Chapter 7

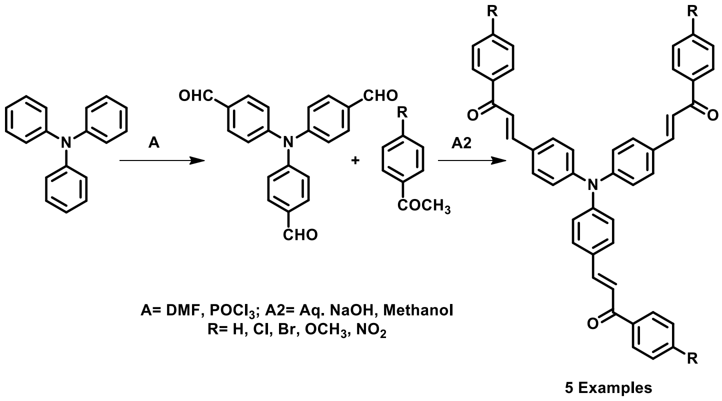
DESIGN AND SYNTHESIS OF TRIPHENYLAMINE BASED BRANCHED CHALCONES

7.1 Introduction:

Trigonal branched octupolar systems create a separate group of 2PA-active compounds. Many research groups have used the triphenylamine core to explore many phenomena including (a) NLO properties (b) electrochromic properties (c) redox properties (d) hole transport behavior for solar cells etc [1-7]. Trigonally branched chalcones with triphenylamine core were synthesized in order to explore its behavioral change when attached to cross-conjugated branch segments. The objective of this work is solely focused to investigate the up-conversion photoluminescence properties of the chalcones and its potential application.

7.2 Synthesis of branched chalcone derivatives:

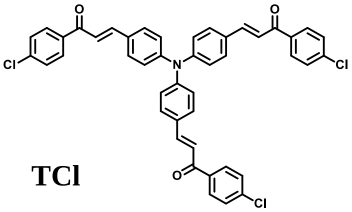
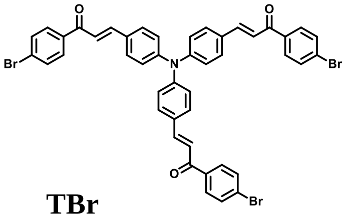
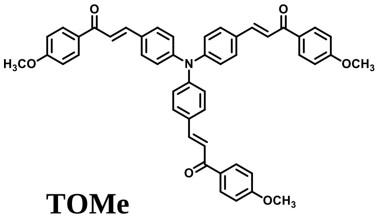
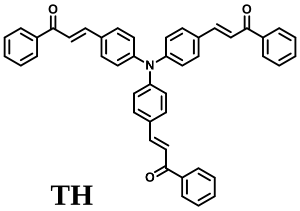
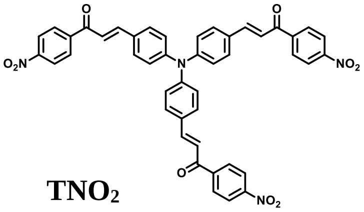
Synthesis of 4,4',4''-nitrilotribenzaldehyde was accomplished with formylation of triphenylamine by Vilsmeier Haack reaction by a known procedure [8].



Scheme 7.1: **Synthesis of branched chalcone derivative from triphenylamine.**

4,4',4''-nitrilotribenzaldehyde (1 mmol) was dissolved in warm methanol. Then, the acetophenone/ acetophenone derivative (3 mmol) was added followed by dropwise addition of a solution of NaOH (10% w/v) and methanol. The mixture was stirred for an appropriate time (mentioned in Table 7.1) with gentle reflux. The progress of the reaction was monitor by TLC using gradient of hexane and DCM as the mobile phase. After completion of the reaction mixture, it was acidified with conc. HCl. The precipitate was collected, washed with cold water, dried and purified by flash column chromatography (silica gel 230-400 mesh) with hexane and DCM as eluent to get the pure product in (80-89) % yield. The reaction approach is produced in scheme 7.1. Table 7.1 contains the reaction time and physical data of the synthesized compounds.

Table 7.1: Reaction time and physical data of the synthesized compounds.

