Electronic Supplementary Information

Highly dispersed silica supported nanocopper as efficient heterogeneous catalyst: Application in the synthesis of 1,2,3-triazoles and thioethers

Pitchaimani Veerakumar,[a] Murugasan Velayudham,[b] Kuang-Lieh Lu[b] and Seenivasan Rajagopal[a*]

[*a]*Department of Physical Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai, 625 021, India.*

[b]*Institute of Chemistry, Academia Sinica, Taipei, 115, Taiwan.*

Table of Contents	*Pages*

[*]*Corresponding author. Tel.: +91 452 2458246; Fax: +91 452 2459105.*

E-mail address: rajagopalseenivasan@yahoo.com (Prof. S. Rajagopal).

S1. Materials

Copper(II) chloride, highly branched polyethyleneimine (PEI) (MW~25 000), tetraethyl orthosilicate (TEOS), sodium azide (NaN_3), 3-aminopropyl triethoxysilane (APTES), phenylacetylene, thiols, iodo- and bromo benzene derivatives and $NaBH_4$ (Merck) were purchased from Sigma Aldrich and used as received. Water purified through a double distilled system was used.

S2. Synthesis of SiNPs

Spherical SiNPs were synthesized using Stöber method[1] from tetraethyl orthosilicate using liq.NH_3 as catalyst. First, 70 mL of ethanol and 30 mL of doubled distilled were taken in an Erlenmeyer flask and 1.2 mL of tetraethyl orthosilicate (TEOS) was added to the solution and stirred for 30 min. Then, 6-7 mL of liq. NH_3 was added drop by drop to this solution and stirred vigorously. The solution was initially clear, after 15-20 min the solution turned cloudy and the final solution was very turbid and after ageing overnight, the solution was filtered and washed.

S3. Amine functionalized SiNPs

Various reported literatures[2-4] are available for the synthesis of the amine functionalized SiNPs. The SiNPs were redispersed in 150 mL water and 1.0 mmol (0.221g) of 3-aminopropyl triethoxysilane (APTES) was added to it. The solution was stirred at 80^{o}C for one hour and allowed to cool. The surface-modified silica nanoparticles were collected by centrifugation, washed three times with water, and dried at room temperature in air.

S4. Experimental details of catalyst A catalyzed alkyne homocoupling

To a solution of alkyne (2.4 mmol) in dry DMSO (5.0 ml), catalyst **A** (0.05 mol %) were added successively stirred at room temperature for 15 mins. Progress of this reaction was monitored by TLC. After completion of the reaction, 10 ml of ethyl acetate was added. The filtrate was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was then purified by column

chromatography on silica gel using petroleum ether as eluent to afford corresponding pure homocoupling product.

S5. Synthesis of Azides

General Procedure: NaN_3 (715 mg, 11 mmol) and DMSO (20 mL) were added to a double-necked round-bottomed flask under nitrogen. The solution was stirred for 24 h at room temperature followed by the addition of the benzyl/alkyl halide (10 mmol) and additional stirring until disappearance of the reagents (TLC). The resulting mixture was treated with H_2O (50 mL), extracted with Et_2O (3 × 20 mL), and washed with H_2O (2 × 20 mL) and saturated brine solution (20 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and the filtrate was concentrated under reduced pressure to give the corresponding pure azides.[5-7]

S6. XRD spectra of catalyst A

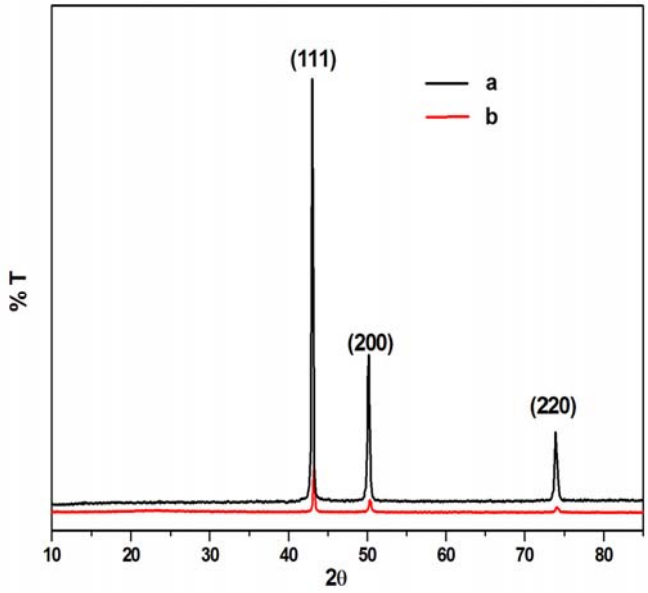


Figure 1. XRD spectra of catalyst **A** before (a) and after (b) the usage reaction.

S7. HRTEM images of catalyst A before and after the reaction

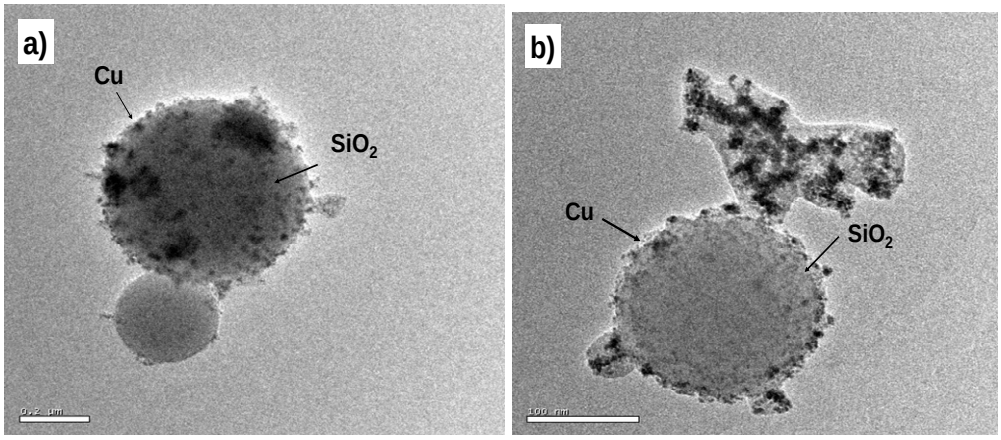


Figure 2. HRTEM images (a) before and (b) after the third cycle.

S8. BET analysis

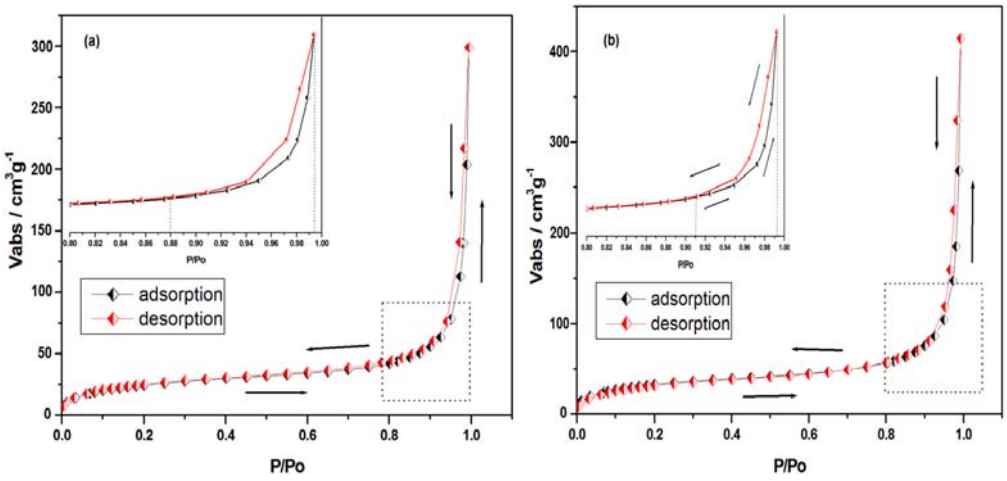


Figure 4.6 N_2 adsorption-desorption isotherms (a) amine functionalized SiO_2 and (b) corresponding catalyst II (Cu/SiO_2).

S9. SEM images

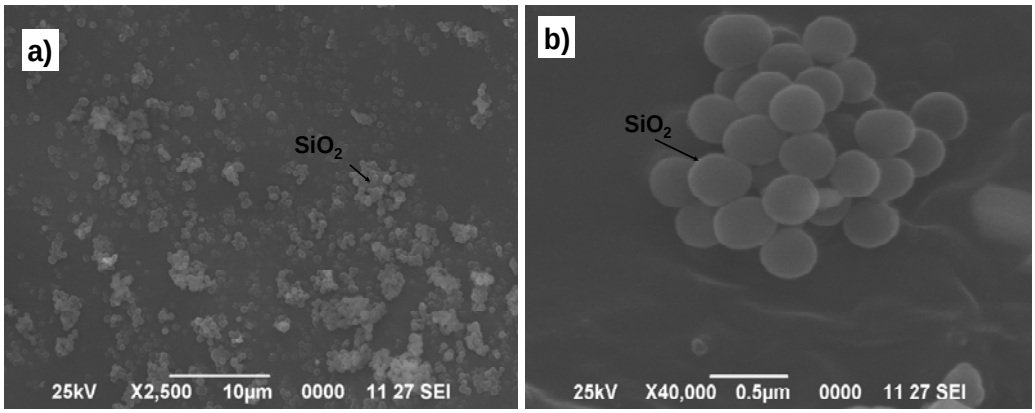


Figure 3. SEM images of the pure SiNPs in different magnifications (a) × 2500 and (b) × 40000.

S10. AFM images

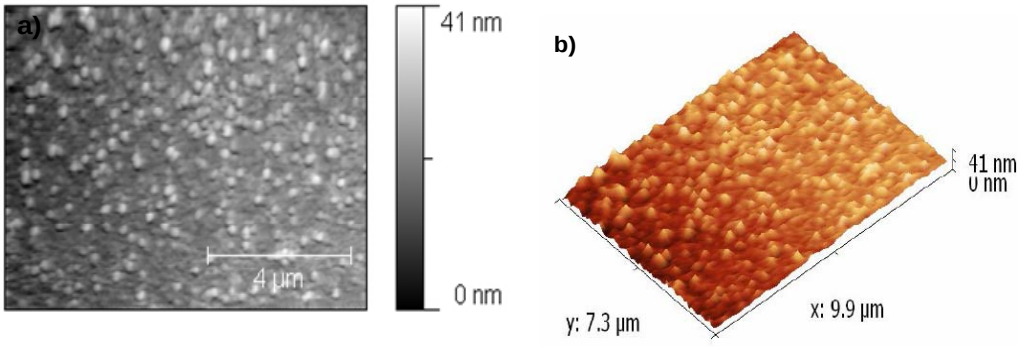


Figure 4. AFM images of catalyst A (a) in two-dimension (2-D) and (b) three-dimension (3-D).

S11. FT-IR Peak assignments and wavenumbers for SiO_2, NH_2-SiO_2, and catalyst A.

SiO_2		NH_2-SiO_2		catalyst A	
Assignment	**cm^{-1}**	**Assignment**	**cm^{-1}**	**Assignment**	**cm^{-1}**
ν(O-H)	3441	ν(O-H)	3427	ν(O-H)	3415
ν_{as}(Si-O-Si)	1103	ν_{as}(Si-O-Si)	1076	ν_{as}(Si-O-Si)	1076
ν_s(Si-O-Si)	800	ν_s(Si-O-Si)	788	ν_s(Si-O-Si)	790
δ(Si-O-Si)	427	δ(Si-O-Si)	459	δ(Si-O-Si)	462
ν(Si-O-(H))	954	ν(Si-O-(H))	-	ν(Si-O-(H))	-
ν_s(C-H) of-CH_2-	-	ν_s(C-H) of-CH_2 -	2856	ν_s(C-H) of-CH_2 -	2929
δ(NH) of the NH_2	-	δ(NH) of the NH_2	1544	δ(NH) of the NH_2	1542

S12. TGA measurement

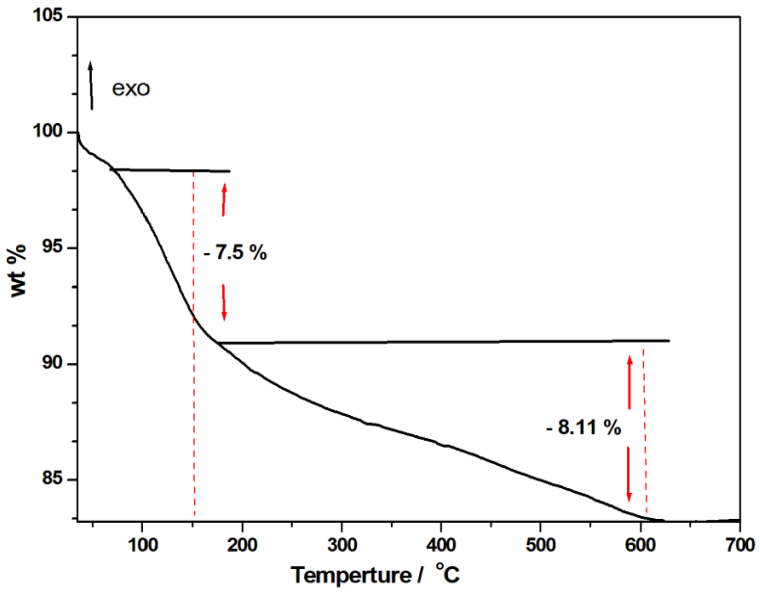


Figure 5. TGA curve of catalyst A under N_2 atmosphere at heating rate of 20 ^oC min^{-1}

S13. Additional HRTEM images

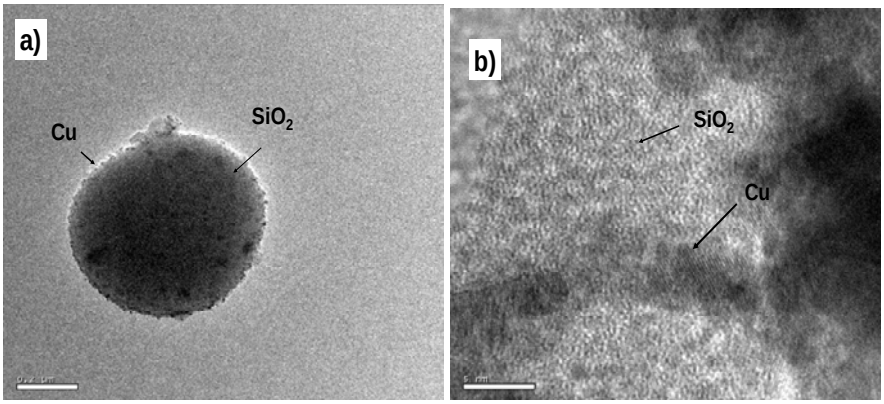


Figure 6. Additional HRTEM images of the catalyst **A** (a and b).

S14. UV-visible absorption spectrum of catalyst A.

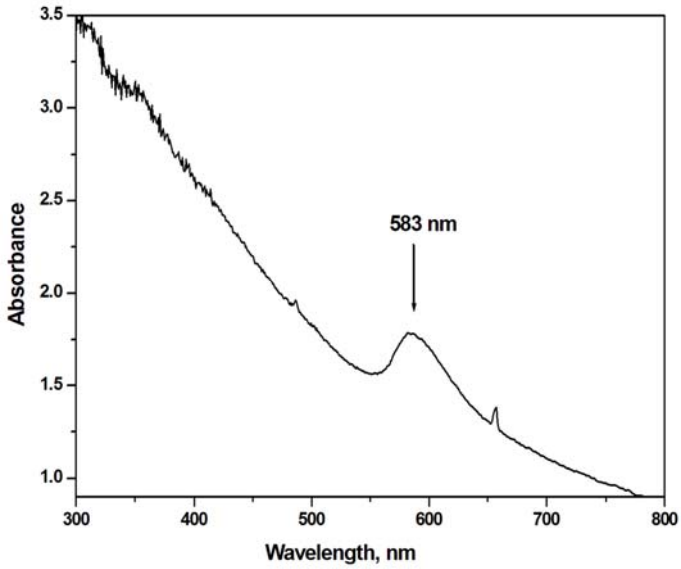


Figure 7. **UV-visible absorption spectrum of catalyst A.**

S15. Influence of different solvents on catalyst A catalyzed Click reaction[a]

Entry	Solvent	Time (min)	Yield (%)[b]
1	Toluene	60	45
2	EtOH	25	90
3	CH_3CN	50	60
4	CH_2Cl_2	90	50
5	H_2O	75	85
6	DMSO	10	98
7	Dioxane	85	38

[a]Reaction conditions: The reaction condition: Phenyl acetylene (1.2 mmol), benzyl bromide (1.2 mmol), NaN_3 (1.2 mmol), catalyst **A** (0.05 mol %) and DMSO (5.0 mL) at room temperature.

[b]Isolated yields.

S16. Catalytic amount of catalyst A screening for the C-S coupling reaction[a]

Entry	catalyst A (mol %)	Yield (%)[b]
1	0	Trace
2	0.5	60
3	1.0	85
4	1.5	96
5	2.0	96

[a]Reaction conditions: **catalyst A** (1.5 mol%), benzenethiol (1.0 mmol), aryl halide (1.2 mmol), KOH (1.5 mmol), and DMSO (3 ml) were stirred at 110°C for 9 h under a N_2 atmosphere.

[b]Isolated yields.

S17. Screening of solvents for the catalyst A catalyzed C-S coupling reaction[a]

Entry	Solvent	Yield (%)[b]
1	H_2O	Trace
2	EtOH	Trace
3	DMF	70
4	Toluene	28
5	MeOH	Trace
6	DMSO	96
7	THF	Trace
8	Benzene	Trace
9	TEA	75[c]

[a]Reaction conditions: C**atalyst A** (1.5 mol%), benzenethiol (1.0 mmol), aryl halide (1.2 mmol), KOH (1.5 mmol), and solvent (3 ml) were stirred at 110°C for 9 h, under a N_2 atmosphere.

