Electronic Supplementary Material (ESI) for RSC Advances.

An efficient facile one-pot multicomponent synthesis of diazepines and benzimidazole using magnetically retrievable Fe_3O_4 nanocatalyst under solvent free condition

Ramen Jamatia[a], Mithu Saha[a], Amarta Kumar Pal[a]*

[a]*Department of Chemistry, North-Eastern Hill University, Mawlai Campus, Shillong 793022, India.*

Tel: +91 364 2307930 ext 2636, E-mail: amartya_pal22@yahoo.com, akpal@nehu.ac.in

Fax: +91 364 2550076

Table of content **Page No.**

1. Experimental Section 2-3
2. **Table S.I. 1.** X-ray crystallography data for compound **3b** 4
3. Spectral data of the compound **3a-h** and **5a-f** 5-10
4. **Fig. S.I. 1.** I.R spectra of Fe_3O_4 NPs 11
5. ^1H & ^{13}C NMR Spectra of compounds **3a-h** and **5a-f** 12-30

1. Experimental Section

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on Spectrum BX FT-IR, Perkin Elmer (υ_{max} in cm^{-1}) on KBr disks. ^{1}H NMR and ^{13}C NMR (400/300 MHz and 100/75 MHz respectively) spectra were recorded on Bruker Avance II-400 and 300 spectrometer in $CDCl_3$ (chemical shifts in δ with TMS as internal standard). Mass spectra were recorded on Waters ZQ-4000. Transmission Electron Microscope (TEM) was recorded on JEOL JSM 100CX. Scanning electron microscope (SEM) was recorded on JSM-6360 (JEOL). XRD was recorded on Bruker D8 XRD instrument SWAX .CHN were recorded on CHN-OS analyzer (Perkin Elmer 2400, Series II). Silica gel G (E-mark, India) was used for TLC. Hexane refers to the fraction boiling between 60 ^{o}C and 80 ^{o}C. Absorption spectra were recorded in Lambda25 (PerkinElmer Inc.) spectrometers.

X-ray crystallography

The X-ray diffraction data were collected at 293 K with Mo Kα radiation (λ = 0.71073 Å) using Agilent Xcalibur (Eos, Gemini) diffractometer equipped with a graphite monochromator. The software used for data collection CrysAlis PRO (Agilent, 2011), data reduction CrysAlis PRO and cell refinement CrysAlis PRO. The structure were solved by direct methods and refined by full-matrix least-squares calculation using SHELXS-97 and SHELXL-97 (CCDC 933681). Absorption spectra were recorded in Lambda25 (PerkinElmer Inc.) spectrometers.

General procedure for 3a-h.

Fe_3O_4 (6 mol %) was added to a mixture of *o*-phenylenediamine **1** (1mmol) and acetophenone **2a-h** (2.2 mmol) and heated at 80 ^{o}C under solvent free condition. After completion of the reaction, monitored by TLC, the reaction mixture was cooled to room temperature and dissolved in 10 mL ethyl acetate. The Fe_3O_4 NPs was then separated by external magnetic field. The

separated Fe_3O_4 NPs was washed with ethyl acetate and dried. Then it was used for another set of reaction under similar condition. The reaction mixture was then washed with water (3 ×5mL), brine (1 × 5 mL) and dried over anhydrous Na_2SO_4. The reaction mass was concentrated under vacuum and the pure product was obtained by purification through column chromatography using ethyl acetate: hexane as eluent.

General procedure for 5a-h.

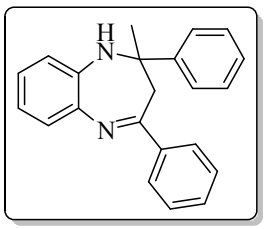
In a round bottom flask, *o*-phenylenediamine **1** (1mmol) and aldehyde **4a-f** (2.2 mmol), was taken and Fe_3O_4 NPs (6 mol %) was added. The reaction was carried out at 80 ^oC under solvent free condition. After completion (TLC), the reaction mixture was cooled to room temperature and dissolved in 10 mL ethyl acetate. The Fe_3O_4 NPs was then separated by external magnetic field and washed with ethyl acetate and dried. The separated Fe_3O_4 NPs was then used for another set of reaction under similar condition. The reaction mixture was then washed with water (3 × 5mL), brine (1 × 5 mL) and dried over anhydrous Na_2SO_4. The reaction mass was concentrated under vacuum. The crude mixture was purified by column chromatography using ethyl acetate: hexane as eluent.

Table S.I.1. X-ray crystallography data for compound **3b**.

Empirical formula	$C_{22}H_{18}Cl_2N_2$
Formula weight	381.28
Crystal system	Monoclinic
Space group	$P2_1/n$
a(Å)	14.0976(12)
b(Å)	10.0170(7)
c(Å)	14.9301(13)
α(°)	90.00
β(°)	116.746(11)
γ(°)	90.00
Volume (Å)	1882.8(3)
ρ (calculated) (g cm^{-3})	1.345
T(K)	293(2)
Absorption coefficient (mm^{-1})	0.353
Total reflection collected	9789
Independent reflection	4403
Refine parameter	336
θ range (°)	6.6 to 58.22
Final R Indexes [1>=2σ(I)]	R1 = 0.0548, wR2 = 0.1174
Final R indexes [all data]	R1 = 0.0979, wR2 = 0.1375
Goodness-of-fit on F^2	1.018

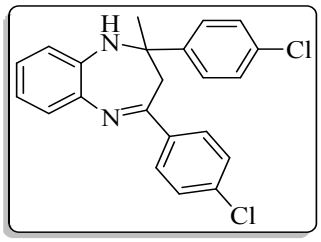
SPECTRAL DATA

1. Compound 3a



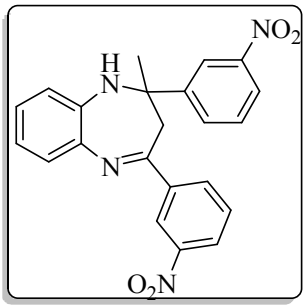
White solid. IR (KBr): 3281, 3066, 1635, 1468 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.53 (t, *J* = 7.6 Hz, 4H), 7.26-7.08 (m, 7H), 7.03-6.95 (m, 2H), 6.78-6.76 (dd, *J* = 7.6, 1.2 Hz, 1H), 3.4 (brs, 1H), 3.08 (d, *J* = 13.2 Hz, 1H), 2.92 (d, *J* = 13.2 Hz, 1H), 1.68 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.7, 147.6, 140.1, 139.5, 138.1, 129.7, 128.6, 128.3, 128.0, 127.1, 126.3, 125.4, 121.6, 121.4, 73.7, 43.1, 29.8. ESI- MS: *m/z* 313 $[M + H]^+$. Anal. Cacld for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.47; H, 6.39; N, 8.80.

2. Compound 3b



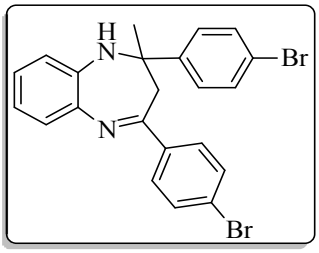
Yellow solid. IR (KBr): 3496, 3025, 1686, 1493, 751 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.51-7.45 (m, 4H), 7.30-7.25 (m, 1H), 7.20-7.17 (m, 4H), 7.07-7.01 (m, 2H), 6.82-6.76 (m, 1H), 3.41 (s, 1H), 3.07 (d, *J* = 13.3 Hz, 1H), 2.88 (d, *J* = 13.5, 1H), 1.71 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.1, 145.7, 139.8, 137.6, 136.1, 133.0, 128.5, 128.38, 128.31, 127.0, 126.6, 122.0, 121.5, 73.5, 42.9, 29.7. ESI- MS: *m/z* 381, 383 $[M + H]^+$. Anal. Cacld for $C_{22}H_{18}Cl_2N_2$: C, 69.30; H, 4.76; N, 7.35. Found: C, 69.53; H, 4.64; N, 7.44.

3. Compound 3c



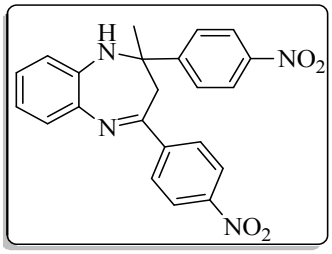
Orange solid. IR (KBr): 3278, 3088, 1604, 1473, 1349 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.47 (s, 1H), 8.16 (s, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.99-7.96 (m, 3H), 7.42-7.32 (m, 3H), 7.18-7.08 (m, 2H), 6.93-6.91 (dd, *J* = 7.5 Hz, 1.2 Hz, 1H), 3.55 (s, 1H), 3.28 (d, *J* = 13.5 Hz, 1H), 3.02 (d, *J* = 13.5, 1H), 1.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 164.1, 149.0, 148.1, 148.0, 140.4, 139.2, 137.1, 132.5, 131.9, 129.5, 129.2, 128.9, 127.4, 124.4, 122.4, 122.2, 121.6, 120.8, 74.1, 42.8, 29.9. ESI- MS: *m/z* 403 $[M + H]^+$. Anal. Cacld for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.61; H, 4.62; N, 13.80.

4. Compound 3d



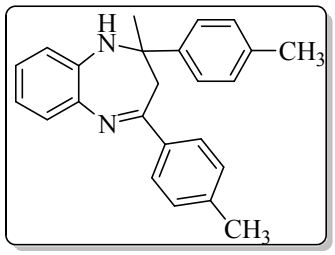
Pale brown solid. IR (KBr): 3370, 2979 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.46-7.27 (m, 9H), 7.11-7.01 (m, 2H), 6.83-6.80 (m, 1H), 3.42 (s, 1H), 3.07 (d, *J* = 13.2 Hz, 1H), 2.89 (d, *J* = 13.2 Hz, 1H), 1.72 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.2, 146.5, 140.0, 138.3, 137.7, 131.5, 131.4, 128.8, 128.7, 127.6, 126.8, 124.7, 122.2, 121.7, 121.4, 73.7, 43.0, 29.9. ESI-MS: *m/z* 469, 471 $[M + H]^+$. Anal. Cacld for $C_{22}H_{18}Br_2N_2$: C, 56.20; H, 3.86; N, 5.96. Found: C, 56.12; H, 3.88; N, 5.77.

5. Compound 3e



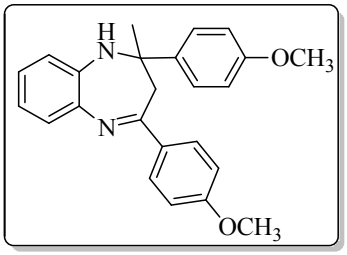
Orange solid. IR (KBr): 3310, 3071, 1606, 1348 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.00 (d, *J* = 8.8 Hz, 4H), 7.69 (d, *J* = 8.8 Hz), 7.62 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.11-7.09 (m, 1H), 7.08-7.00 (m, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 3.58 (s, 1H), 3.24 (d, *J* = 13.2 Hz, 1H), 2.95 (d, *J* = 13.6, 1H), 1.77 (s, 3H). ESI- MS: *m/z* 403 $[M + H]^+$. Anal. Cacld for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.38; H, 4.46; N, 13.79.

6. Compound 3f



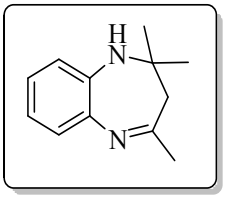
Orange solid. IR (KBr): 3319, 3023, 1600, 1463 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.50-6.74 (m, 12H), 3.44 (brs, 1H), 3.02 (d, *J* = 13.2 Hz, 1H), 2.92 (d, *J* = 13.2 Hz, 1H), 2.26 (s, 3H), 2.33 (s, 3H), 1.65 (s, 3H). ESI- MS: *m/z* 341 $[M + H]^+$. Anal. Cacld for $C_{24}H_{24}N_2$: C, 84.67; H, 7.11; N, 8.23. Found: C, 84.71; H, 6.97; N, 8.44.

