 (s, 12H), 2.10 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 204.6, 149.7, 141.2, 132.2, 127.6, 114.8, 111.8, 40.6, 30.1; IR (KBr): 2856, 1680, 1605, 1541, 1497, 1445, 1360, 816 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{24}N_2O_2$ (M+H)$^+$: 325.1911; found: 325.1912.

*4.2.12. N^4,N^4,$N^{4'}$,$N^{4'}$-tetramethyl-2,2'-dinitro-[1,1'-biphenyl]-4,4'-diamine (**2l**)*

White solid; 10.0 mg, 15% yield; mp: 238.5-239.4 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 (d, J = 3.0 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 6.89 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 2H), 3.06 (s, 12H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 150.2, 149.1, 132.3, 120.9, 116.2, 107.3, 40.5; IR (KBr): 2853, 1625, 1522, 1443, 1360, 1340, 819 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{18}N_4O_4$ (M+H)$^+$: 331.1401; found: 331.1406.

*4.2.13. 4,4'-bis(dimethylamino)-[1,1'-biphenyl]-3,3'-dicarbonitrile (**2m**)*

White solid; 11.1 mg, 19% yield; mp: 157.6-158.4 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.63 (d, J = 2.0 Hz, 2H), 7.54 (dd, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 2H), 6.93 (d, J = 9.0 Hz, 2H), 3.10 (s, 12H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 154.0, 132.4, 131.2, 129.7, 119.6, 117.2, 101.0, 43.0; IR (KBr): 3052, 2853, 2212, 1610, 1506, 1460, 1350, 812 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{18}N_4$ (M+H)$^+$: 291.1604; found: 291.1614.

*4.2.14. N^4,N^4,$N^{4'}$,$N^{4'}$-tetramethyl-[1,1'-binaphthalene]-4,4'-diamine (**2n**)*[7]

White solid; 50.8 mg, 75% yield; mp: 132.3-133.4 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.33 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 7.5 Hz, 2H), 7.25 (t, J = 8.5 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 2.98 (s, 12H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 150.6, 134.5, 133.6, 128.9, 128.1, 127.4, 125.8, 125.1, 124.4, 113.7, 45.5; IR (KBr): 3036, 2865, 1611, 1579, 1507, 1476, 1454, 1378, 845 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{24}N_2$ (M+H)$^+$: 341.2012; found: 341.2017.

*4.2.15. 2,2',5,5'-tetramethoxy-N^4,$N^{4'}$-dimethyl-[1,1'-biphenyl]-4,4'-diamine (**2o**)*

White solid; 39.9 mg, 60% yield; mp: 149.8-151.7 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.73 (s, 2H), 6.32 (s, 2H), 4.26 (brs, 2H), 3.79 (s, 6H), 3.75 (s, 6H), 2.90 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 152.0, 140.9, 139.2, 114.9, 113.6, 96.1, 56.9, 56.1, 30.5; IR (KBr): 3439, 3016, 2879, 1616, 1520, 1483, 1465, 1210, 1040 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{24}N_2O_4$ (M+H)$^+$: 333.1809; found: 333.1797.

*4.2.16. N^4,$N^{4'}$-diethyl-3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diamine (**2p**)*

White solid; 15.0 mg, 28% yield; mp: 94.5-95.8 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.26 (s, 2H), 6.66 (d, J = 8.5 Hz, 2H), 3.49 (brs, 2H), 3.23 (q, J = 7.0 Hz, 4H), 2.19 (s, 6H), 1.32 (t, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 145.1, 130.6, 128.5, 125.1, 122.2, 110.2, 38.8, 17.8, 15.2; IR (KBr): 3448, 3027, 2969, 2925, 2854, 1610, 1506, 1467, 1369, 809 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{24}N_2$ (M+H)$^+$: 269.2012; found: 269.2017.

*4.2.17. 2,2'-dichloro-N^4,$N^{4'}$-dimethyl-[1,1'-biphenyl]-4,4'-diamine (**2q**)*

White solid; 20.2 mg, 36% yield; mp: 103.4-104.2 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.06 (d, J = 8.0 Hz, 2H), 6.69 (d, J = 2.5 Hz, 2H), 6.53 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 2H), 3.83 (brs, 2H), 2.86 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.5, 134.8, 132.3, 127.1, 112.1, 110.8, 30.6; IR (KBr): 3434, 2865, 1613, 1560, 1505, 1430, 1312, 810, 611 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{14}Cl_2N_2$ (M+H)$^+$: 281.0607; found: 281.0608.

*4.2.18. 2,2'-diiodo-N^4,$N^{4'}$-dimethyl-[1,1'-biphenyl]-4,4'-diamine (**2r**)*

White solid; 30.3 mg, 32% yield; mp: 114.5-115.6 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.14 (d, J = 2.5 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 6.62 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 2H), 3.82 (brs, 2H), 2.85 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.2, 138.2, 130.7, 121.4, 112.2, 102.2, 30.6; IR (KBr): 3405, 3034, 2873, 1599, 1557, 1493, 1425, 1317, 830, 479 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{14}I_2N_2$ (M+H)$^+$: 464.9319; found: 464.9333.

*4.2.19. dimethyl 4,4'-bis(methylamino)-[1,1'-biphenyl]-2,2'-dicarboxylate (**2s**)*

White solid; 7.2 mg, 11% yield; mp: 117.6-117.9 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.15 (d, J = 3.0 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 6.74 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 2H), 3.82 (brs, 2H), 3.62 (s, 6H), 2.89 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 168.3, 147.5, 132.2, 131.7, 130.6, 115.6, 113.4, 51.8, 30.9; IR (KBr): 3428, 2986, 2887, 1723, 1608, 1557, 1500, 1446, 1363, 1230, 799 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{20}N_2O_4$ (M+H)$^+$: 329.1496; found: 329.1485.

*4.2.20. 1,1'-dimethyl-1,1',2,2',3,3',4,4'-octahydro-6,6'-biquinoline (**2t**)*

Yellow solid; 34.5 mg, 59% yield; mp: 114.2-114.7 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.25 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 2H), 7.14 (d, J = 2.0 Hz, 2H), 6.63 (d, J = 8.5 Hz, 2H), 3.22 (t, J = 6.0 Hz, 4H), 2.90 (s, 6H), 2.82 (t, J = 6.5 Hz, 4H), 2.03-1.98 (m, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 145.3, 129.8, 126.9, 124.9, 123.0, 111.4, 51.4, 39.3, 28.0, 22.6; IR (KBr): 3024, 2936, 2862, 1611, 1502, 1461, 1320, 809 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{24}N_2$ (M+H)$^+$: 293.2012; found: 293.2014.

4.3. General Procedure for the oxidative self-bridged assembling reactions

To a stirred mixture of aniline **1** (0.4 mmol) and 2.0 mL toluene was added triethylamine (56 μL, 0.4 mmol) and $FeCl_3 \cdot 6H_2O$ (270.3 mg, 1.0 mmol) successively at room temperature. The reaction was stirred at 85 °C for 3.5 h in atmosphere. After it was cooled to room temperature, the reaction mixture was quenched by aqueous ammonia solution (mass fraction: 25%-28%, 10 mL) and extracted with dichloromethane (10 mL per time) until no product was observed in the extract, monitored by TLC. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give crude product, which was chromatographed on silica gel column using 1:100 to 1:70 (*v*/*v*) EtOAc-petroleum ether solution as eluent to afford isolated product **3**.

*4.3.1. 4,4'-methylenebis(N,N-dimethylaniline) (**3a**)*[12a,c]

White solid; 29.8 mg, 88% yield; mp: 90.0-91.0 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.05 (d, J = 9.0 Hz, 4H), 6.68 (d, J = 8.5 Hz, 4H), 3.80 (s, 2H), 2.89 (s, 12H); ^{13}C NMR (125 MHz, CDCl$_3$) δ

149.3, 130.5, 129.6, 113.2, 41.1, 40.1; IR (KBr): 3005, 2888, 1614, 1522, 1444, 1343, 795 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{23}N_2$ (M+H)$^+$: 255.1856; found: 255.1863.

*4.3.2. 4,4'-methylenebis(N-methylaniline) (**3b**)*

Slightly yellow solid; 15.1 mg, 50% yield; mp: 55.2-56.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, *J* =8.0 Hz, 4H), 6.50 (d, *J* = 8.5 Hz, 4H), 3.76 (s, 2H), 3.49 (brs, 2H), 2.74 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 130.9, 129.6, 112.6, 40.2, 31.0; IR (KBr): 3439, 2926, 2856, 1614, 1521, 1444, 1342, 829 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{18}N_2$ (M+H)$^+$: 227.1543; found: 227.1536.

*4.3.3. 4,4'-methylenebis(N-ethyl-N-methylaniline) (**3c**)*

Slightly yellow solid; 11.7 mg, 31% yield; mp: 89.6-91.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.5 Hz, 4H), 6.65 (d, *J* = 9.0 Hz, 4H), 3.79 (s, 2H), 3.35 (q, *J* = 7.0 Hz, 4H), 2.86 (s, 6H), 1.09 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 130.0, 129.7, 112.9, 47.2, 40.0, 37.8, 11.4; IR (KBr): 2918, 2884, 1614, 1522, 1444, 1343, 830 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{26}N_2$ (M+H)$^+$: 283.2169; found: 283.2162.

*4.3.4. 4,4'-methylenebis(3-chloro-N,N-dimethylaniline) (**3d**)*[11b]

Slightly yellow solid; 18.1 mg, 42% yield; mp: 99.5-101.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 2.5 Hz, 2H), 6.53 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 2H), 3.99 (s, 2H), 2.90 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1, 134.9, 131.1, 125.5, 113.2, 111.4, 40.7, 34.9; IR (KBr): 2988, 2853, 1612, 1510, 1445, 1358, 823, 792 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{20}Cl_2N_2$ (M+H)$^+$: 323.1077; found: 323.1080.

*4.3.5. 4,4'-methylenebis(3-bromo-N,N-dimethylaniline) (**3e**)*

Slightly yellow solid; 16.5 mg, 30% yield; mp: 97.1-98.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (s, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 8.5 Hz, 2H), 4.00 (s, 2H), 2.91 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 130.9, 127.3, 125.8, 116.4, 112.0, 40.7, 40.0; IR (KBr): 2920, 2853, 1608, 1509, 1442, 1360, 805, 500 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{20}Br_2N_2$ (M+H)$^+$: 411.0066; found: 411.0072.

*4.3.6. 4,4'-methylenebis(3-iodo-N,N-dimethylaniline) (**3f**)*

Slightly yellow solid; 23.6 mg, 35% yield; mp: 120.2-121.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (s, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 8.5 Hz, 2H), 4.00 (s, 2H), 2.91 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 130.9, 127.3, 125.8, 116.4, 112.0, 40.7, 40.0; IR (KBr): 2918, 2897, 2853, 1607, 1509, 1442, 1359, 824, 443 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{20}I_2N_2$ (M+H)$^+$: 485.9994; found: 485.9981 (^{116}I, ^{117}I).

*4.3.7. N^4,$N^{4\prime}$-dibenzyl-N^4,$N^{4\prime}$-dimethyl-[1,1'-biphenyl]-4,4'-diamine (**2u**)*[12a]

White solid; 12.6 mg, 24% yield; mp: 146.0-147.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 4H), 7.32-7.30 (m, 4H), 7.26 (m, 6H), 6.78 (d, *J* = 8.5 Hz, 4H), 4.54 (s, 4H), 3.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 139.3, 129.8, 128.7, 127.2, 127.04, 126.95, 112.9, 56.9, 38.8. ; IR (KBr): 3026, 2926, 2891, 1610, 1511, 1450, 1369, 808 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{29}N_2$ (M+H)$^+$ 393.2326, found 393.2331.

4.4. General Procedure for the synthesis of 4

4.4.1 Preparation of amalgamated zinc

To a round-bottom flask was added zinc powder (480 mg, 7.3 mmol) and mercuric chloride (48 mg, 0.2 mmol), followed by H_2O (800 µL, 44.4 mmol) and con. hydrochloric acid (24 µL, 0.8 mmol). The reaction mixture was stirred at room temperature for 10 min, the solution was decanted, and amalgamated zinc was obtained.

*4.4.2 Clemmensen reduction of **2k***[16]

To freshly prepared amalgamated zinc was added diacetyldiphenyl **2k** (65 mg , 0.2 mmol), H_2O (280 µL, 15.6 mmol) and con. hydrochloric acid (720 µL, 23.3 mmol) successively. The resulting mixture was boiled under reflux for 2 h. The reaction mixture was washed by diethyl ether (5 mL) and the solid residue was removed. The solution was alkalized by saturated $NaHCO_3$ and extracted by diethyl ether (5 mL×3). The organic layers were combined, dried over anhydrous Mg_2SO_4, filtered and concentrated under reduced pressure to give crude product, which was chromatographed on silica gel column using EtOAc-petroleum ether (1: 60, *v*/*v*) solutions as eluent to afford white solid **4**. 15.2 mg, 26% yield; mp: 195.5-196.6 °C; ^{1}H NMR (500 MHz, DMSO) δ 8.44 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 5.0 Hz, 2H), 7.08 (s, 2H), 3.03 (s, 12H), 2.61 (s, 6H);^{13}C NMR (125 MHz, DMSO) δ 148.1, 131.1, 128.4, 122.8, 120.7, 113.9, 105.1, 40.5, 15.9; ; IR (KBr): 2960, 2924, 1609, 1500, 1430, 1385, 829 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{24}N_2$ (M+H)$^+$ 293.2012, found 293.2005.

Acknowledgments

We gratefully acknowledge funding from the National Natural Science Foundation of China (No. 21372265 and No. 61271059), the Scientific Research Fundings of the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, the Natural Science Foundation Project of CQ CSTC (No. cstc2013jcyjA10037), and the Fundamental Reseach Funds for the Central Universities (No. CDJZR14225502 and No. CQDXWL-2013-Z012).

References and notes

1. (a) Bissell, R. A.; Córdova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature.* **1994**, *369*, 133. (b) Ballardini, R.; Balzani, V.; Gandolfi, M. T.; Prodi, L.; Venturi, M.; Philip, D.; Ricketts, H. G.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **1993**, *32*, 1301.
2. (a) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science.* **1992**, *258*, 1474. (b) Johnson, G. E.; McGrane, K. M.; Stolka, M. *Pure Appl. Chem*. **1995**, *67*, 175. (c) Horowitz, G. *Adv. Mater*. **1998**, *10*, 365. (d) O'Brien, D. F.; Burrows, P. E.; Forrest, S. R.; Koene, B. E.; Loy, D. E.; Thompson, M. E. *Adv. Mater*. **1998**, *10*, 1108. (e) Noda, T.; Ogawa, H.; Noma, N.; Shirota, Y. *J. Mater. Chem*. **1999**, *9*, 2177. (f) Goodbrand, H. B.; Hu, N.-X. *J. Org. Chem*. **1999**, *64*, 670. (g) Getautis, V.; Stanisauskaite, A.; Paliulis, O.; Uss, S.; Uss, V. *J. Prakt. Chem.* **2000**, *342*, 58. (h) Hmadeh, M.; Traboulsi, H.; Elhabiri, M.; Braunstein, P.; Albrecht-Gary, A.; Siri, O. *Tetrahedron*, **2008**, *64*, 6522.
3. (a) Holland, V. R.; Saunders, B. C.; Rose, F. L.; Walpole, A. L. *Tetrahedron*. **1974**, *30*, 3299. (b) Liu, L.-F.; Zhang, Y.-L.; Qian, X.-H. *Dyes Pigments*. **2004**, *60*, 17.
4. Khademi, S.; Song, J. Y.; Wyatt, P. B.; Kreouzis, T.; Gillin, W. P.; *Adv. Mater*. **2012**, *24*, 2278.
5. (a) Nelson, T. D.; Crouch, R. D. *Org. React.***2004**, *63*, 265.
6. (a) Cheng, J.-D.; Shine, H. J. *J. Org. Chem*. **1975**, *40*, 703. (b) Gündüz, T.; Kiliç, E.; Kenar, A.; Öztaş, S. G. *Analyst*. **1989**, *114*, 727. (c) Zhu-Ohlbach, Q.; Gleiter, R.; Rominger, F.; Schmidt, H. L.; Reda, T. *Eur. J. Org. Chem*. **1998**, 2409. (d) Buncel, E. *Can. J. Chem*. **2000**, *78*, 1251. (e) Kang, H.-M.; Lim, Y.-K.; Shin, I.-J.; Kim, H.-Y.; Cho, C.-G. *Org. Lett*. **2006**, *8*, 2047. (f) De, C. K.; Pesciaioli, F.; List, B. *Angew. Chem. Int. Ed*. **2013**, *52*, 9293.
7. Periasamy, M.; Jayakumar, K. N.; Bharathi, P. *J. Org. Chem*. **2000**, *65*, 3548.
8. (a) Xi, C.-J.; Jiang, Y.-F.; Yang, X.-H. *Tetrahedron Lett*. **2005**, *46*, 3909. (b) Yang, X.-H.; Xi, C.-J.; Jiang, Y.-F. *Synth. Commun*. **2006**, *36*, 2413.
9. Jiang, Y.-F.; Xi, C.-J.; Yang, X.-H. *Synlett* **2005**, 1381.
10. Kirchgessner, M.; Sreenath, K.; Gopidas, K. R. *J. Org. Chem*. **2006**, *71*, 9849.

11. (a) Murata, S.; Miura, M.; Nomura, M. *J. Chem. Soc., Chem. Commun*. **1989**, 116. (b) Murata, S.; Miura, M.; Nomura, M. *J. Org. Chem*. **1989**, *54*, 4700. (c) Li, X.-L.; Huang, J.-H.; Yang, L.-M. *Org. Lett*. **2011**, *13*, 4950.
12. (a) Ling, X.-G.; Xiong, Y.; Huang, R-F.; Zhang, X-H.; Zhang, S-T.; Chen, C.-G. *J. Org. Chem.* **2013**, *78*, 5218. Also see: (b) Li, H.-J.; He, Z.-H.; Guo, X.-W.; Li, W.-J.; Zhao, X.-H.; Li, Z. *Org. Lett*. **2009**, *11*, 4176. (c) Zhang, L.; Peng, C.; Zhao, D.; Wang, Y.; Fu, H.-J.; Shen, Q.; Li, J-X. *Chem. Commun*. **2012**, *48*, 5928.
13. (a) Saitoh, T.; Yoshida, S.; Ichikawa, J. *Org. Lett*. **2004**, *6*, 4563. (b) Saitoh, T.; Yoshida, S.; Ichikawa, J. *J. Org. Chem*. **2006**, *71*, 6414.
14. For constructing diphenylmethane, see our former work: (a) Zhang, S.-T.; Zhang, X.-H.; Ling, X.-G.; He, C.; Huang, R.-F.; Pan, J.; Li, J. Q.; Xiong, Y. *RSC Adv*. **2014**, *4*, 30768. (b) Li Y.; Xiong, Y.; Li, X.-M.; Ling, X.-G.; Huang, R.-F.; Zhang, X.-H.; Yang, J.-C. *Green Chem.* **2014**, *16*, 2976. (c) Huang, R.-F.; Zhang, X.-H.; Pan, J.; Li, J.-Q.; Shen, H.; Ling, X.-G.; Xiong, Y. *Tetrahedron* **2015**, *71*, 1540.
15. For the detail of optimization, see supporting information.
16. Hall, D.-M.; Ladbury, J.-E.; Lesslie, M.-S.; Turner, E.-E. *J. Chem. Soc.* **1956**, 3475.

Electronic Supplementary Information

Extension studies on iron(III)-promoted free radical oxidation of anilines: self-coupling and self-bridged assembling reactions

Jing Pan[a] , *Jiaqiang Li*[a] , *Ruofeng Huang*[a] , *Xiaohui Zhang*[a] , *Hang Shen*[a] , *Yan Xiong*[a,]* *and Xiangming Zhu*[b]

[a] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China.

[b] UCD School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland.

Table of contents

---

* Corresponding author. Tel.: +86-15086903431; fax: +86-023 65112134; e-mail: xiong@cqu.edu.cn

1. Experimental Section

1.1. General Information

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

1.2. General Procedure for the oxidative self-coupling reactions

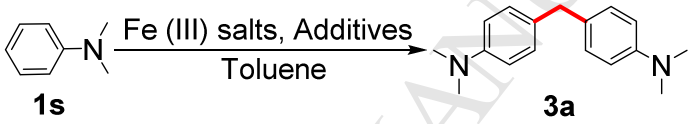
To a stirred mixture of $FeCl_3 \cdot 6H_2O$ (270.3 mg, 1.0 mmol) and 2.0 mL toluene was added aniline **1** (0.4 mmol) at room temperature. The reaction was stirred at 85 °C for 2 h in atmosphere. After it was cooled to room temperature, the reaction mixture was quenched by aqueous ammonia solution (mass fraction: 25%-28%, 10 mL) and extracted with dichloromethane (10 mL per time) until no product was observed in the extract, monitored by TLC. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give crude product, which was chromatographed on silica gel column using 1:100 to 1:70 (*v*/*v*) EtOAc-petroleum ether solution as eluent to afford isolated product **2**.

1.3. General Procedure for the oxidative self-bridged assembling reactions

To a stirred mixture of aniline **1** (0.4 mmol) and 2.0 mL toluene was added triethylamine (56 μL, 0.4 mmol) and $FeCl_3 \cdot 6H_2O$ (270.3 mg, 1.0 mmol) successively at room temperature. The reaction was stirred at 85 °C for 3.5 h in atmosphere. After it was cooled to room temperature, the reaction mixture was quenched by aqueous ammonia solution (mass fraction: 25%-28%, 10 mL) and extracted with dichloromethane (10 mL per time) until no product was observed in the extract, monitored by TLC. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give crude product, which was chromatographed on silica gel column using 1:100 to 1:70 (*v*/*v*) EtOAc-petroleum ether solution as eluent to afford isolated product **3**.

2. Optimization of reaction conditions

Table S1. Optimization conditions for the self-bridged assembling reaction of *N*,*N*-dimethylaniline[a]



Entry	Oxidant (eq.)	Additives (eq.)	*T* (°C)	*t* (h)	Yield (%)[b]
1	$FeCl_3$ (2.5)	Et_3N (1.0)	85	4.5	41
2	$Fe_2(SO_4)_3$ (2.5)	Et_3N (1.0)	85	4.5	0
3	$Fe(NO_3)_3$ (2.5)	Et_3N (1.0)	85	4.5	-[c]
4	$FeCl_3\cdot 6H_2O$ (2.5)	Et_3N (1.0)	85	4.5	77
5	$FeCl_3\cdot 6H_2O$ (2.5)	K_2CO_3 (1.0)	85	4.5	49
6	$FeCl_3\cdot 6H_2O$ (2.5)	DIEA (1.0)	85	4.5	76
7	$FeCl_3\cdot 6H_2O$ (2.5)	NaOH (1.0)	85	4.5	13
8	$FeCl_3\cdot 6H_2O$ (2.5)	Phen (1.0)	85	4.5	35
9	$FeCl_3\cdot 6H_2O$ (1.0)	Et_3N (1.0)	85	4.5	31
10	$FeCl_3\cdot 6H_2O$ (2.0)	Et_3N (1.0)	85	4.5	53
11	$FeCl_3\cdot 6H_2O$ (3.0)	Et_3N (1.0)	85	4.5	76
12	$FeCl_3\cdot 6H_2O$ (2.5)	Et_3N (0.5)	85	4.5	62
13	$FeCl_3\cdot 6H_2O$ (2.5)	Et_3N (1.5)	85	4.5	64
14	$FeCl_3\cdot 6H_2O$ (2.5)	Et_3N (1.0)	85	2.5	77
15	$FeCl_3\cdot 6H_2O$ (2.5)	Et_3N (1.0)	85	3.0	83
16	$FeCl_3\cdot 6H_2O$ (2.5)	Et_3N (1.0)	**85**	**3.5**	**88**
17	$FeCl_3\cdot 6H_2O$ (2.5)	Et_3N (1.0)	85	4.0	80
18	$FeCl_3\cdot 6H_2O$ (2.5)	Et_3N (1.0)	100	3.5	87
19	$FeCl_3\cdot 6H_2O$ (2.5)	Et_3N (1.0)	120	3.5	52

[a] Reaction conditions: *N*,*N*-dimethylaniline (0.4 mmol), iron sources, and additives (specified

amounts) in 2.0 mL of toluene. [b] Isolated yields. [c] Complex mixture.