Compound and Code	Reaction time	M.P (℃)
 **TCl**	1 h	205-207
 **TBr**	2 h	208-209
 **TOMe**	2.2 h	207-208
 **TH**	1 h	190-191
 **TNO_2**	40 min	211-212

7.3 Characterization of branched chalcone derivatives:

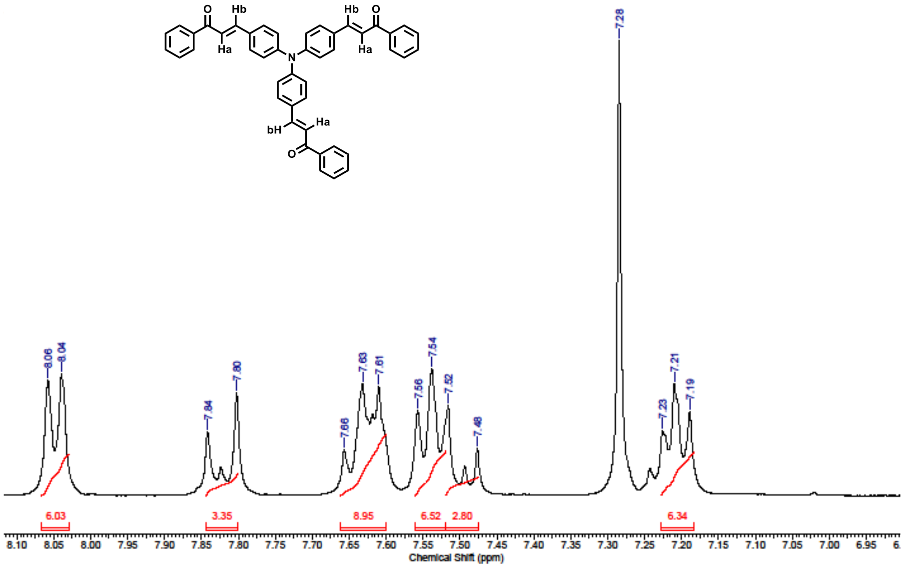


Figure7.1: ^{1}H NMR spectrum of TH [*(2E,2'E,2''E)-3,3',3''-(nitrilotris(benzene-4,1-diyl))tris(1-phenylprop-2-en-1-one)*]

Fig. 7.1 shows The ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of *(2E,2'E,2''E)-3,3',3''-(nitrilotris(benzene-4,1-diyl))tris(1-phenylprop-2-en-1-one)* (**TH**). H^a and H^b are at 7.82 and 7.50 ppm respectively, they have a high coupling constant of 16 Hz, which indicates that the double bond has a *trans*-configuration. ortho aromatic protons of the three phenyl ring attached to nitrogen have J = 8 Hz and appears as a doublet at 8.05 ppm.

The characterization data of other chalcone derivatives are presented in the following section. The spectra of other compounds in the series are available in the Section 7.8.

***(2E,2'E,2''E)-3,3',3''-(nitrilotris(benzene-4,1-diyl))tris(1-(4-chlorophenyl)prop-2-en-1-one)* (TCl): TCl** was synthesized following the procedure mentioned in Section 7.2 and Scheme 7.1 from 4,4',4''-nitrilotribenzaldehyde (329 mg) and 4-chloroacetophenone (465 mg) and the reaction time is mentioned in Table 7.1. TLC (Hexane: DCM= 4:1) Orange solid. Yield: 560 mg (80%). (^{1}H NMR**,** 400 MHz, $CDCl_3$) δ 7.99 (d, J = 8 Hz, 6H), 7.82 (d, J = 16 Hz, 3H), 7.61 (d, J = 8 Hz, 6H), 7.51 (d, J = 8 Hz, 6H), 7.44 (d, J = 16 Hz, 3H), 7.20 (d, J = 8 Hz, 6H).

(2E,2'E,2''E)-3,3',3''-(nitrilotris(benzene-4,1-diyl))tris(1-(4-bromophenyl)prop-2-en-1-one) **(TBr): TBr** was synthesized following the procedure mentioned in Section 7.2 and Scheme 7.1 from 4,4',4"-nitrilotribenzaldehyde (329 mg) and 4-bromoacetophenone (597 mg) and the reaction time is mentioned in Table 7.1. TLC (Hexane: DCM= 4: 1). Orange solid. Yield: 741 mg (85%). (^{1}H NMR**,** 400 MHz, $CDCl_3$) δ 7.91 (d, J = 8 Hz, 6H), 7.82 (d, J = 16 Hz, 3H), 7.68 (d, J = 8 Hz, 6H), 7.61 (d, J = 8 Hz, 6H), 7.43 (d, J = 16 Hz, 3H), 7.20 (d, J = 8 Hz, 6H).