7. **Compound 3g**



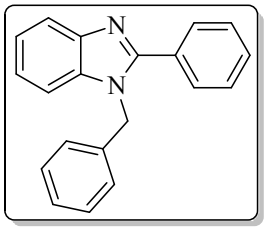
Orange solid. IR (KBr): 3321, 1606, 1467, 1245, 1030 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.60 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.30-7.26 (m, 1H), 7.05-7.02 (m, 2H), 6.81-6.74 (m, 5H), 3.79 (s, 3H), 3.75 (s, 3H), 3.41 (s, 1H), 3.06 (d, *J* = 12.9 Hz, 1H), 2.92 (d, *J* = 13.2 Hz, 1H), 1.71 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.3, 161.2, 158.7, 140.8, 140.2, 138.2, 132.4, 129.0, 128.3, 126.7, 126.0, 121.9, 121.7, 113.7, 113.5, 73.5, 55.49, 55.47, 43.0, 29.9. ESI-MS: *m/z* 373 $[M + H]^+$. Anal. Cacld for $C_{24}H_{24}N_2O_2$: C, 77.39; H, 6.49; N, 7.52. Found: C, 77.57; H, 6.37; N, 7.64.

8. Compound 3h



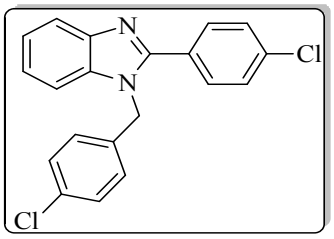
Pale brown solid. IR (KBr): 3283, 1467, 1639 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.14-7.11 (m, 1H), 7.01-6.97 (m, 2H), 6.75-6.72 (m, 1H), 2.97 (brs, 1H), 2.37 (s, 3H), 2.22 (s, 2H), 1.35 (s, 6H). ESI- MS: *m/z* 189 $[M + H]^+$. Anal Cacld for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.82; H, 8.70; N, 14.83.

9. Compound 5a



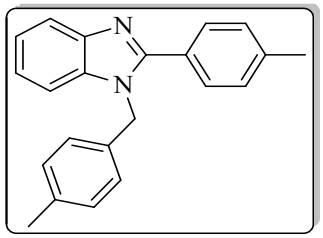
Pale white solid. IR (KBr): 3083, 3029, 2957, 1611, 1276 cm^{-1}. NMR ($CDCl_3$, 300 MHz): δ = 7.83 (d, *J* = 8 Hz, 1H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.40-7.05 (m, 9H), 5.40 (s, 2H). ESI-MS: *m/z* 285 $[M + H]^+$. Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.37; H, 5.55; N, 9.68.

10. Compound 5b



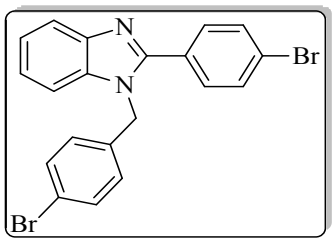
Pale white solid. IR (KBr): 3075, 2928, 2852, 1611, 1250, 744 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.29-7.19 (m, 4H), 7.14 (d, *J* = 8 Hz, 1H), 6.96 (d, *J* = 8 Hz, 2H), 5.33 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.8, 142.9, 136.3, 135.8, 134.6, 133.8, 130.4, 129.3, 129.1, 128.2, 127.2, 123.5, 123.1, 120.1, 110.3, 47.8. ESI- MS: *m/z* 353, 355 $[M + H]^+$. Anal. Calcd for $C_{20}H_{14}Cl_2N_2$: C, 68.00; H, 3.99; N, 7.93. Found: C, 68.21; H, 4.03; N, 7.82.

11. Compound 5c



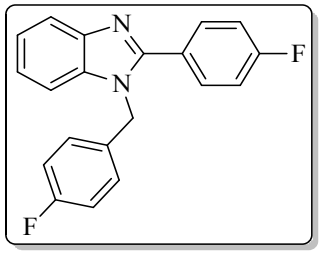
White solid. IR (KBr): 3073, 2924, 2857, 1607, 1281 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.32-7.20 (m, 5H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 5.41 (s, 2H), 2.40 (s, 3H), 2.33 (s, 3H). ESI- MS: *m/z* 313 $[M + H]^+$. Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.78; H, 6.31; N, 8.70.

12. Compound 5d



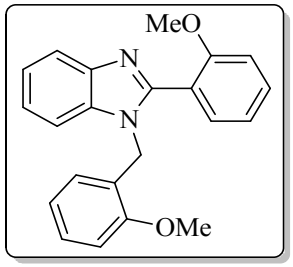
Pale white solid. IR (KBr): 3072, 2928, 2851, 1610, 1251, 617 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 8 Hz, 1H), 7.60-7.56 (m, 2H), 7.29-7.07 (m, 5H), 6.97-6.93 (m, 4H), 5.34 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.8, 142.9, 135.8, 135.1, 132.3, 132.1, 130.6, 128.7, 127.5, 124.7, 123.5, 123.1, 121.9, 120.1, 110.3, 47.8. ESI- MS: *m/z* 441, 443 $[M + H]^+$. Anal. Calcd for $C_{20}H_{14}Br_2N_2$: C, 54.33; H, 3.19; N, 6.34. Found: C, 54.25; H, 3.25; N, 6.17.

13. Compound 5e



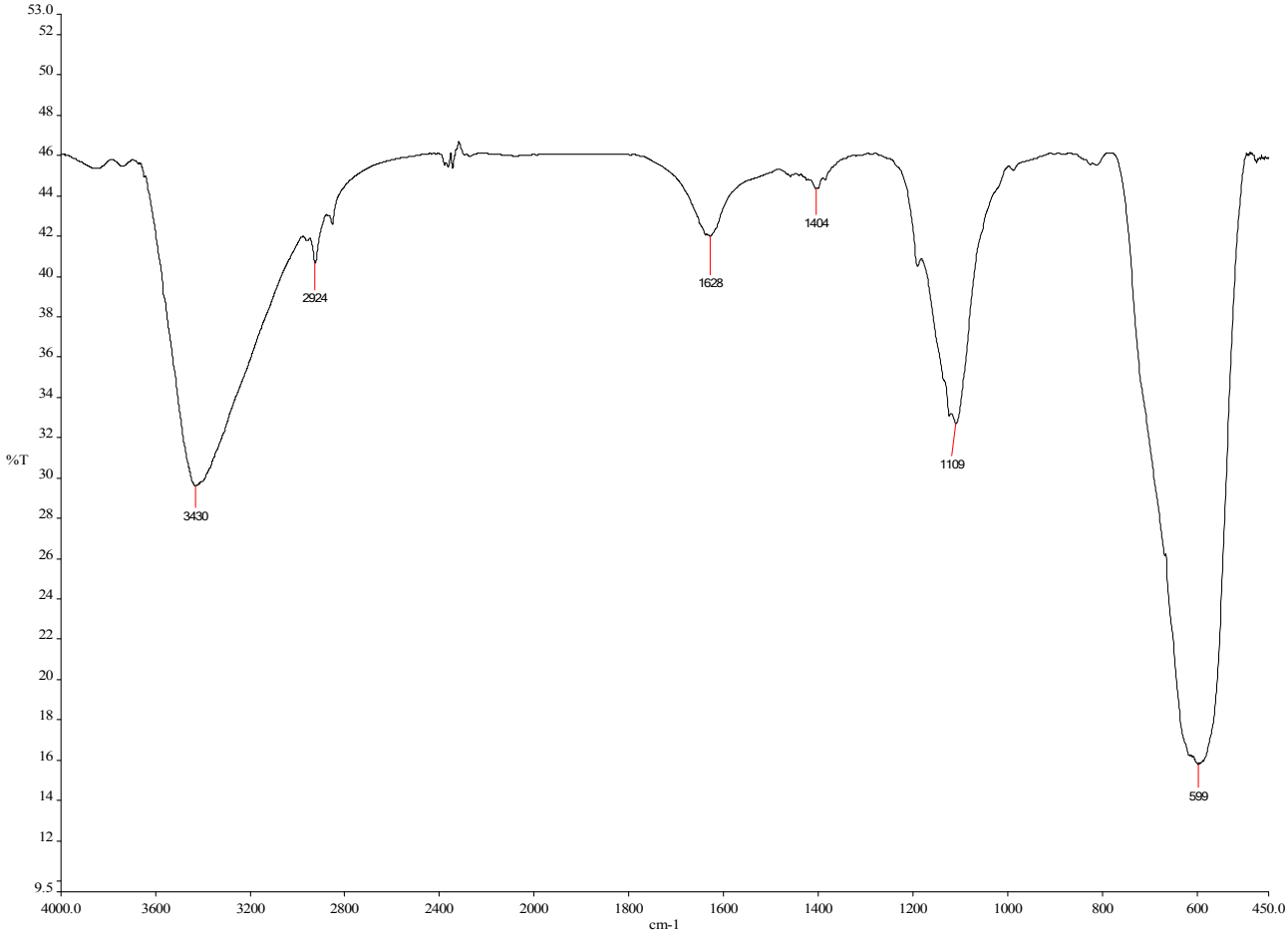
Yellow solid. IR (KBr): 3050, 2923, 2871, 1624, 1243 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.83 (d, *J* = 8 Hz, 1H), 7.55(d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.30-7.19 (m, 2H), 7.14 (d, *J* = 8 Hz, 1H), 6.90 (d, *J* = 8 Hz, 2H), 5.32 (s, 2H). ESI- MS: *m/z* 321 $[M + H]^+$ Anal. Calcd for $C_{20}H_{14}F_2N_2$: C, 74.99; H, 4.41; N, 8.75. Found: C, 75.23; H, 4.29; N, 8.72.

14. Compound 5f



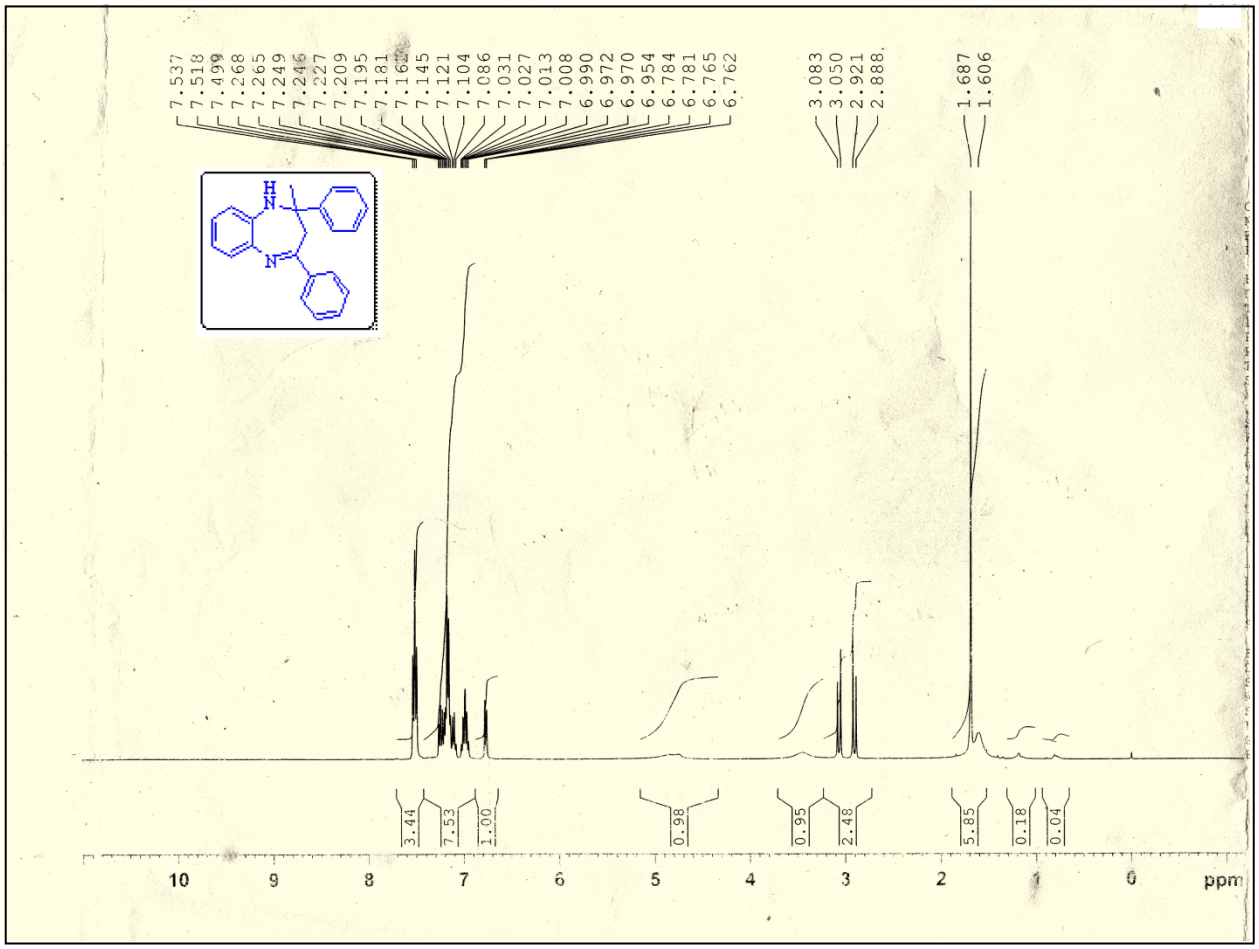
Pale white solid. IR (KBr): 3063, 2936, 2838, 1604, 1246, 1110 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.80 (d, *J* = 8 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.22-7.10 (m, 4H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 8 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.63 (d, J = 7.2 Hz, 1H), 5.17 (s, 2H), 3.70 (s, 3H), 3.52 (s, 3H). ESI- MS: *m/z* 345 $[M + H]^+$. Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.83; H, 5.81; N, 7.93.