3. General Procedure for the synthesis of 4

3.1. Preparation of amalgamated zinc

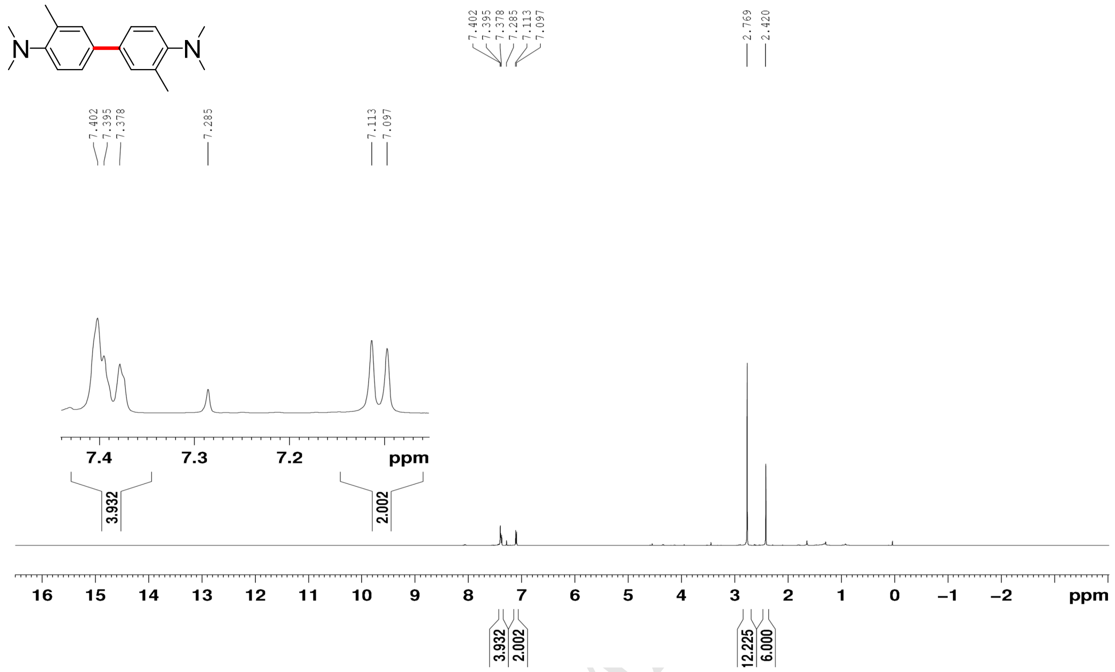
To a round-bottom flask was added zinc powder (480 mg, 7.3 mmol) and mercuric chloride (48 mg, 0.2 mmol), followed by H_2O (800 μL, 44.4 mmol) and con. hydrochloric acid (24 μL, 0.8 mmol). The reaction mixture was stirred at room temperature for 10 min, the solution was decanted, and amalgamated zinc was obtained.

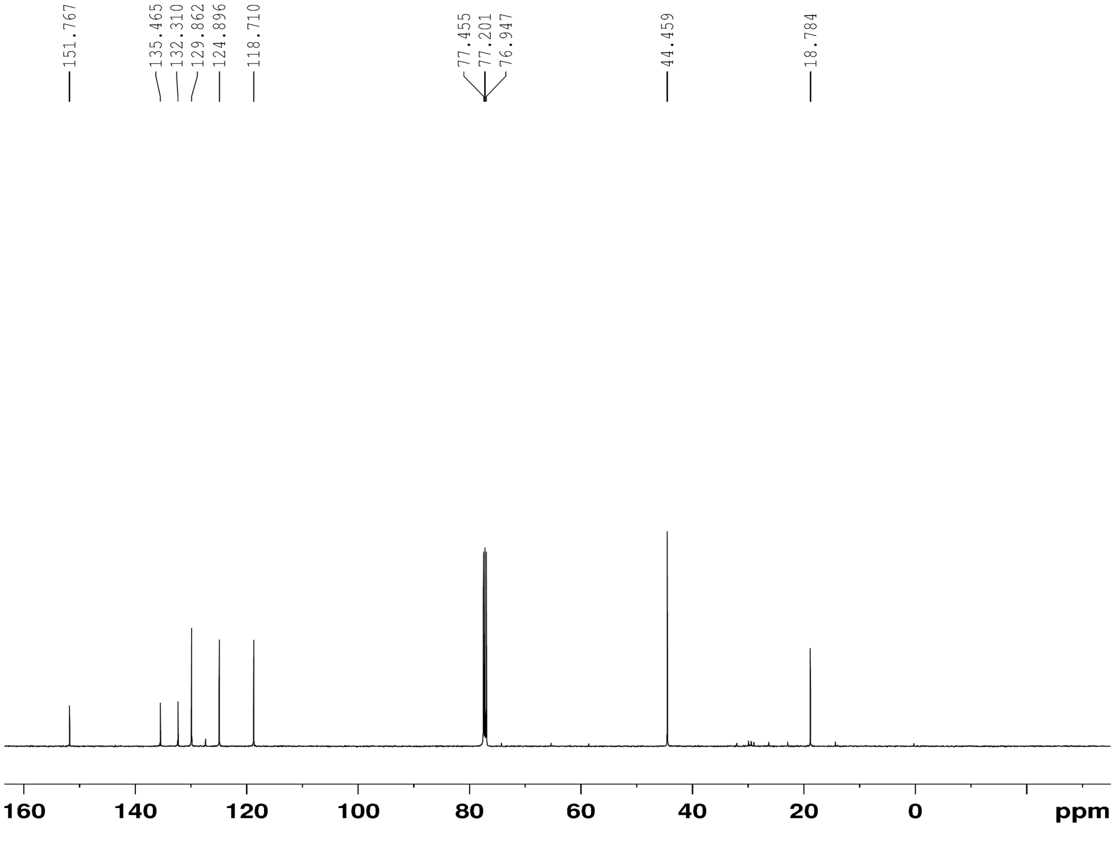
3.2. Clemmensen reduction of 2k

To freshly prepared amalgamated zinc was added diacetyldiphenyl **2k** (65 mg , 0.2 mmol), H_2O (280 μL, 15.6 mmol) and con. hydrochloric acid (720 μL, 23.3 mmol) successively. The resulting mixture was boiled under reflux for 2 h. The reaction mixture was washed by diethyl ether (5 mL) and the solid residue was removed. The solution was alkalized by saturated $NaHCO_3$ and extracted by diethyl ether (5 mL×3). The organic layers were combined, dried over anhydrous Mg_2SO_4, filtered and concentrated under reduced pressure to give crude product, which was chromatographed on silica gel column using EtOAc-petroleum ether (1: 60, v/v) solutions as eluent to afford white solid **4**.

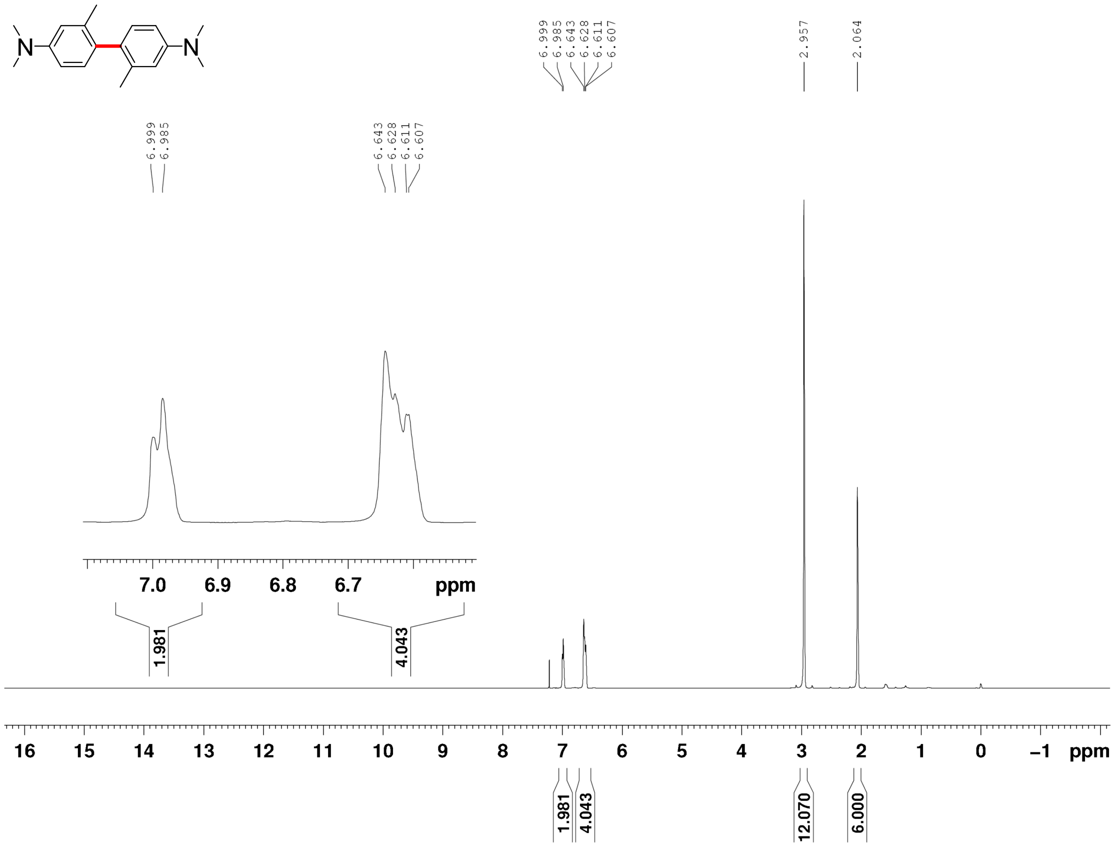
4. Copies of of ^{1}H- and ^{13}C-NMR

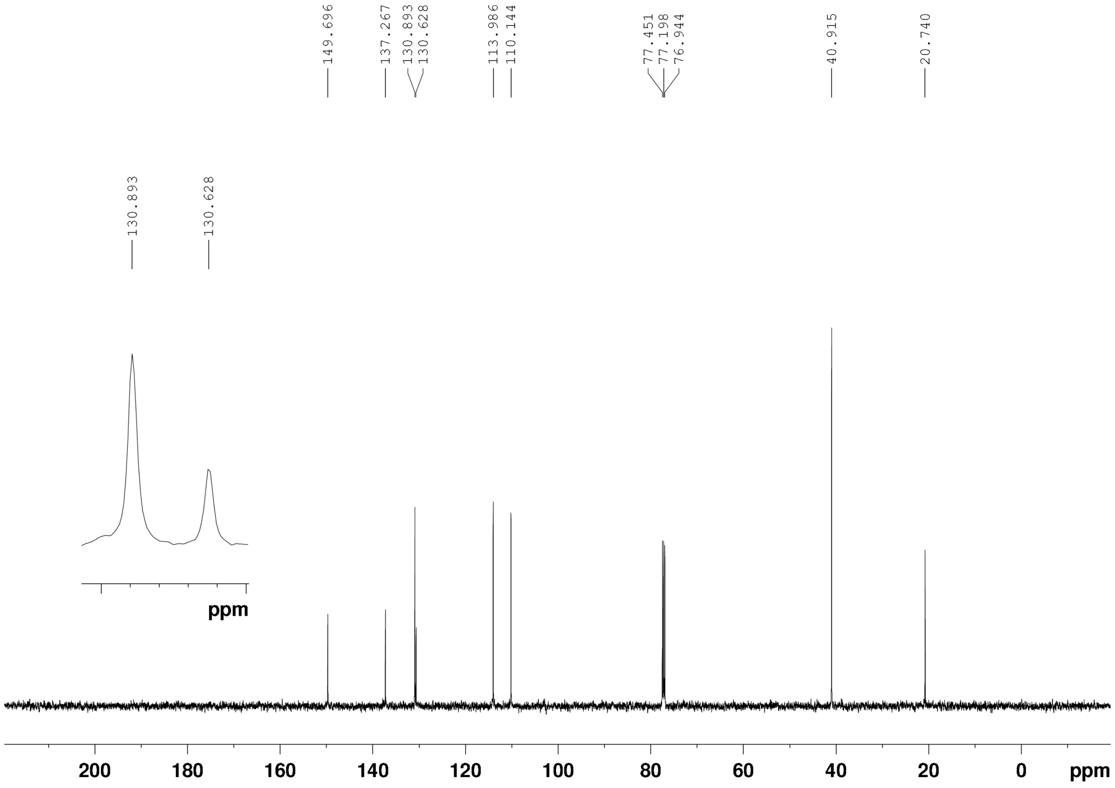
N^4,*N*^{4},*N*$^{4'}$,*N*$^{4'}$,3,3'-hexamethyl-[1,1'-biphenyl]-4,4'-diamine (2a)



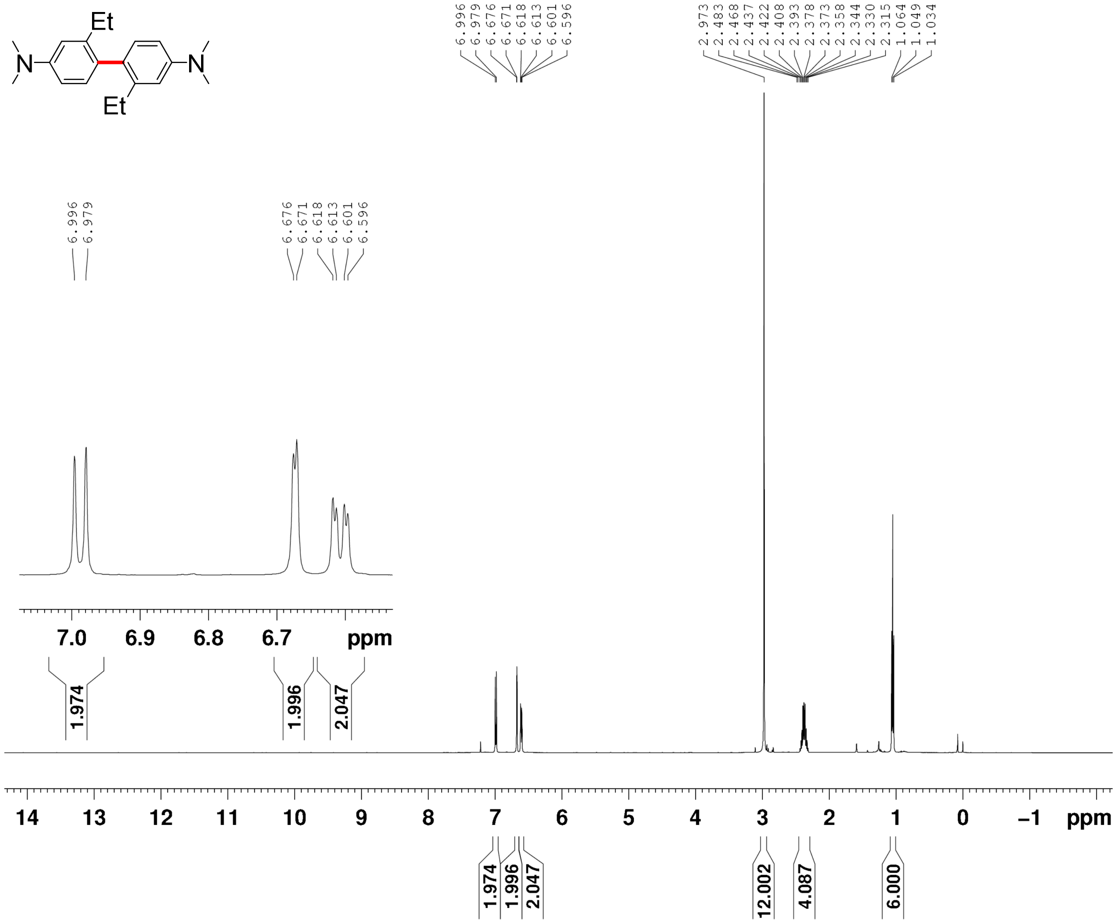


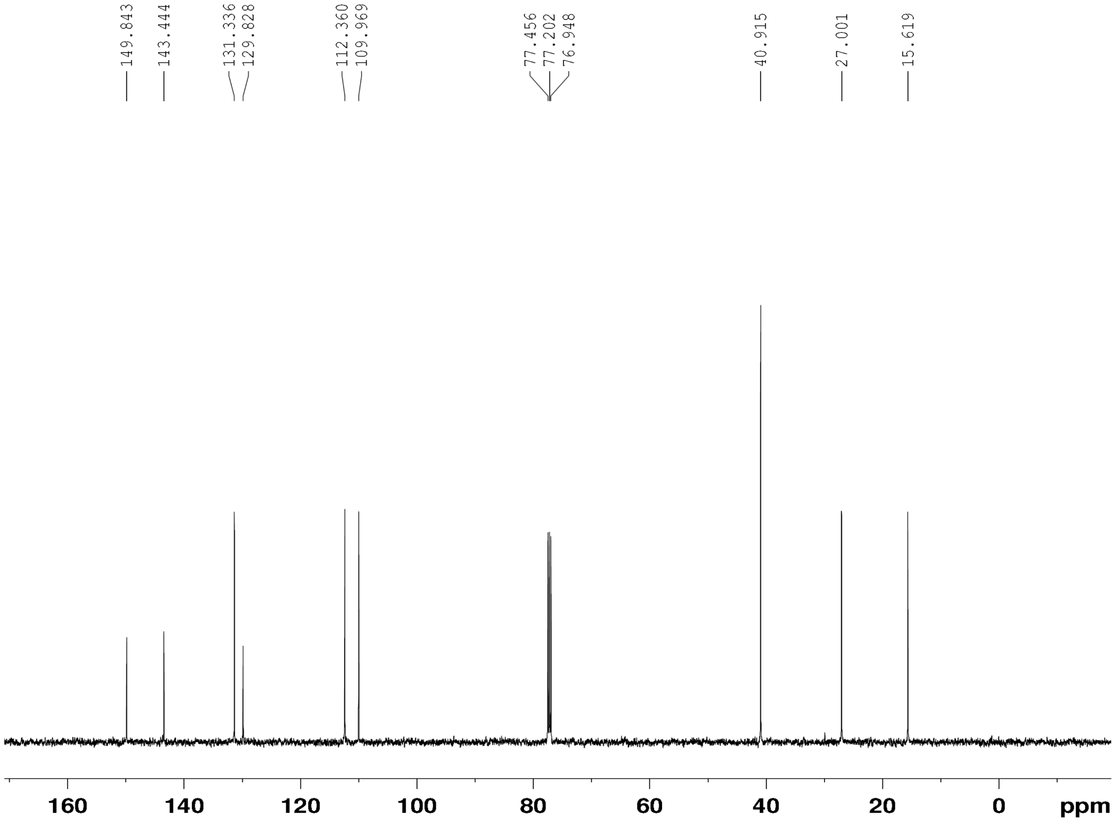
N^{4},N^{4},$N^{4\prime}$,$N^{4\prime}$,2,2'-hexamethyl-[1,1'-biphenyl]-4,4'-diamine (2b)



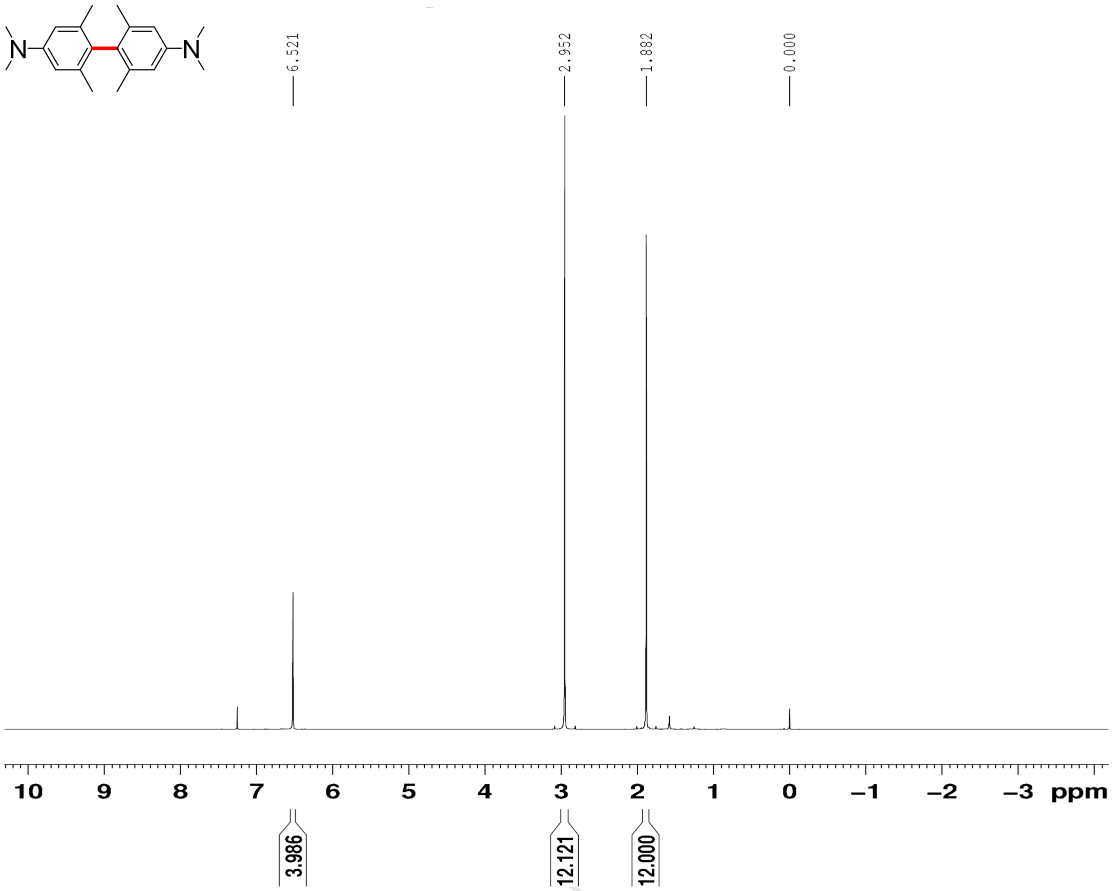


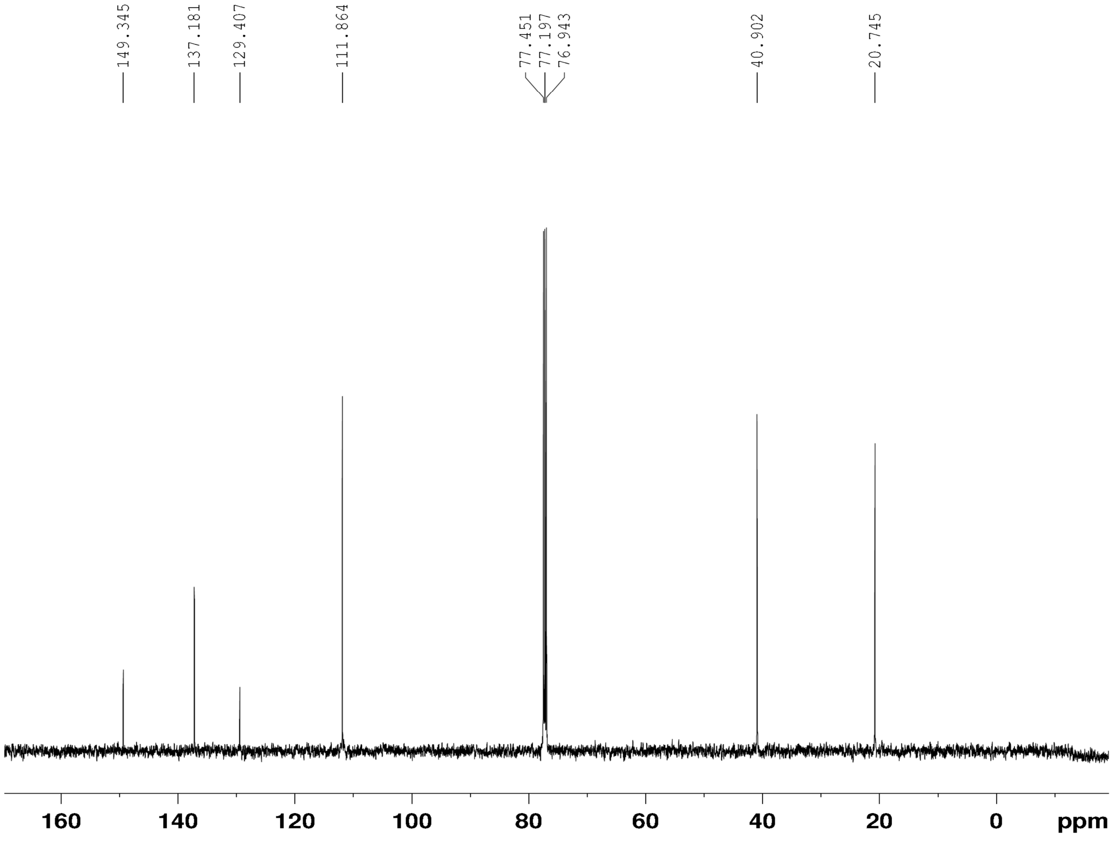
2,2'-diethyl-N^4,N^4,$N^{4'}$,$N^{4'}$-tetramethyl-[1,1'-biphenyl]-4,4'-diamine (2c)