[b]Isolated yields.

[c]Triethyl amine acting as a base as well as a solvent.

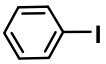
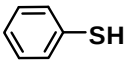
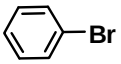
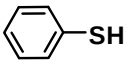
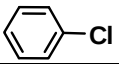
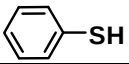
S18. Screening of bases for the catalyst A catalyzed C-S coupling reaction[a]

Entry	Base	Yield(%)[b]
1	NaOAc	Trace
2	NaOH	78
3	Na_2CO_3	Trace
4	KOH	96
5	Pyridine	50
6	K_2CO_3	65

[a]Reaction conditions: **Catalyst A** (1.5 mol%), benzenethiol (1.0 mmol), aryl halide (1.2 mmol), base (1.5 mmol), and DMSO (3 ml) were stirred at 110°C for under a N_2 atmosphere.

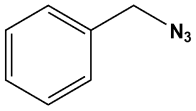
[b]Isolated yields.

S19. C-S coupling of thiophenol with different aryl halides[a]

Entry	Halides	Thiol	Time (h)	Yield (%)[b]
1			9	96
2			9	60
3			9	30

[a]Reaction conditions: **Catalyst A** (1.5 mol %), benzenethiol (1.0 mmol), aryl halide (1.2 mmol), KOH (1.5 mmol), and DMSO (3.0 ml) were stirred at 110 ^{o}C under a N_2 atmosphere.
[b]Isolated yields.

S20. NMR data of azides



Benzyl azide: Yellow oil[8] ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.3 (s, 2H), 7.27-7.39 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 54.8, 128.2, 128.3, 128.8, 135.4.

C_6H_{13}-N_3 **1-Azido hexane: Colorless oil**, ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.25 (t, 2H, *J* =7.0 Hz), 1.55-1.64 (m, 2H), 1.25-1.41 (m, 6H), 0.89 (t, 3H, *J* =6.8 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 51.4 (-CH_2N_3).

$C_{10}H_{21}$-N_3 **1-Azido decane: Colorless oil**, ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.88 (m, 5H), 1.54-1.62 (m, 14H), 3.25 (t, *J* = 7.2 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 51.5 (-CH_2N_3).

N_3-$C_{10}H_{20}$-N_3 **1,10-diazidodecane: Yellow oil**, ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.38-1.54 (m, 18H); 3.40 (t, *J* = 6.9 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 51.4 (-CH_2N_3).

$C_{12}H_{25}$-N_3 **1-Azido dodecane: Yellow oil**[9] ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.88-1.12 (m, 8H), 1.62-1.27 (m, 15H), 3.40 (t, *J* = 6.3 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 51.4 (-CH_2N_3).

$C_{16}H_{33}$-N_3 **1-Azido hexadecane: Colorless oil**, ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.88-0.96 (m, 3H), 1.54-1.62 (m, 28H), 3.40 (t, *J* = 6.9 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 51.5 (-CH_2N_3).

S21. NMR spectra of azides

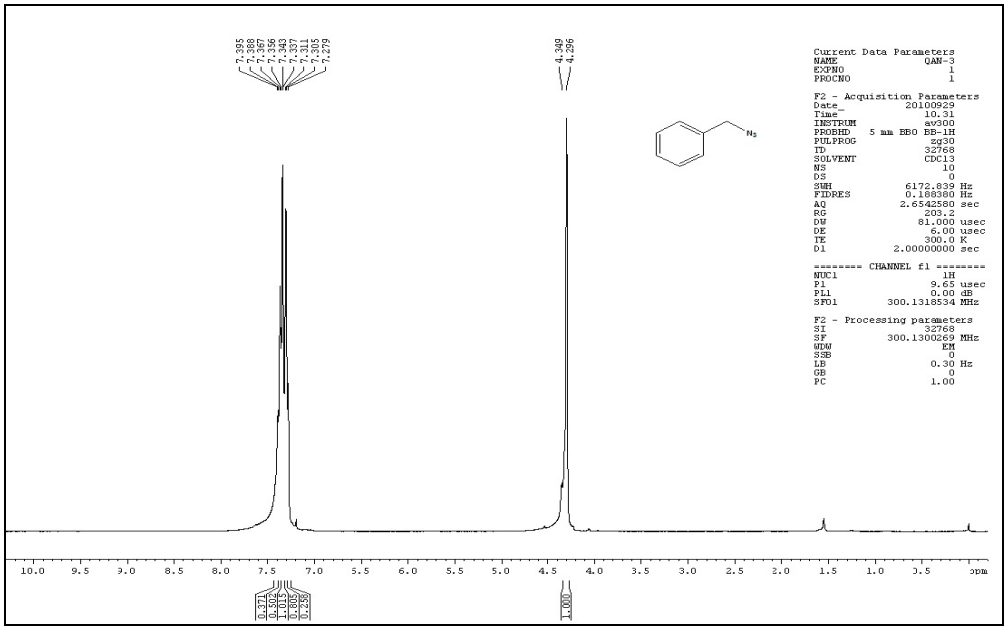


Figure 8. ^{1}H-NMR spectrum of benzyl azide.

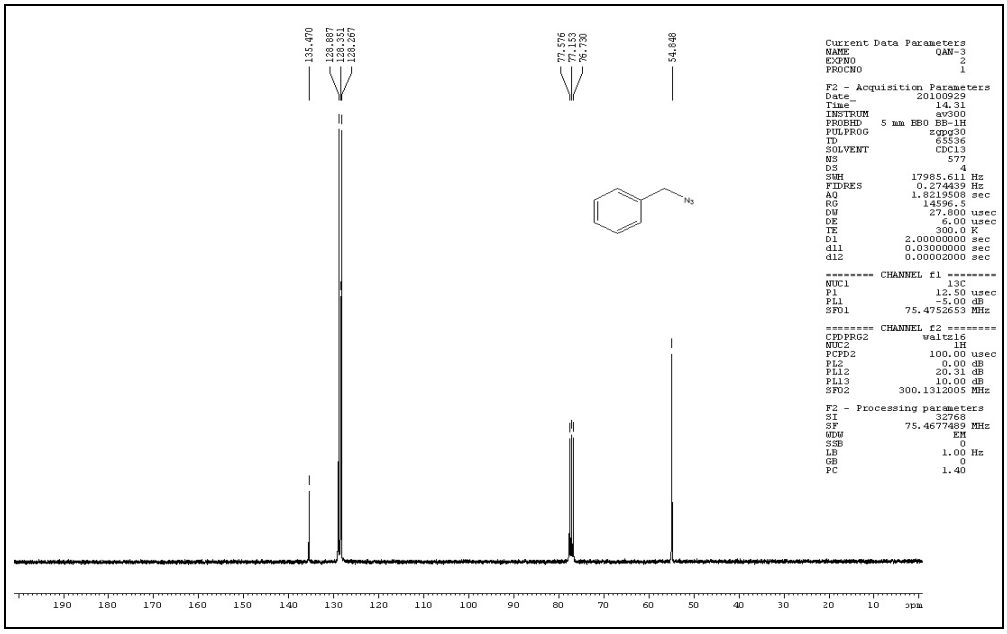


Figure 9. ^{13}C-NMR spectrum of benzyl azide.

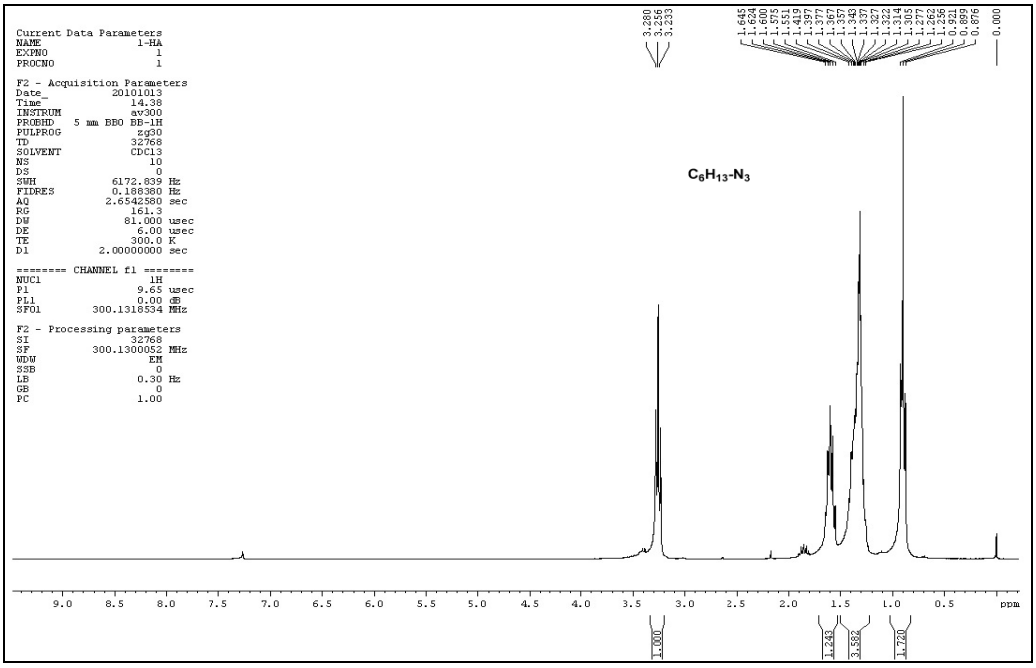


Figure 10. ^{1}H-NMR spectrum of 1-azido hexane.

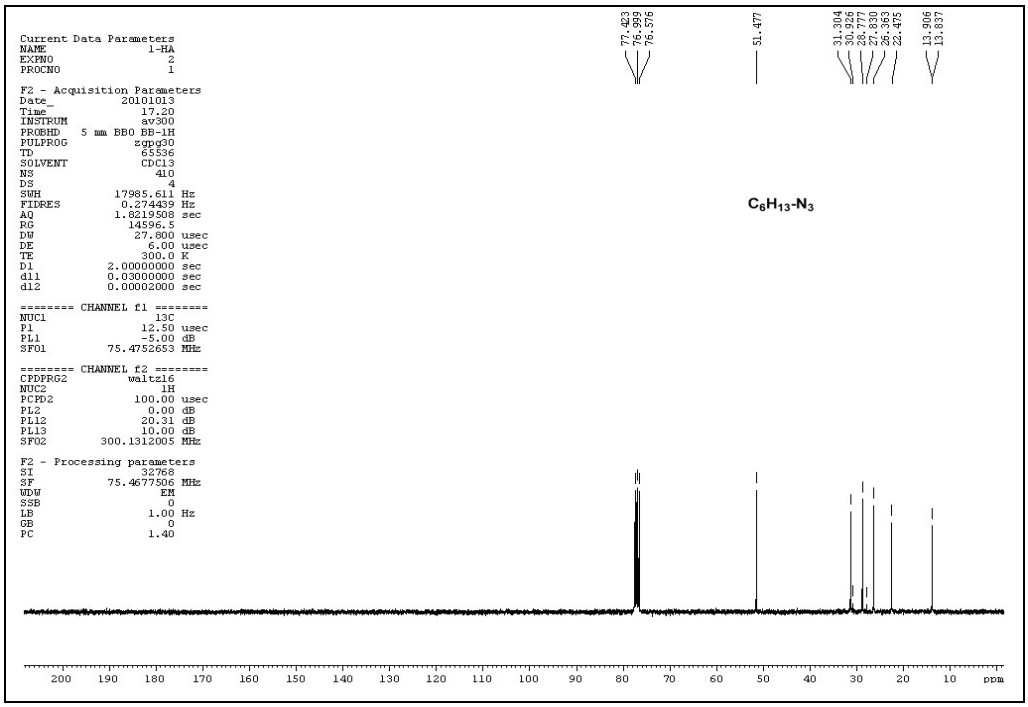


Figure 11. ^{13}C-NMR spectrum of 1-azido hexane.

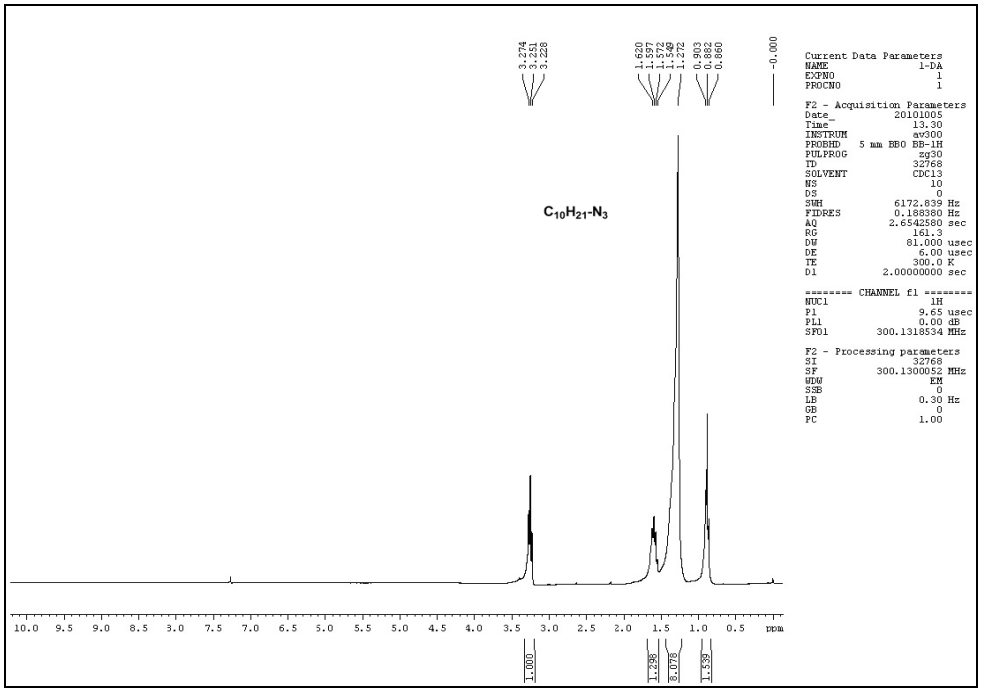


Figure 12. ^{1}H-NMR spectrum of 1-azido decane.

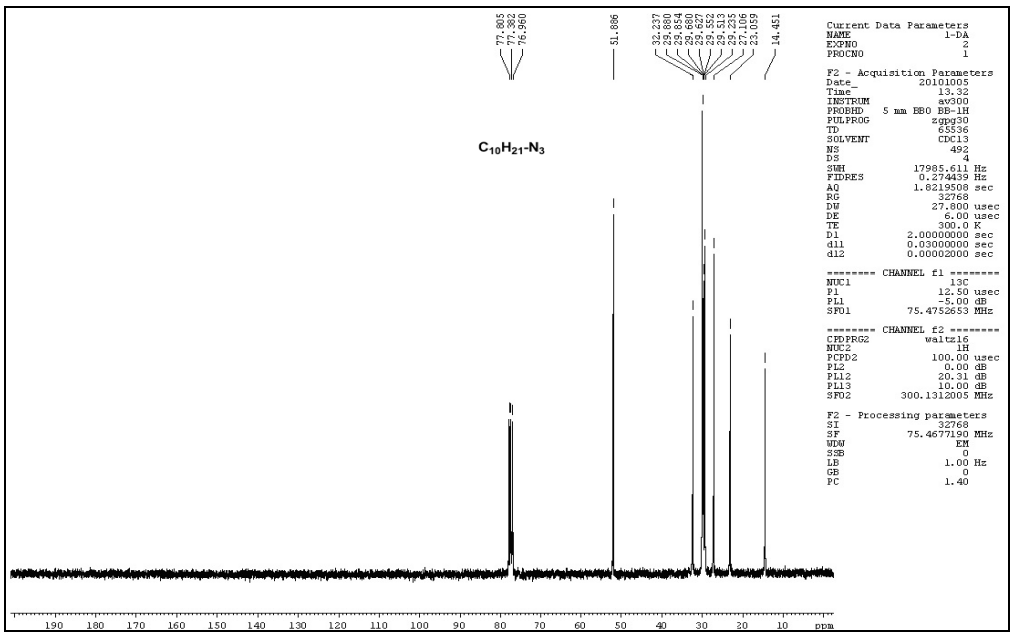


Figure 13. ^{13}C-NMR spectrum of 1-azido decane.

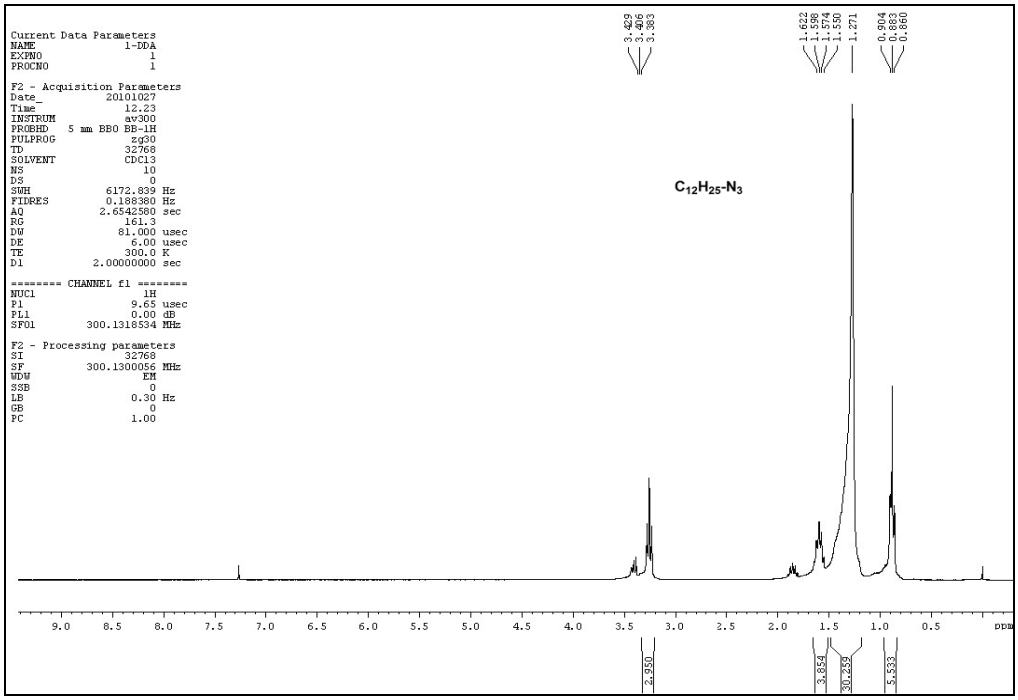


Figure 14. ^{1}H-NMR spectrum of 1-azido dodecane.