(2E,2'E,2''E)-3,3',3''-(nitrilotris(benzene-4,1-diyl))tris(1-(4-methoxyphenyl)prop-2-en-1-one) **(TOMe): TOMe** was synthesized following the procedure mentioned in Section 7.2 and Scheme 7.1 from 4,4',4"-nitrilotribenzaldehyde (329 mg) and 4-methoxyacetophenone (450 mg) and the reaction time is mentioned in Table 7.1. TLC (Hexane: DCM= 1:1). Orange solid. Yield: 600 mg (83%). (^{1}H NMR**,** 400 MHz, $CDCl_3$) δ 8.07 (d, J = 8 Hz, 6H), 7.81 (d, J = 16 Hz, 3H), 7.61 (d, J = 8 Hz, 6H), 7.51 (d, J = 16 Hz, 3H), 7.19 (d, J = 8 Hz, 6H), 7.01 (d, J = 8 Hz, 6H), 3.92 (s, 9H).

(2Z,2'Z,2''Z)-3,3',3''-(nitrilotris(benzene-4,1-diyl))tris(1-(4-nitrophenyl)prop-2-en-1-one) **(TNO_2): TNO_2** was synthesized following the procedure mentioned in Section 7.2 and Scheme 7.1 from 4,4',4"-nitrilotribenzaldehyde (329 mg) and 4-nitroacetophenone (495 mg) and the reaction time is mentioned in Table 7.1. TLC (Hexane: DCM= 1:1). Orange solid. Yield: 685 mg (89%). (^{1}H NMR**,** 400 MHz, $CDCl_3$) δ 8.45 (d, J = 8 Hz, 6H), 8.09-8.06 (m, 8H), 7.74 (d, J = 8 Hz, 6H), 7.61-7.55 (m, 7H), 7.34 (d, J = 12 Hz, 3H)

(2E,2'E,2''E)-3,3',3''-(nitrilotris(benzene-4,1-diyl))tris(1-phenylprop-2-en-1-one) **(TH): TH** was synthesized following the procedure mentioned in Section 7.2 and Scheme 7.1 from 4,4',4"-nitrilotribenzaldehyde (329 mg) and acetophenone (360 mg) and the reaction time is mentioned in Table 7.1. TLC (Hexane: DCM= 4: 1). Orange solid. Yield: 551 mg (87%). (^{1}H NMR**,** 400 MHz,

$CDCl_3$) δ 8.05 (d, J = 8 Hz, 6H), 7.82 (d, J = 16 Hz, 3H), 7.66-7.61 (m, 9H), 7.54 (t, J = 8 Hz, 6H), 7.50 (d, J = 16 Hz, 3H), 7.20 (d, J = 8 Hz, 6H).

7.4 Linear Optical Properties of branched chalcone derivatives:

The absorption spectra of **TH, TCl, TBr, TOMe** and **TNO_2** were recorded in chloroform with 0.2×10^{-8} M concentration. Figure 7.2 shows the absorption spectra and Table 7.2 contains the absorption maxima values of the compounds.

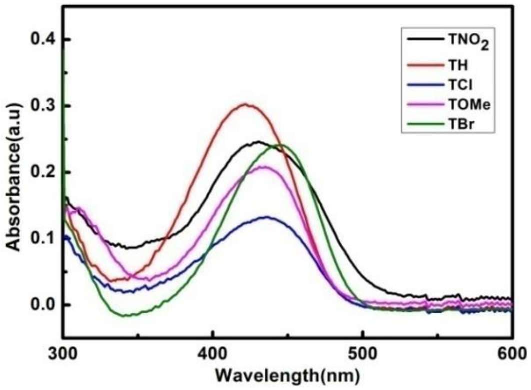


Figure 7.2: Absorption spectra of TH, TCl, TBr, TOMe and TNO_2.

Table 7.2: Absorption maxima of TH, TCl, TBr, TOMe & TNO_2.

Compound	λ_{abs} (nm)
TH	422
TCl	437
TBr	445
TOMe	434
TNO_2	430

The branched chalcones with triphenylamine core were substituted in ring A with donor and acceptor groups to create a push-pull system. The absorption in the range 422-445 nm is due to the $n - \pi^*$ transition, as the carbonyl group is present in the molecules. **TH** has unsubstituted ring A while **TBr** has –Br substitution; Fig. 7.2 illustrates that the maximal peak is bathochromically shifted from 422 nm **(TH)**, to 445 nm **(TBr)** and, to 437 nm **(TCl)** nm and their absorption coefficients also increases significantly owing to the increased π-conjugated length. The compounds are highly transparent in the near infrared range (800 nm).