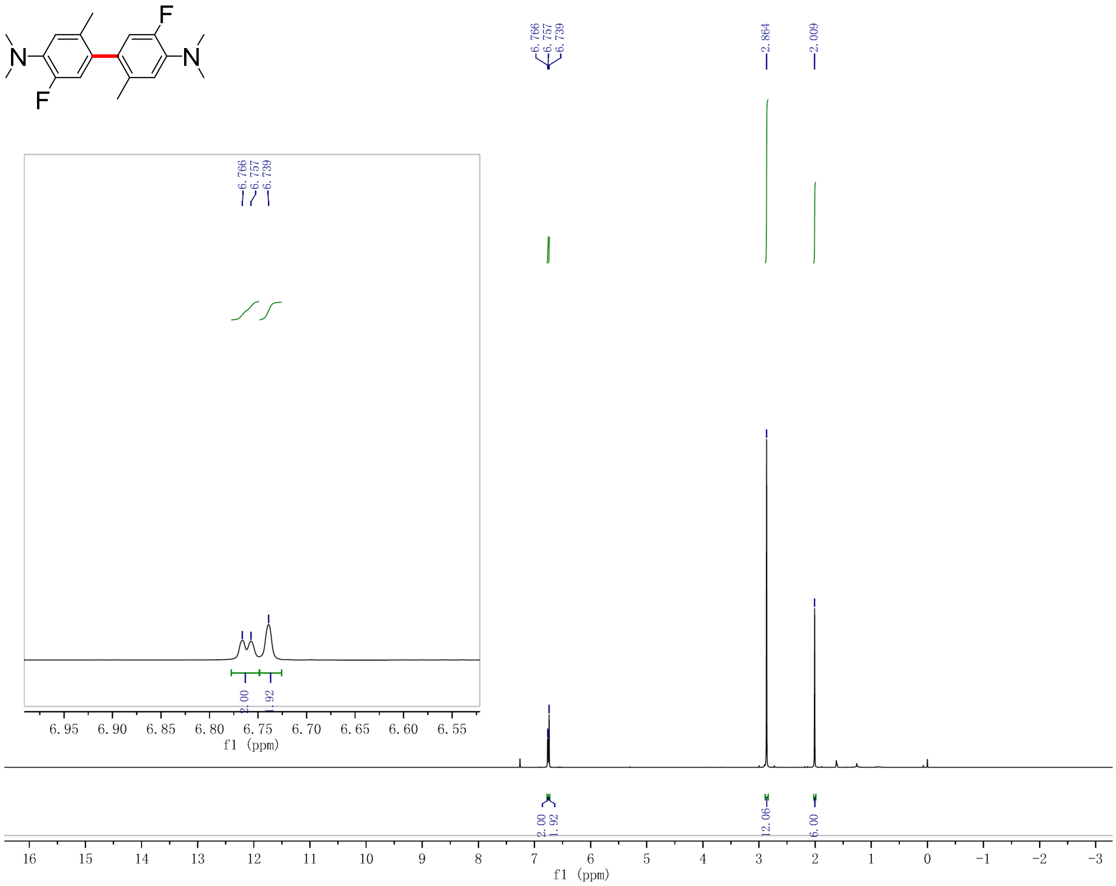


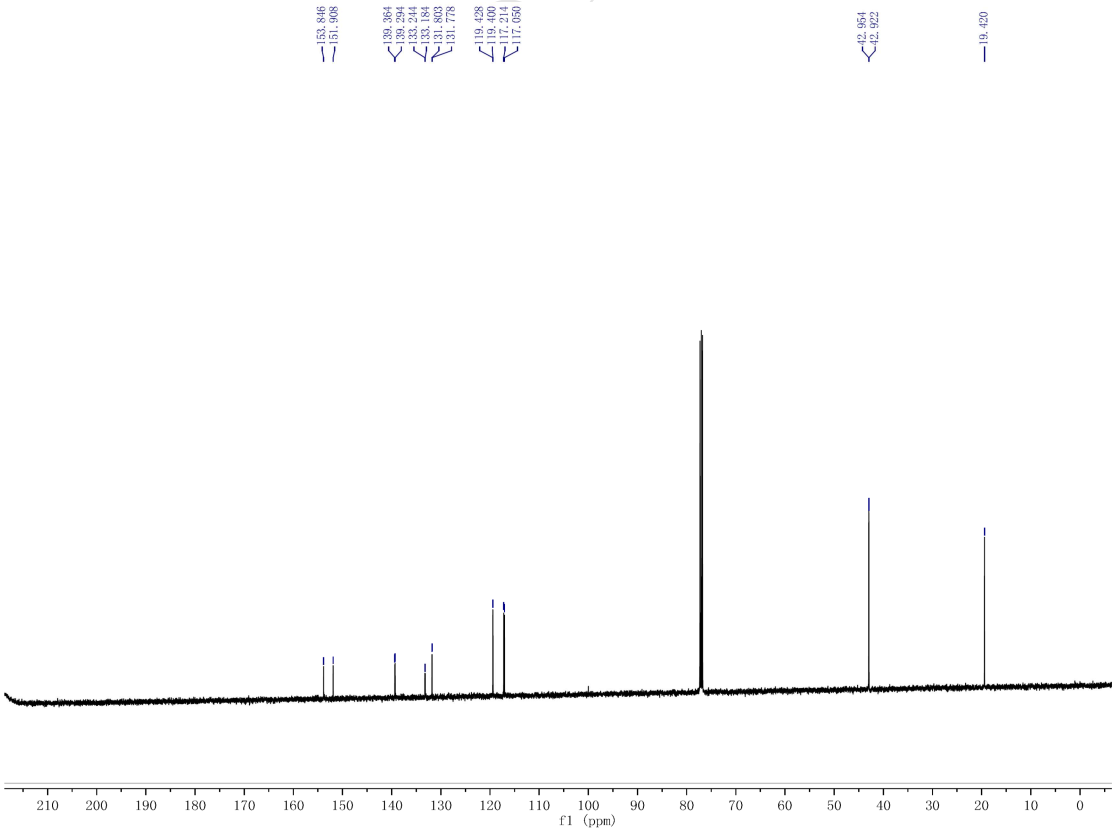
N^4,N^4,$N^{4'}$,$N^{4'}$,2,2',6,6'-octamethyl-[1,1'-biphenyl]-4,4'-diamine (2d)



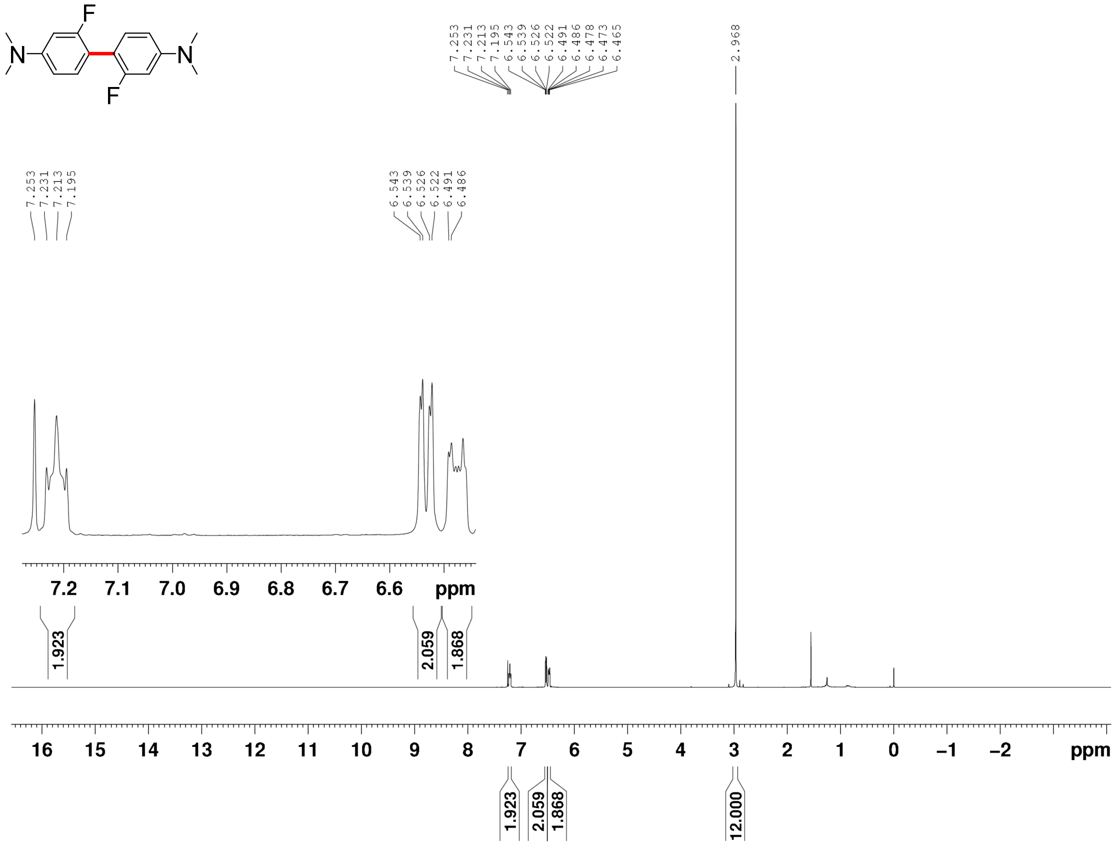


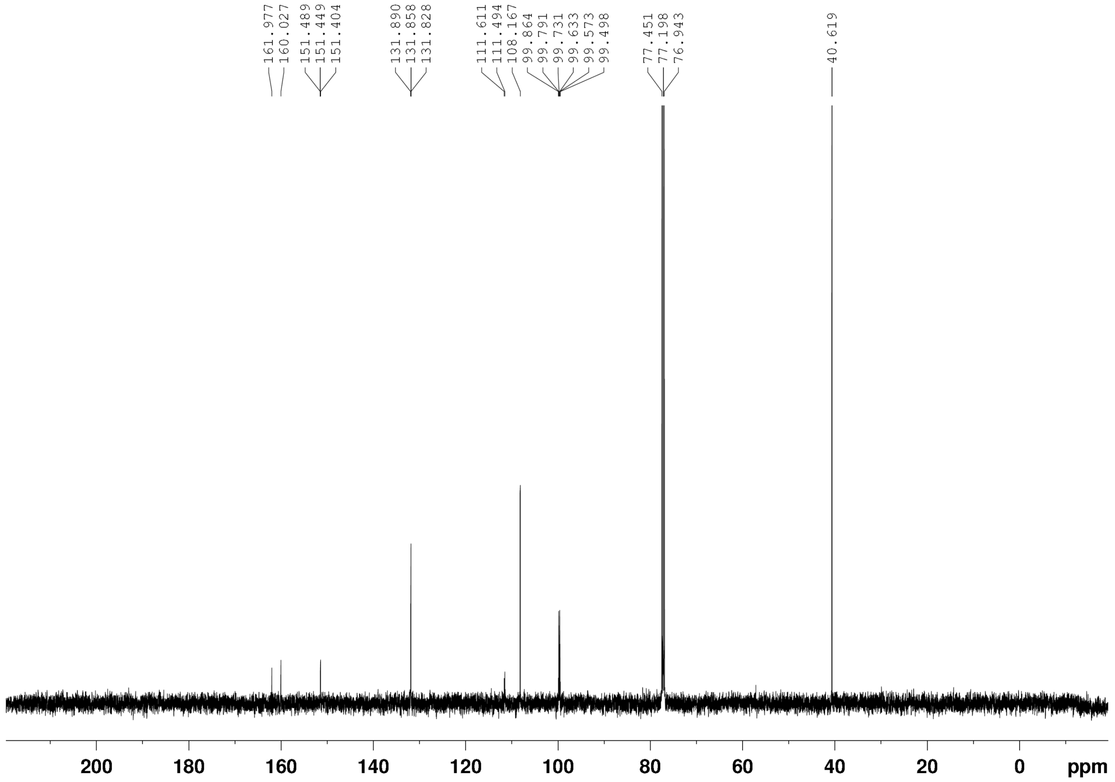
5,5'-difluoro-N^4,N^4,$N^{4\prime}$,$N^{4\prime}$,2,2'-hexamethyl-[1,1'-biphenyl]-4,4'-diamine (2e)



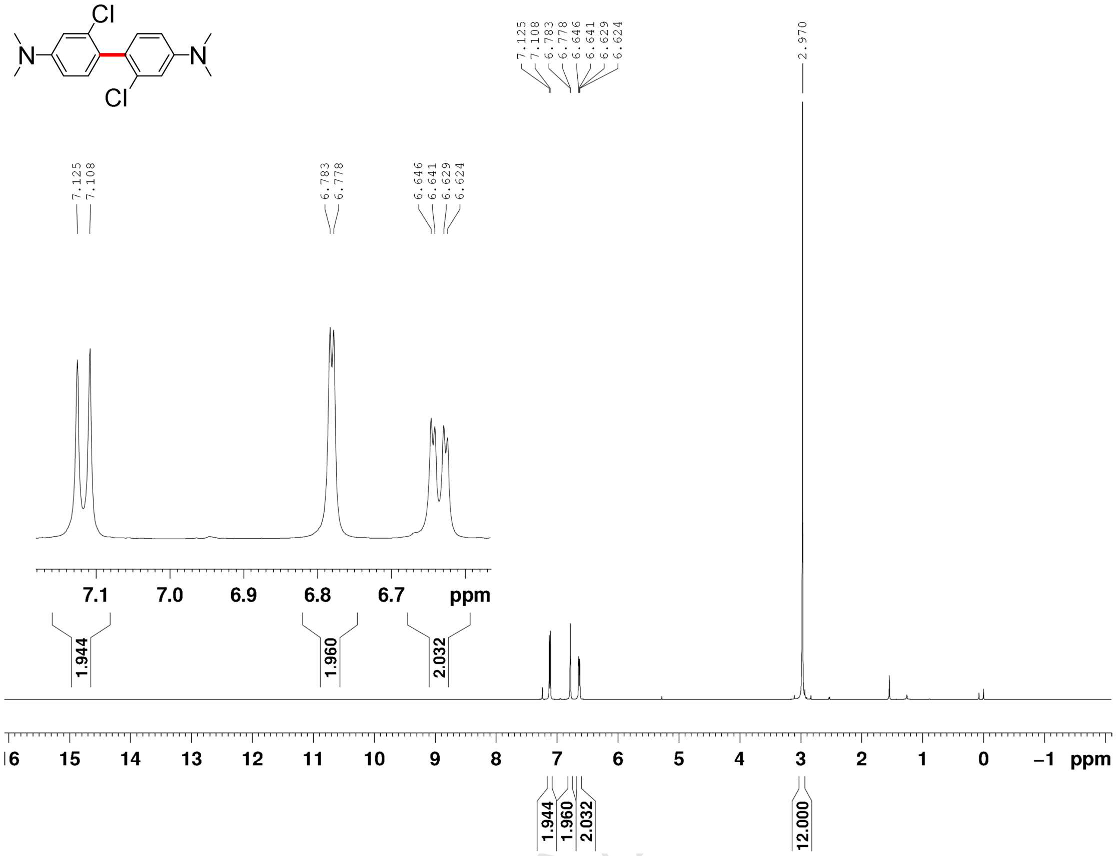


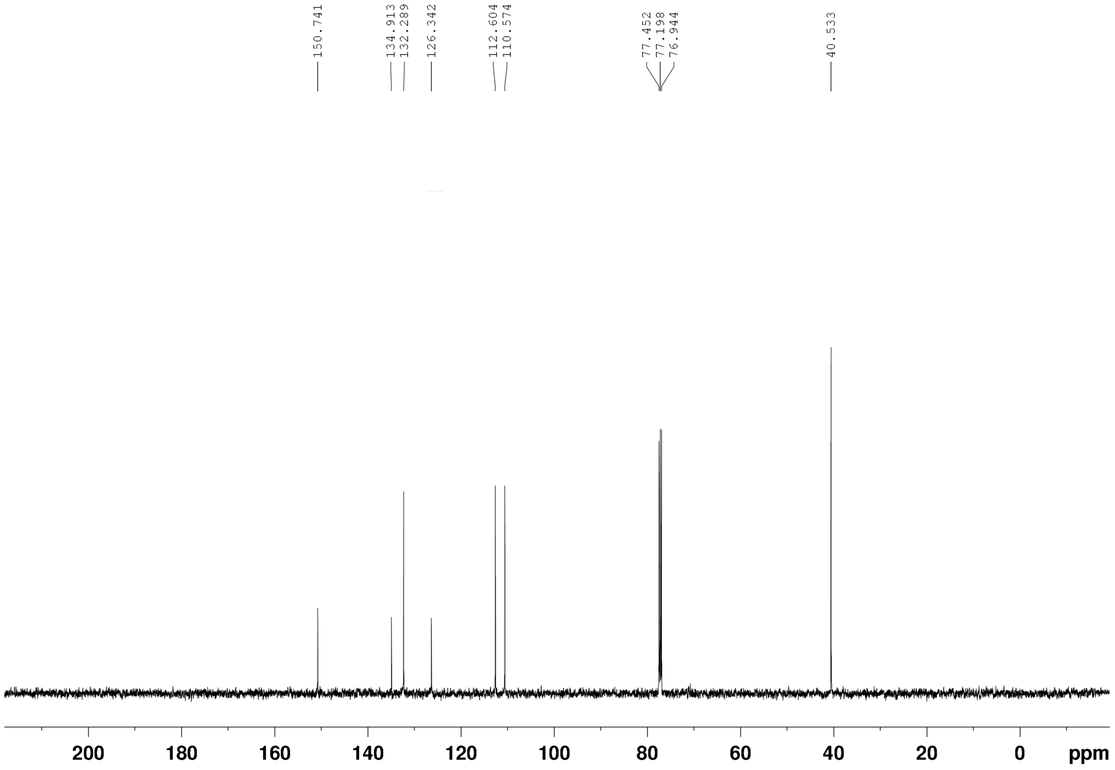
2,2'-difluoro-N^4,N^4,$N^{4'}$,$N^{4'}$-tetramethyl-[1,1'-biphenyl]-4,4'-diamine (2f)