Fig. S.I. I.R Spectra of Fe_3O_4 NPs.

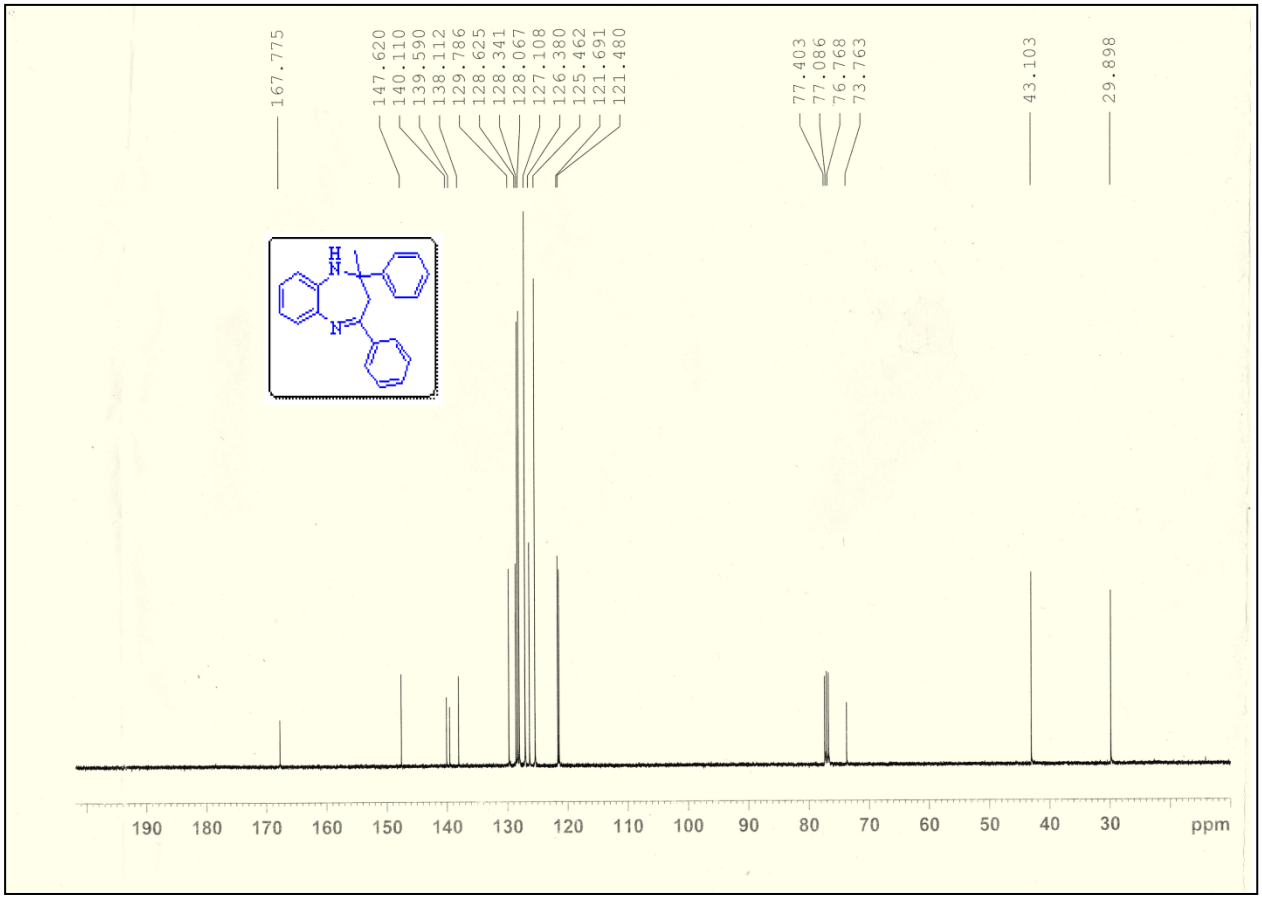


^{1}H & ^{13}C NMR Spectra of compounds 3a-h and 5a-f

1. Compound 3a

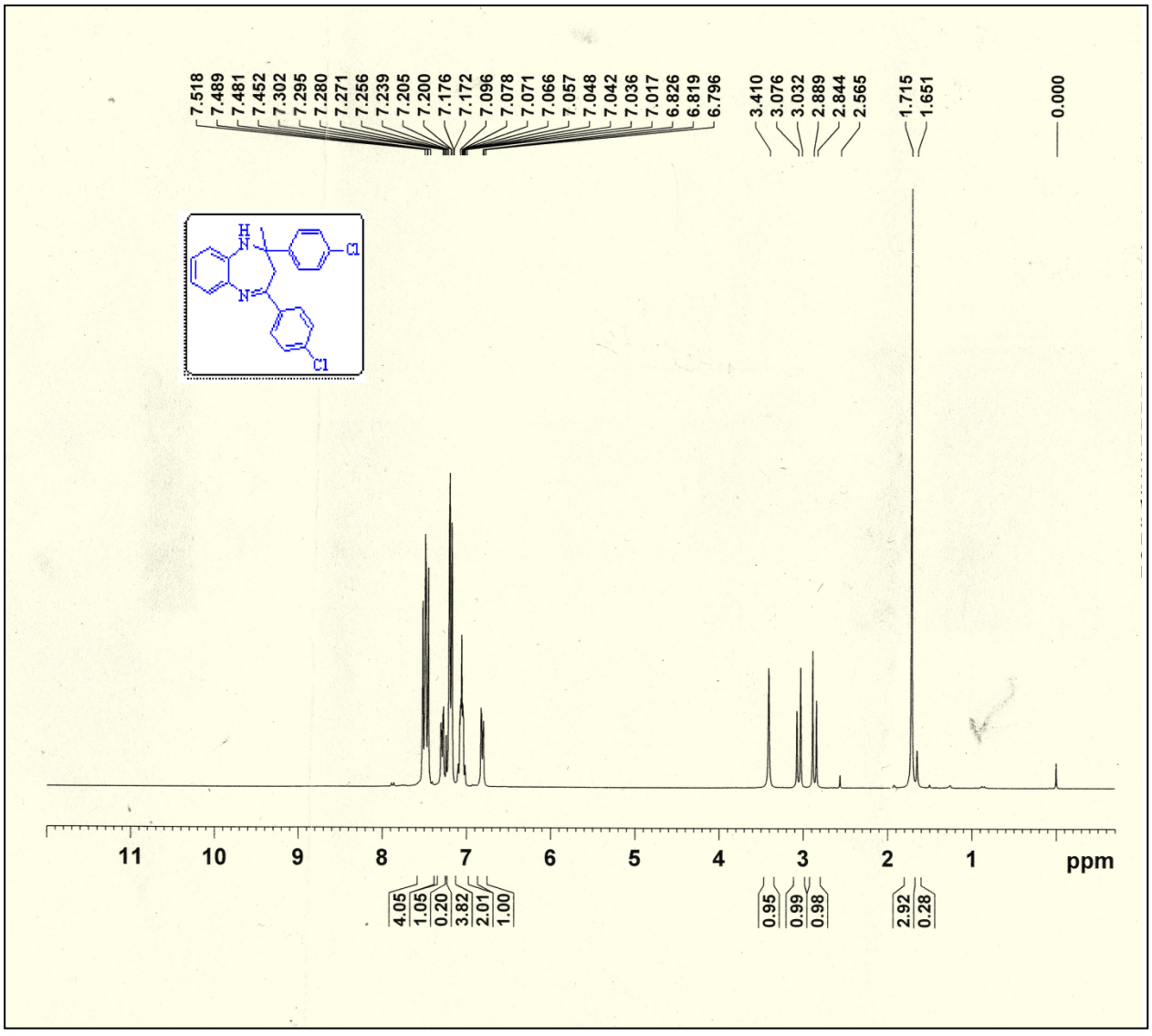


^{1}H NMR Spectra of Compound 3a



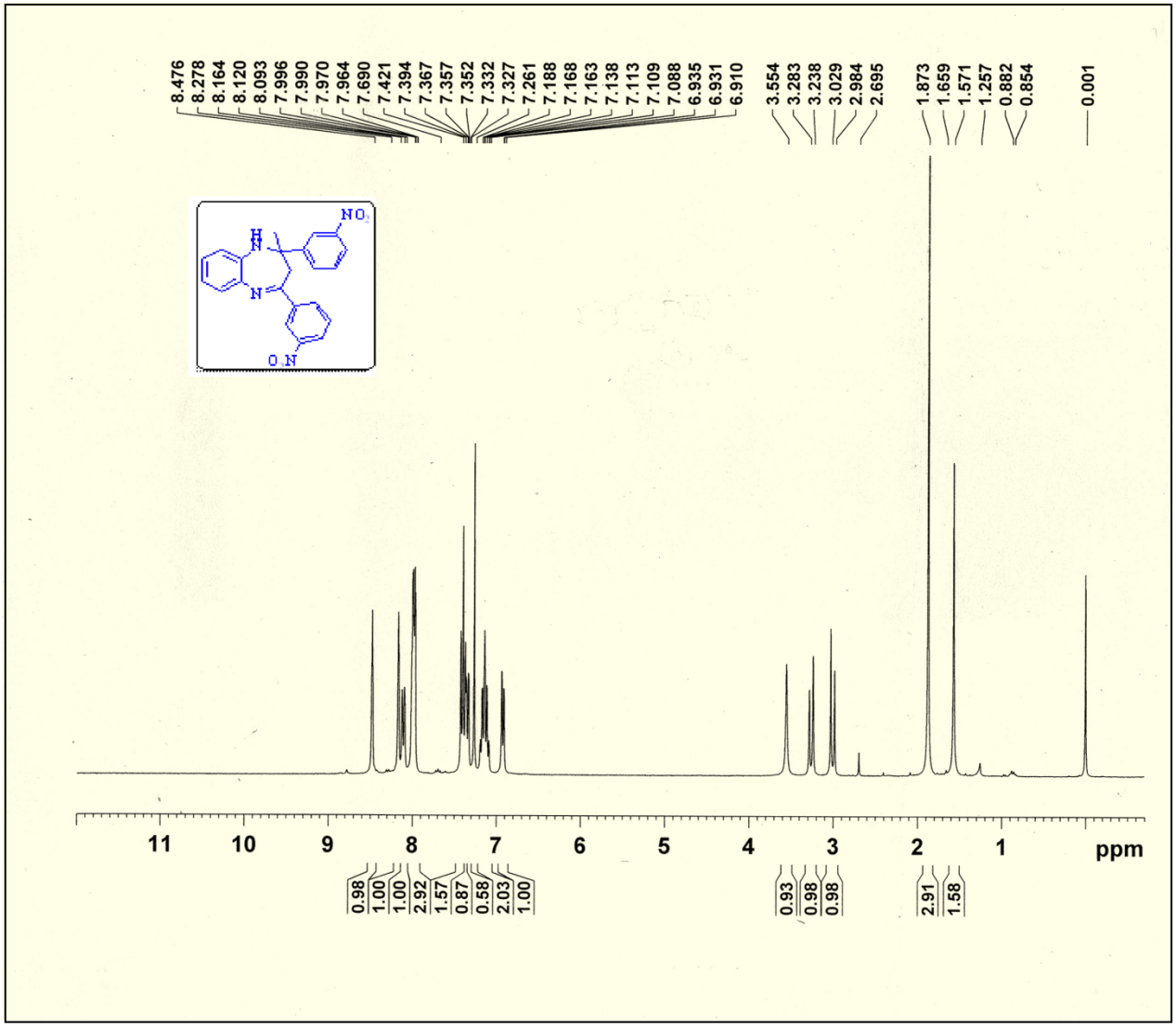
^{13}C NMR Spectra of Compound 3a

2. Compound 3b



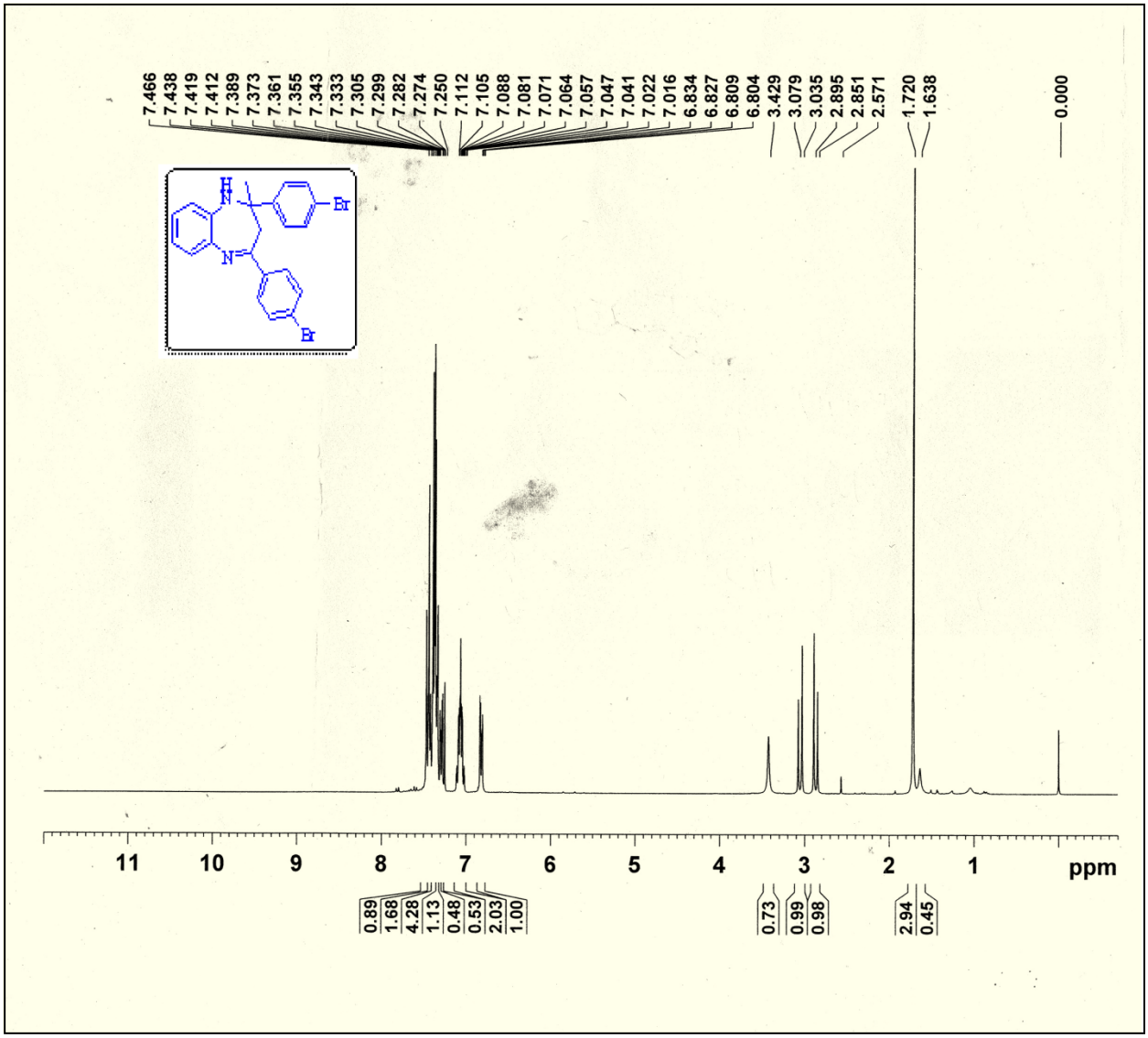
^{1}H NMR Spectra of Compound 3b