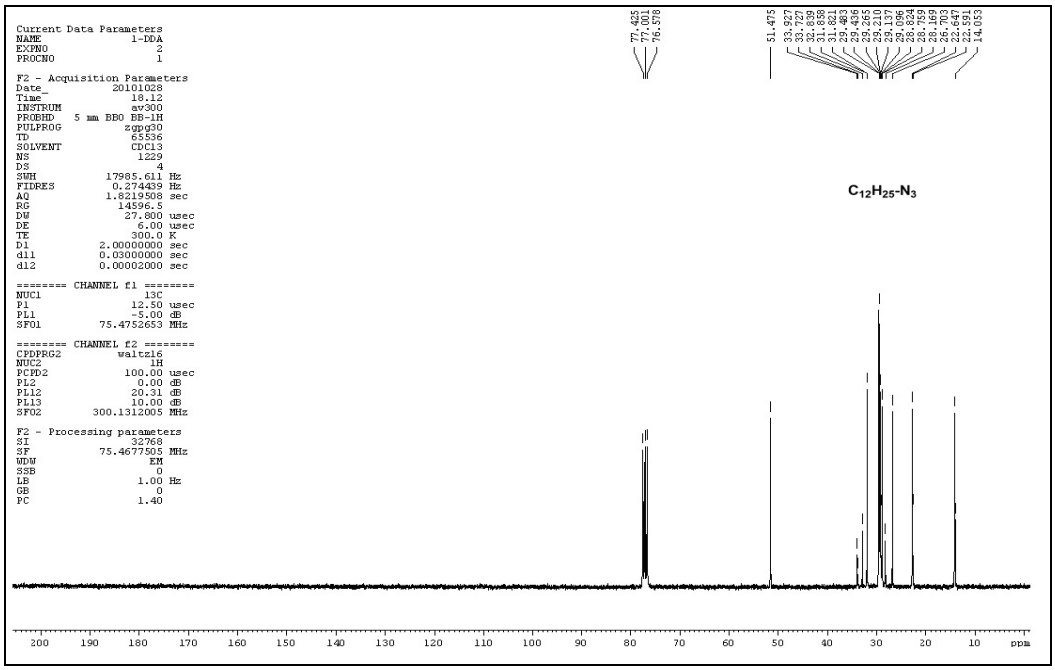


Figure 15. ^{13}C-NMR spectrum of 1-azido dodecane.

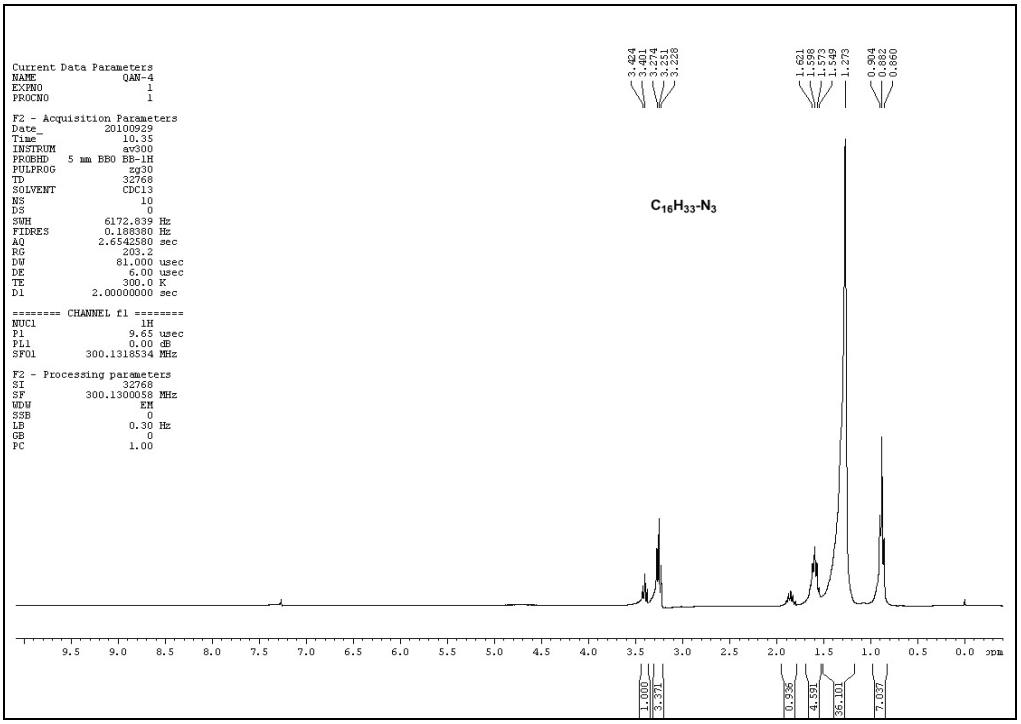


Figure 16. ^{1}H-NMR spectrum of 1- azido hexadecane.

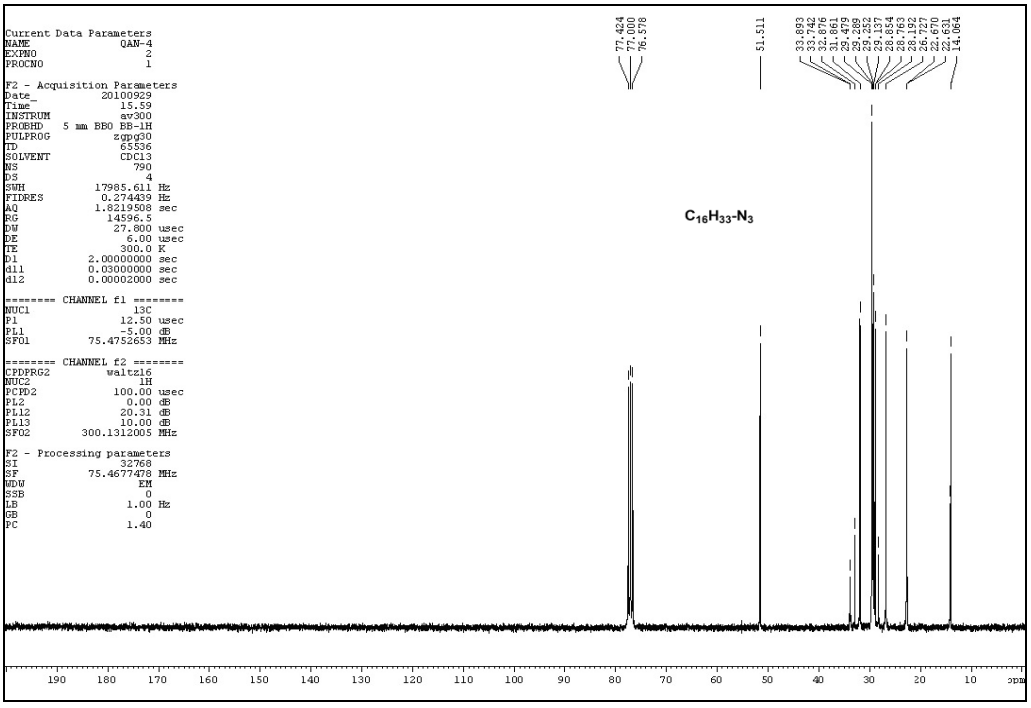


Figure 17. ^{13}C-NMR spectrum of 1- azido hexadecane.

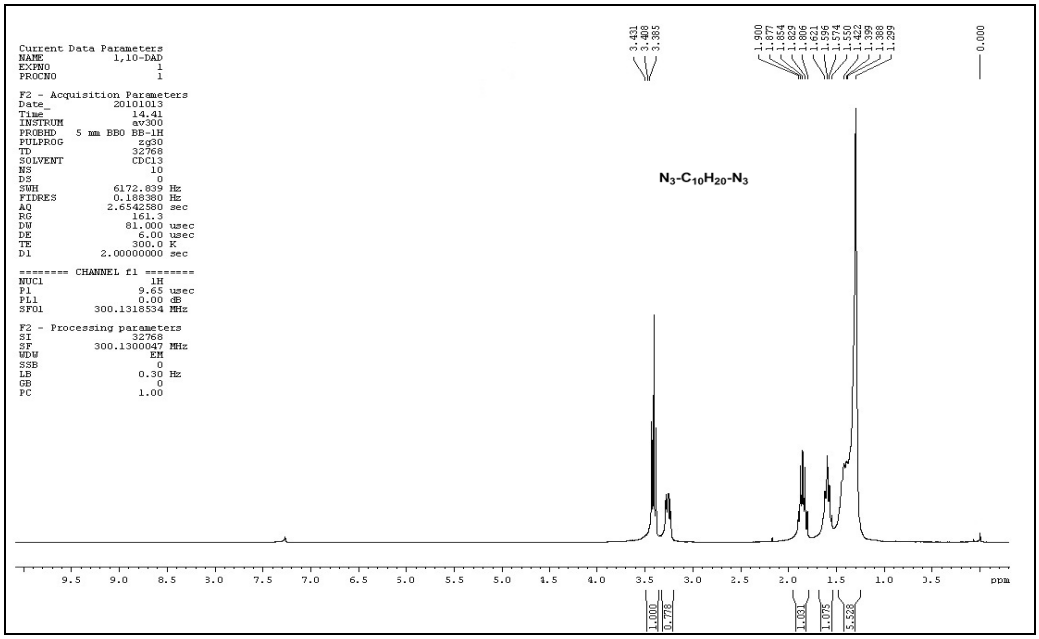


Figure 18. ^{1}H-NMR spectrum of 1,10-diazidodecane.

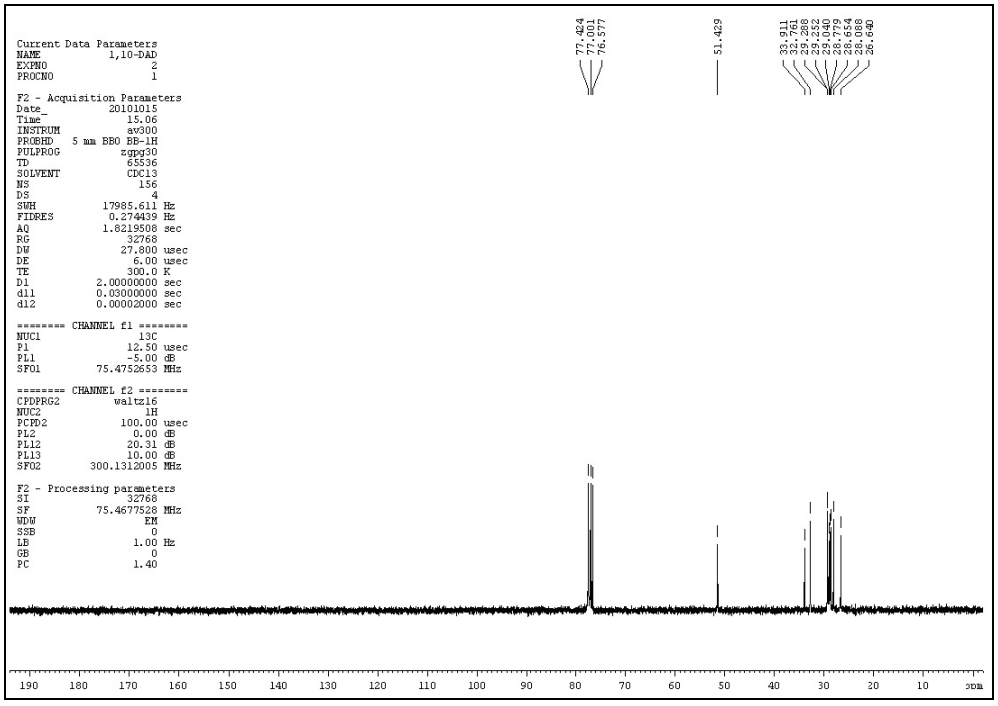
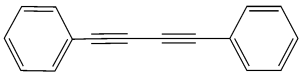
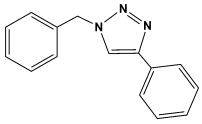


Figure 19. ^{13}C-NMR spectrum of 1,10-diazidodecane.

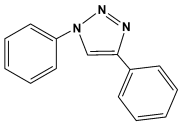
S22. NMR data of 1,2,3-triazole products



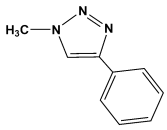
1,4-diphenylbuta-1,3-diyne:[10] Colorless solid (Table 1, Entry 1) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.38-7.28 (m, 6H), 7.53-7.47 (m, 4H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 73.9, 81.5, 121.7, 128.4, 129.1, 132.4.



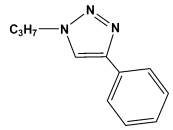
1-benzyl-4-phenyl-*1H*-1,2,3-triazole:[11]Colorless solid (Table 1, Entry 2) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.58 (s, 2H), 7.43-7.26 (m, 8H), 7.66 (s, 1H), 7.81 (d, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 54.2. 119.4, 125.6, 128.0, 128.1, 128.7, 129.5, 130.5, 134.6, 137.5, 147.6.



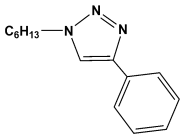
1-phenyl-4-phenyl-1H-1,2,3-triazole:[12] Colorless (Table 1, Entry 3) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.13-7.49 (m, 7H), 7.70-7.86 (m, 3H), 8.14 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 117.8, 126.4, 128.6, 128.9, 129.3, 129.6, 129.9, 130.4, 137.2, 148.5.



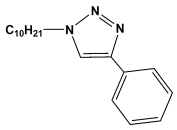
1-methyl-4-phenyl-1H-1,2,3-triazole:[12] Colorless (Table 1, Entry 4) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 4.13 (s, 3H), 7.33-7.45 (m, 5H), 7.83 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 46.8, 128.6, 128.3, 128.2, 125.8, 120.7, 137.6.



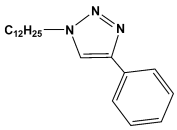
1-propyl-4-phenyl-1H-1,2,3-triazole:[12] Colorless solid (Table 1, Entry 5) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.99-1.12 (m, 3H), 1.88-1.99 (m, 2H), 4.34 (t, 2H), 7.36-7.63 (m, 5H), 7.74 (s, 1H); -^{13}C-NMR ($CDCl_3$, 75 MHz) δ 11.0, 23.7, 51.9, 119.5, 125.6, 128.0, 128.8, 130.7, 147.6.



1-hexyl-4-phenyl-1H-1,2,3-triazole:[13] Colorless solid (Table 1, Entry 6) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, 3H), 1.25-1.32 (m, 2H), 1.89-1.96 (m, 2H), 4.39 (t, 2H), 7.26-7.38 (m,1H), 7.39-7.47 (m, 2H), 7.74 (s, 1H), 7.85 (d, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 13.9, 22.3, 26.1, 30.2, 31.1, 50.4, 119.3, 125.6, 128.0, 128.7, 130.6, 147.6.



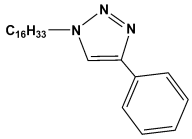
1-docyl-4-phenyl-1H-1,2,3-triazole:[12,14] Colorless solid (Table 1, Entry 7) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.87 (t, 3H), 1.25-1.35 (m, 14H), 1.69-1.96 (m, 2H), 4.39 (t, 2H), 7.26-7.35 (m, 1H), 7.40-7.45 (m, 2H), 7.74 (s, 1H), 7.82-7.85 (m, 2H); ^{13}C -NMR ($CDCl_3$, 75 MHz) δ 14.4, 22.7, 26.6, 29.8, 30.5, 31.7, 50.8, 119.7, 126.1, 128.0, 128.4, 131.6, 148.1.



1-dodecyl-4-phenyl-1H-1,2,3-triazole:[14] Colorless soild (Table 1, Entry 8) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.87 (t, 3H), 1.24-1.33 (m, 18H), 1.93-2.01 (m, 2H), 4.38 (t, 2H), 7.32-7.34 (m, 1H), 7.39-7.44 (m, 2H), 7.74 (s, 1H), 7.84-7.82 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.0, 22.5, 22.6, 26.4, 28.9,

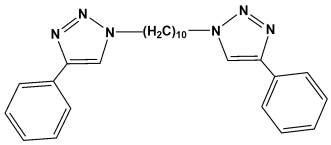
29.2, 29.3, 29.4, 29.5, 30.3, 31.8, 50.3, 119.3, 125.0, 128.0, 128.7, 130.6, 147.6.

1-hexadecyl-4-phenyl-1H-1,2,3-triazole:



Colorless (Table 1, Entry 9) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.87 (t, 3H), 1.24-1.31 (m, 26H), 1.92 (m, 2H), 4.36 (t, 2H), 7.33-7.31 (m, 1H), 7.43-7.38 (m, 2H), 7.73 (s, 1H), 7.83-7.81 (m, 2H),^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.0, 22.6, 26.4, 28.1, 28.7, 28.9, 29.3, 29.4, 29.6, 30.3, 30.8, 31.8, 32.7, 34.0, 50.3, 119.3, 128.0, 128.7, 129.1, 130.6, 147.6.