7.5 Nonlinear optical properties of branched chalcone derivatives:

Up-conversion photoluminescence studies on the trigonally branched chalcone derivatives were carried out with 2.6 × 10^{-3}M solution in chloroform at near IR wavelength of 990 nm. The spectra are presented in Fig. 7.3-7.6. Interestingly, among the five chalcones all of them, except the nitro derivative (**TNO_2**), exhibited UCPL and emitted green light in the visible range. **TBr** has emission at 549 nm, **TCl** at 554 nm, **TH** at 552 nm and **TOMe** 546 nm wavelength. So, with branching chalcone moiety with triphenylamine as a core can be accepted as an effective 2PA chromophore for further application.

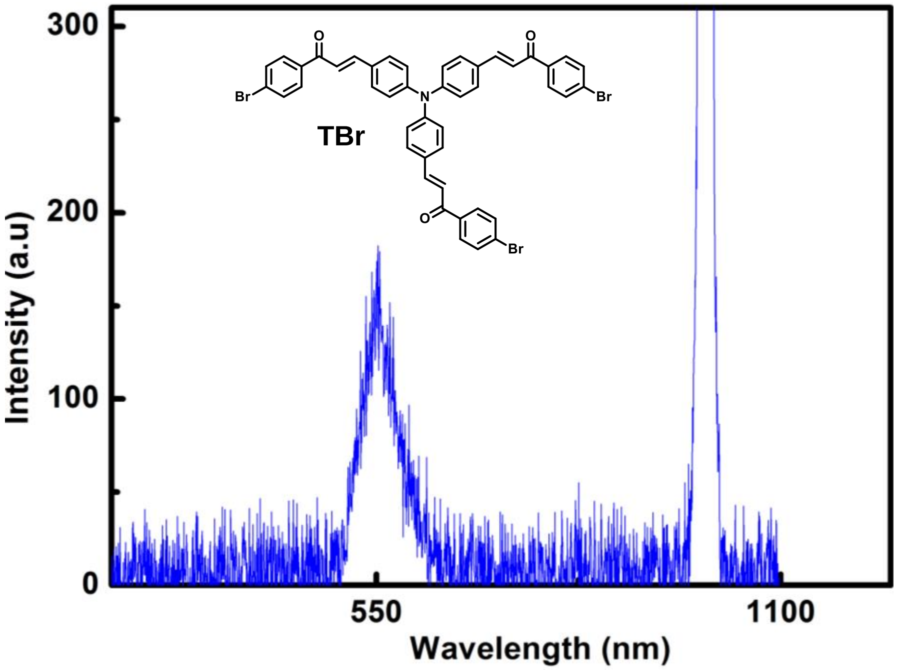


Figure 7.3: UCPL spectrum of TBr when excited at 990 nm.

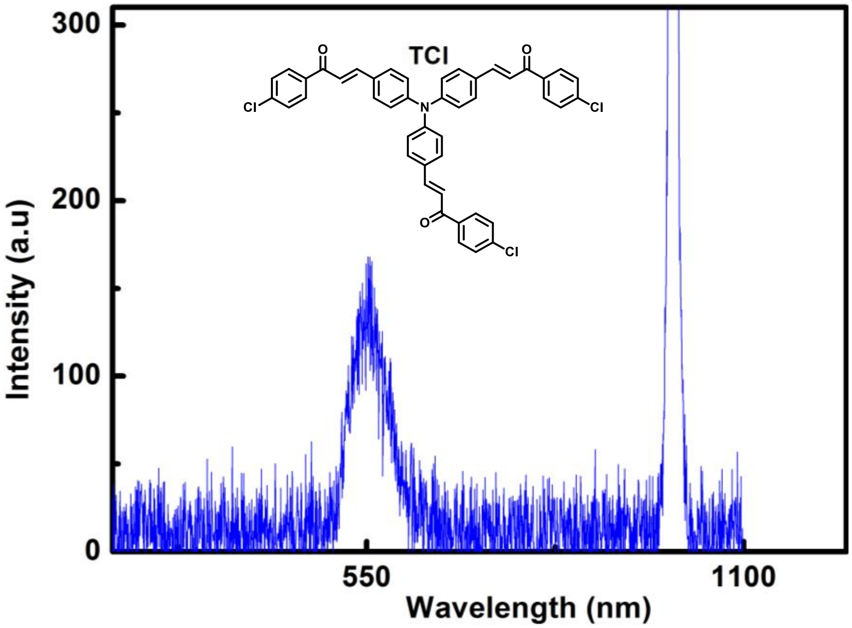


Figure7.4: UCPL spectrum of TCl when excited at 990 nm.