3. Compound 3c

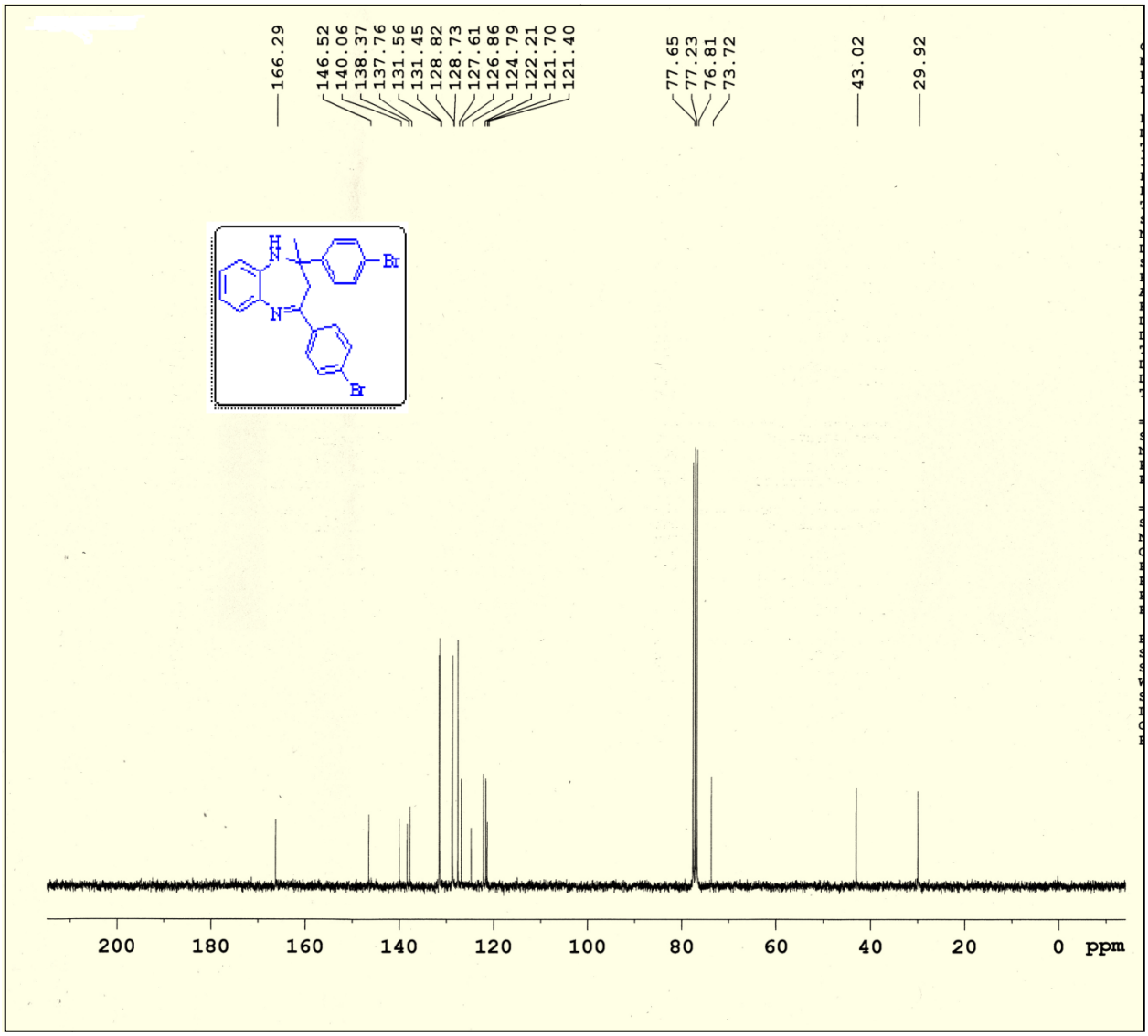


^{1}H NMR Spectra of Compound 3c

4. Compound 3d

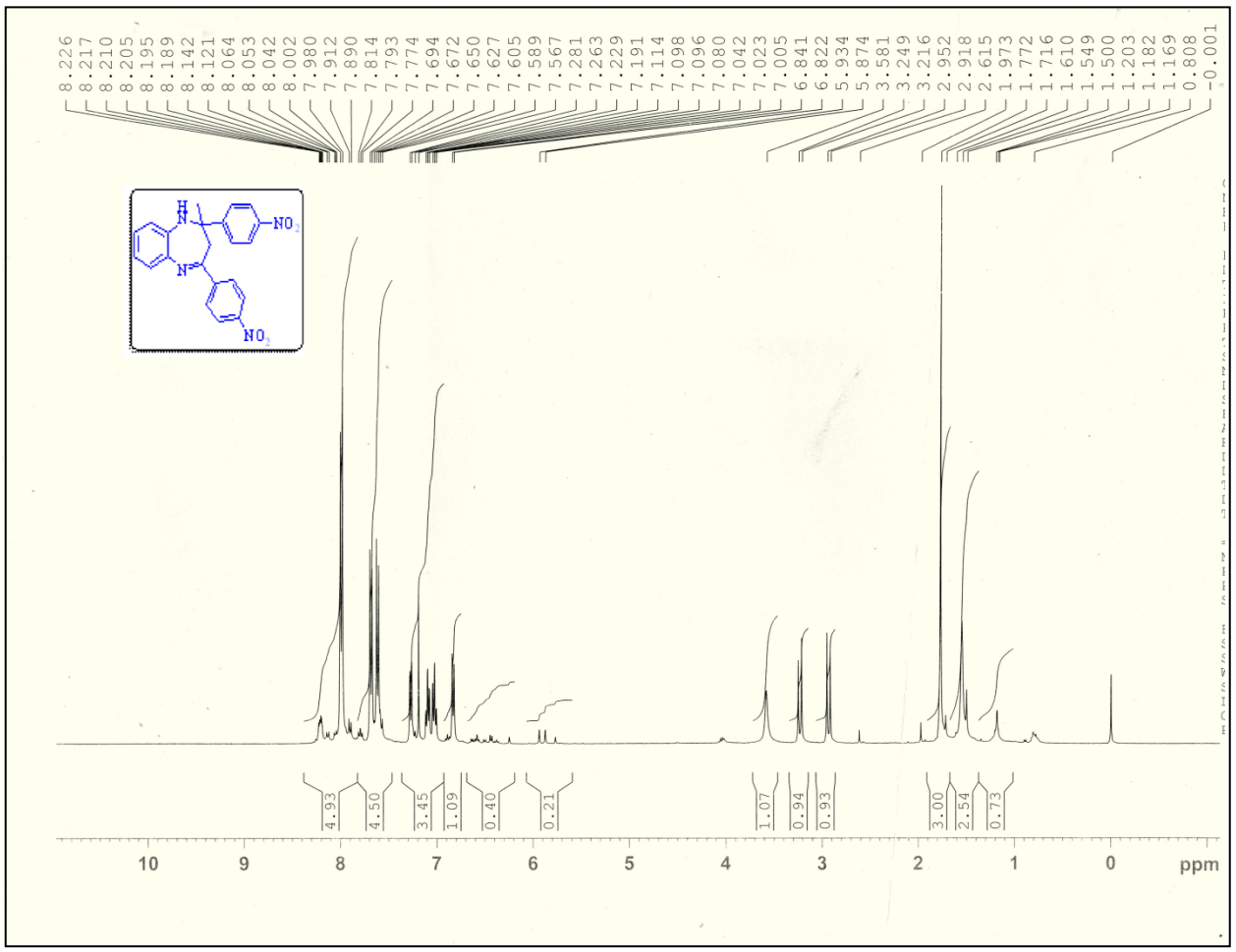


^{1}H NMR Spectra of Compound 3d


166.29
146.52
140.06
138.37
137.76
131.56
131.45
128.82
128.73
127.61
126.86
124.79
122.21
121.70
121.40
77.65
77.23
76.81
73.72
43.02
29.92
H
N
N
Br
Br
200
180
160
140
120
100
80
60
40
20
0
ppm