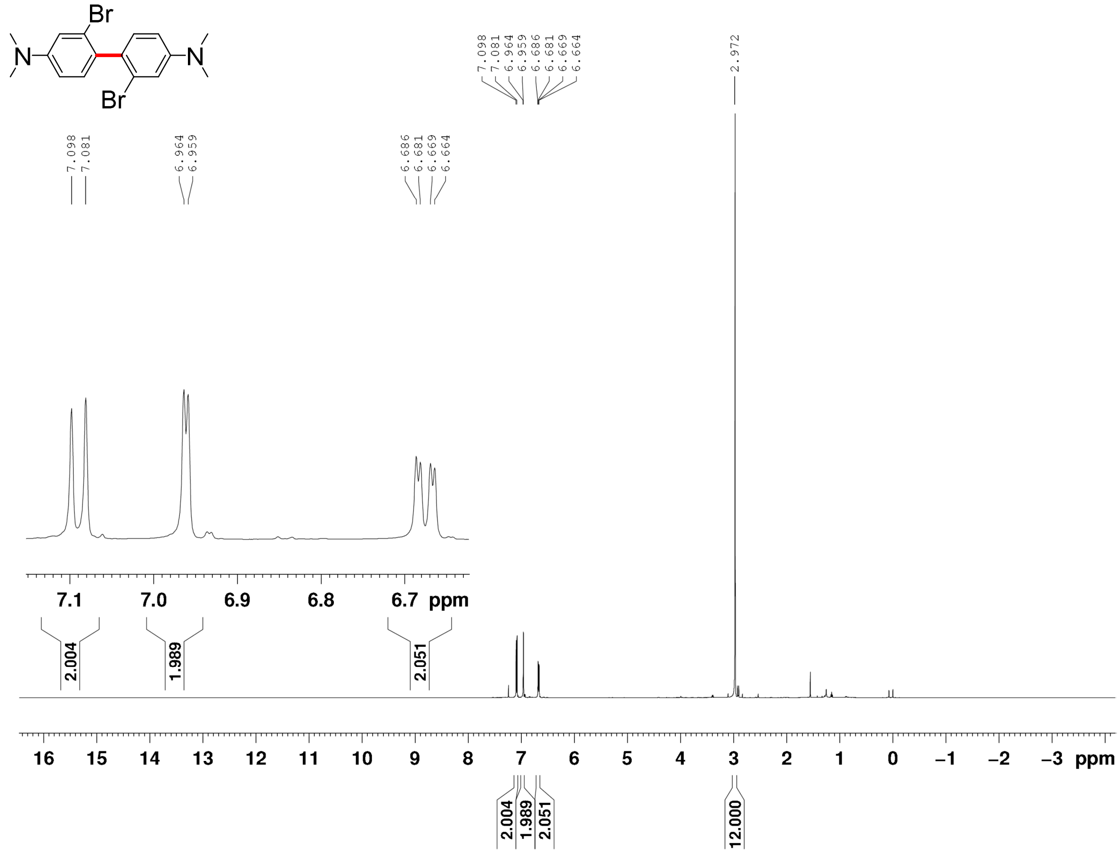


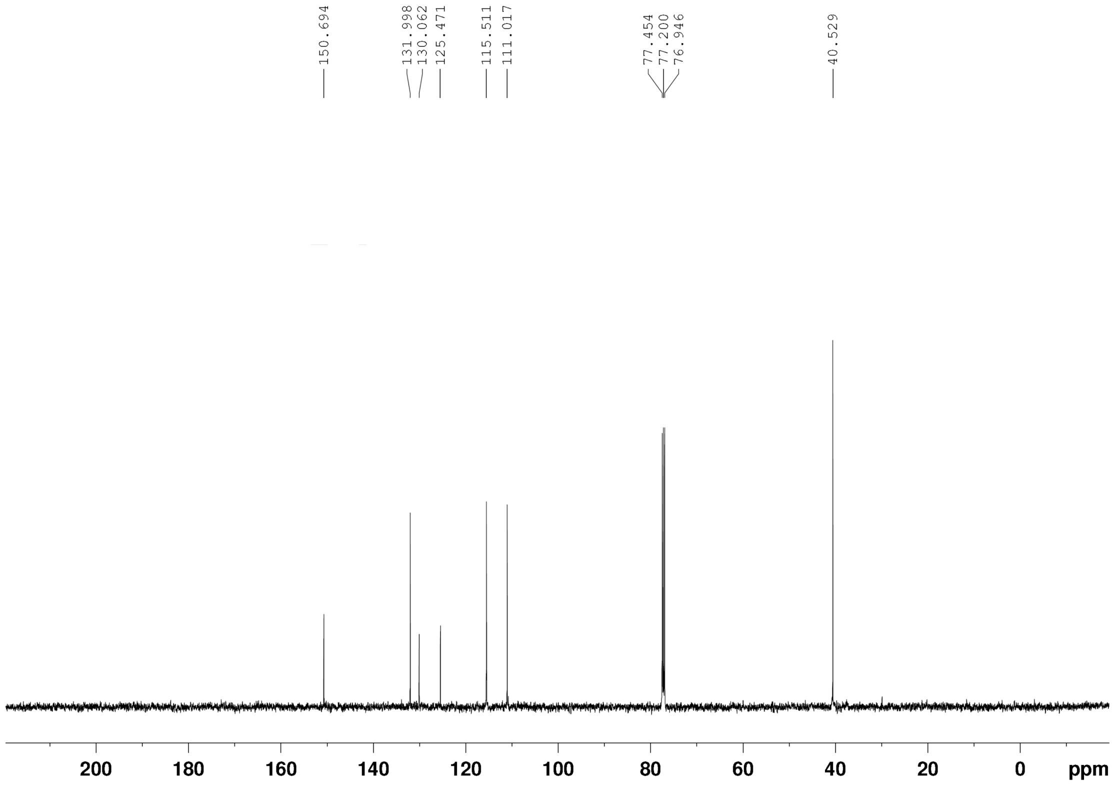
2,2'-dichloro-*N*^{4},*N*^{4},*N*$^{4'}$,*N*$^{4'}$-tetramethyl-[1,1'-biphenyl]-4,4'-diamine (2g)



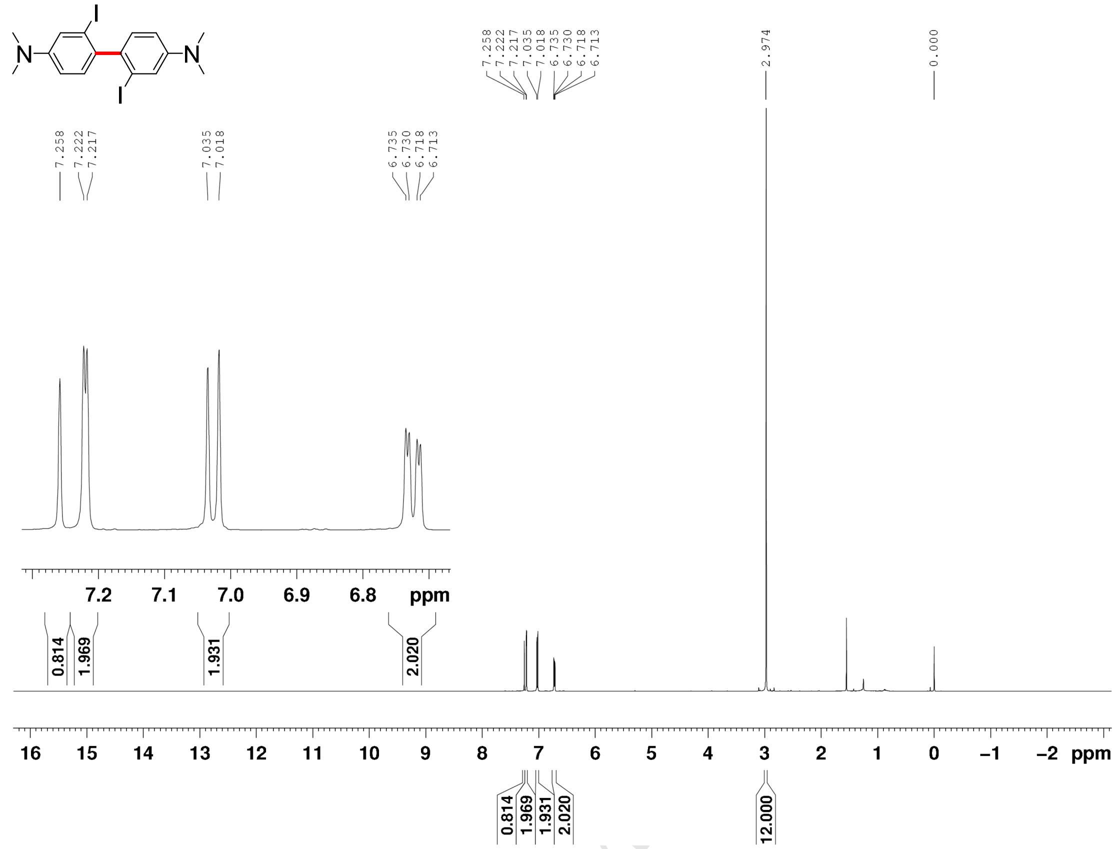


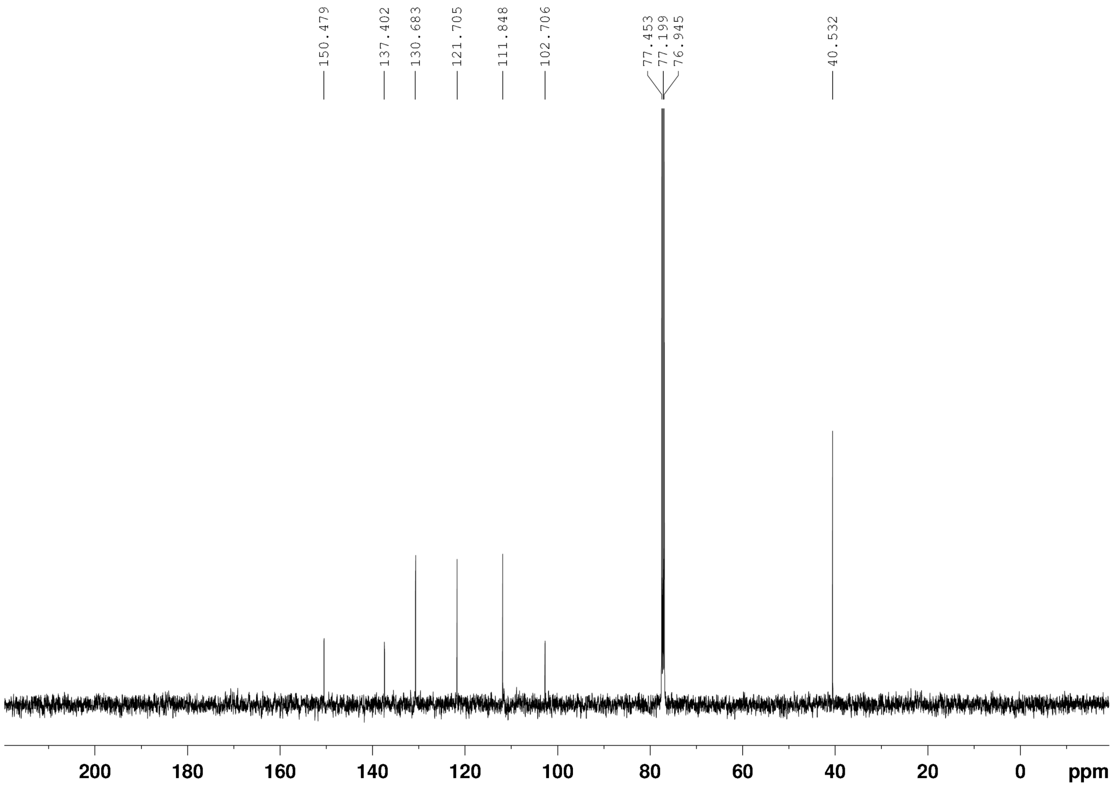
2,2'-dibromo-N^4,N^4,$N^{4'}$,$N^{4'}$-tetramethyl-[1,1'-biphenyl]-4,4'-diamine (2h)



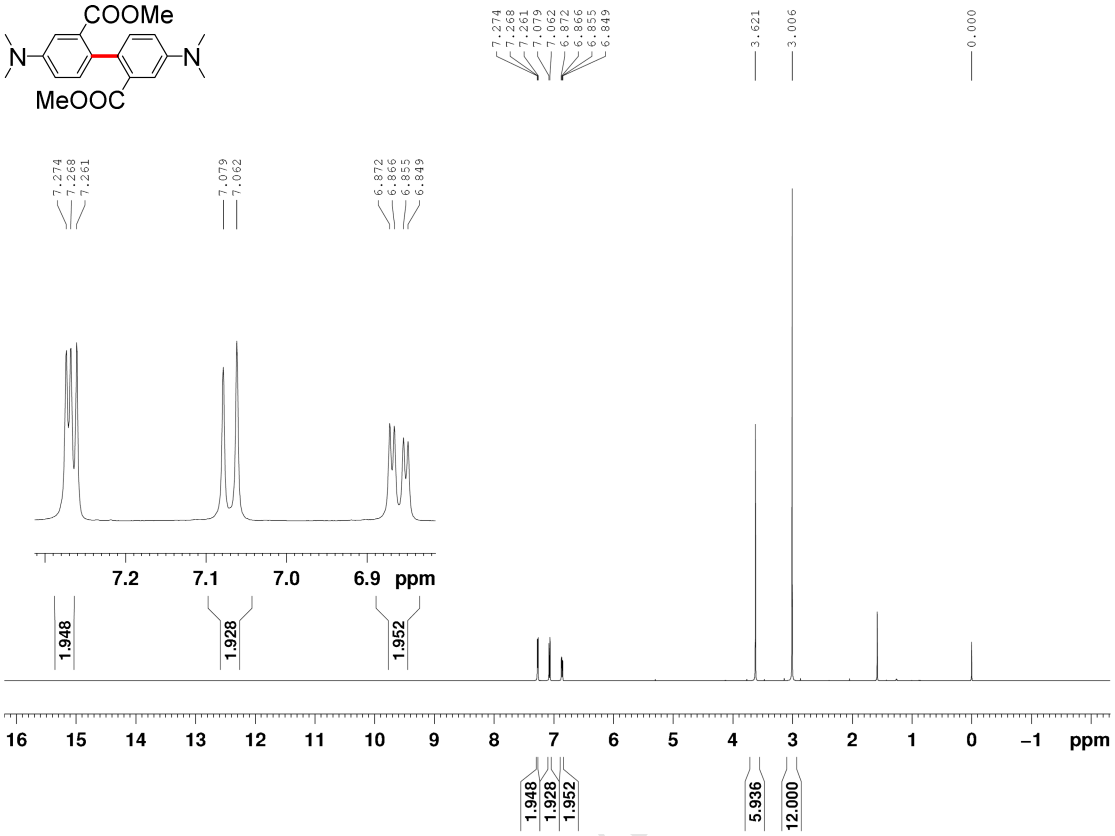


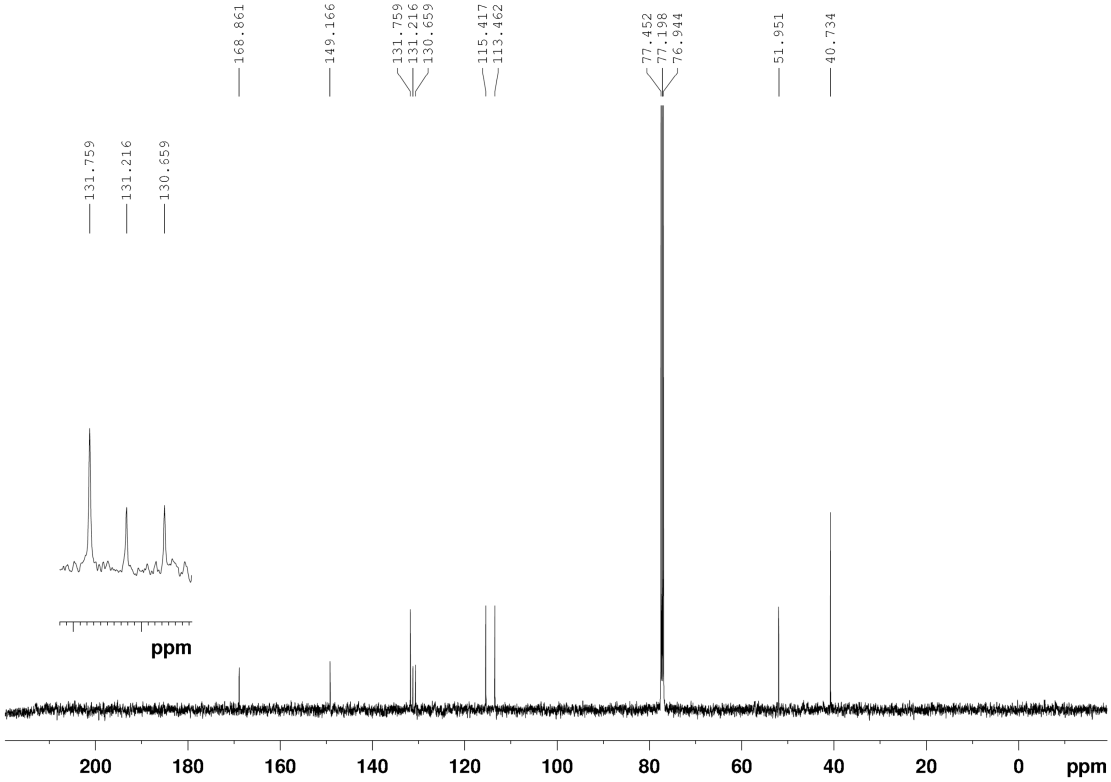
2,2'-diiodo-N^4,N^4,$N^{4'}$,$N^{4'}$-tetramethyl-[1,1'-biphenyl]-4,4'-diamine (2i)



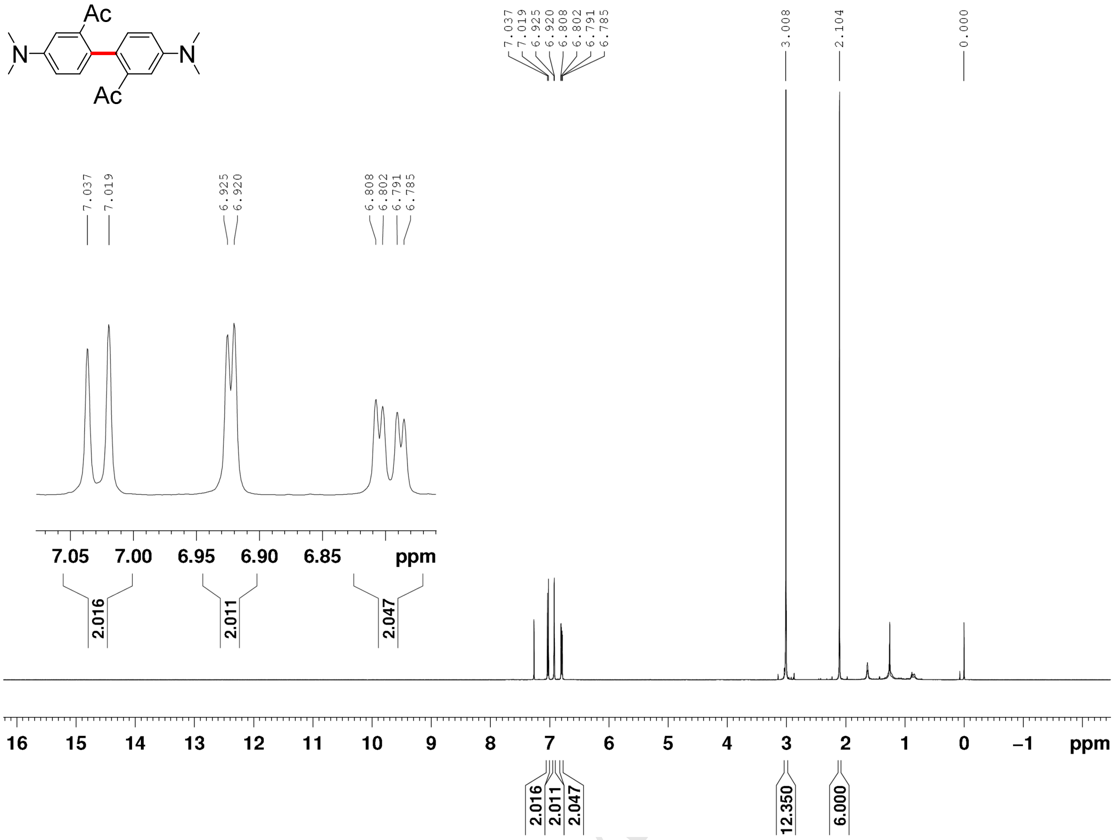


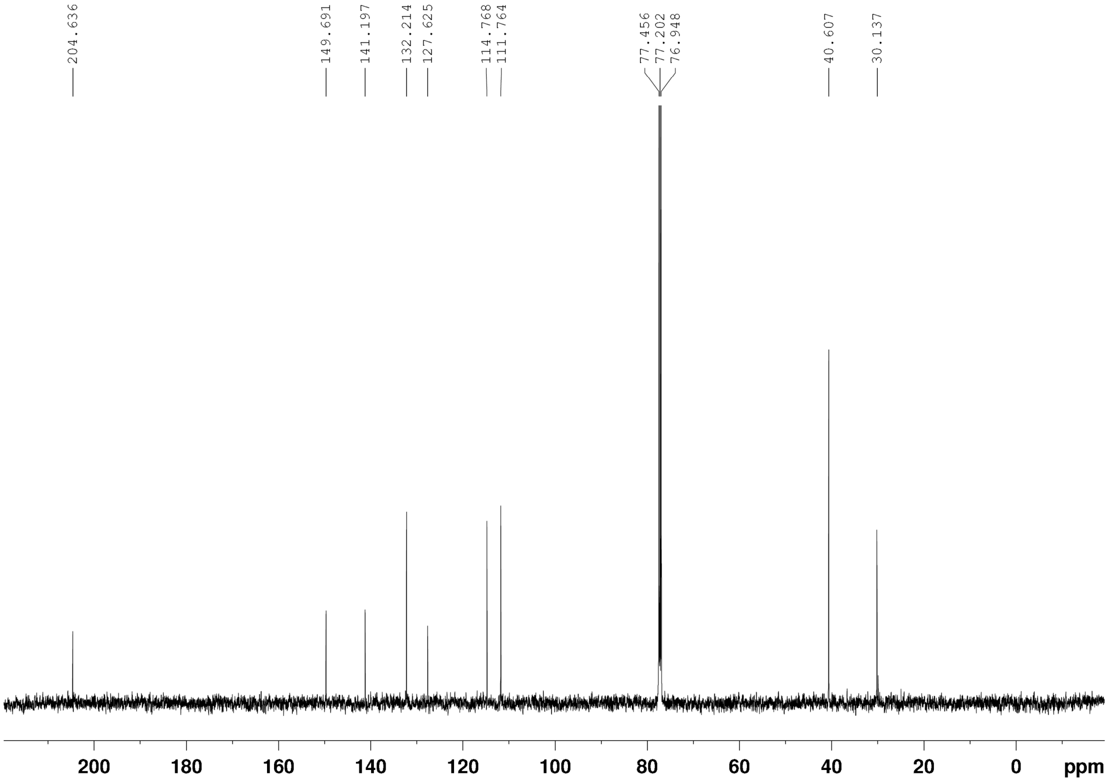
dimethyl 4,4'-bis(dimethylamino)-[1,1'-biphenyl]-2,2'-dicarboxylate (2j)



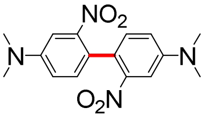


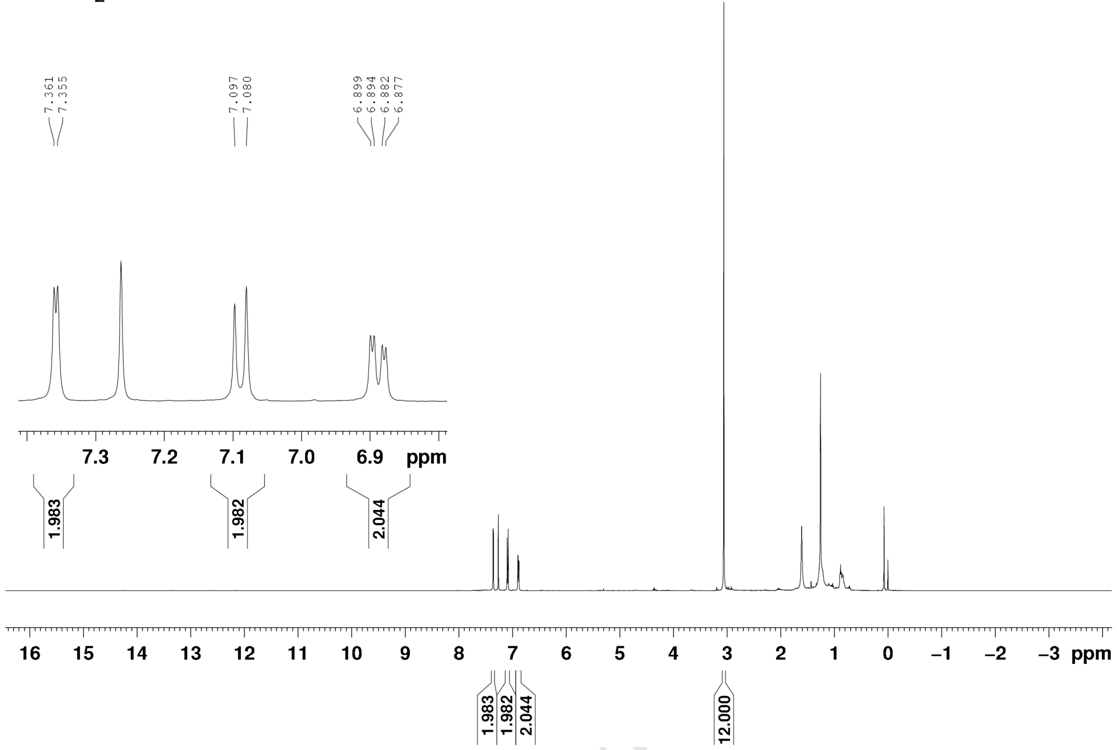
1,1'-(4,4'-bis(dimethylamino)-[1,1'-biphenyl]-2,2'-diyl)bis(ethan-1-one) (2k)