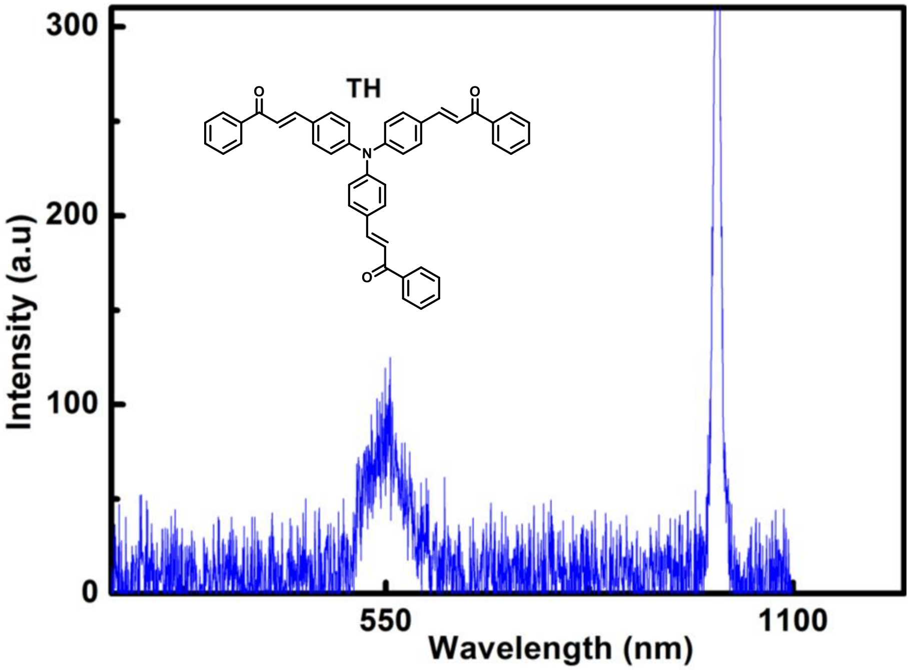


Figure 7.5: UCPL spectrum of TH when excited at 990 nm.

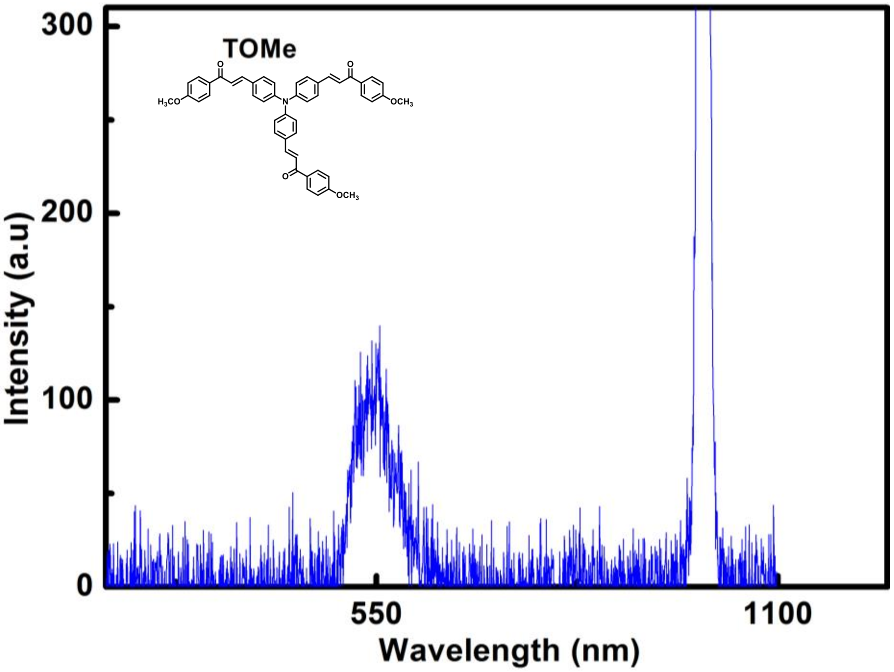


Figure 7.6: UCPL spectrum of TOMe when excited at 990 nm.