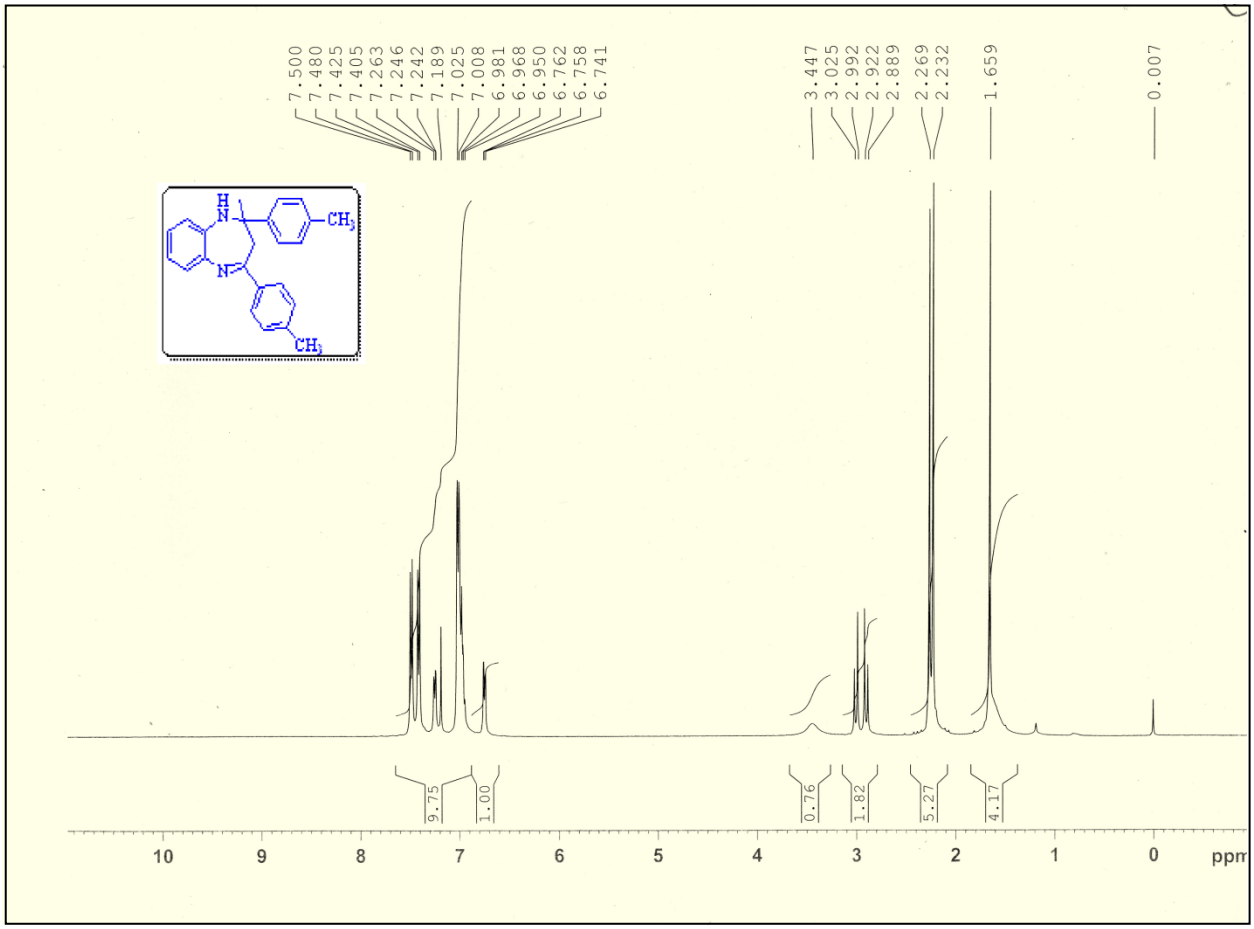
^{13}C NMR Spectra of Compound 3d

5. Compound 3e



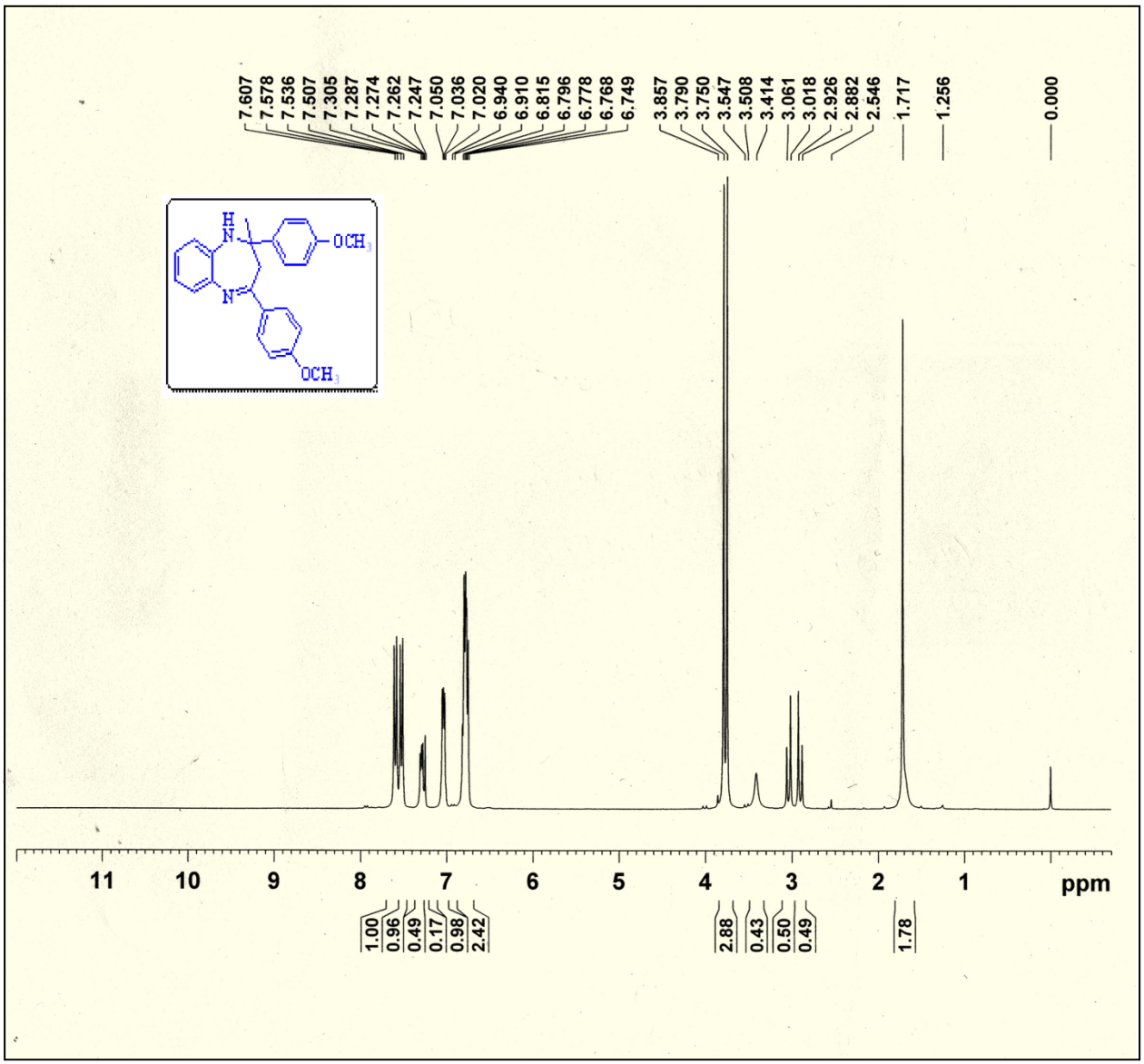
^{1}H NMR Spectra of Compound 3e

6. Compound 3f

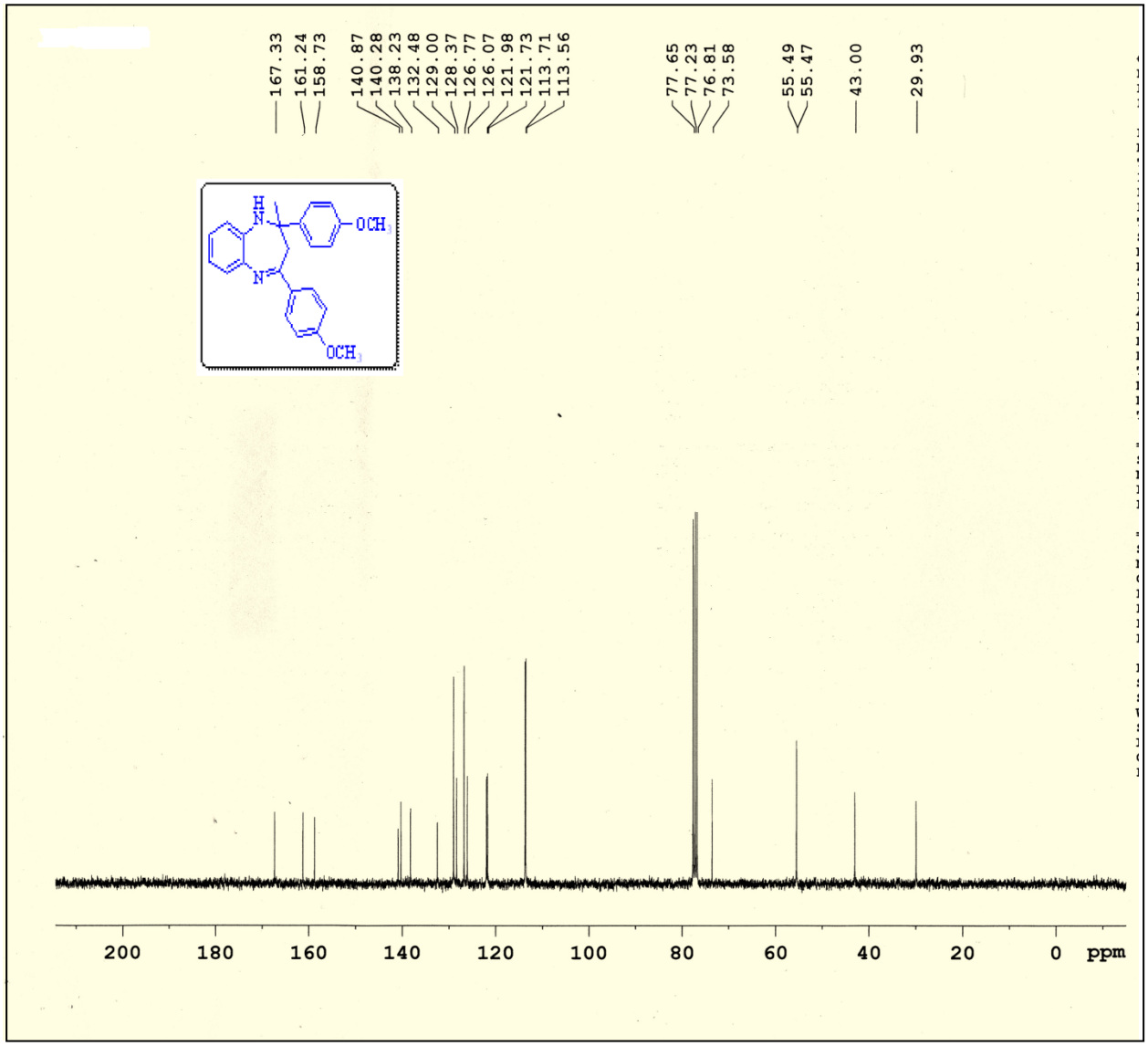


^{1}H NMR Spectra of Compound 3f

7. Compound 3g

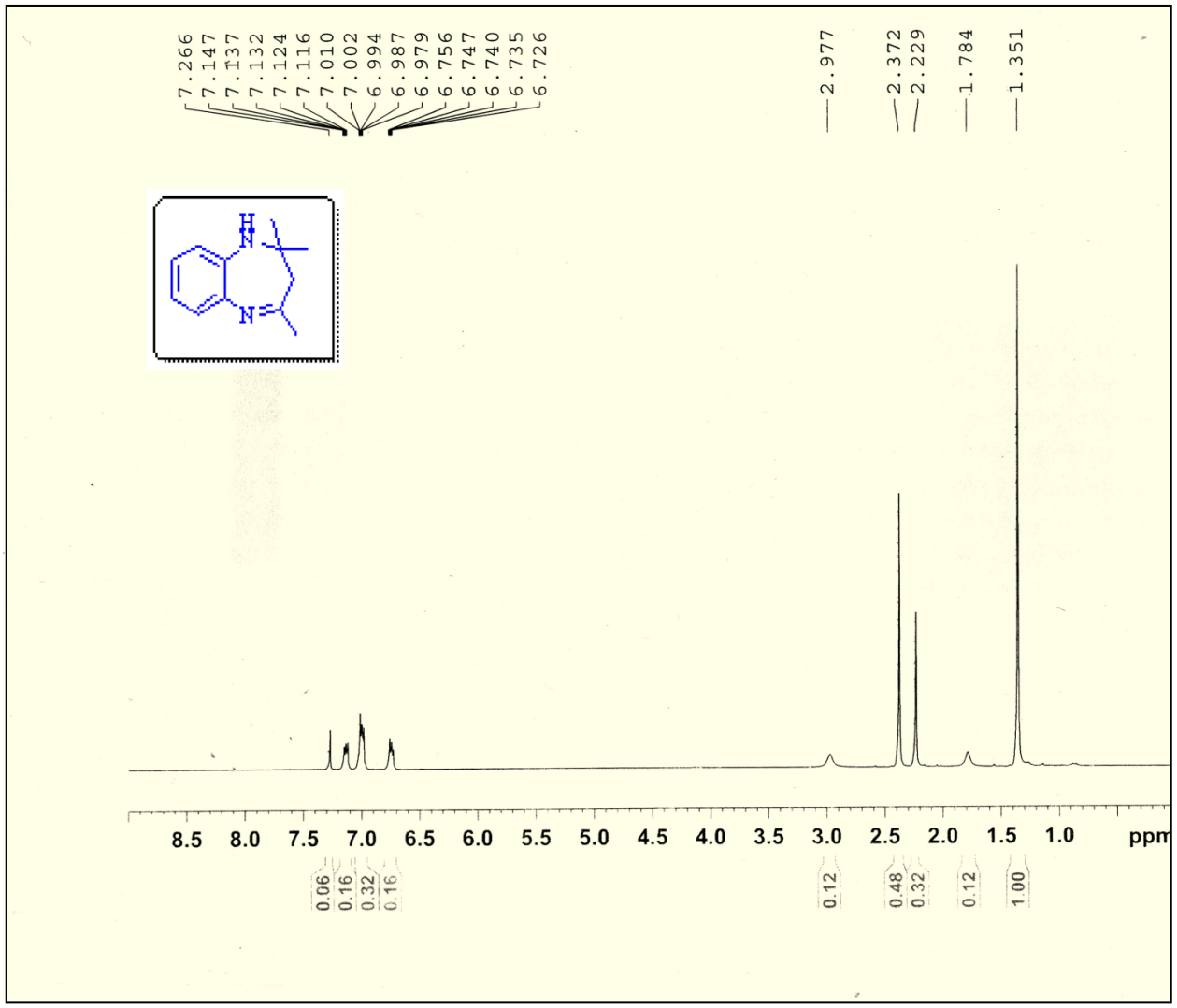