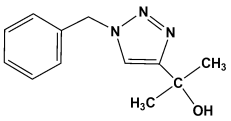
1,10-bis(4-phenyl-*1H*-1,2,3-triazol-1-yl)decane:



Colorless (Table 1, Entry 10) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.68-1.25 (m, 14H), 1.97-1.94 (m, 2H), 4.39 (t, 4H), 7.36-7.31 (m, 1H), 7.45-7.40 (m, 2H), 7.74 (s, 1H), 7.85-7.82 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 26.3, 28.6, 28.8, 29.1, 51.3, 119.2, 125.5, 128.0, 128.7, 130.5, 147.5.

2,7-dimethylocta-3,5-diyne-2,7-diol:[15] Colorless solid (Table 1, Entry 11) ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.04 (s, 2H), 1.54 (s, 12H). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 31.0, 66.5, 66.3, 83.9.

2-(1-Benzyl-1H-1,2,3-triazol-4-yl)-2-propanol[15]



Colorless solid (Table 1, Entry 12) ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.57 (s, 6 H), 3.20 (s, 1H), 5.49 (s, 2H), 7.25-7.39 (m, 5H), 7.42 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 30.6, 54.6, 68.8, 119.9, 128.6, 128.8, 129.5, 134.5, 152.9.

S23. NMR spectra 1,2,3-triazoles

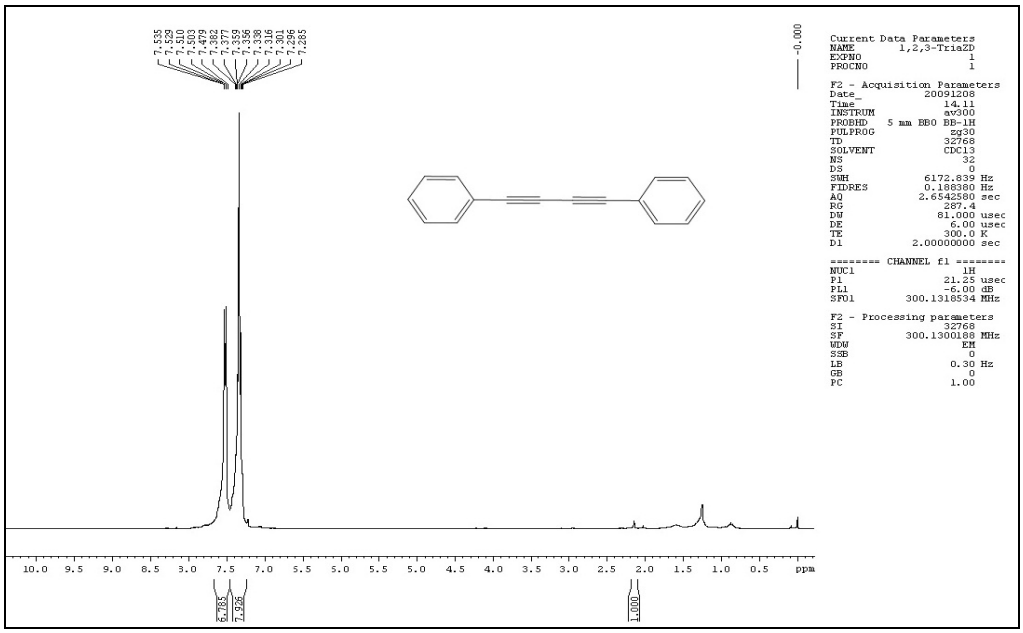


Figure 20. ^{1}H-NMR spectrum of 1,4-diphenylbuta-1,3-diyne (Table 1 Entry 1).

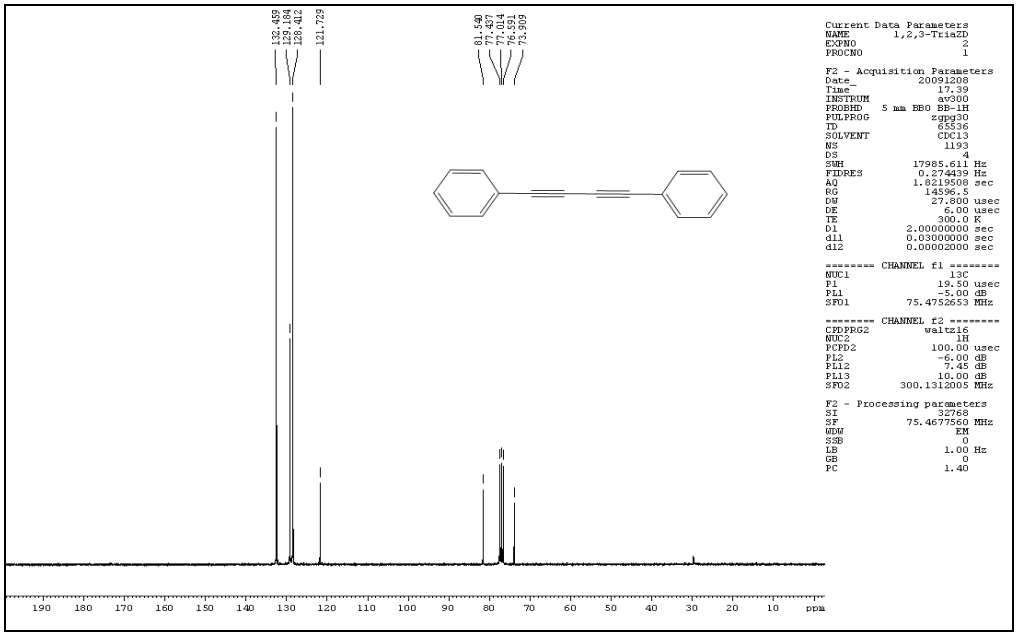


Figure 21. ^{13}C-NMR spectrum for 1,4-diphenylbuta-1,3-diyne (Table 1 Entry 1).

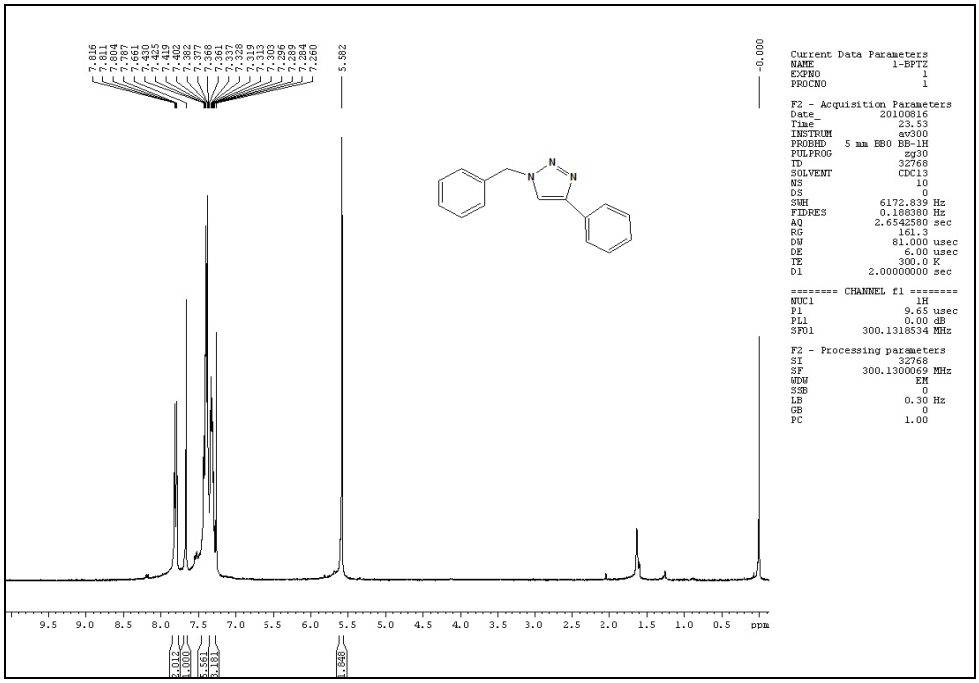


Figure 22. ^{1}H-NMR spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 2).

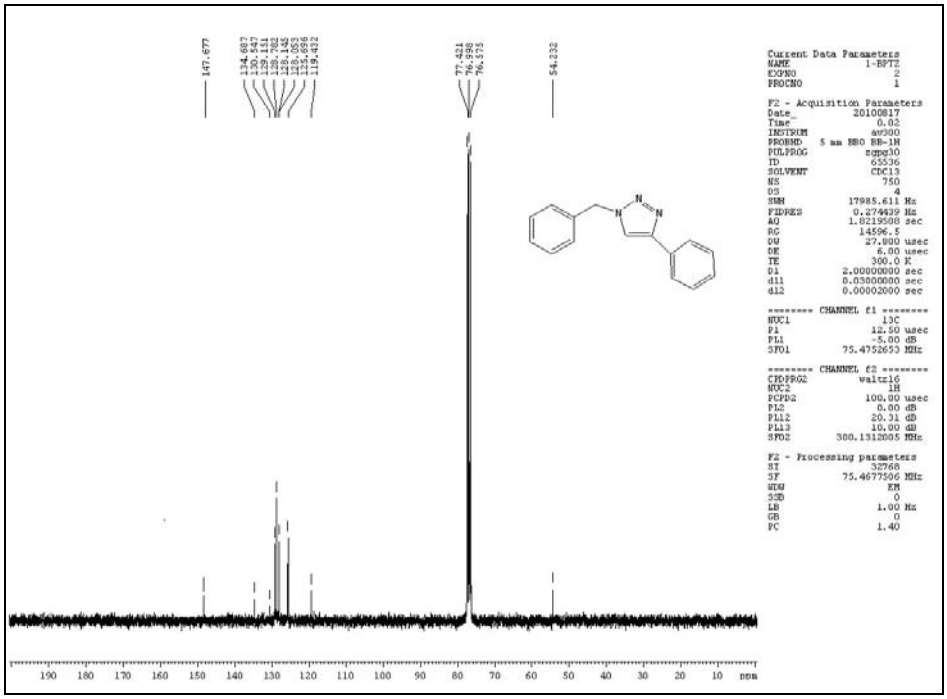


Figure 23. ^{13}C-NMR spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 2).

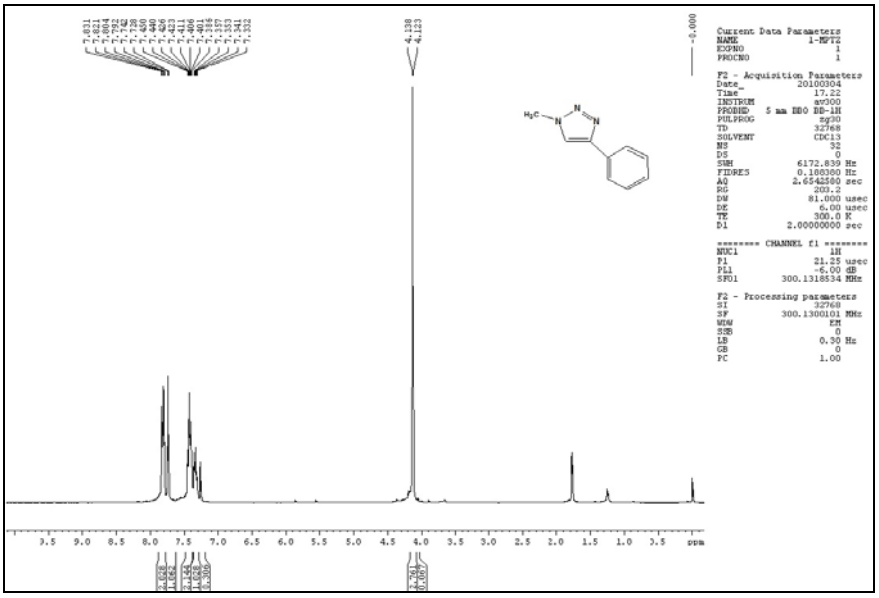


Figure 24. ^{1}H-NMR spectrum of 1-methyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 4).

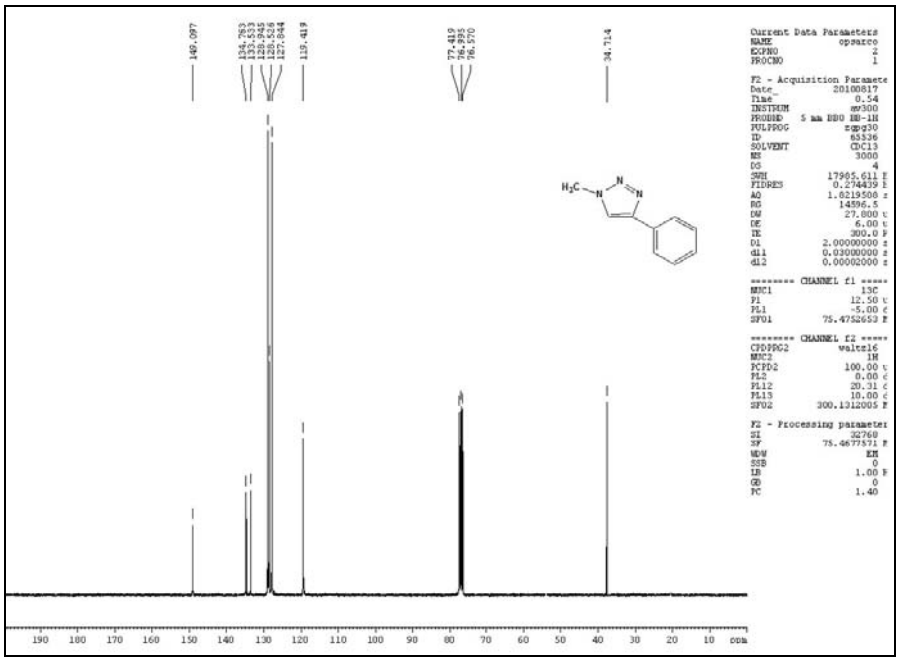


Figure 25. ^{13}C-NMR spectrum of 1-methyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 4).

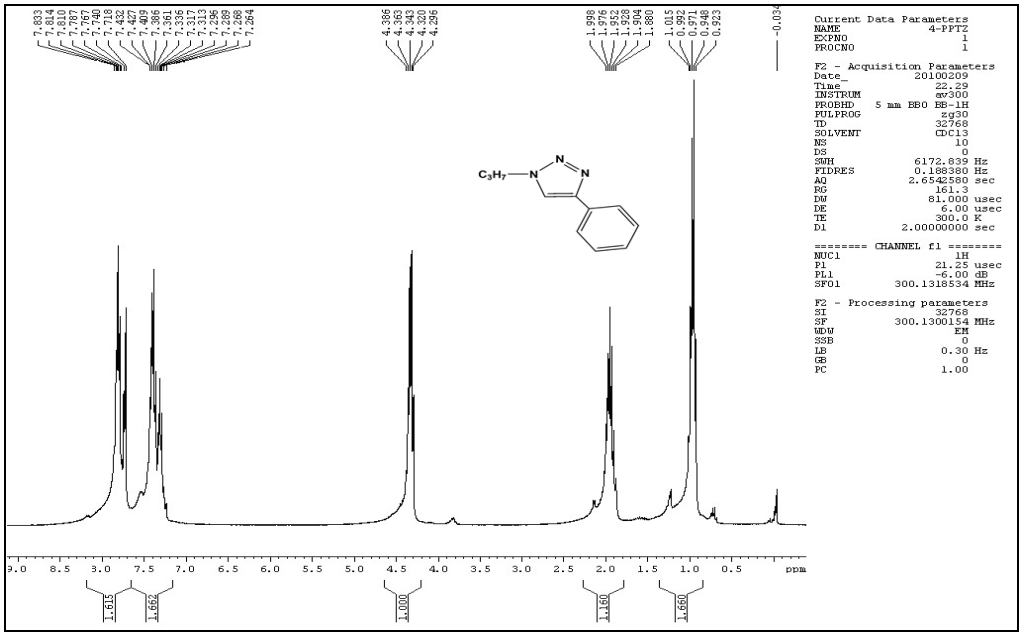


Figure 26. ^{1}H-NMR spectrum of 1-propyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 5).

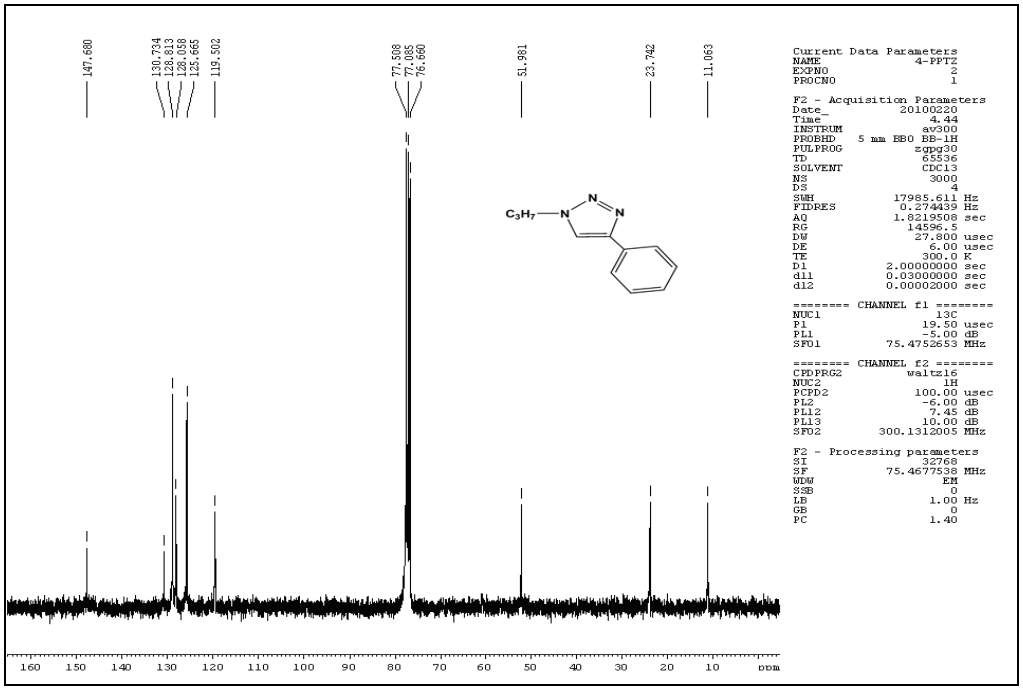


Figure 27. ^{13}C-NMR spectrum of 1-propyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 5).