7.6 Conclusion:

Efficient two-photon chromophores have molecular structures either $D - \pi - A - \pi - D$ type i.e., symmetrically end capped or $D - \pi - A - \pi - A$ type i.e., asymmetrically substituted terminating groups [9-14]. The synthesis of five new chalcones, where asymmetrically substituted three chromophore units have been linked through a common amino group, was accomplished. This additional group in the middle changes the charge redistribution, which is the key to improve nonlinear optical properties. Moreover, the method used for the synthesis was green with high yielding products.

The potential applications of UCPL in the near IR region cover photovoltaic energy conversion [15-21] photoluminescence bioimaging [20, 22-25] displays [26], lasers [27] and optical refrigeration of solids [18] etc. But in the near-infrared optical range, limitations in material's stability, the symphony between range and compatibility of available excitation and emission photon energies for photon up-conversion have decreased the array of applications. Further studies with these chalcones are ongoing to look at the scope for well-suited industrial and daily life applications.

7.7 References:

1. Zeng, S.; Ouyang, X.; Zeng, H.; Ji, W.; Ge, Z. *Dyes and Pigments*. **2012**. *94*. 290.

2. Jin, H.; Li, X.; Tan, T.; Wang, S.; Xiao, Y.; Tian, J. *Dyes and Pigments*. **2014**. *106*. 154.

3. Beaupre´, S.; Dumas, J.; Leclerc, M.; *Chem. Mater.* **2006.** *18.* 4011.

4. Wu, X.; Davis, A.P.; Lambert, P.C.; Kraig Steffen, L.; Toy, O.; Fry, A.J. *Tetrahedron*. **2009.** *65*. 2408.

5. Xu, Q.; Chen, H.Z.; Wang, M. *Materials Chemistry and Physics*. **2004**. *87.* 446.

6. Liang, M.; Xu, W.; Cai, F.; Chen, P.; Peng, B.; Chen, J.; Li, Z. *J. Phys. Chem. C.* **2007**. *111*. 4465.

7. Xue, L.; He, J.; Gu, X.; Yang, Z.; Xu, B.; Tian, W. *J. Phys. Chem. C.* **2009**. *113*. 12911.

8. Lai, G.; Bu, X.R.; Santos, J.; Mintz, E.A. *SYNLETT*. **1997**. 1275

9. He, G.S.; Bhawalkar, J.D.; Zhao, C.F.; Prasad, P.N. *Appl. Phys. Lett.* **1995**. *67.* 2433.

10. He, G.S.; Yuan, L.; Cheng, N.; Bhawalkar, J.D.; Prasad, P.N.; Brott, L.L.; Clarson, S.J.; Reinhardt, B.A. *J. Opt. Soc. Am. B* **1997**. *B14*. 1079.

11. Reinhardt, B.A.; Brott, L.L.; Clarson, S.J.; Dillard, A.G.; Bhatt, J.C.; Kannan, R.; Yuan, L.; He, G.S.; Prasad, P.N. *Chem. Mater*. **1998**. *10.* 1863.

12. Ehrlich, J.B.; Wu, X.L.; Lee, I.Y.S.; Hu, Z.Y.; Rockel, H.; Marder, S.R.; Perry, J. W. *Opt. Lett.* **1997**. *22 (24)*. 1843.

13. Albota, M.; Beljonne, D.; Bredas, J.L.; Ehrlich, J.E.; Fu, J.Y.; Heikal, A.A.; Hess, S.E.; Kogej, T.; Levin, M.D.; Marder, S.R.; McCord-Maughan, D.; Perry, J.W.; Rockel, H.; Rumi, M.; Subramaniam, G.; Webb, W.W.; Wu, X.L.; Xu, C. *Science.* **1998**. *281.* 1653.

14. Bhawalkar, J.D.; He, G.S.; Prasad, P.N. *Rep. Prog. Phys*. **1996**. *59*. 1041.

15. Baluschev, S. *Phys. Rev. Lett.* **2006**. *97*, 143903.

16. Zhao, J.; Ji, S.; Guo, H. *RSC Adv. 1*. **2011**. 937.

17. Joly, A.G.; Chen, W.; McCready, D.E.; Malm, J.O.; Bovin, J.O. *Phys. Rev. B.* **2005**. *71*. 165304.

18. Sheik-Bahae, M.; Epstein, R.I. *Nat. Photon. 1*. **2007**. 693.

19. Rakovich, Y.P.; Donegan, J.F. in *Semiconductor Nanocrystal Quantum Dots* Ch. 9 (ed. Andrey, L. Rogach). (Springer Vienna, **2008**). pp 257−275.