^{1}H NMR Spectra of Compound 3g



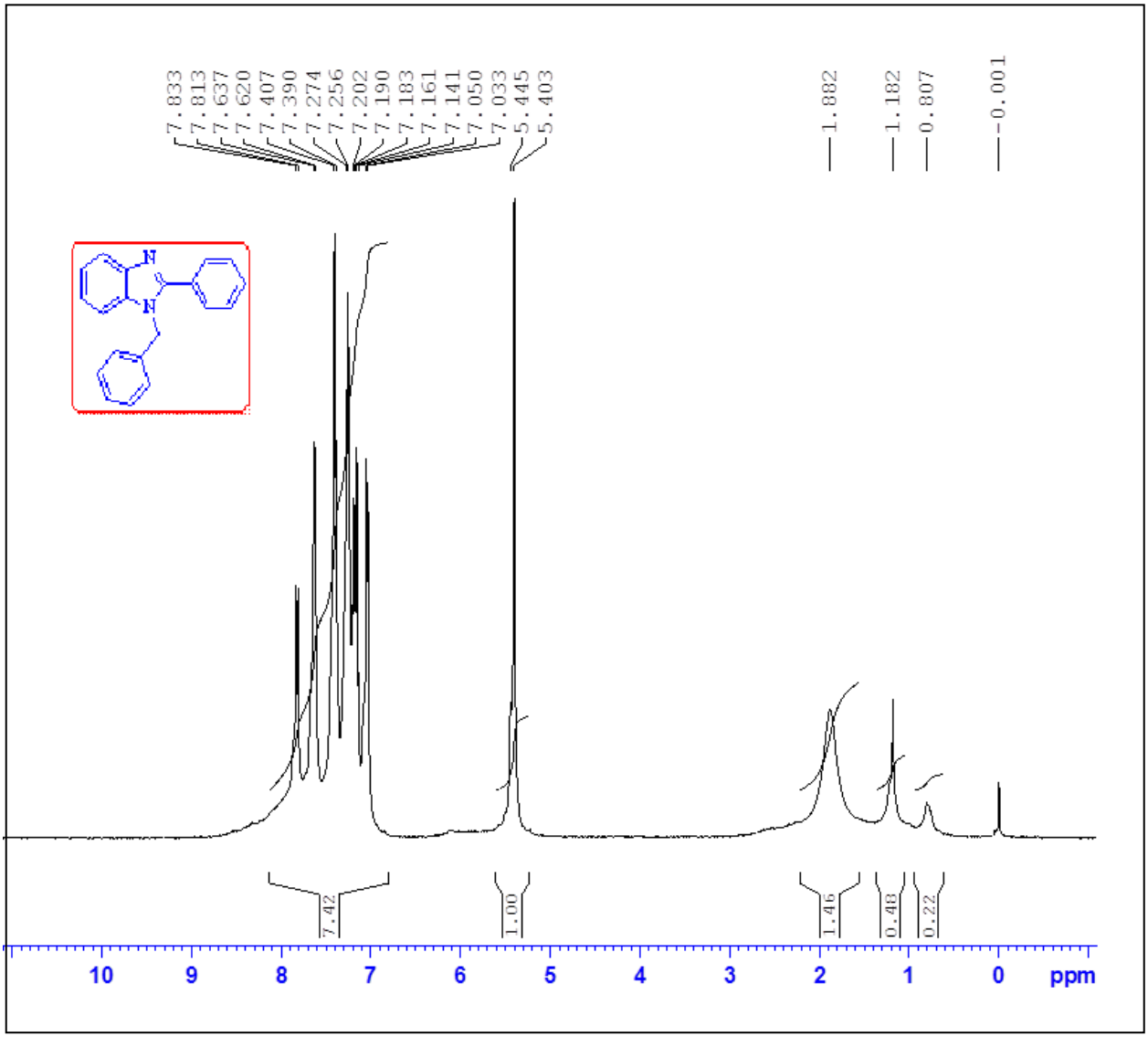
^{13}C NMR Spectra of Compound 3g

8. Compound 3h



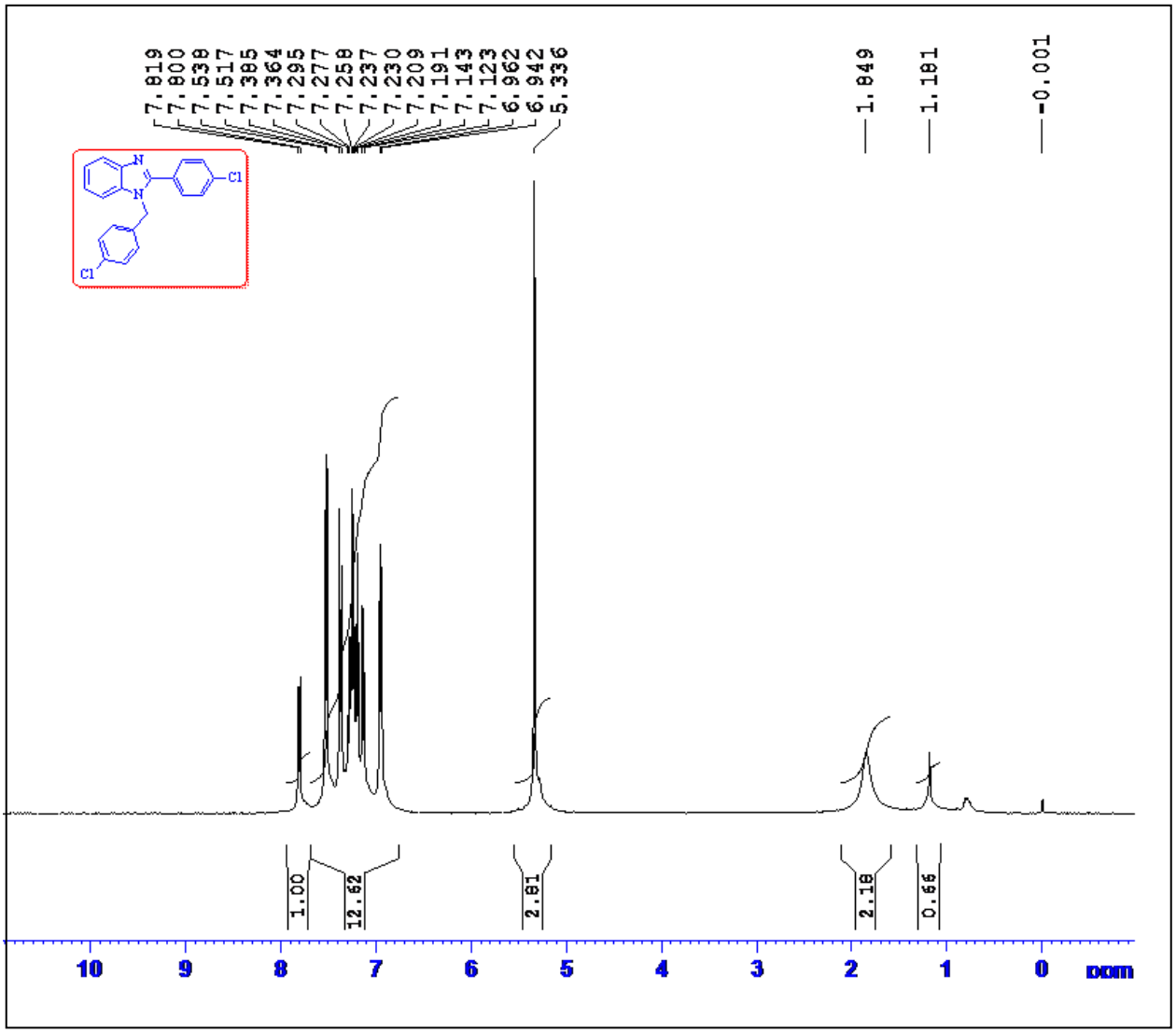
^{1}H NMR Spectra of Compound 3h

9. Compound 5a

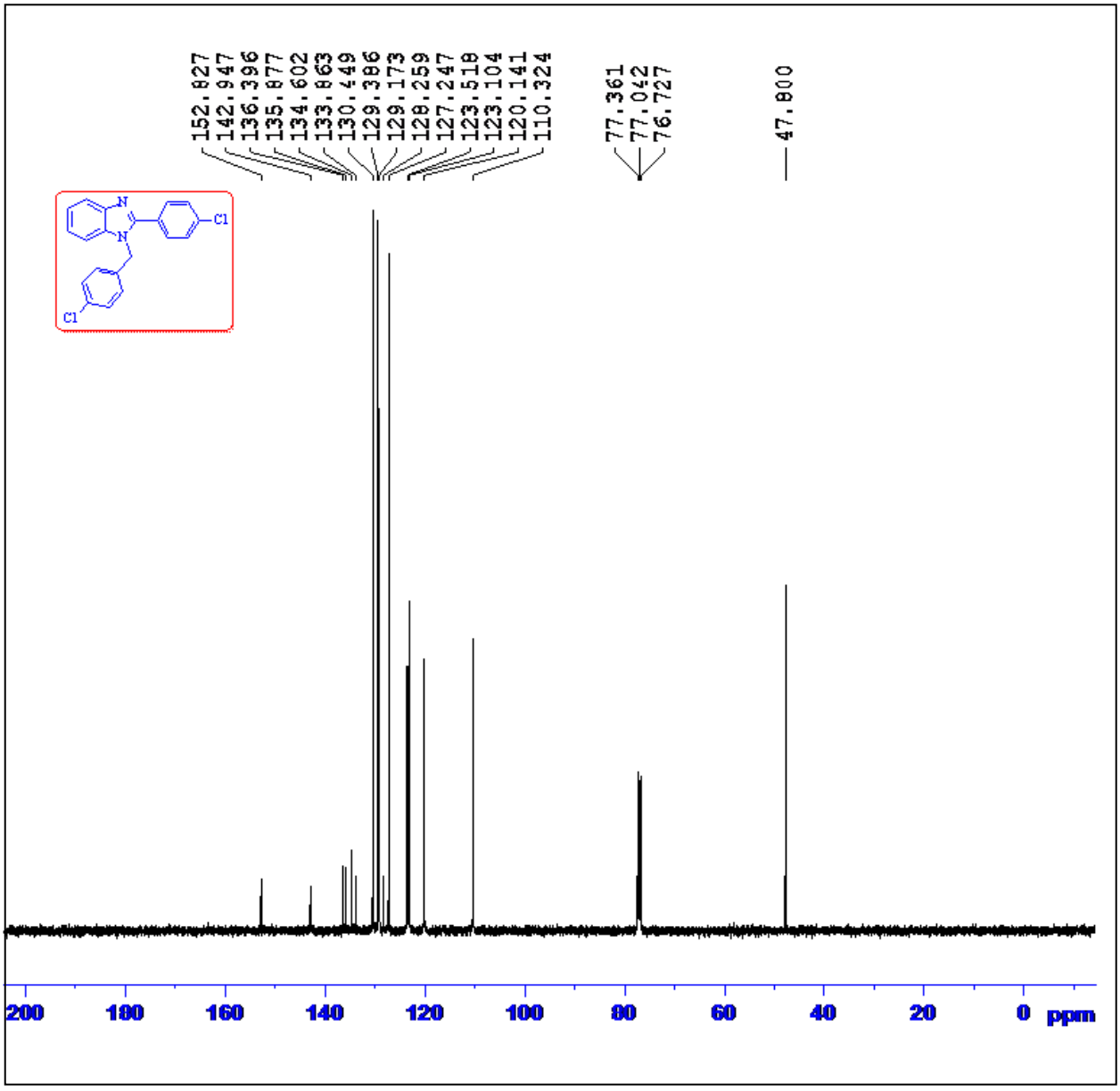


^{1}H NMR Spectra of Compound 5a