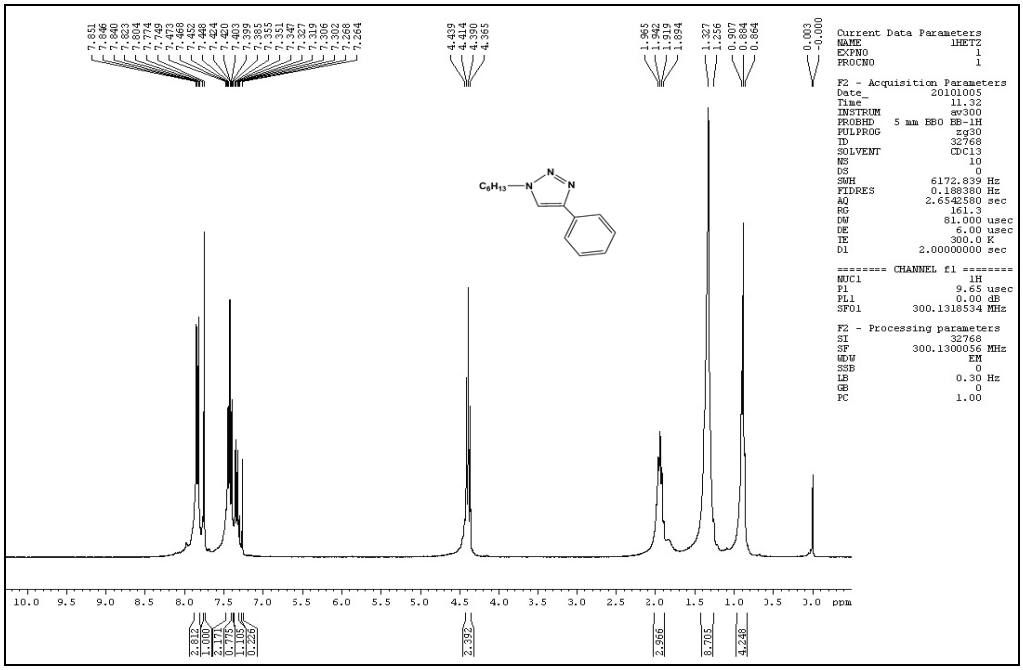


Figure 28. [1]H-NMR spectrum of 1-hexyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 6).

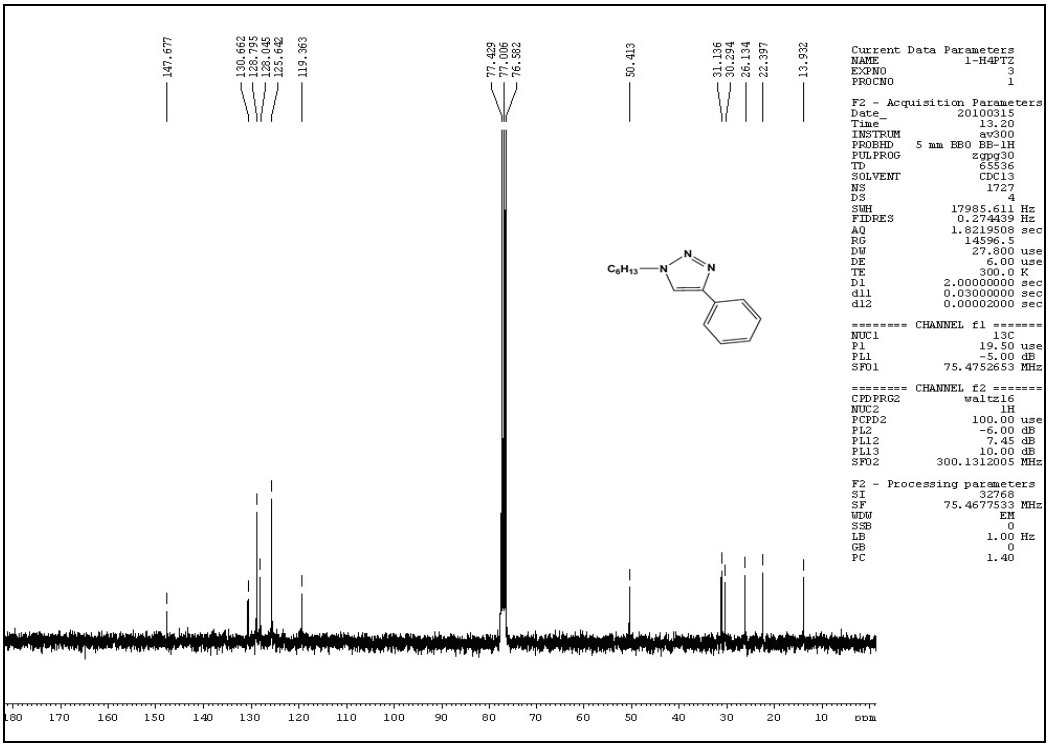


Figure 29.[13]C-NMR spectrum of 1-hexyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 6).

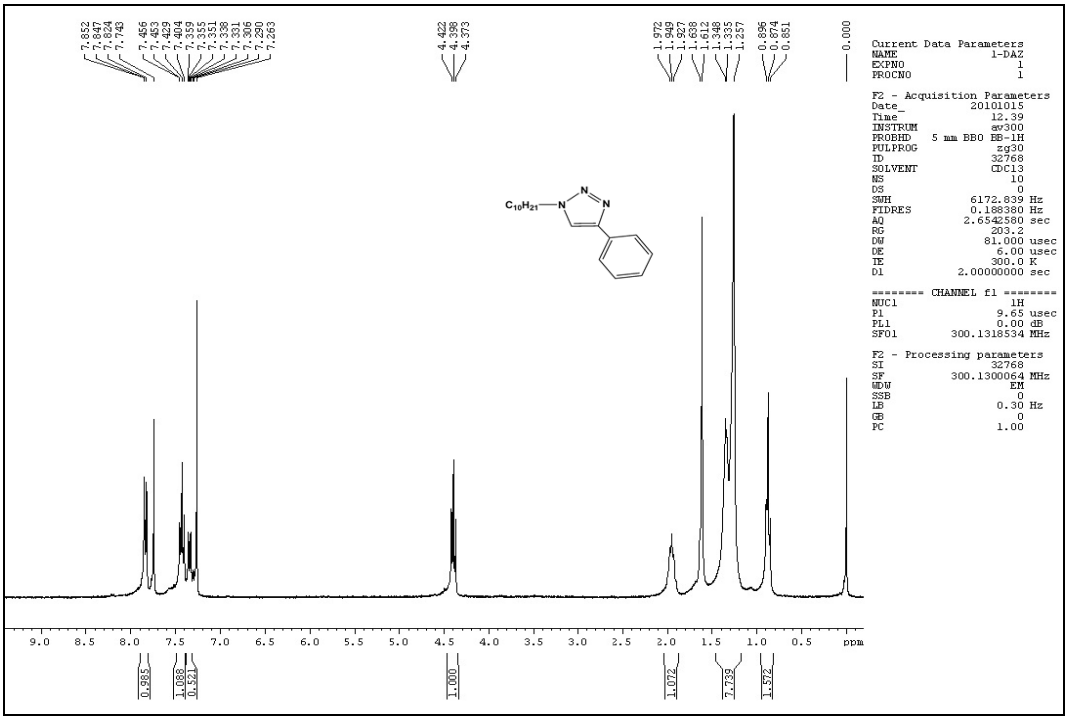


Figure 30.[1]H-NMR spectrum of 1-decyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 7).

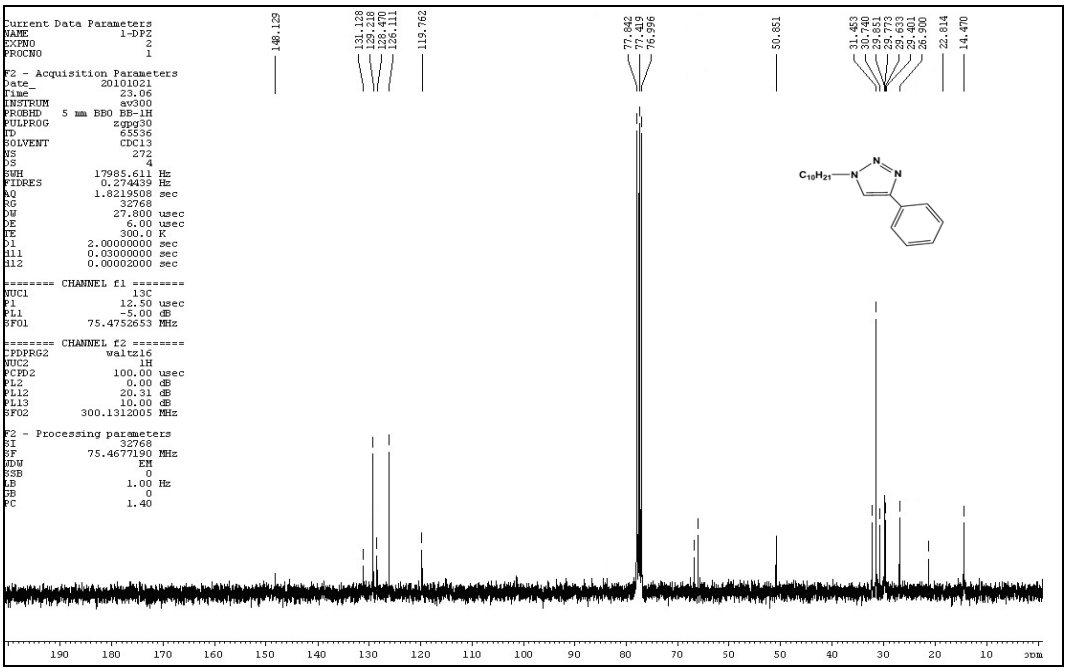


Figure 31. [13]C-NMR spectrum of 1-decyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 7).

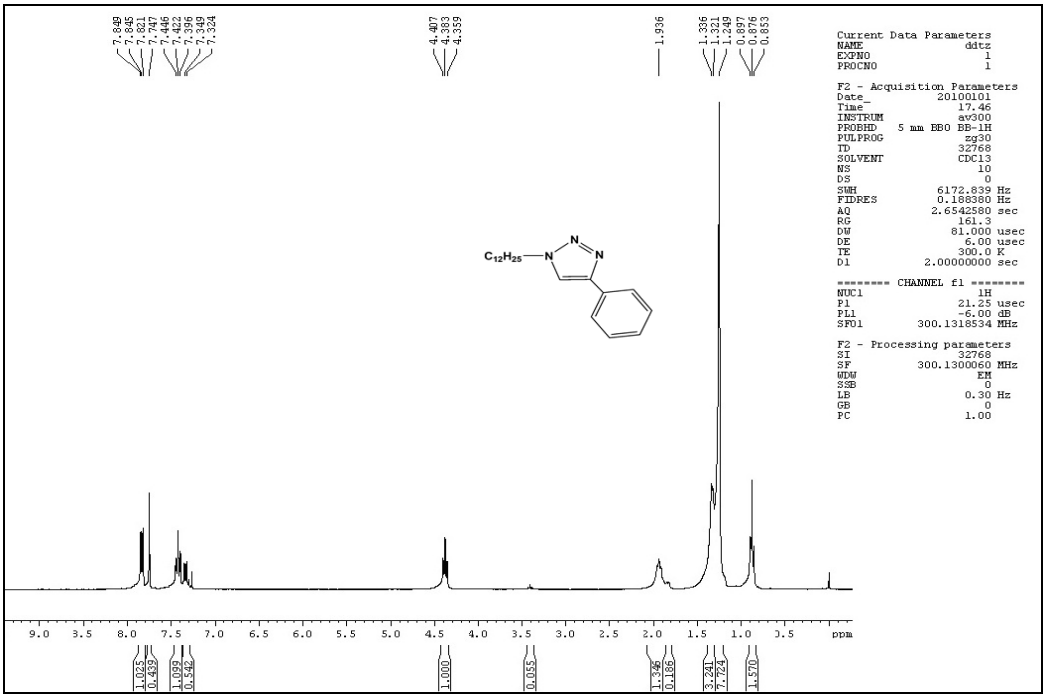


Figure 32. ^{1}H-NMR spectrum of 1-dodecyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 8).

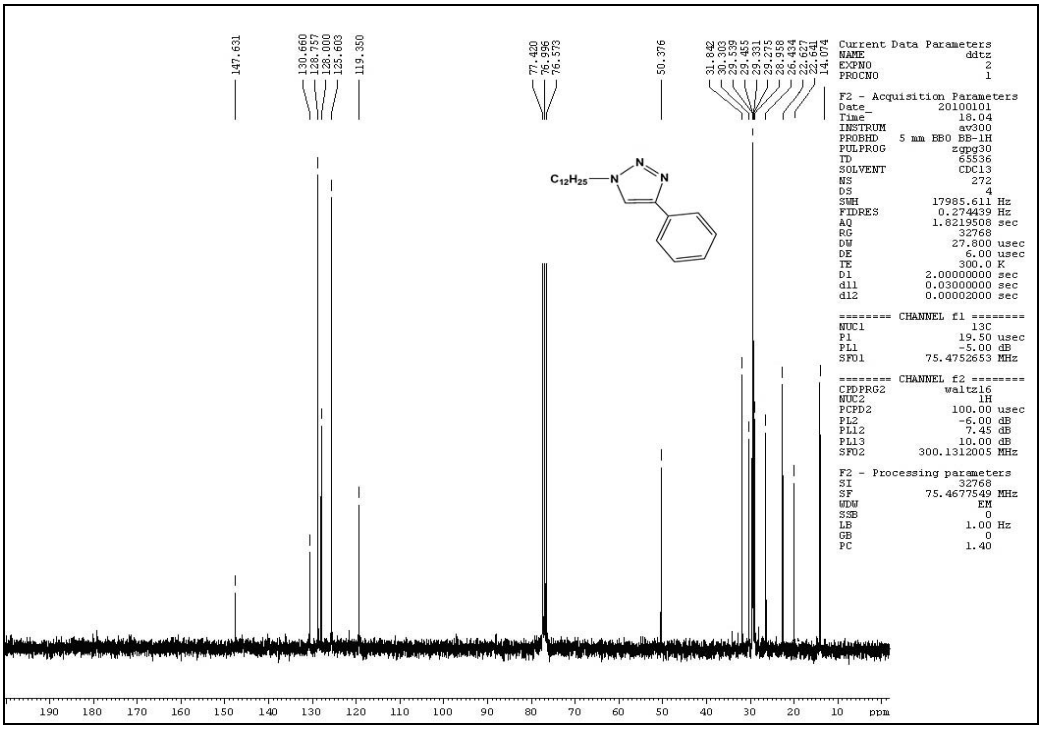


Figure 32. ^{1}H-NMR spectrum of 1-dodecyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 8).

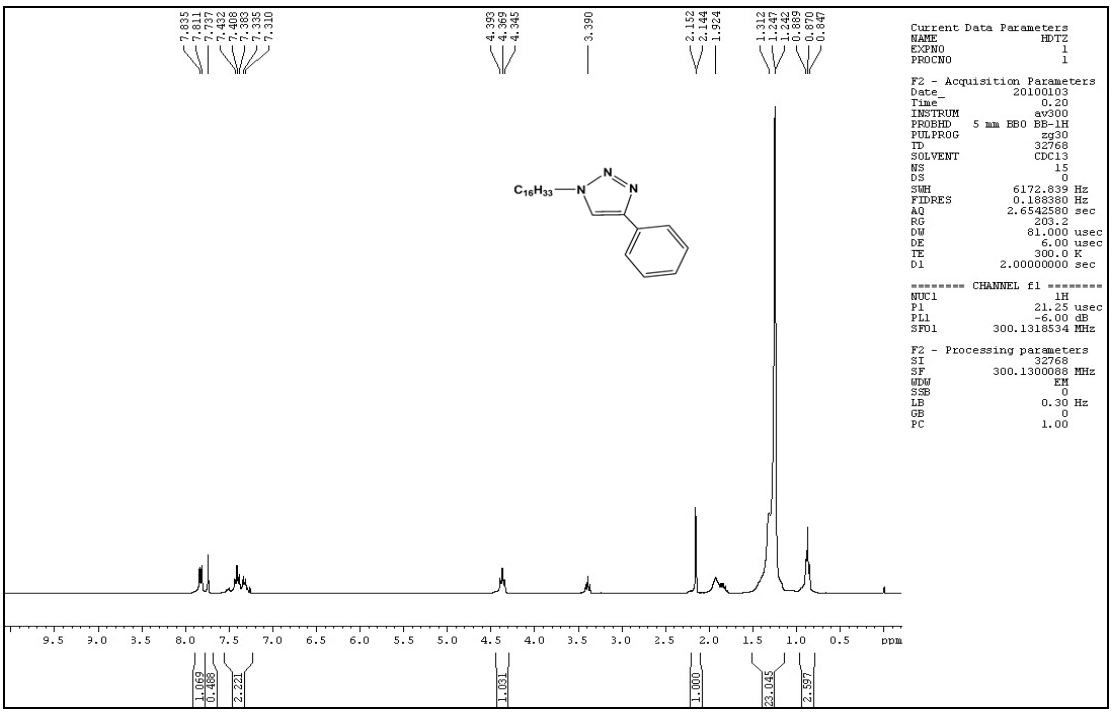


Figure 33. ^{1}H-NMR spectrum of 1-hexadecyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 9).