20. Wang, F. *Nat. Mater.* **2011**. *10*. 968.

21. Gray, V.; Dzebo, D.; Abrahamsson, M.; Albinsson, B.; Moth-Poulsen, K. *Phys. Chem. Chem. Phys.* **2014**. *16*. 10345.

22. Xu, C.T. *Appl. Phys. Lett.* **2008**. *93*. 171103.

23. Vinegoni, C. *Opt. Lett.* **2009**. *34*. 2566.

24. Kotov, N. *Nat. Mater.* **2011**. *10*. 903.

25. Dou, Q.Q.; Guo, H.C.; Ye, E. *Mater. Sci. Eng. C Mater. Biol. Appl.* **2014**. *45*. 635.

26. Downing, E.; Hesselink, L.; Ralston, J.; Macfarlane, R.A. *Science.* **1996**. *273*. 1185.

27. He, G.S.; Markowicz, P.P.; Lin, T.C.; Prasad, P.N. *Nature.* **2002**. *415*. 767.

7.8 Spectral data of branched chalcone derivatives:

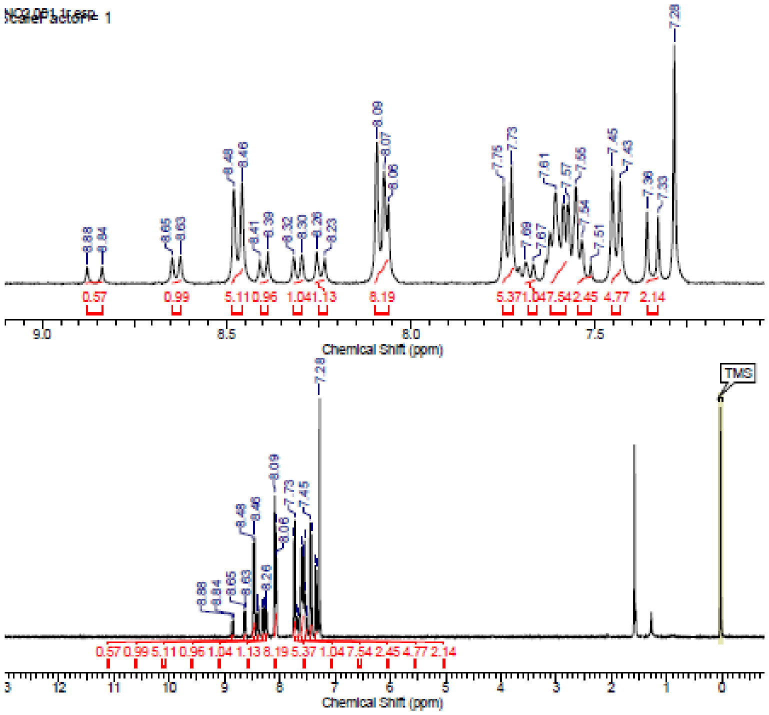


Figure 7.7: ^{1}H NMR spectrum of *(2Z,2'Z,2''Z)-3,3',3''-(nitrilotris(benzene-4,1-diyl))tris(1-(4-nitrophenyl)prop-2-en-1-one)* (**TNO$_2$**).