10. Compound 5b

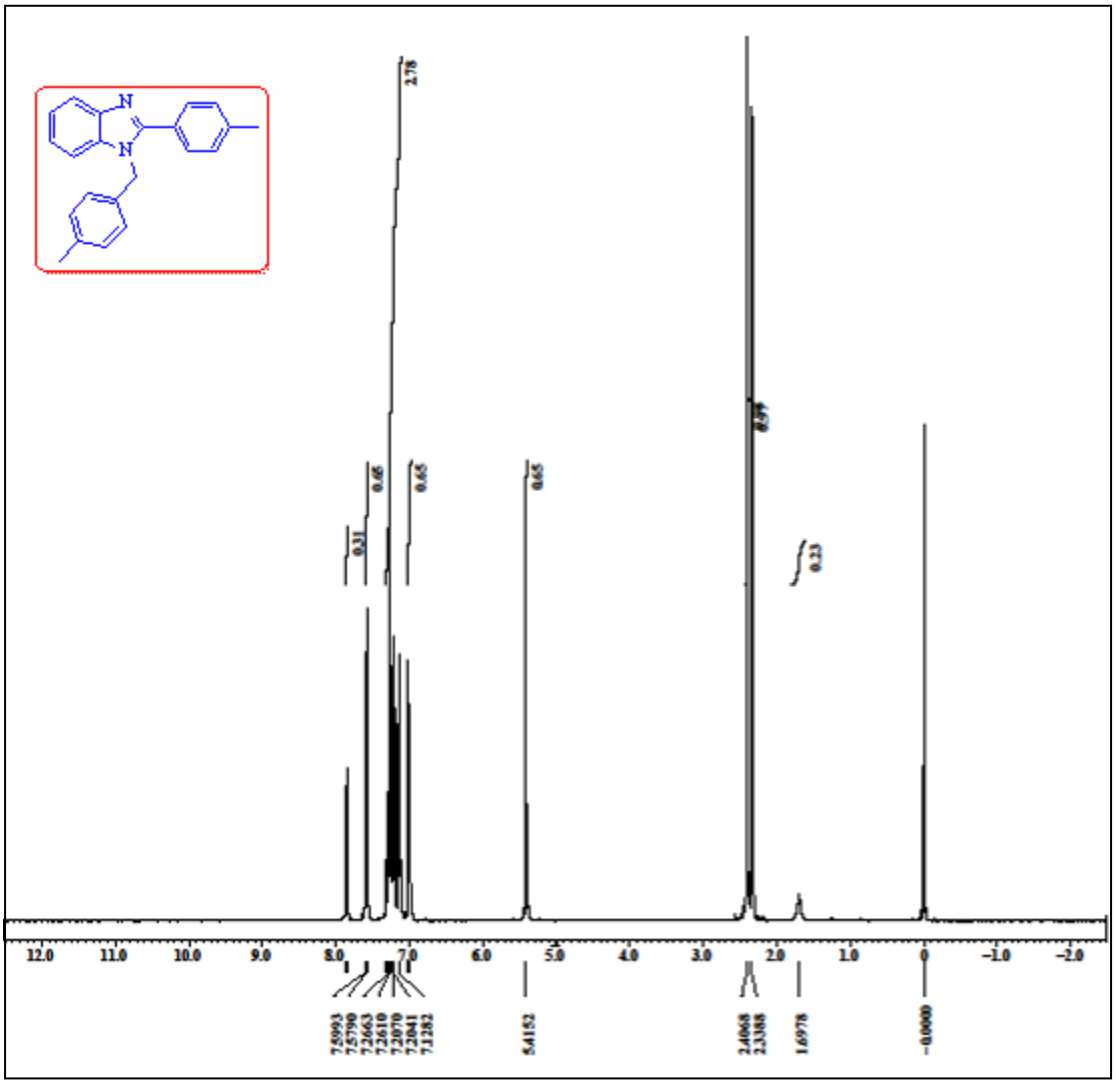


^{1}H NMR Spectra of Compound 5b


152.827
142.947
136.396
135.877
134.602
133.863
130.449
129.386
129.173
128.259
127.247
123.518
123.104
120.141
110.324
77.361
77.042
76.727
47.800
Cl
Cl
200
180
160
140
120
100
80
60
40
20
0
ppm