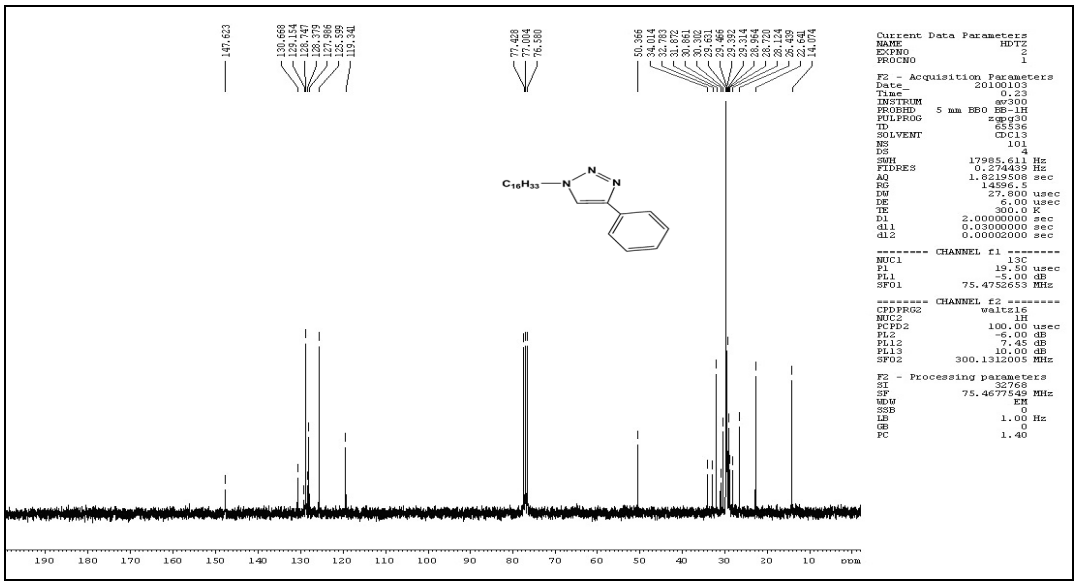


Figure 34. ^{13}C-NMR spectrum of 1-hexadecyl-4-phenyl-1H-1,2,3-triazole (Table 1 Entry 9).

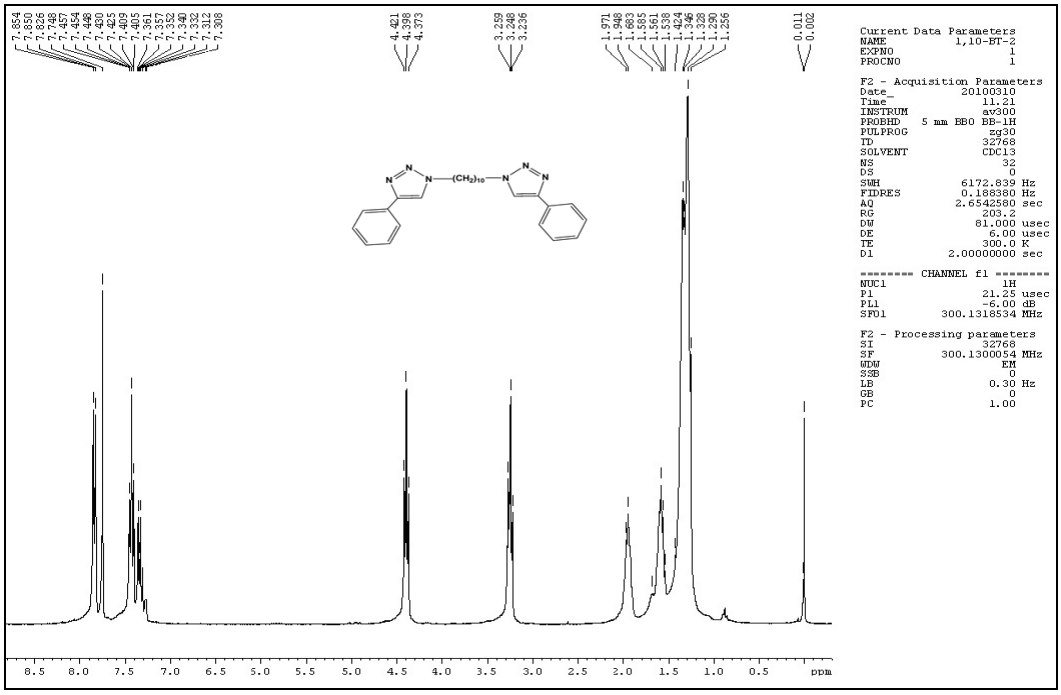


Figure 35. ^{1}H-NMR spectrum of 1, 10-bis(4-phenyl-1H-1, 2, 3-triazol-1-yl)decane (Table 1 Entry 10).

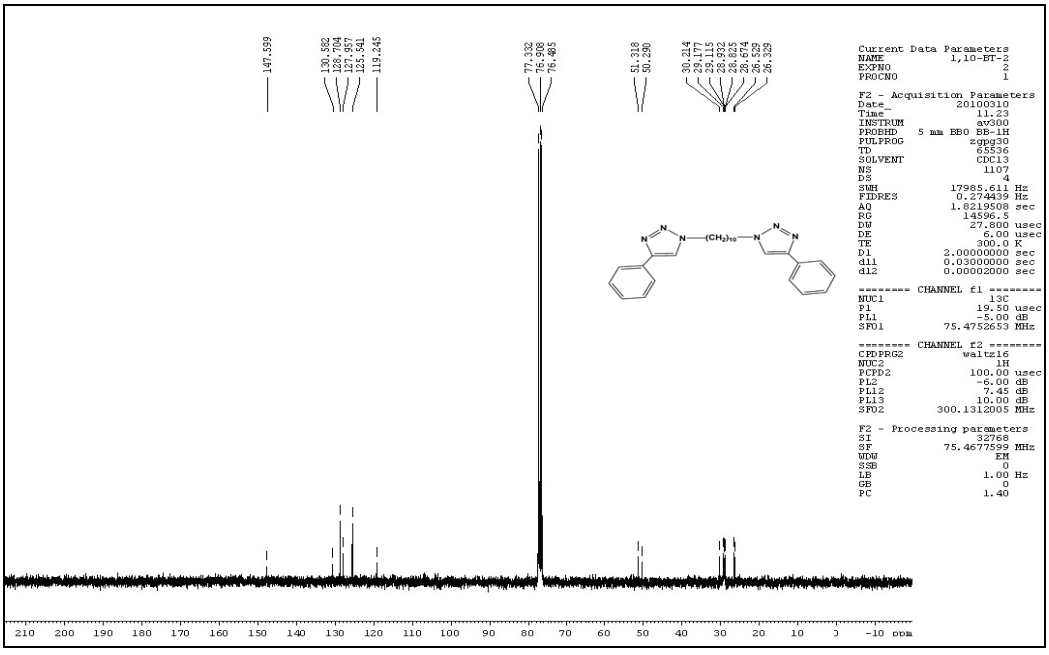


Figure 36. ^{13}C-NMR spectrum of 1, 10-bis(4-phenyl-1H-1, 2, 3-triazol-1-yl)decane (Table 1 Entry 10).

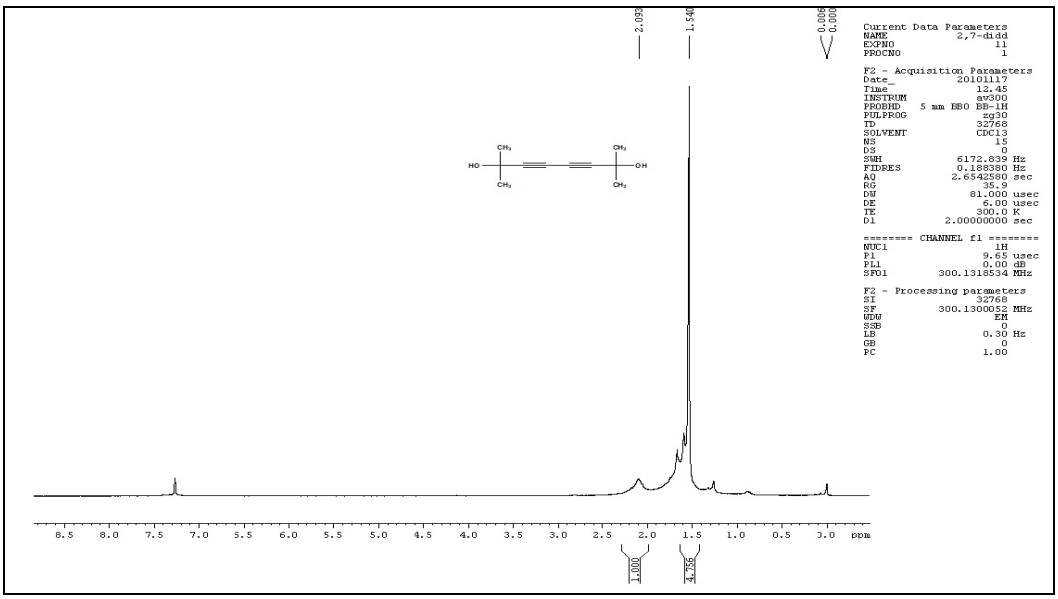


Figure 37. ^{1}H-NMR spectrum of 2,7-Dimethyl octa-3,5-diyne-2,7-diol (Table 1 Entry 11).

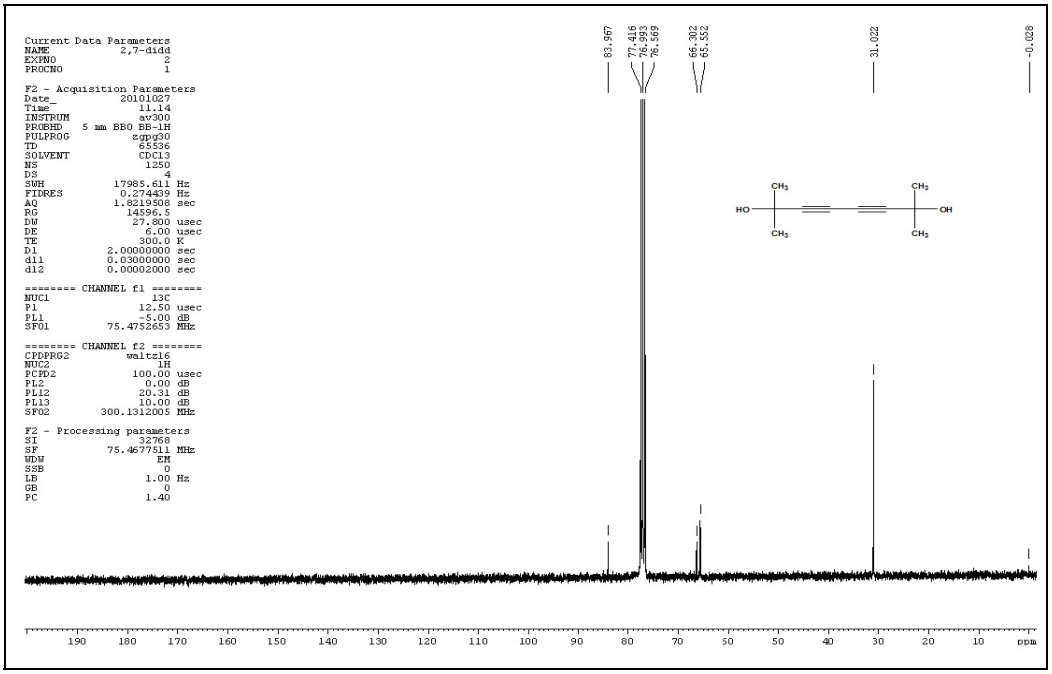
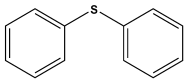
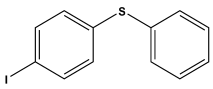


Figure 38. ^{13}C-NMR spectrum of 2,7-Dimethyl octa-3,5-diyne-2,7-diol (Table 1 Entry 11).

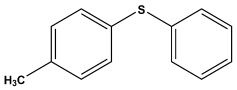
S24. NMR data of C-S coupling products



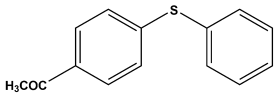
Diphenyl sulfide:[16] Colorless liquid (Table 2, Entry1) ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.49-7.71 (10H, m); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 126.7, 128.9, 130.7, 135.5.



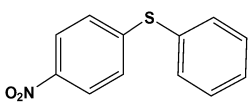
4-Iodo diphenyl sulfide:[16] Colorless liquid (Table 2, Entry 2) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.20 -7.44 (m, 5H), 7.46 (d, J = 6.8Hz, 2H), 7.12 (d, J = 6.8Hz, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 117.3, 120.8, 122.3, 128.7, 129.0, 130.0, 136.2, 136.5,



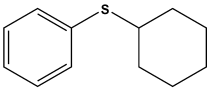
4-Tolylphenyl sulfide:[16] Colorless liquid (Table 2, Entry 3) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 3H), 7.10-7.26 (m, 5H), 7.32 (d, J = 7.2Hz, 2H), 7.46 (d, J = 7.2Hz, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.1, 126.4, 129.2, 129.7, 130.0, 131.2, 132.3, 137.1, 137.6



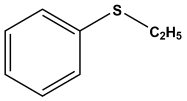
4-Acetyl-diphenyl phenyl sulfide:[17] Colorless liquid (Table 2, Entry 4) ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.54 (s, 3H), 7.21 (d, J = 7.2Hz, 2H), 7.38-7.39 (m, 3H), 7.90-7.47 (m, 2H), 8.09 (d, J = 7.2Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 26.45, 127.37, 128.77, 128.25, 129.64, 131.99, 133.85, 134.39, 144.90, 196.13.



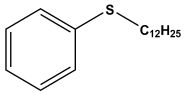
4-Nitrophenyl phenyl sulfide:[17] Light yellow color liquid (Table 2, Entry 6) ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.18 (d, J = 9.0 Hz, 2H), 7.47-7.55 (m, 5H), 8.07 (d, J = 9.0 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 124.0, 126.7, 129.6, 130.0, 130.5, 134.7, 145.4, 148.4.



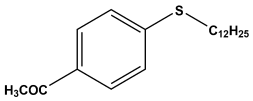
Cyclohexyl phenyl sulfide:[17] Colorless liquid (Table 2, Entry 8) ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.25-1.42 (m, 5H), 1.61-1.59 (m, 1H), 1.77-1.75 (m, 2H), 1.97-1.99 (m, 2H), 3.05-3.13 (m, 1H), 7.19-7.24 (m, 1H), 7.26-7.29 (m, 2H), 7.31-7.40 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 126.7, 128.9, 130.7, 135.5.



Ethyl phenyl sulfide:[16] Colorless liquid (Table 2, Entry 10) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.31 (t, 3H), 2.94 (q, 2H), 7.19-7.10 (m, 1H), 7.30 -7.21 (m, 4H); ^{13}C-NMR ($CDCl_3$ 75 MHz) δ 14.3, 27.5, 125.9, 128.4, 129.23, 136.79,



Dodecyl phenyl sulfide:[18] Colorless liquid (Table 2, Entry 11) ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H), 1.26-132 (m 16H), 1.58-160 (m, 2H), 1.61-1.69 (m, 2H), 2.91 (t, 2H), 7.08-7.13 (m, 1H), 7.26-7.35 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.0, 22.6, 28.5, 29.1, 29.2, 29.3, 29.5, 29.6, 30.8, 31.8, 33.6, 39.1, 127.3, 128.7, 130.1, 137.4.



1-(4-(dodecylthio)phenyl)ethanone:[19] Colorless liquid (Table 2, Entry 12) ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H) 1.26-1.59 (m, 16H), 1.60-1.69 (m, 2H), 2.65(t, 2H), 7.27 (d, 2H), 7.84 (d, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.7, 22.2, 26.1, 28.8, 28.8, 29.1, 29.2, 29.2, 31.5, 38.7, 127.8, 129.4, 131.4, 135.3, 196.5.

S25. NMR Spectra of C-S coupling products.

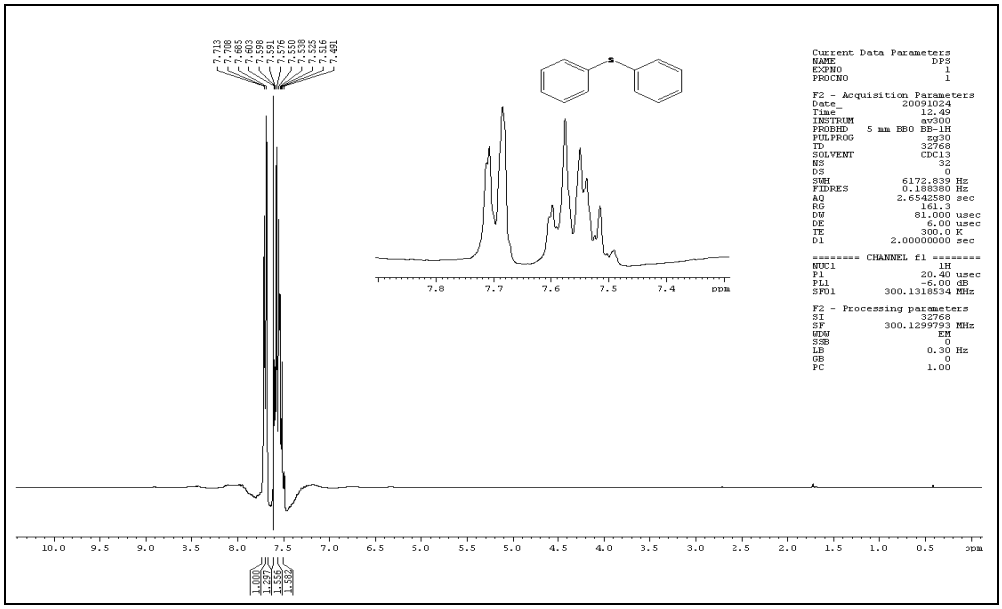


Figure 39. [1]H-NMR spectrum of diphenyl sulfide (Table 2 Entry1).