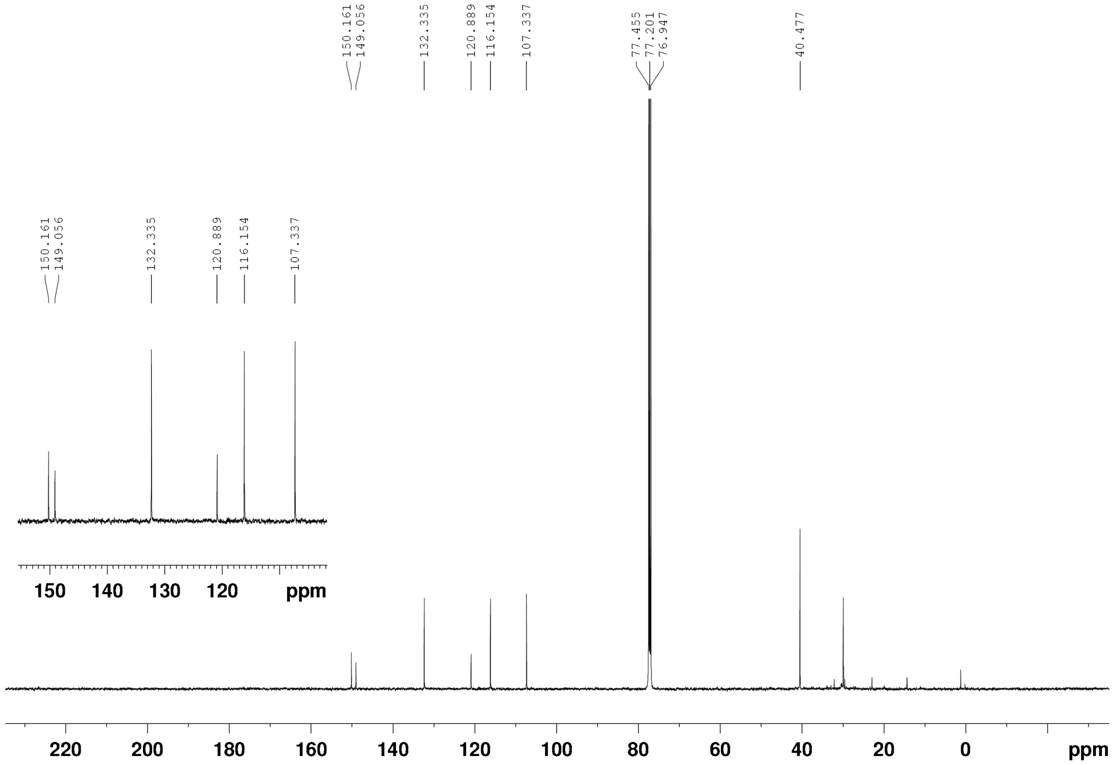




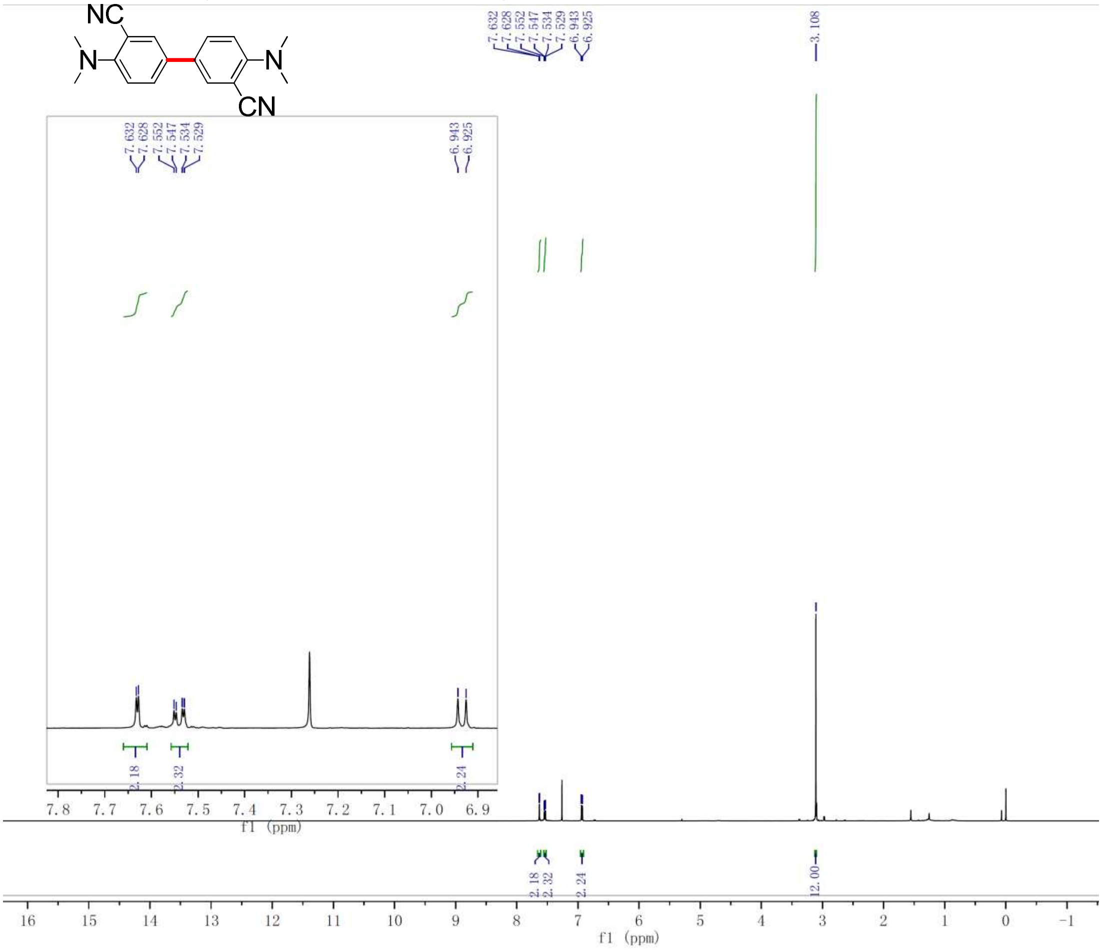
N^4,*N*^{4},*N*$^{4'}$,*N*$^{4'}$-tetramethyl-2,2'-dinitro-[1,1'-biphenyl]-4,4'-diamine (2l)

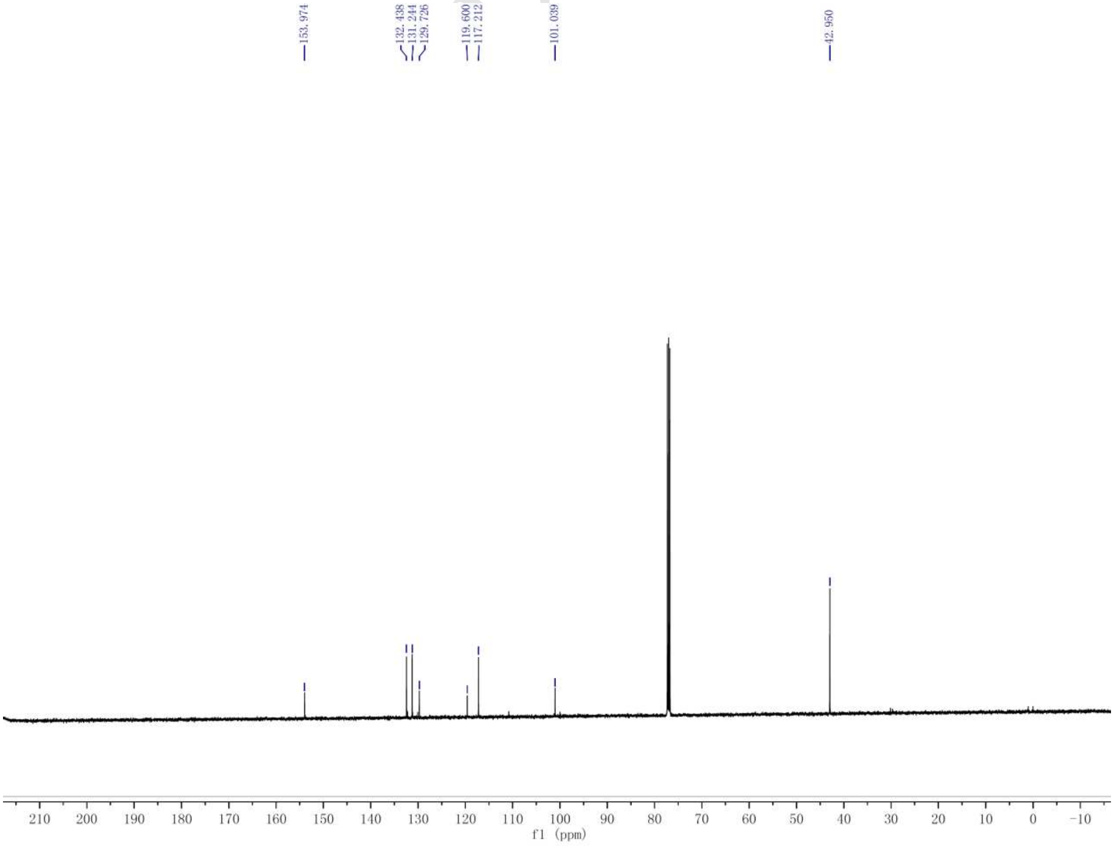




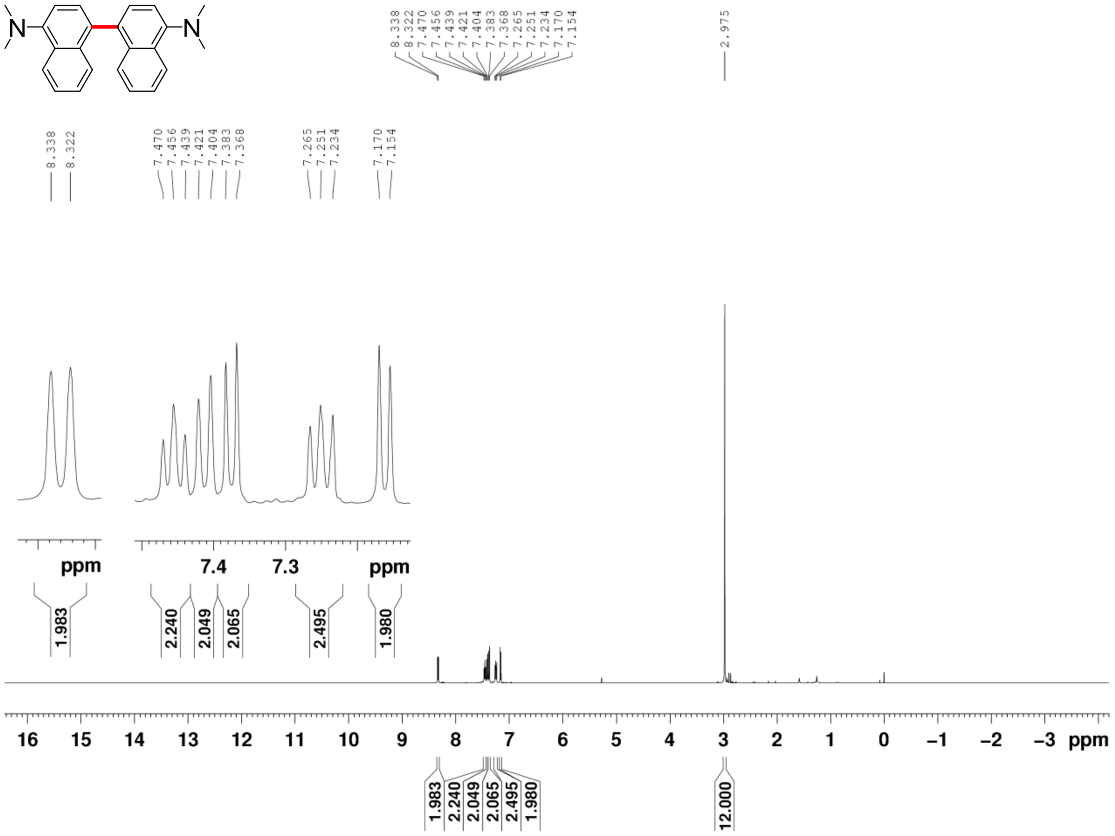


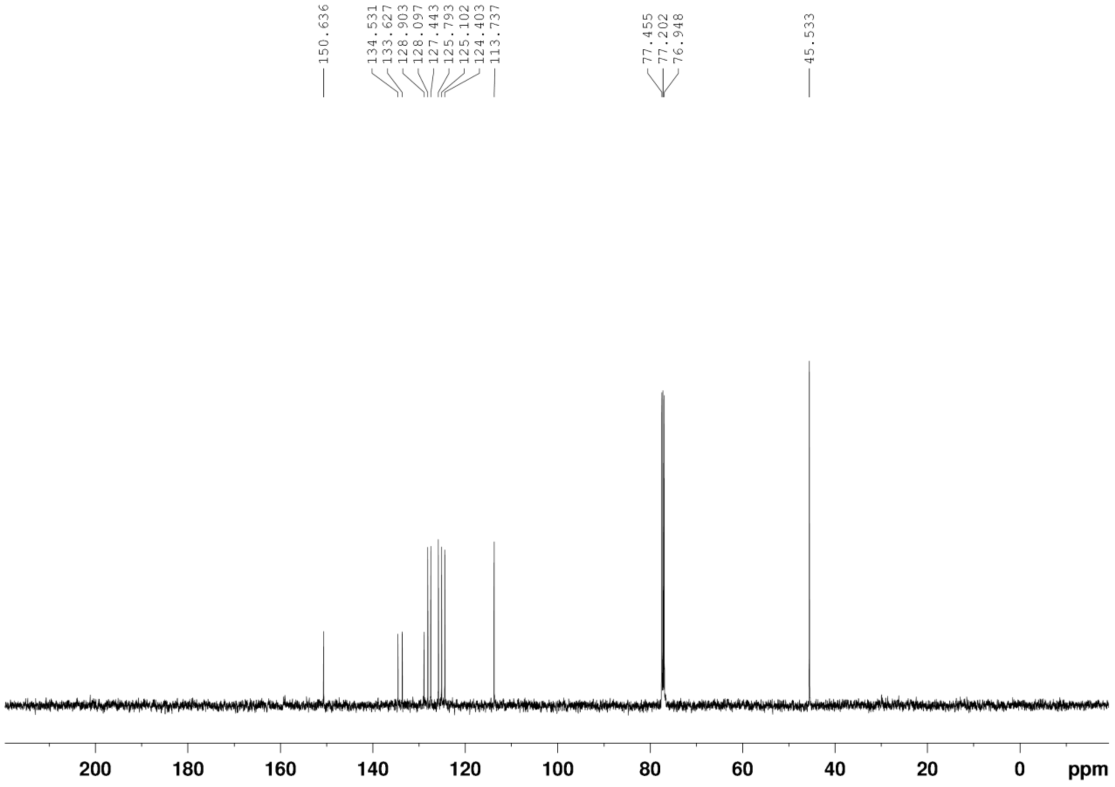
4,4'-bis(dimethylamino)-[1,1'-biphenyl]-3,3'-dicarbonitrile (2m)



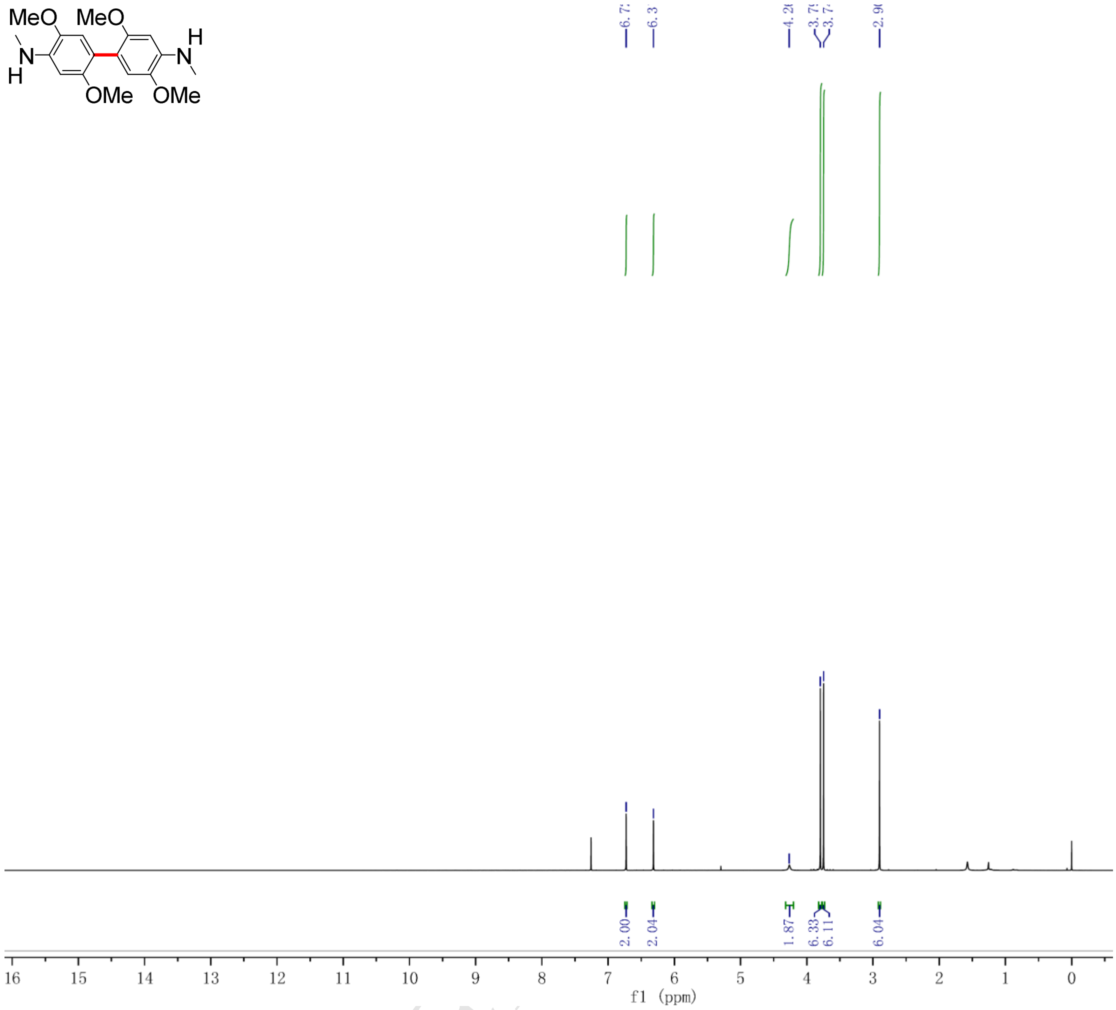


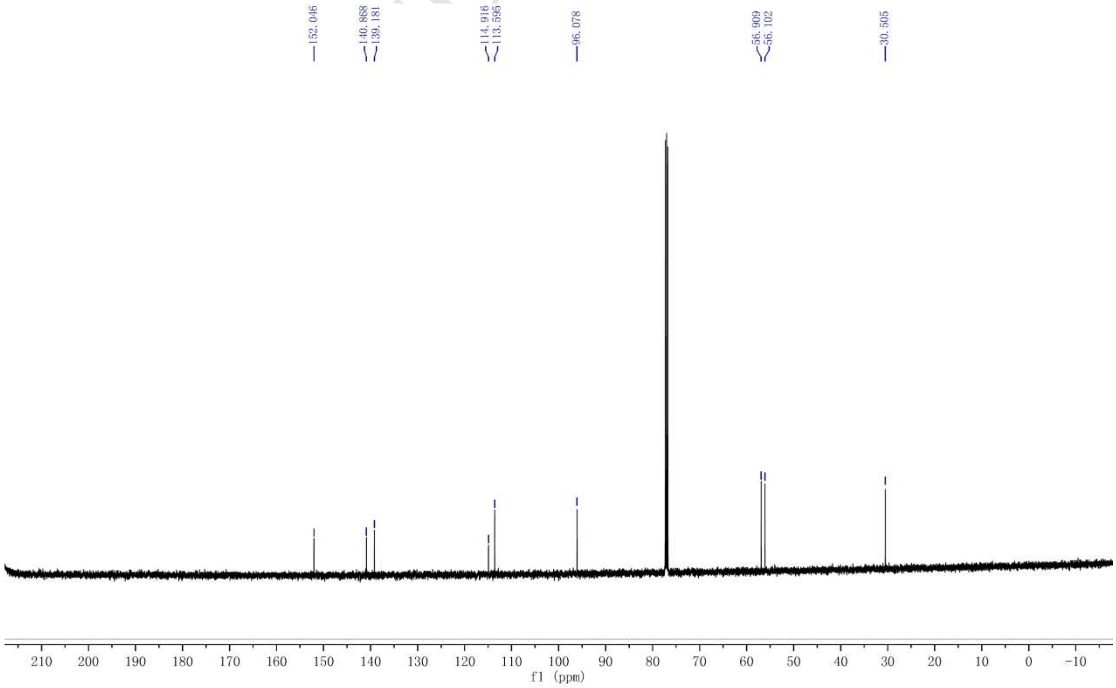
N^4,*N*^{4},*N*$^{4'}$,*N*$^{4'}$-tetramethyl-[1,1'-binaphthalene]-4,4'-diamine (2n)