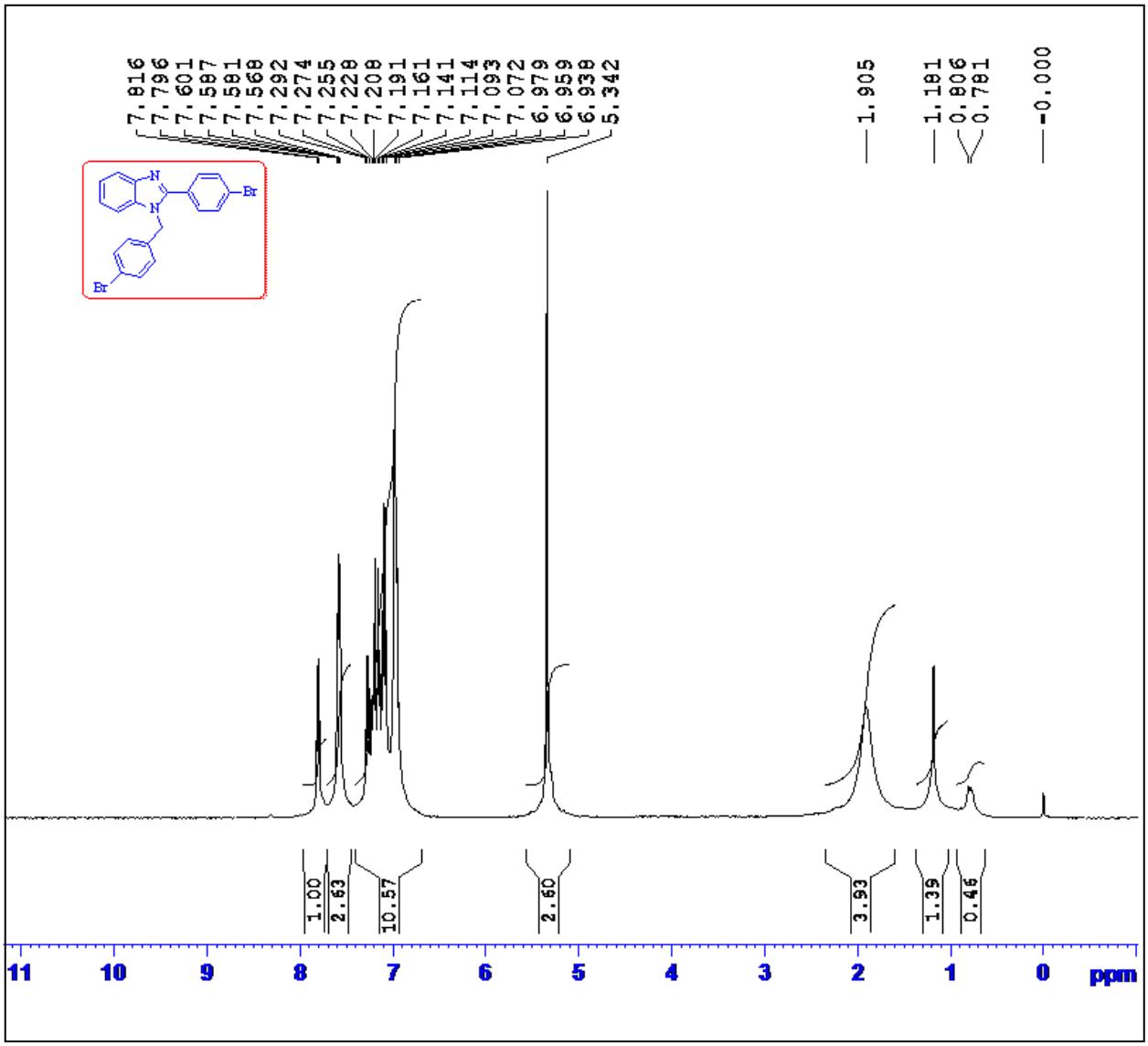
^{13}C NMR Spectra of Compound 5b

11. Compound 5c

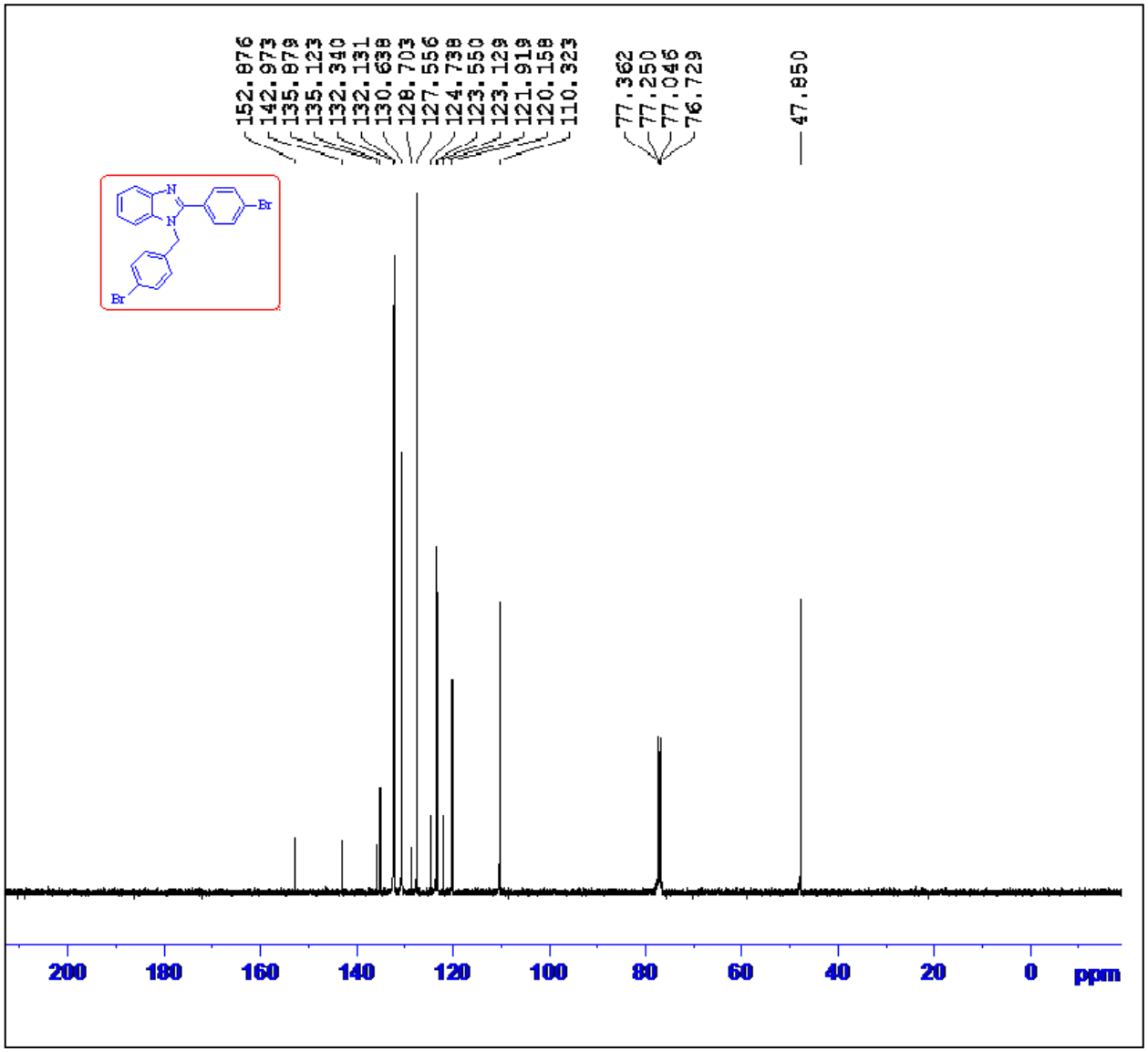


^{1}H NMR Spectra of Compound 5c

12. Compound 5d

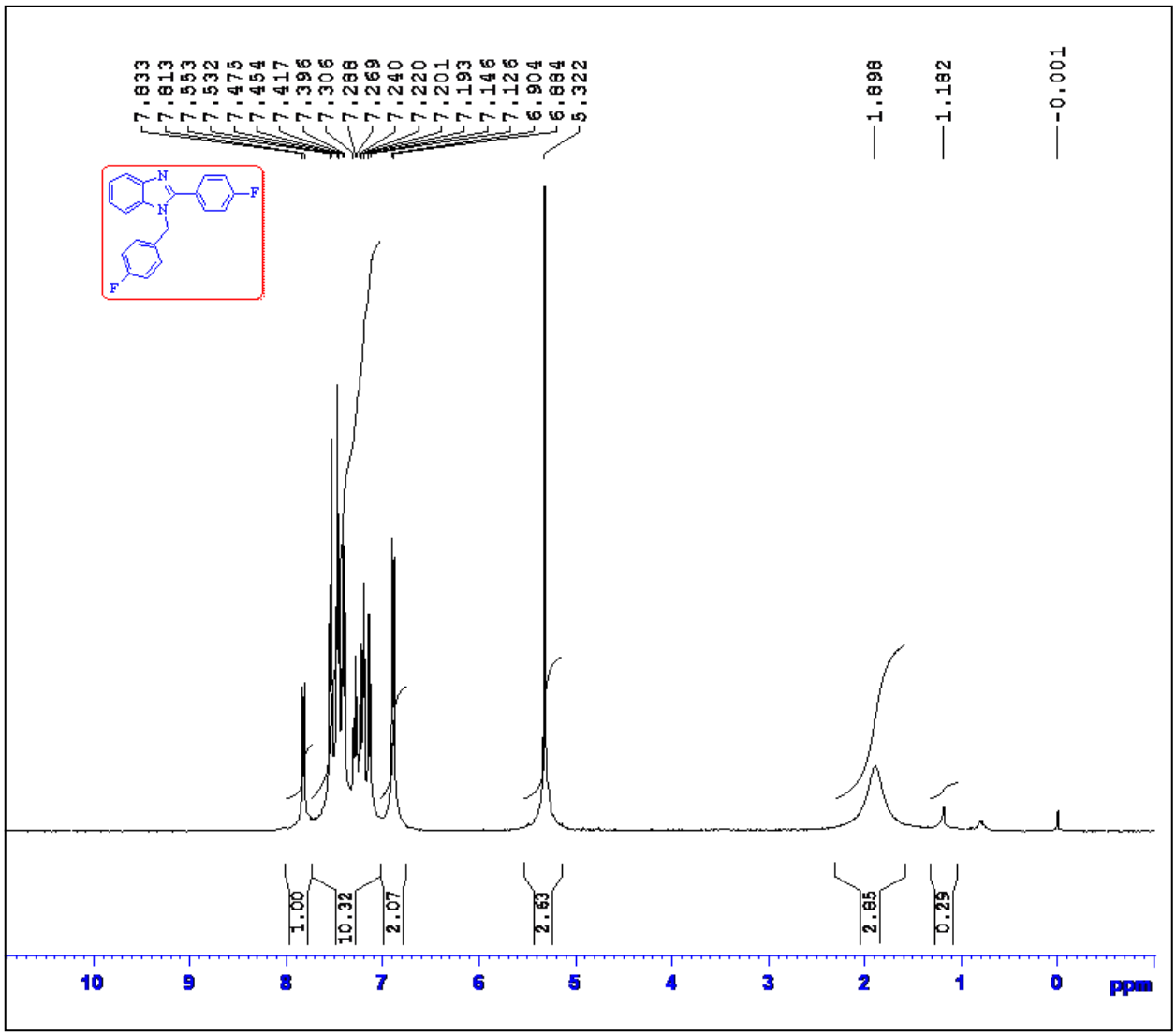


^{1}H NMR Spectra of Compound 5d



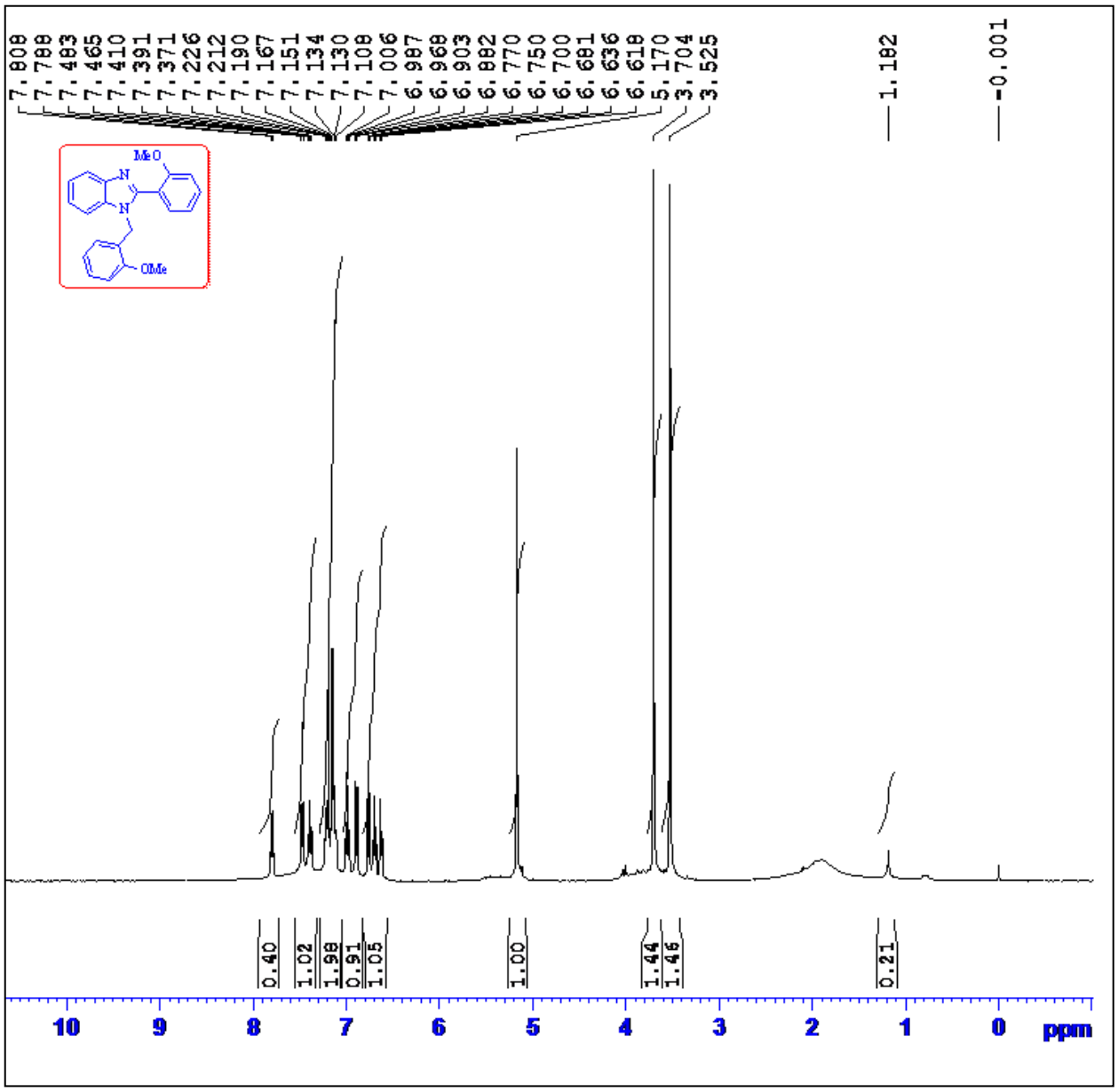
^{13}C NMR Spectra of Compound 5d

13. Compound 5e



^{1}H NMR Spectra of Compound 5e

14. Compound 5f



^{1}H NMR Spectra of Compound 5f