Figure 40. [13]C-NMR spectrum of diphenyl sulfide (Table 2, Entry1).

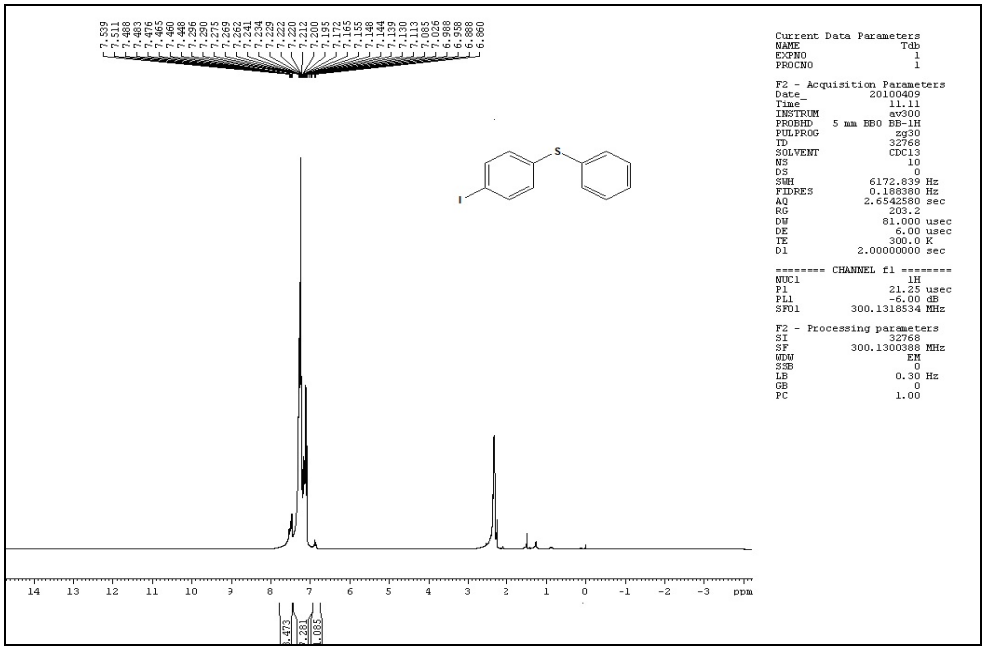


Figure 42. ^{1}H-NMR spectrum of 4-iodo diphenyl sulfide (Table 2, Entry 2).

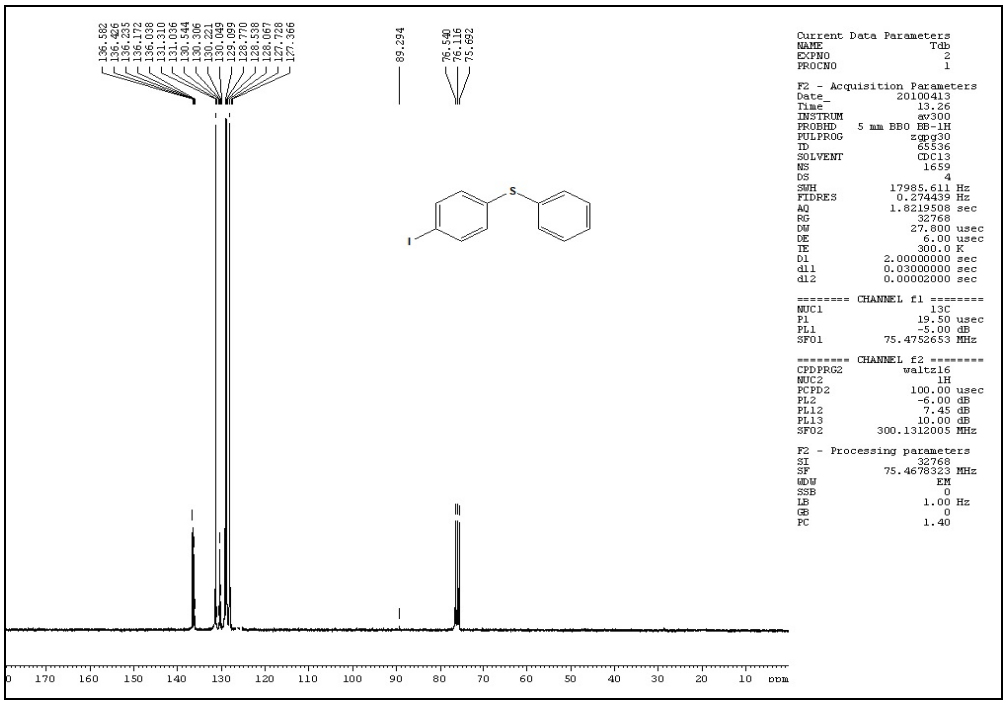


Figure 43. ^{13}C-NMR spectrum of 4-iodo diphenyl sulfide (Table 2, Entry 2).

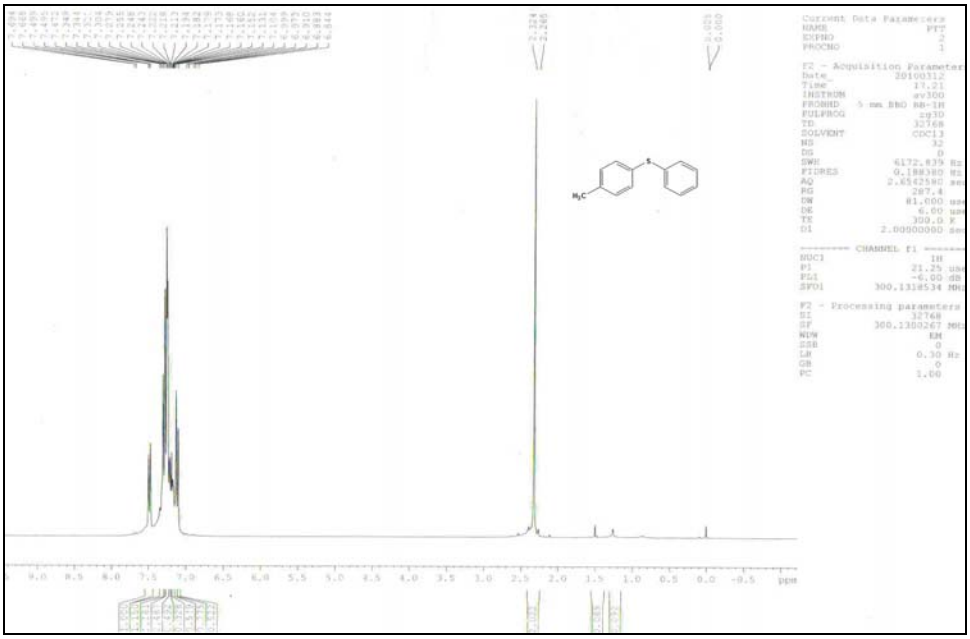


Figure 44. ^{1}H-NMR spectrum of 4-tolylphenyl sulfide (Table 2, Entry 3).

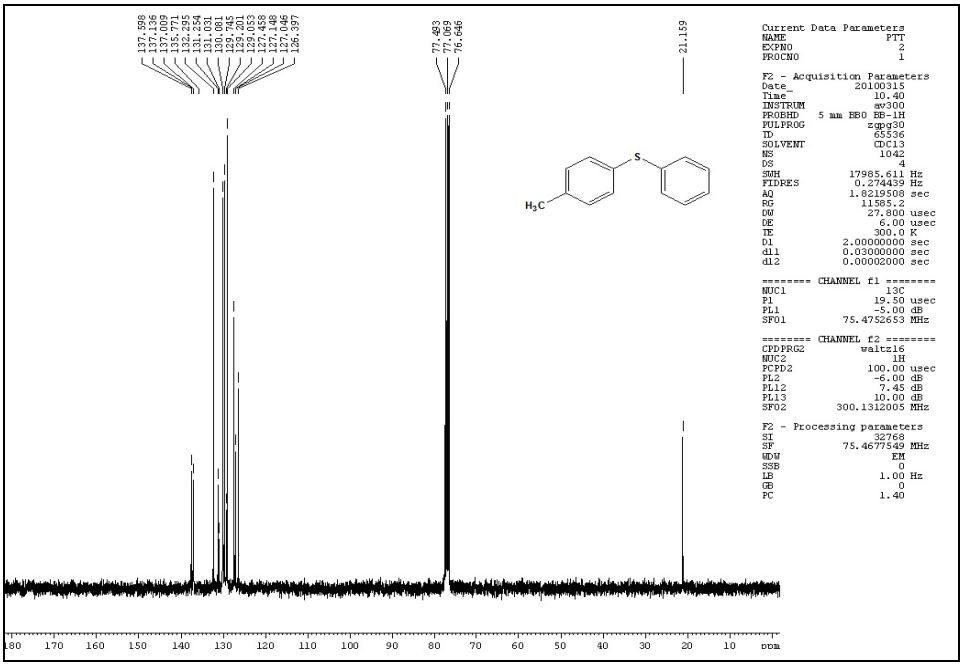


Figure 45. ^{1}H-NMR spectrum of 4-tolylphenyl sulfide (Table 2, Entry 3).

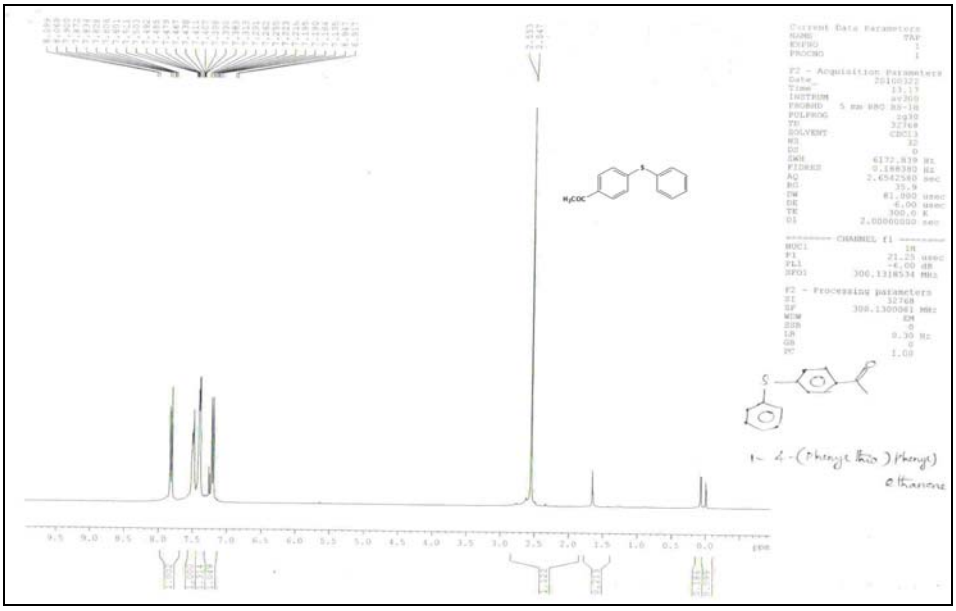


Figure 46. *^{1}H-NMR spectrum of 4-acetyl diphenyl sulfide (Table 2 Entry 4)*

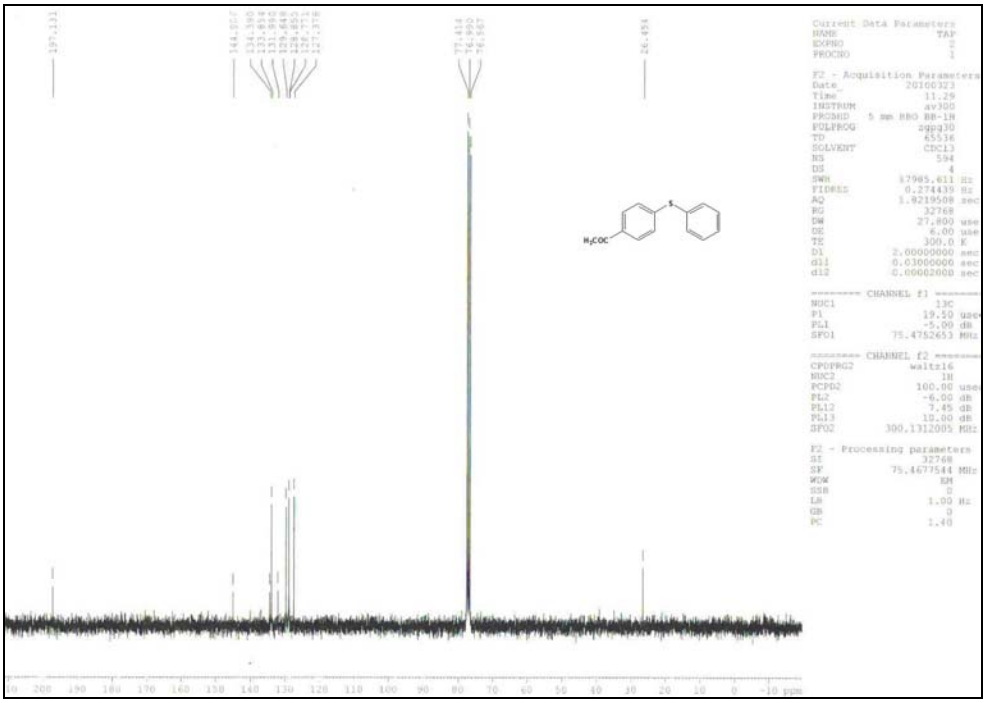


Figure 47. *^{13}C-NMR spectrum of 4-acetyl diphenyl sulfide (Table 2, Entry 4).*

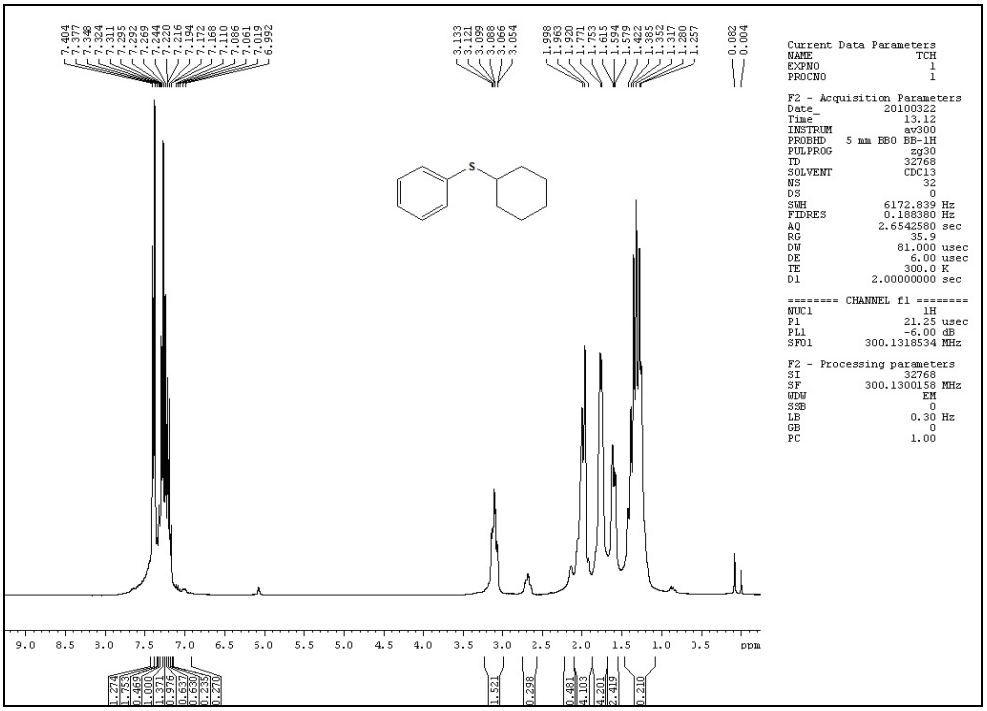


Figure 48. ^{1}H-NMR spectrum of cyclohexyl phenyl sulfide (Table 2 Entry 8).

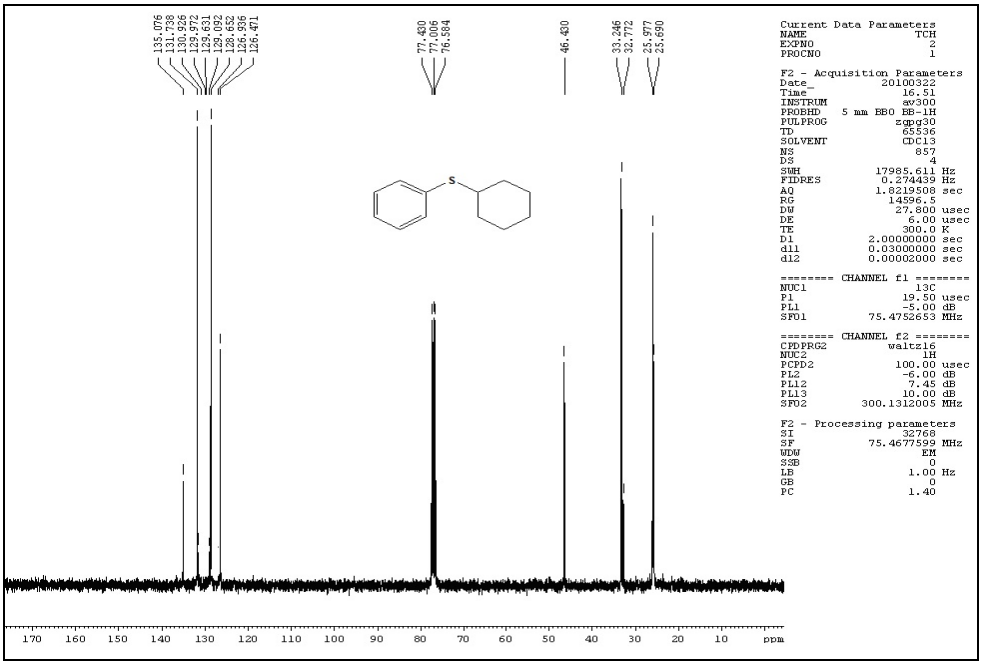


Figure 49. ^{13}C-NMR spectrum of cyclohexyl phenyl sulfide (Table 2 Entry 8).

