Supporting Information

Inter and Intramolecular Mitsunobu Reaction and Metal Complexation Study: Synthesis of *S*-Amino Acids Derived Chiral 1,2,3,4-Tetrahydroquinoxaline, Benzo annulated [9]-N_3 Peraza, [12]-N_4 Peraza-Macrocycles†

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Fig. S-8: ^{13}C Spectra of (2*S*)-4-Methyl-2-(2-nitrophenylamino)pentanoic Acid Methyl Ester (**3c).**

Fig. S-9: ^{1}H Spectra of (2*S*,3*S*)-Methyl-3-methyl-2-(2-nitrophenylamino)pentanoic Acid Methyl Ester **(3d).**

Fig. S-10: ^{13}C Spectra of (2*S*,3*S*)-Methyl-3-methyl-2-(2-nitrophenylamino)pentanoic Acid Methyl Ester **(3d).**

Fig. S-11: ^{1}H Spectra of (2*S*)-3-(1*H*-Indol-3-yl)-2-(2-nitrophenylamino)propionic Acid Methyl Ester **(3e).**

Fig. S-12: ^{13}C Spectra of of (2*S*)-3-(1*H*-Indol-3-yl)-2-(2-nitrophenylamino)propionic Acid Methyl Ester **(3e).**

Fig. S-13: ^{1}H Spectra of (2*S*)-3-Methyl-2-(2-nitrophenylamino)butyric Acid Methyl Ester (**3f)**.

Fig. S-14: ^{13}C Spectra of (2*S*)-3-Methyl-2-(2-nitrophenylamino)butyric Acid Methyl Ester (**3f) .**

Fig. S-15: HPLC Spectra of (2*S*)-3-Methyl-2-(2-nitrophenylamino)butyric Acid Methyl Ester (**3f).**

Fig. S-16: ^{1}H Spectra of (2*S*)-4-Methylsulfanyl-2-(2-nitrophenylamino)butyric Acid Methyl Ester (**3g).**

Fig. S-17: ^{13}C Spectra of (2*S*)-4-Methylsulfanyl-2-(2-nitrophenylamino)butyric Acid Methyl Ester (**3g).**

Fig. S-18: ^{1}H Spectra of (2*S*)-2-(2-Aminophenylamino)propan-1-ol **(4a).**

Fig. S-19: ^{13}C Spectra of (2*S*)-2-(2-Aminophenylamino)propan-1-ol **(4a).**

Fig. S-20: ^{1}H Spectra of (2*S*)-2-(2-Aminophenylamino)-3-phenylpropan-1-ol (**4b).**

Fig. S-21: ^{13}C Spectra of (2*S*)-2-(2-Aminophenylamino)-3-phenylpropan-1-ol (**4b).**

Fig. S-22: ^{1}H Spectra of (2*S*)- 2-(2-Aminophenylamino)-4-methylpentan-1-ol **(4c).**

Fig. S-23: ^{13}C Spectra of (2*S*)- 2-(2-Aminophenylamino)-4-methylpentan-1-ol **(4c).**

Fig. S-24: ^{1}H Spectra of (2*S*,3*S*)-2-(2-Aminophenylamino)-3-methylpentan-1-ol **(4d).**

Fig. S-77: ^{1}H Spectra of (*S*)-2-Benzyl-1,2,3,4-tetrahydroquinoxaline **(8b).**

Fig. S-78: ^{13}C Spectra of (*S*)-2-Benzyl-1,2,3,4-tetrahydroquinoxaline **(8b).**

Fig. S-79: HPLC Spectra of (*S*)-2-Benzyl-1,2,3,4-tetrahydroquinoxaline **(8b).**

Fig. S-80: ^{1}H Spectra of (*S*)-Methyl-2-(4-methyl-N-((*S*)-2-(2-nitrophenylamino)-3-phenylpropyl)phenylsulfonamido) propanoate **(10a).**

Fig. S-81: ^{13}C Spectra of (*S*)-Methyl-2-(4-methyl-N-((*S*)-2-(2-nitrophenylamino)-3-phenylpropyl)phenylsulfonamido) propanoate **(10a).**

Fig. S-82: ^{1}H Spectra of (*S*)-Methyl-3-methyl-2-(4-methyl-N-((*S*)-2-(2-nitrophenylamino)-3-phenylpropyl)phenylsulfonamido)butanoate **(10b).**

Fig. S-83: ^{13}C Spectra of (*S*)-Methyl-3-methyl-2-(4-methyl-N-((*S*)-2-(2-nitrophenylamino)-3-phenylpropyl)phenylsulfonamido)butanoate **(10b).**

Fig. S-84: ^{1}H Spectra of (*S*)-Methyl-4-methyl-2-(4-methyl-N-((*S*)-2-(2-nitrophenylamino)-3-phenylpropyl)phenylsulfonamido)pentanoate **(10c).**