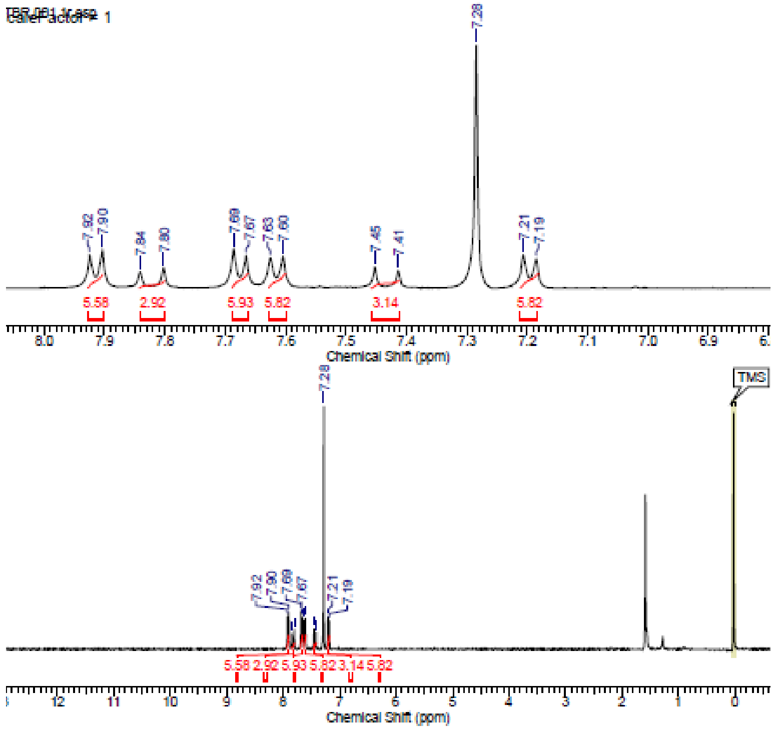


Figure 7.8: ^{1}H NMR spectrum of *(2E,2'E,2''E)-3,3',3''-(nitrilotris(benzene-4,1-diyl))tris(1-(4-bromophenyl)prop-2-en-1-one)* (**TBr**).

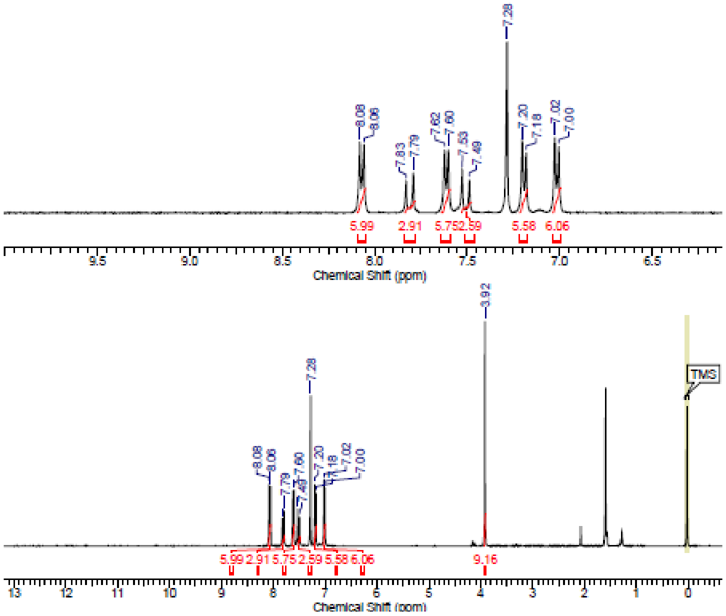


Figure 7.9: ^{1}H NMR spectrum of *(2E,2'E,2''E)-3,3',3''-(nitrilotris(benzene-4,1-diyl))tris(1-(4-methoxyphenyl)prop-2-en-1-one)* (**TOMe**).

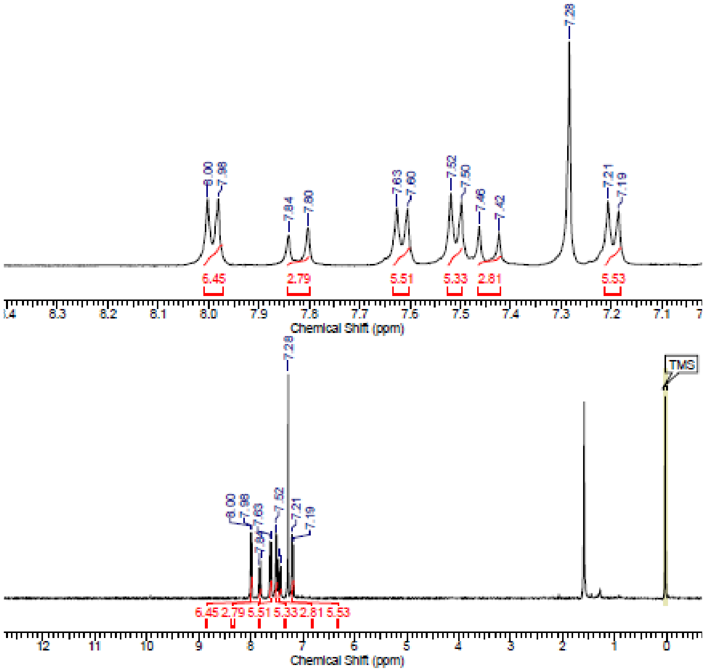


Figure 7.10: ^{1}H NMR spectrum of *(2E,2'E,2''E)-3,3',3''-(nitrilotris(benzene-4,1-diyl))tris(1-(4-chlorophenyl)prop-2-en-1-one)* (**TCl**)