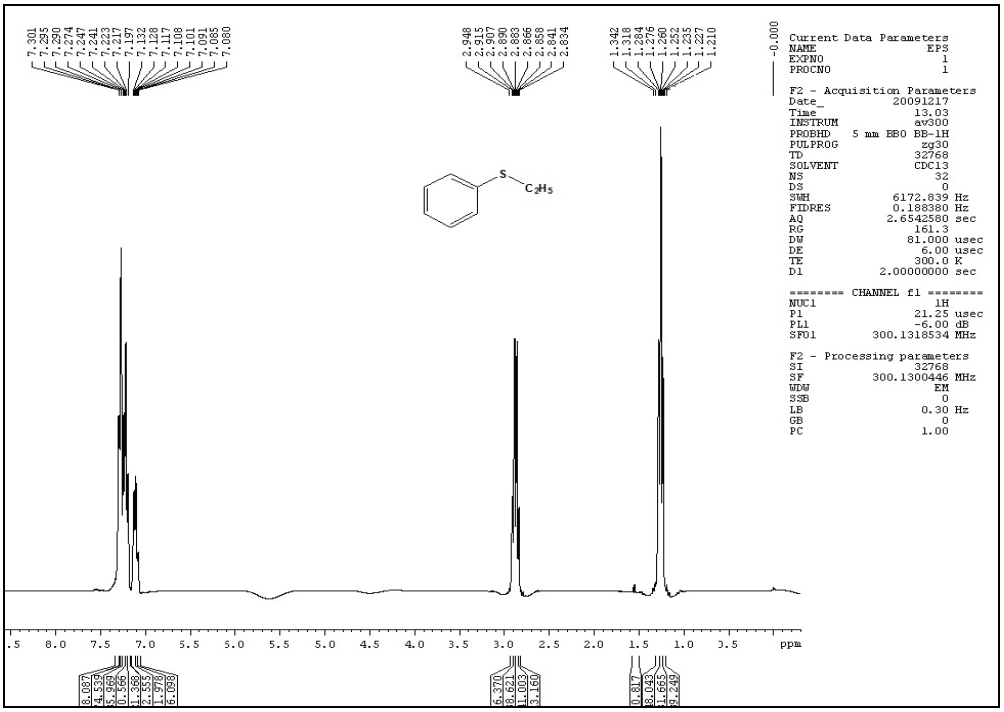


Figure 50. ^{1}H-NMR spectrum of n-ethyl thiobenzene (Table 2, Entry 10).

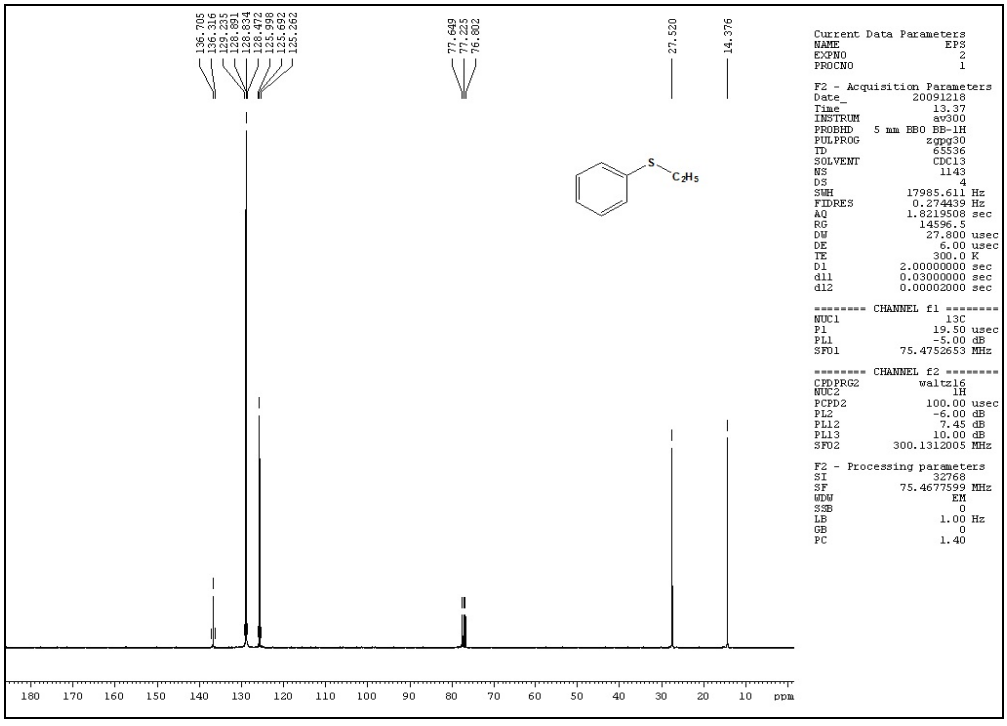


Figure 51. ^{13}C-NMR spectrum of n-ethyl thiobenzene (Table 2, Entry 10).

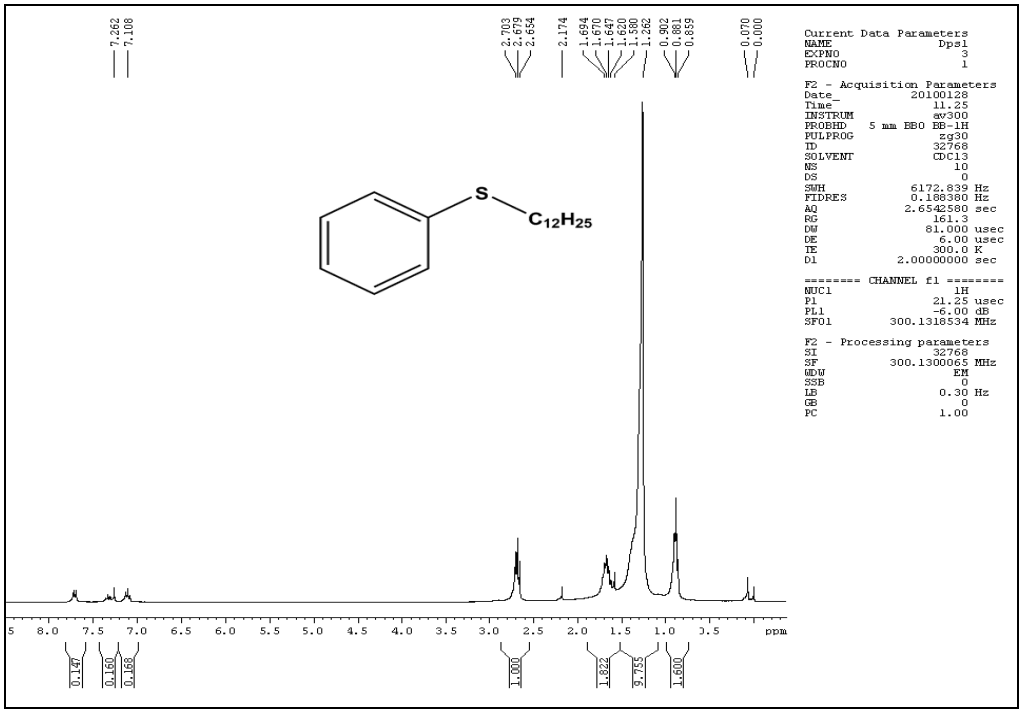


Figure 52. ^{1}H-NMR spectrum of dodecyl phenyl sulfide (Table 2, Entry 11).

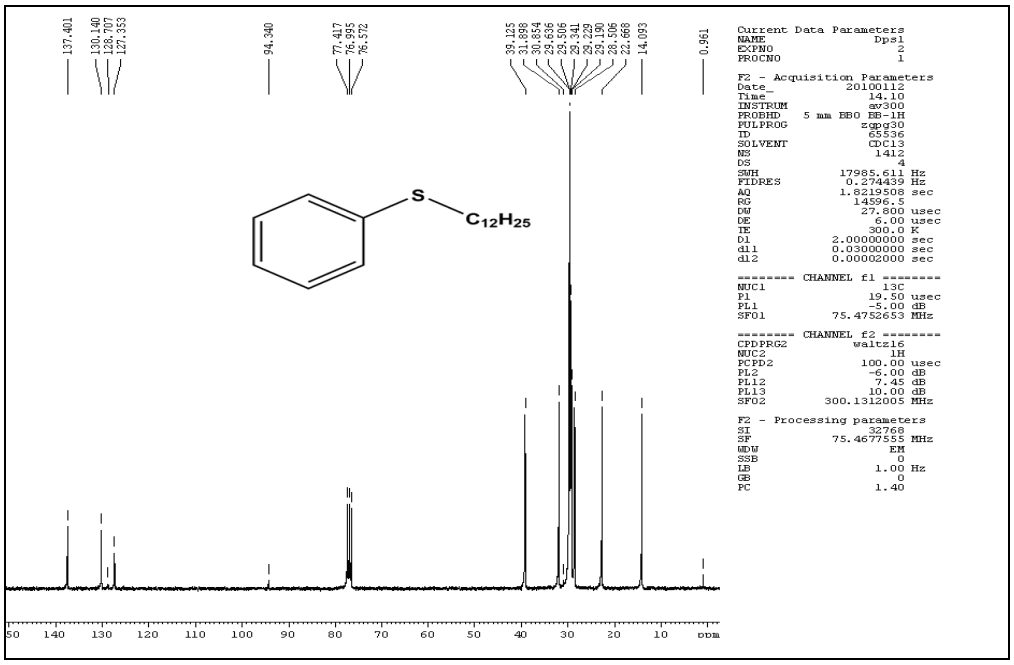


Figure 53. ^{13}C-NMR spectrum of dodecyl phenyl sulfide (Table 2, Entry 11).

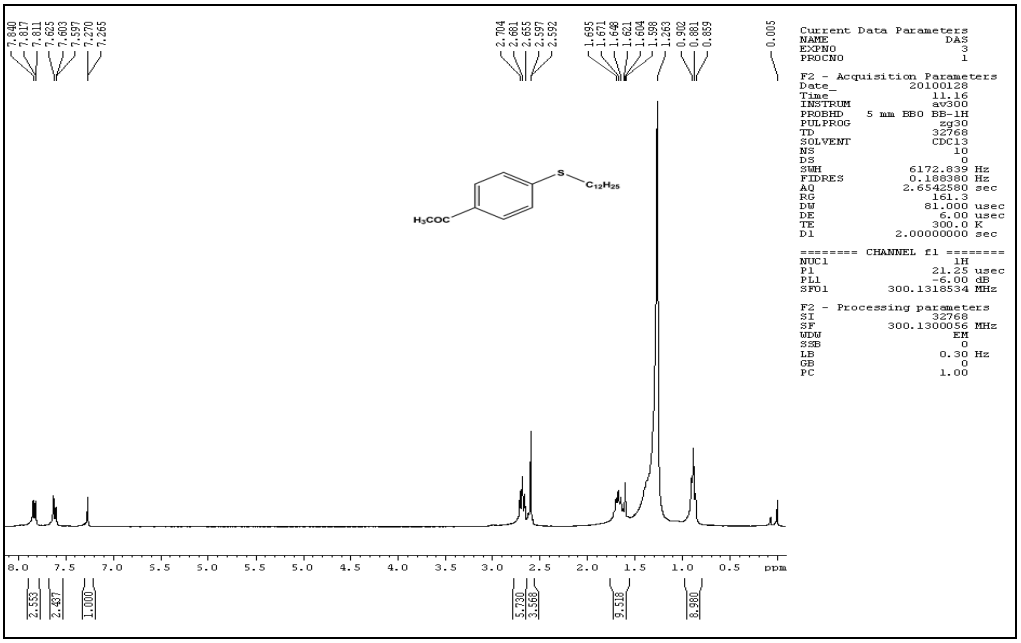


Figure 54. ^{1}H-NMR spectrum of 1-(4-(dodecylthio)phenyl)ethanone (Table 2, Entry 12).

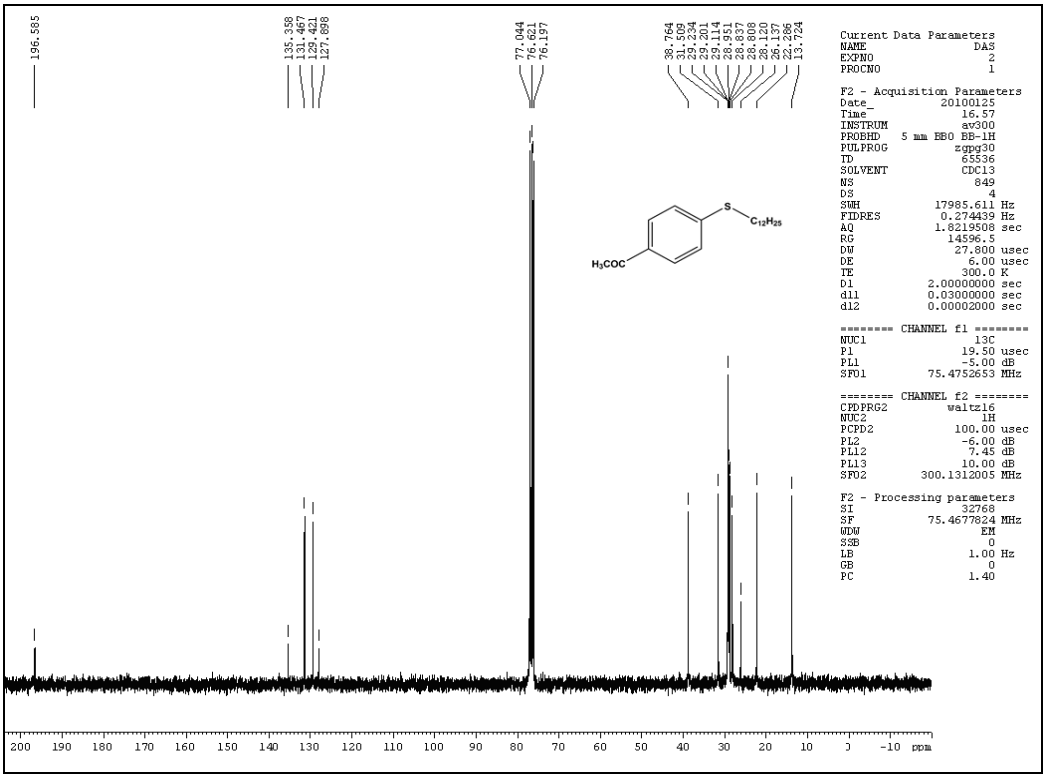


Figure 55. ^{13}C-NMR spectrum of 1-(4-(dodecylthio)phenyl)ethanone (Table 2, Entry 12).

S26. References

1 W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.* 1968, **26**, 62.

2 S. Cheng, X. Wang and S. Y. Chen, *Top Catal.,* 2009, **52**, 681.

3 Y. Kobayashi and T. Sakuraba, *Colloids and Surf., A* 2008, **317**, 756.

4 B. Sreedhar, P. Radhika, B. Neelima and N. Hebalkar, *Chem. Asian J*, 2008, **3**, 1163.

5 S. G. Alvamrez and M. T. Alvarez, *Synthesis* 1997, 413.

6 L. Campbell-Verduyn, P. H. Elsinga, L. Mirfeizi, R. A. Dierckx and B. L. Feringa, *Org. Biomol. Chem.,* 2008, **6**, 3461.

7 S. D. Gonzlez, A. Correa, L. Cavallo and S. P. Nolan, *Chem. Eur. J.* 2006, **12**, 7558.

8 Z. Gonda and Z. Novak, *Dalton Trans.,* 2010, **39**, 726.

9 F. Alonso, Y. Moglie, G. Radivoy, and M. Yus, *Eur. J. Org. Chem.,* 2010, 1875.

10 S.-N. Chen, W-Y. Wu, Fu-Yu Tsai, *Green Chem.*, 2009, **11**, 269.

11 T. Miao, L. Wang, *Synthesis* 2008, 363

12 (a) S. D. Gonzlez, A. Correa, L. Cavallo, S. P. Nolan, *Chem. Eur. J.* 2006, **12**, 7558. (b) P. Appukkuttan, W. Dehaen, V. V. Fokin, E. V. Eycken, *Org.Lett.,* 2004, **6**, 4223.

13 P. Li, L. Wang, Y. Zhang, *Tetrahedron* 2008, **64**, 10825.

14 K. Kacprzak, *Synlett* 2005, 943.

15 B. R. Buckley, S. Dann, E. H. Heaney, *Chem. Eur. J,* 2010, **16**, 6278.

16 (a) L. Rout, T. K. Sen, T. Punniyamurthy, *Angew. Chem. Int. Ed.,* 2007, **46**, 5583. (b) B. C. Ranu, A. Saha, R. Jana, *Adv. Synth. Catal.,* 2007, **349**, 2690.(c) V. P. Reddy, A. Vijay Kumar, K. Swapna, K. Rama Rao, *Org. Lett.,* 2009, **11**, 1697. (d) S. Bhadra, B. Sreedhar, B. C. Ranu, *Adv. Synth. Catal.,* 2009, **351**, 2369. (e) B. C. Ranu, K. Chattopadhyay, L. Adak, A. Saha, S. Bhadra, R. Dey, D. Saha, *Pure Appl. Chem.,* 2009, **81**, 2337.

17 (a) Y.-J. Chen, H.-H. Chen, *Org.Lett.* 2006, **8**, 5609. (b) W.-Y. Wu, J.-C. Wang, F.-Y. Tsai, *Green Chem.,* 2009, **11**, 326.

18 T. Itoh, T. Mase, *Org.Lett.* 2004, **6**, 4587.

19 Z. Jiang, J. She, X. Lin, *Adv. Syn. Catal.,* **2009**, *351*, 2558.