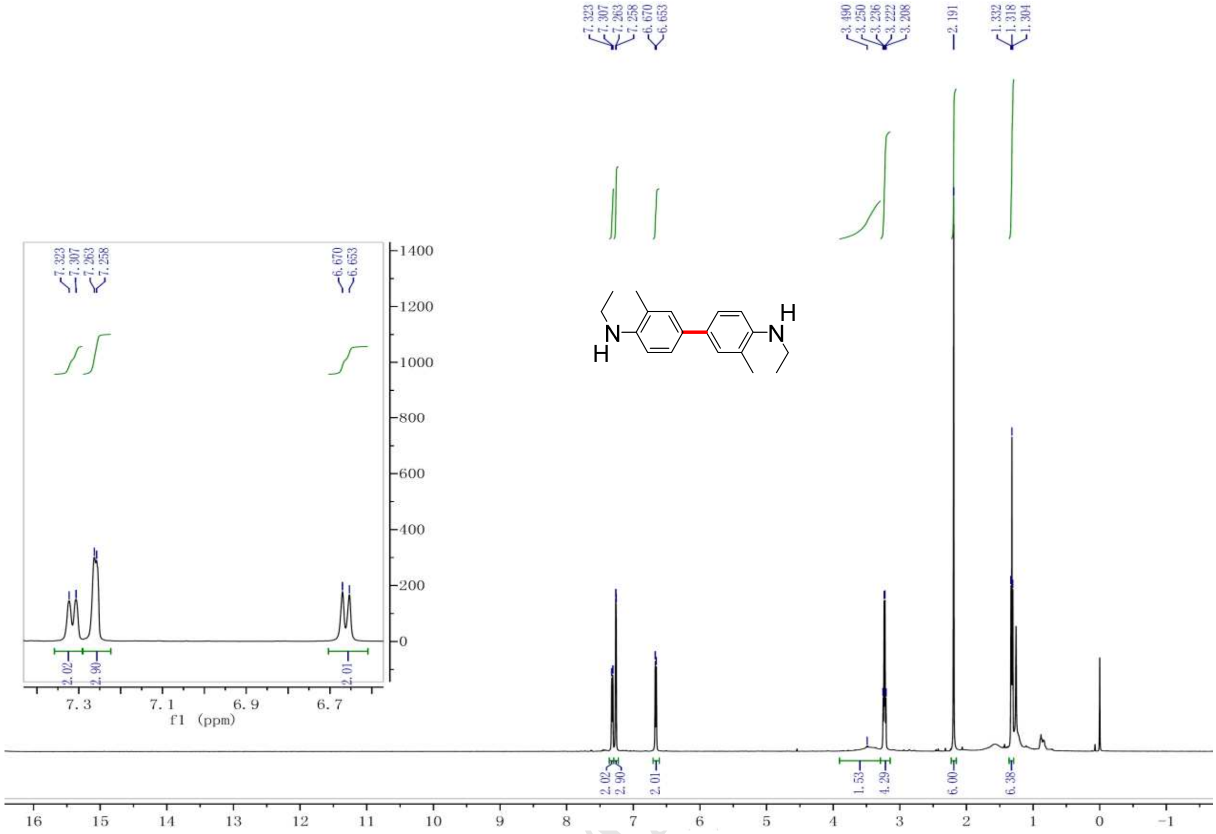


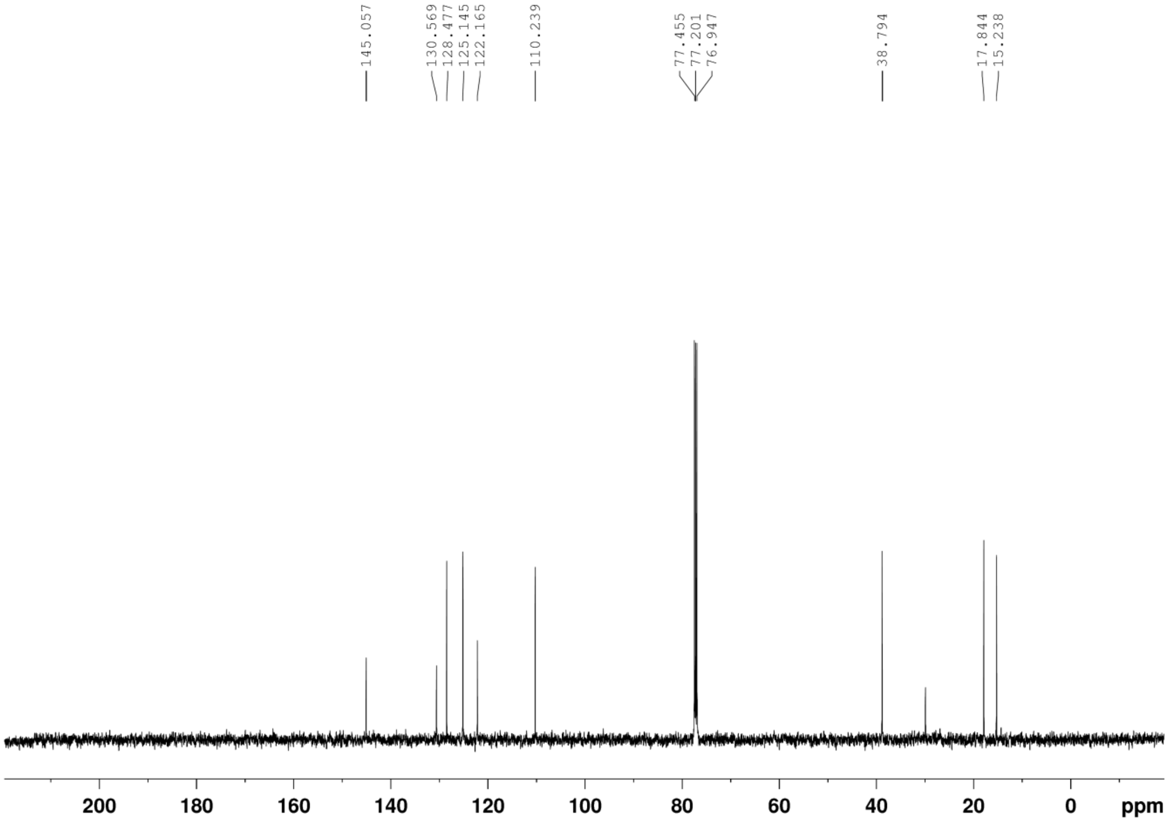
2,2',5,5'-tetramethoxy-*N*^{4},*N*$^{4'}$-dimethyl-[1,1'-biphenyl]-4,4'-diamine (2o)



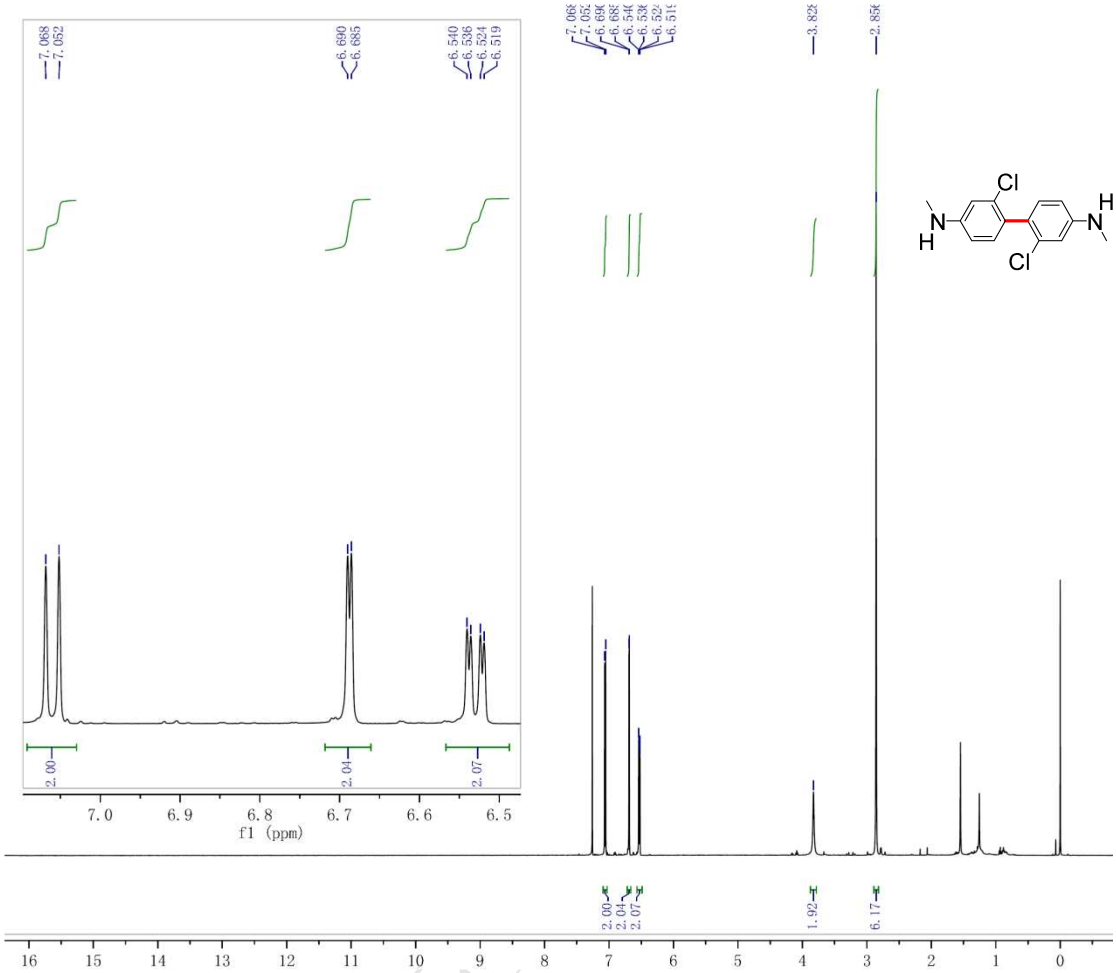


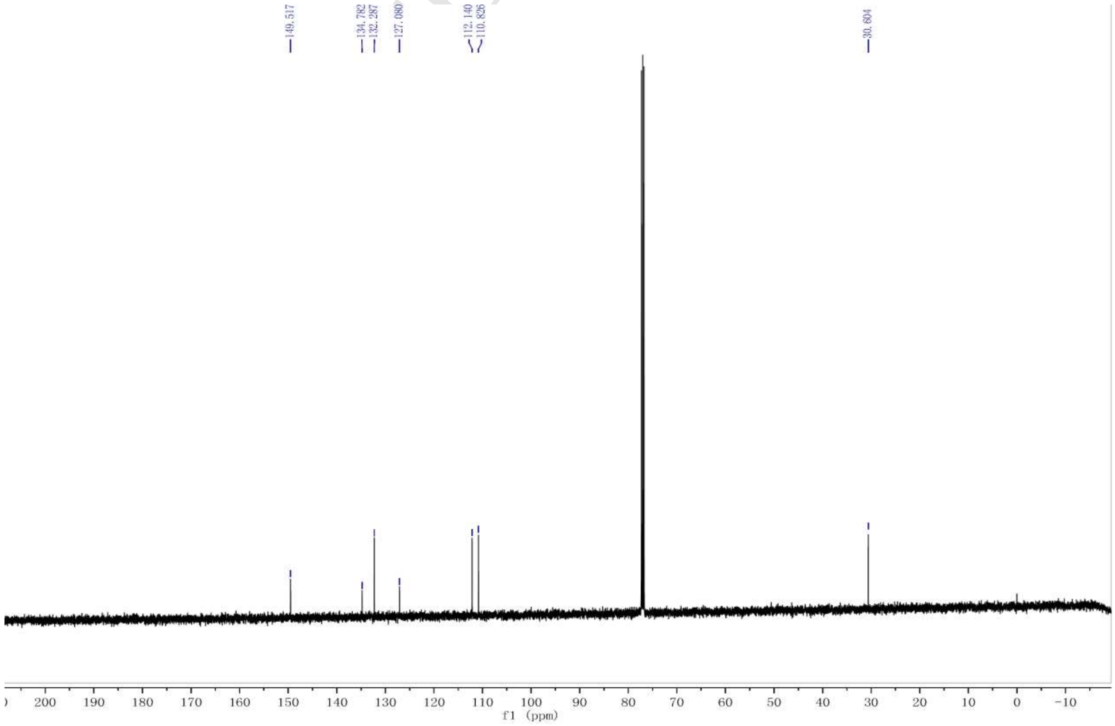
N^4,*N*$^{4'}$-diethyl-3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diamine (2p)



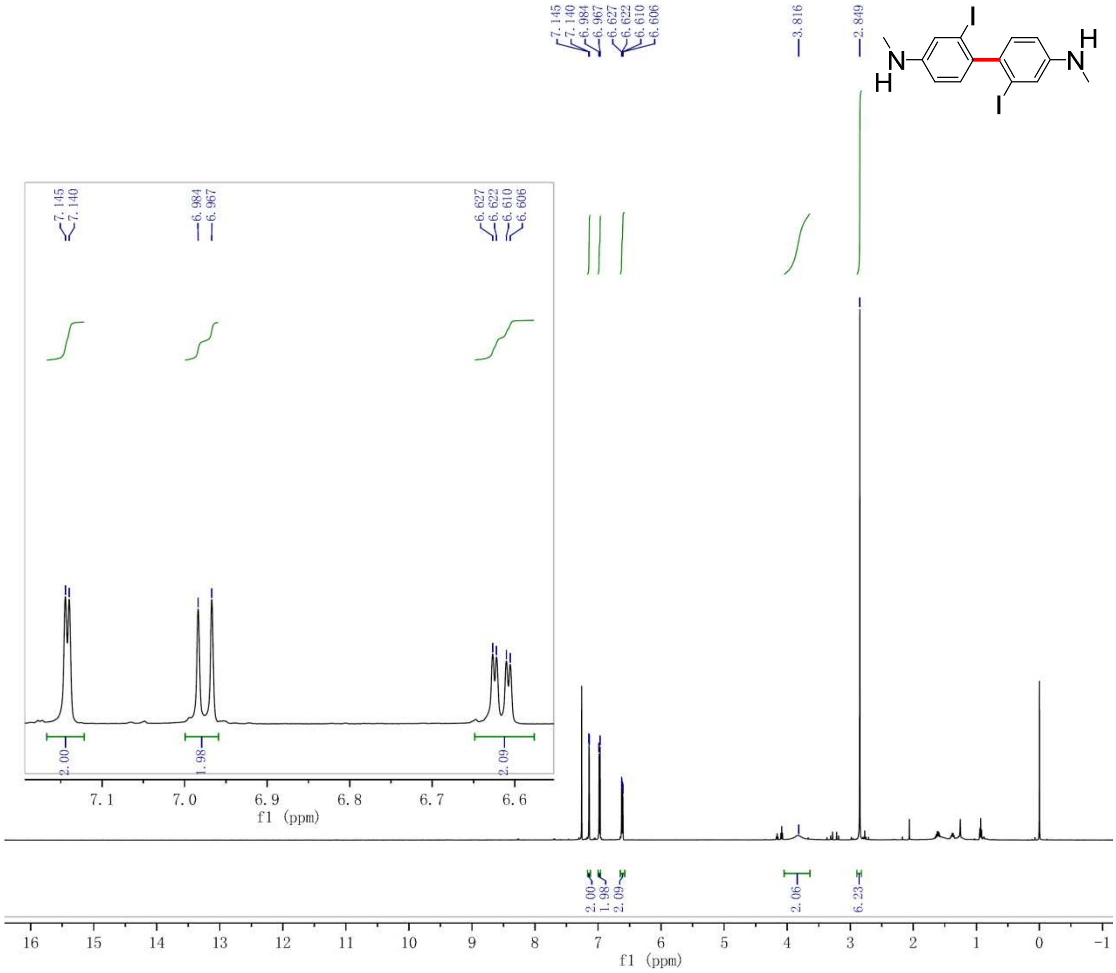


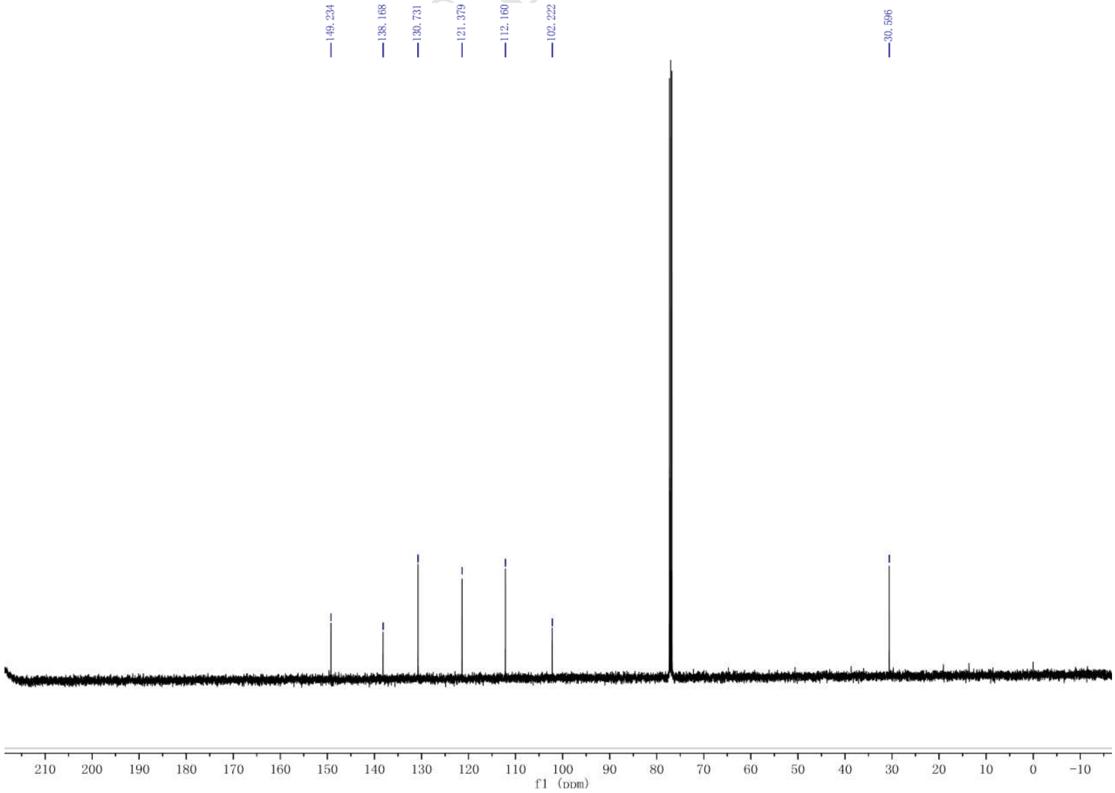
2,2'-dichloro-N^4,N^{4}'-dimethyl-[1,1'-biphenyl]-4,4'-diamine (2q)



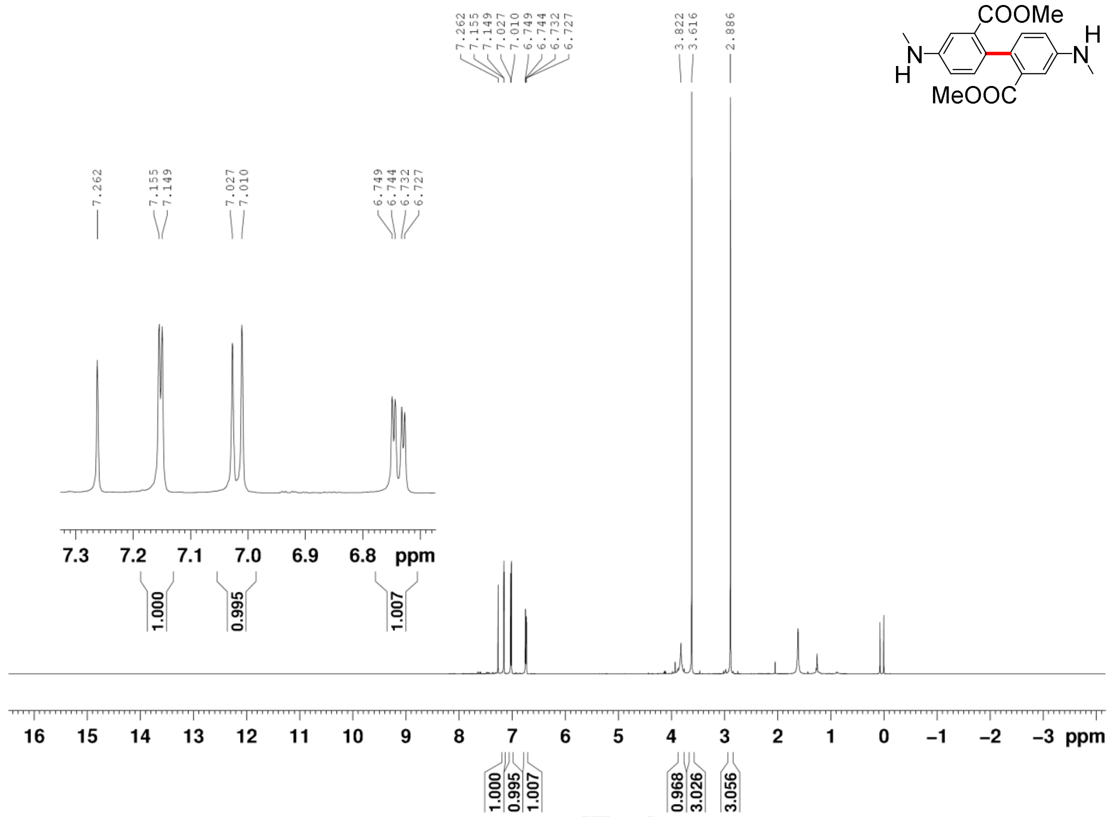


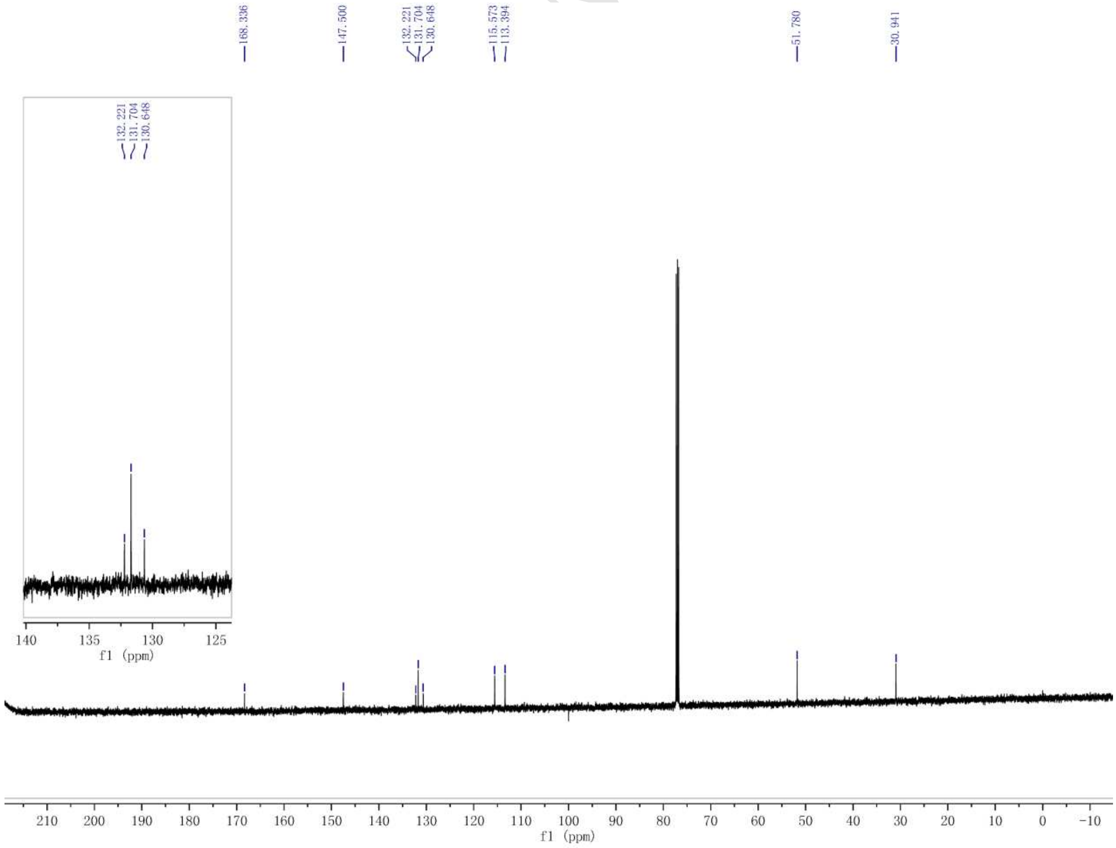
2,2'-diiodo-N^4,$N^{4'}$-dimethyl-[1,1'-biphenyl]-4,4'-diamine (2r)



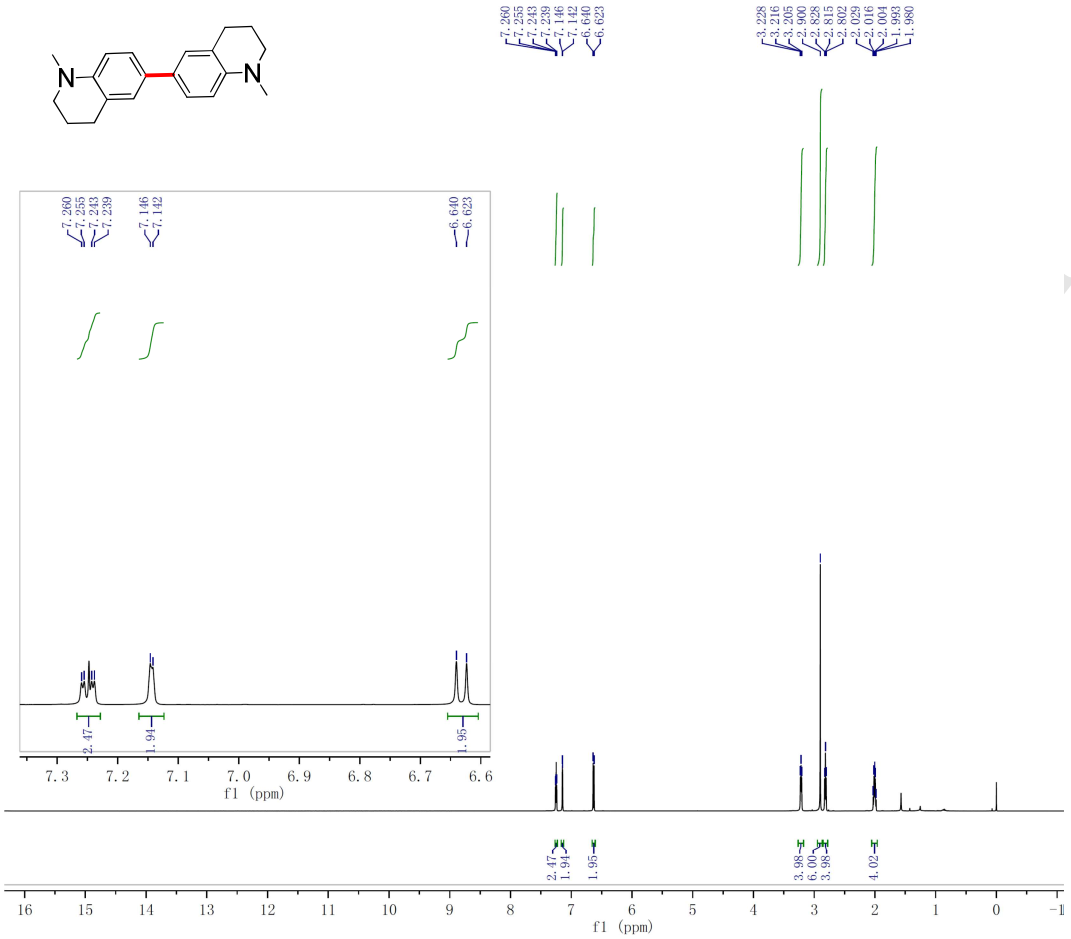


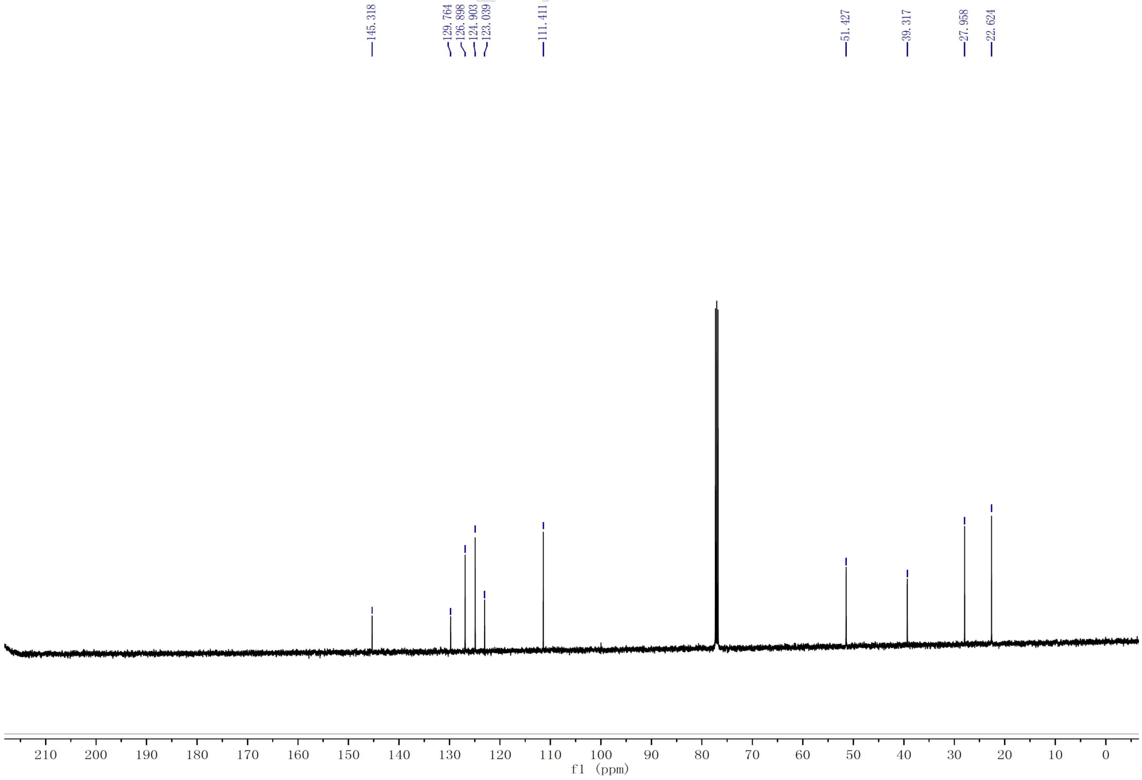
dimethyl 4,4'-bis(methylamino)-[1,1'-biphenyl]-2,2'-dicarboxylate (2s)



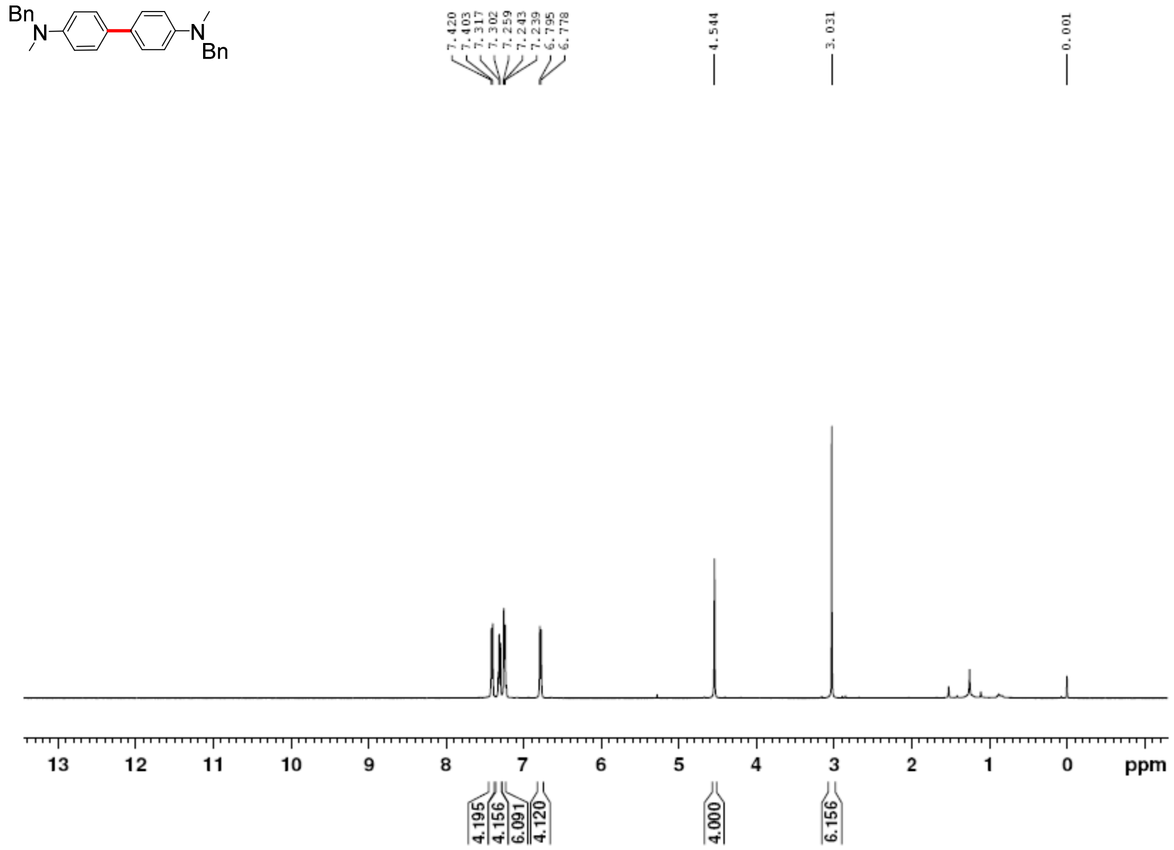


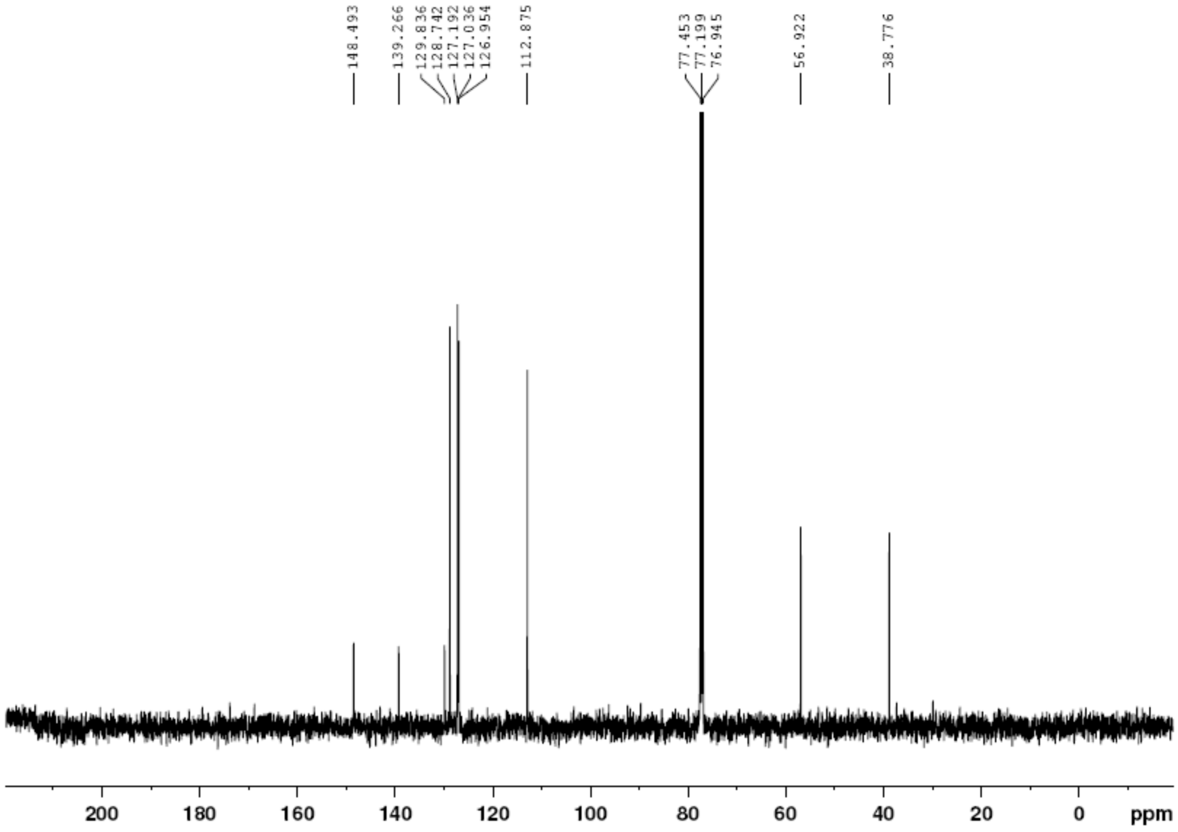
1,1'-dimethyl-1,1',2,2',3,3',4,4'-octahydro-6,6'-biquinoline (2t)



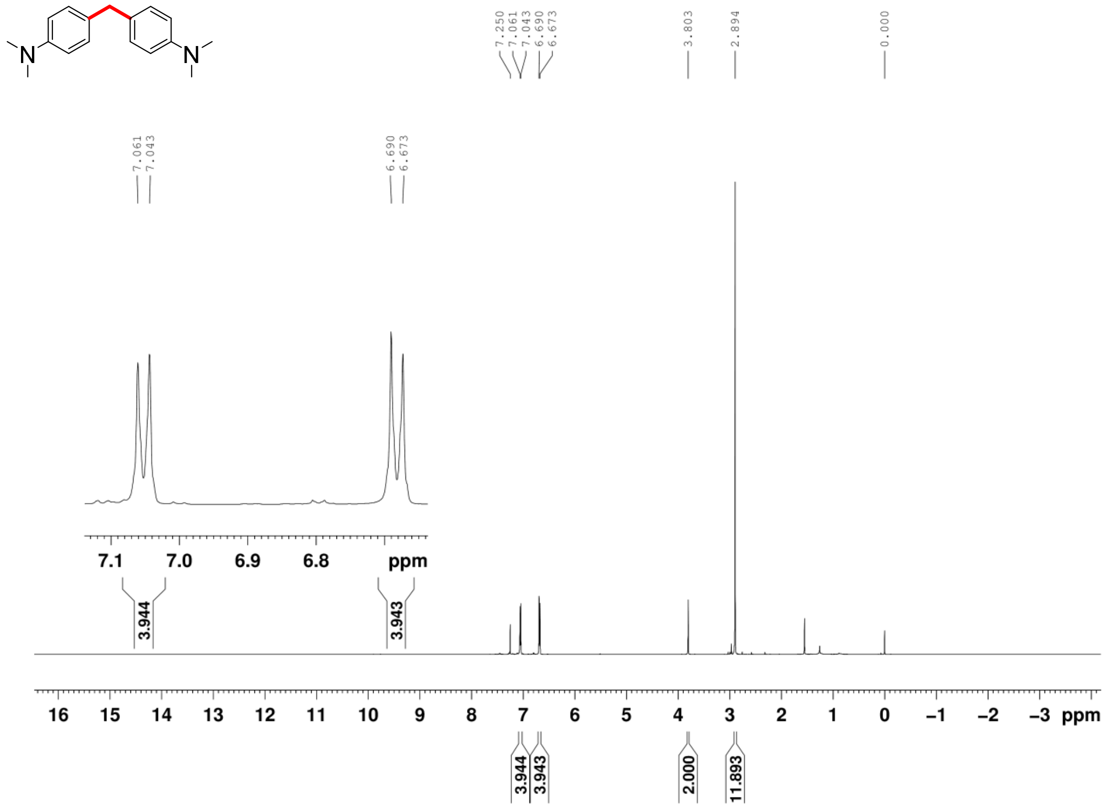


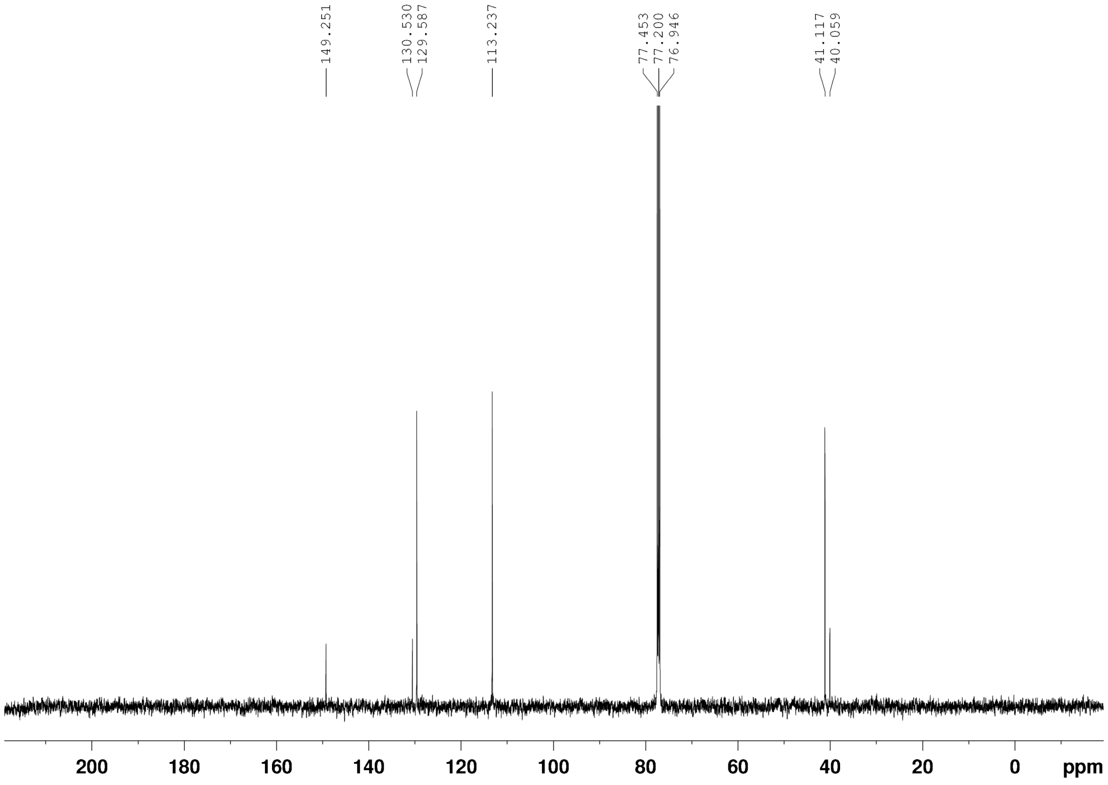
N^4,*N*$^{4'}$-dibenzyl-*N*^{4},*N*$^{4'}$-dimethyl-[1,1'-biphenyl]-4,4'-diamine (2u)



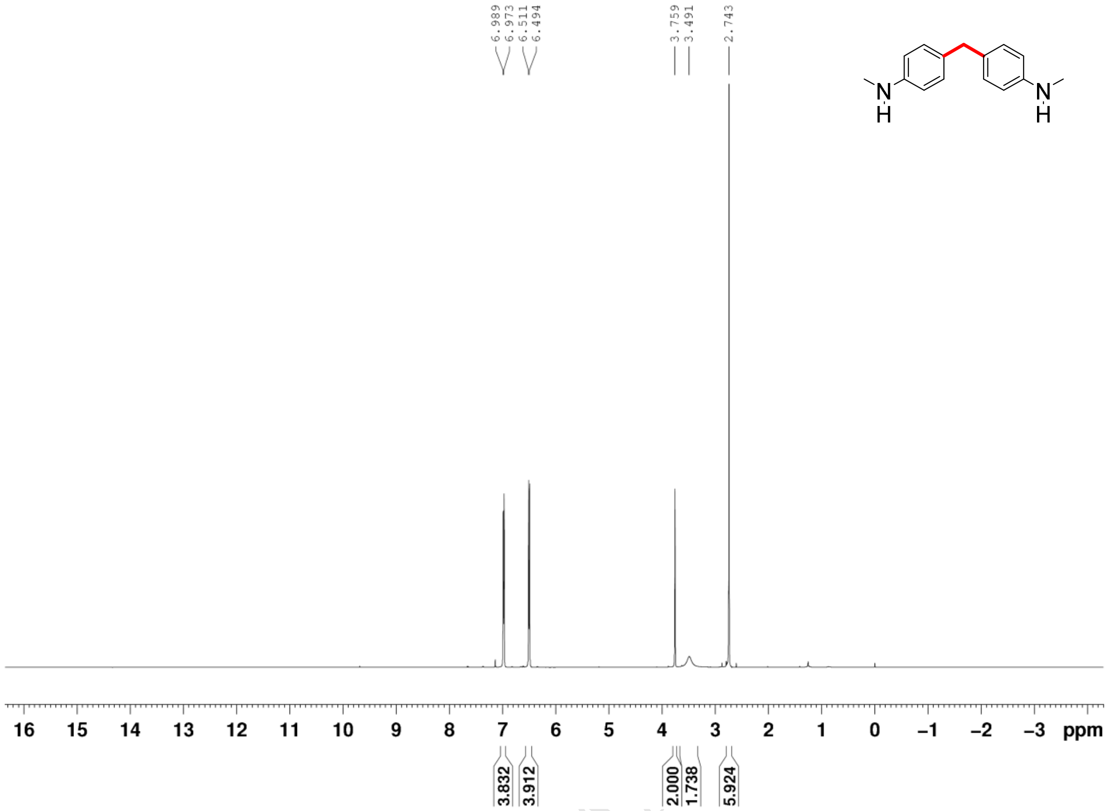


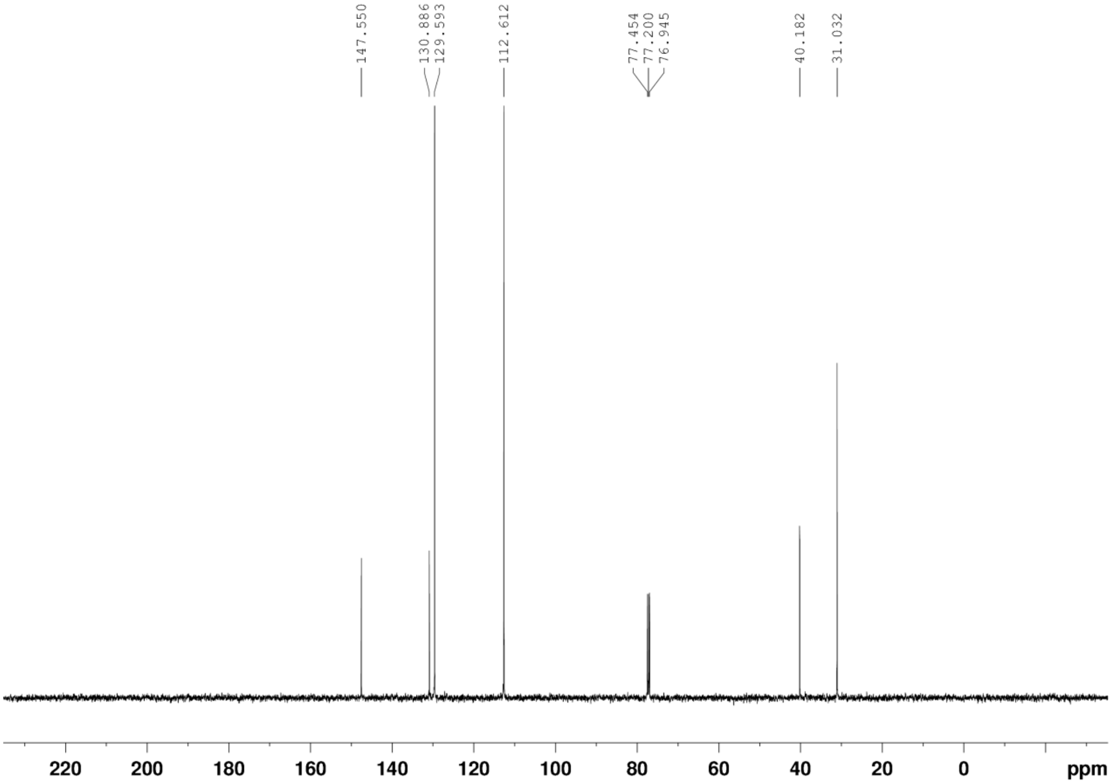
4,4'-methylenebis(*N*,*N*-dimethylaniline) (3a)



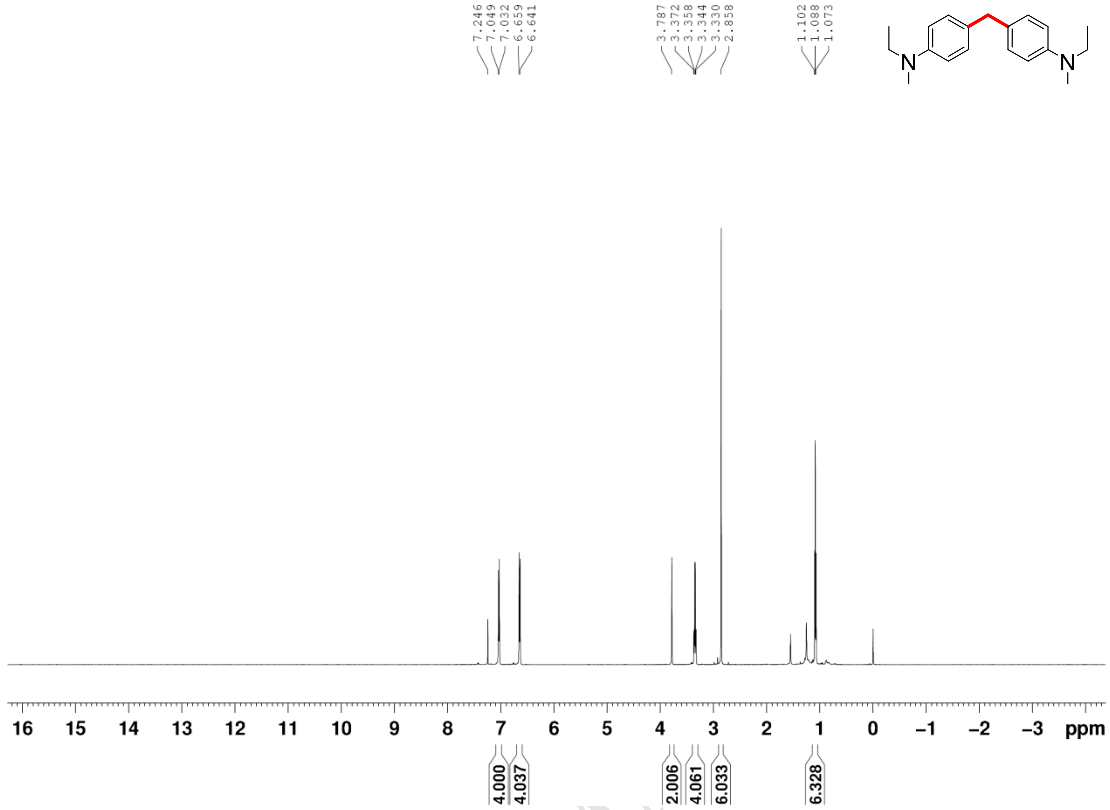


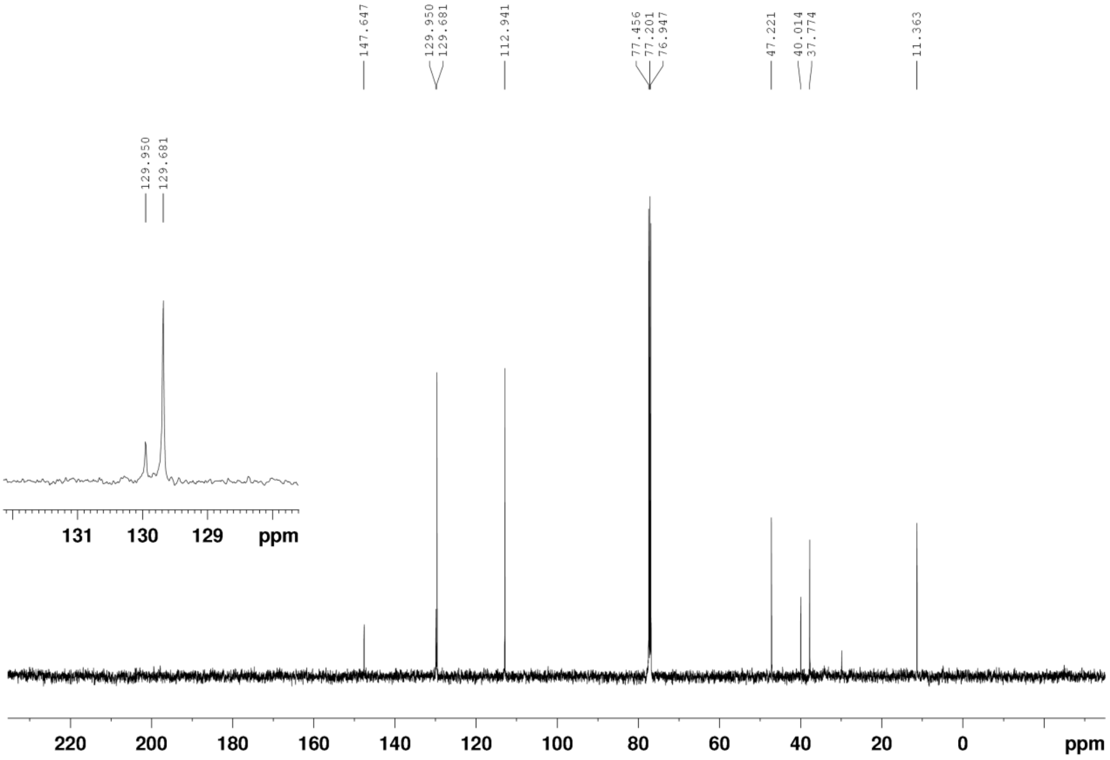
4,4'-methylenebis(*N*-methylaniline) (3b)



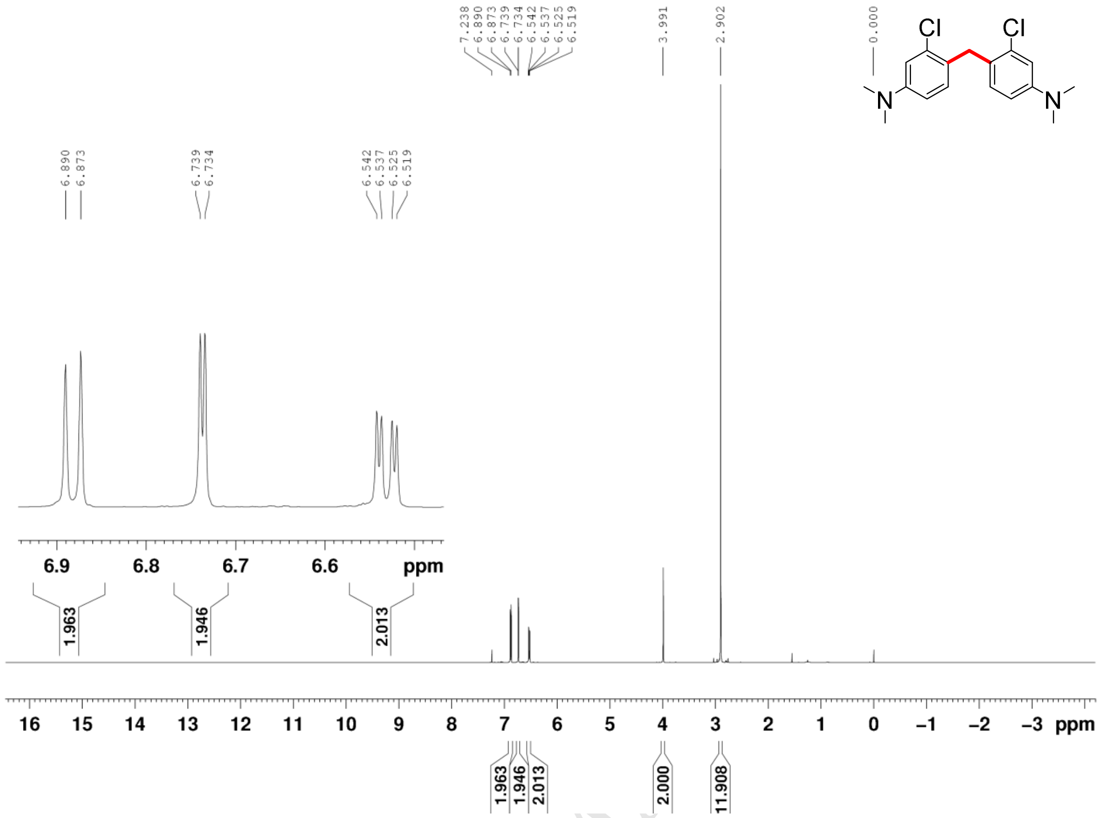


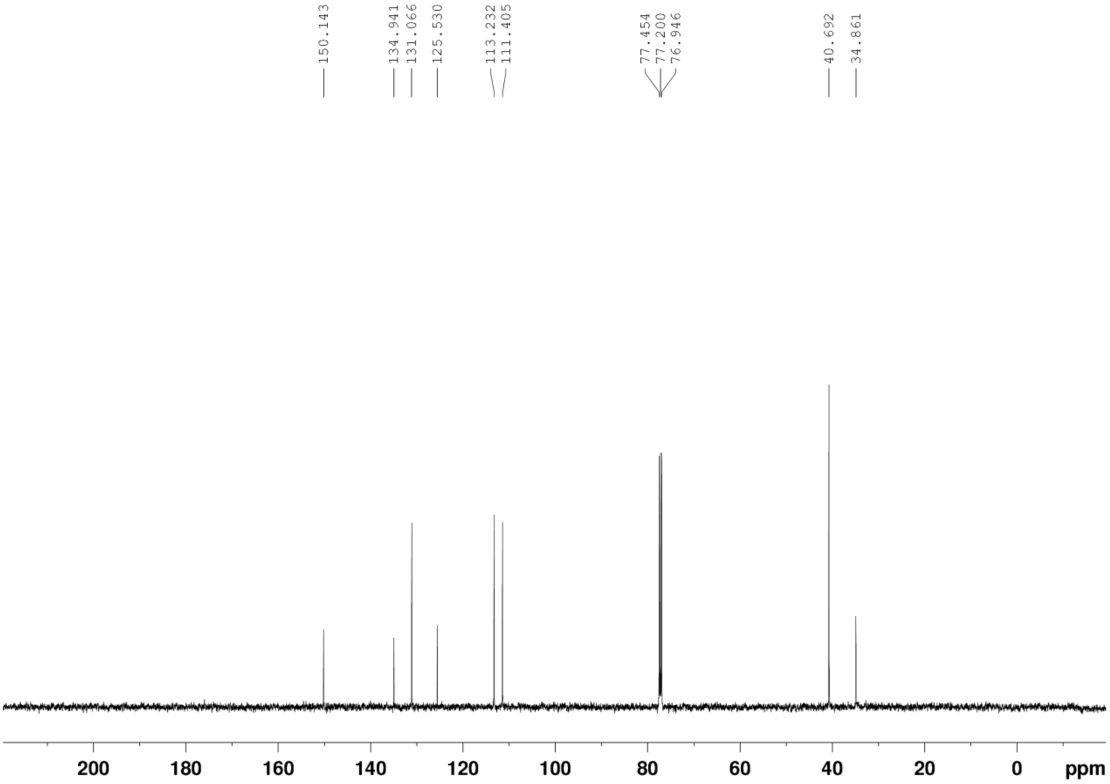
4,4'-methylenebis(*N*-ethyl-N-methylaniline) (3c)



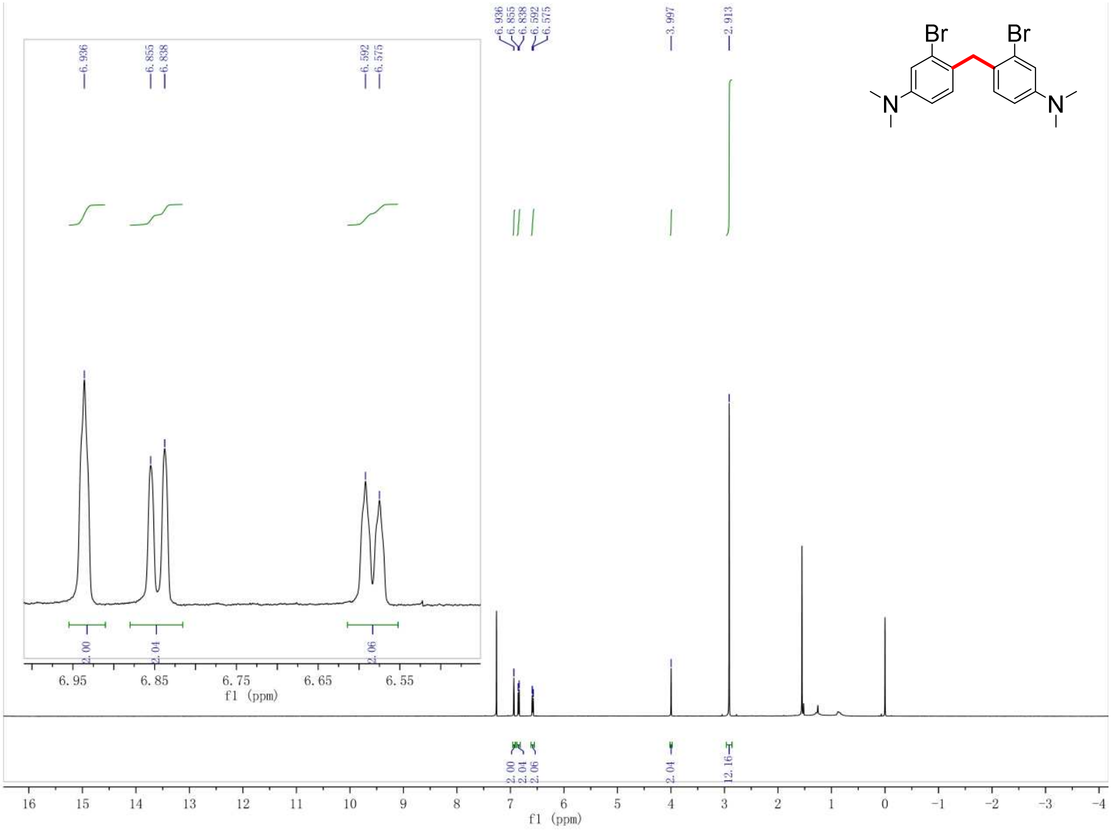


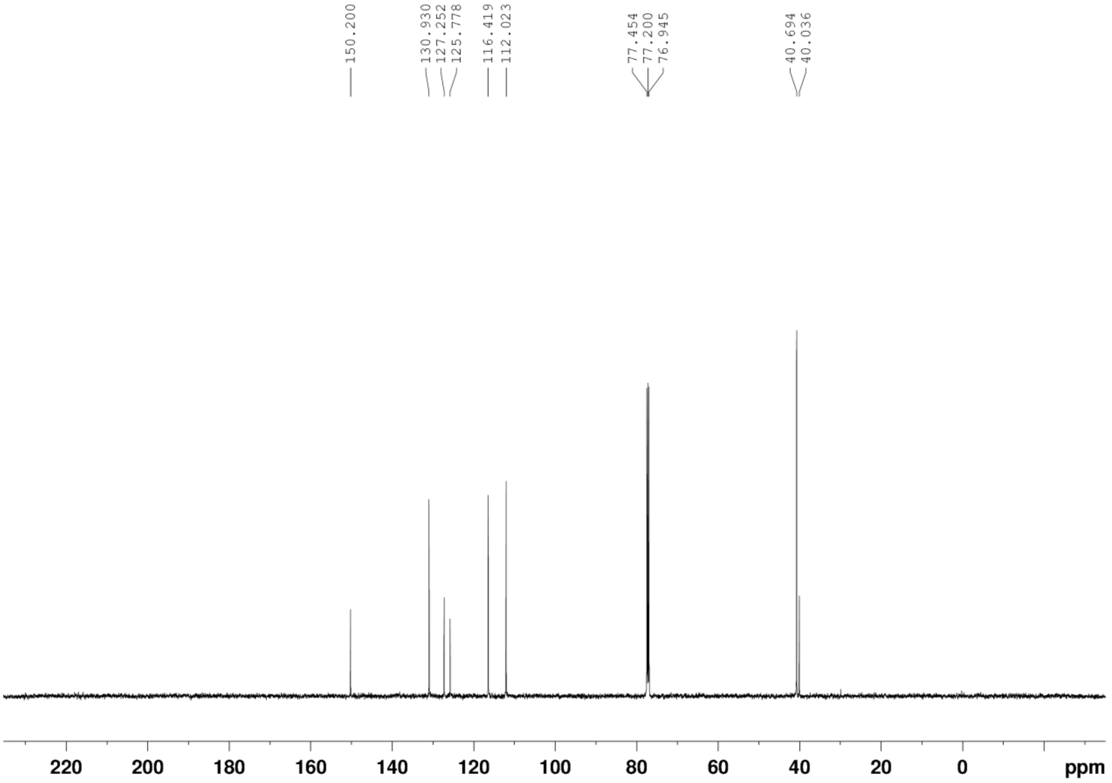
4,4'-methylenebis(3-chloro-*N*,*N*-dimethylaniline) (3d)



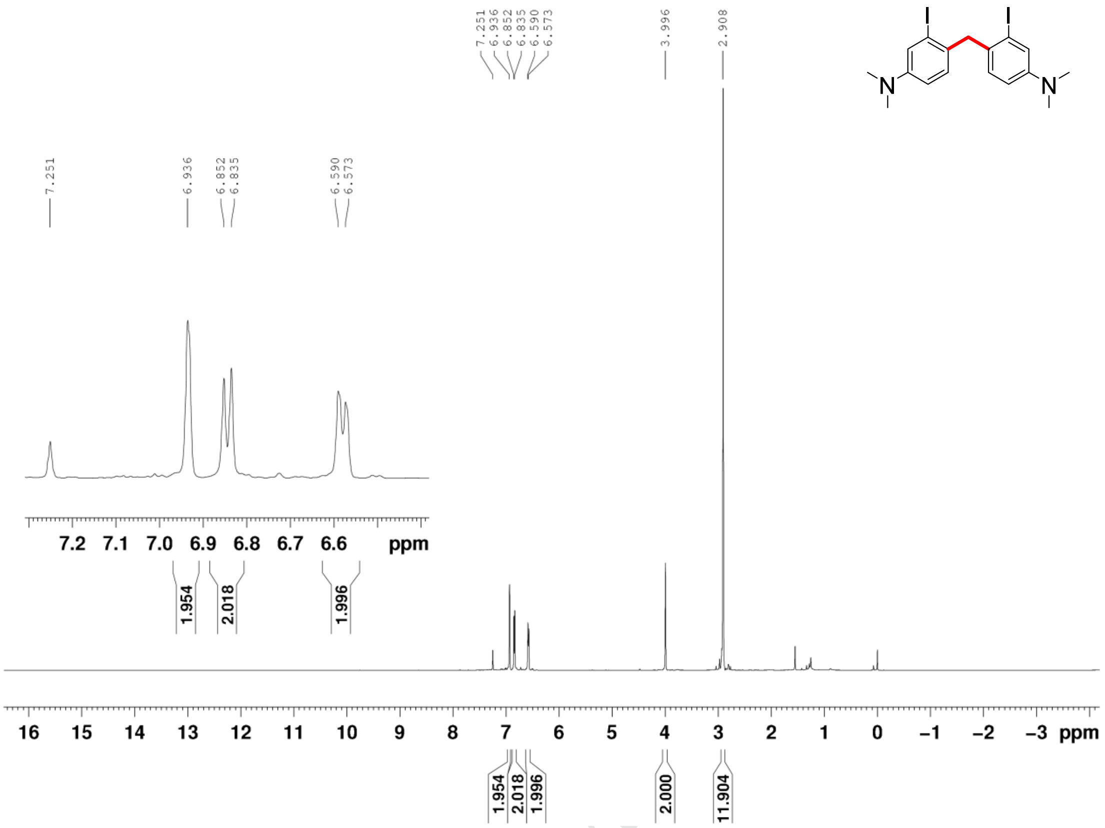


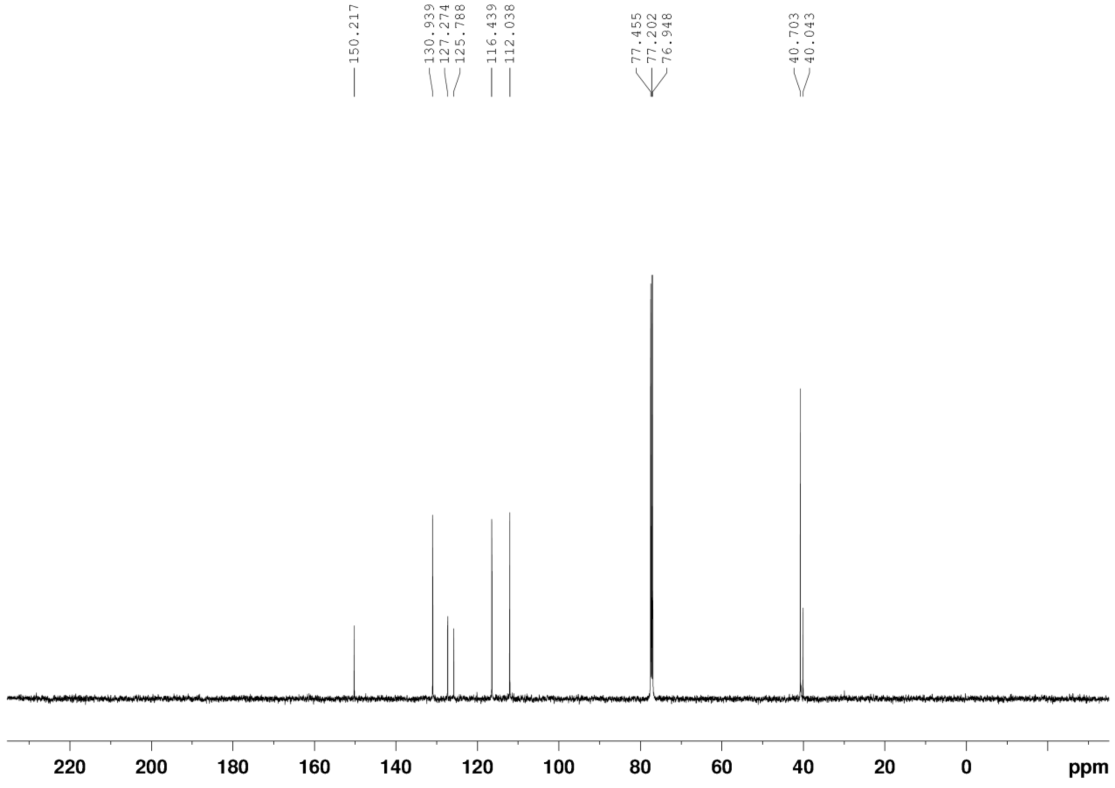
4,4'-methylenebis(3-bromo-*N*,*N*-dimethylaniline) (3e)





4,4'-methylenebis(3-iodo-*N*,*N*-dimethylaniline) (3f)





9,10-dimethyl-2,7-bisdimethaminophenanthrene (4)