Fig. S-85: ^{13}C Spectra of (*S*)-Methyl-4-methyl-2-(4-methyl-N-((*S*)-2-(2-nitrophenylamino)-3-phenylpropyl)phenylsulfonamido)pentanoate **(10c).**

Fig. S-86: ^{1}H Spectra of (*S*)-Methyl-2-(4-methyl-N-((*S*)-2-(2-nitrophenylamino)-3-phenylpropyl)phenylsulfonamido)-3-phenylpropanoate **(10d).**

Fig. S-87: ^{13}C Spectra of (*S*)-Methyl-2-(4-methyl-N-((*S*)-2-(2-nitrophenylamino)-3-phenylpropyl)phenylsulfonamido)-3-phenylpropanoate **10d.**

Fig. S-88: ^{1}H Spectra of (*S*)-Methyl 2-(4-methyl-N-((*S*)-2-(2-nitrophenylamino)propyl) phenylsulfonamido) propanoate (**10e).**

Fig. S-89: ^{13}C Spectra of (*S*)-Methyl 2-(4-methyl-N-((*S*)-2-(2-nitrophenylamino)propyl) phenylsulfonamido) propanoate (**10e).**

Fig. S-90: ^{1}H Spectra of (*S*)-Methyl 3-methyl-2-(4-methyl-N-((*S*)-3-methyl-2-(2-nitrophenylamino)butyl) phenyl sulfonamido)butanoate (**10f).**

Fig. S-91: ^{13}C Spectra (*S*)-Methyl 3-methyl-2-(4-methyl-N-((*S*)-3-methyl-2-(2-nitrophenylamino)butyl) phenyl sulfonamido)butanoate (**10f).**

Fig. S-92: ^{1}H Spectra of (*S*)-Methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)phenylamino)-3-phenylpropyl) phenylsulfonamido)propanoate **(11a).**

Fig. S-93: ^{13}C Spectra of (*S*)-Methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)phenylamino)-3-phenylpropyl) phenylsulfonamido)propanoate **(11a).**

Fig. S-94: ^{1}H Spectra of (*S*)-Methyl-3-methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)phenylamino)-3-phenylpropyl) phenylsulfonamido)butanoate **(11b).**

Fig. S-95: ^{13}C Spectra of (*S*)-Methyl-3-methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)phenylamino)-3-phenylpropyl) phenylsulfonamido)butanoate **(11b).**

Fig. S-96: ^{1}H Spectra of (*S*)-Methyl-4-methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)phenylamino)-3-phenylpropyl)phenylsulfonamido)pentanoate **(11c).**

Fig. S-97: ^{13}C Spectra of (*S*)-Methyl-4-methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)phenylamino)-3-phenylpropyl)phenylsulfonamido)pentanoate **(11c).**

Fig. S-98: ^{1}H Spectra of (*S*)-Methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)phenylamino)-3-phenylpropyl)- phenylsulfonamido)-3-phenylpropanoate **(11d).**

Fig. S-99: ^{13}C Spectra of (*S*)-Methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)phenylamino)-3-phenylpropyl)- phenylsulfonamido)-3-phenylpropanoate **(11d).**

Fig. S-100: ^{1}H Spectra of N-((*S*)-1-Hydroxy-3-methylbutan-2-yl)-4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)phenyl- amino)-3-phenylpropyl)benzenesulfonamide **(12b).**

Fig. S-101: ^{13}C Spectra of N-((*S*)-1-Hydroxy-3-methylbutan-2-yl)-4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)phenyl- amino)-3-phenylpropyl)benzenesulfonamide **(12b).**

Fig. S-102: ^{1}H Spectra of N-((*S*)-1-Hydroxy-4-methylpentan-2-yl)-4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)-

phenylamino) -3-phenylpropyl)benzenesulfonamide **(12c).**

Fig. S-103: ^{1}H Spectra of N-((*S*)-1-Hydroxy-3-phenylpropan-2-yl)-4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)- phenylamino)-3-phenylpropyl)benzenesulfonamide (**12d).**

Fig. S-104: ^{13}C Spectra of N-((*S*)-1-Hydroxy-3-phenylpropan-2-yl)-4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)- phenylamino)-3-phenylpropyl)benzenesulfonamide (**12d).**

Fig. S-136: ^{13}C Spectra of (*S*)-Methyl-2-(N-((*S*)-2-(2-(N-((*S*)-2-(tert-butoxycarbonylamino)-3-phenylpropyl)-4-methylphenyl-sulfonamido)phenylamino)-3-phenylpropyl)-4-methylphenylsulfonamido)-3-methylbutanoate **(16a).**

Fig. S-137: ^{1}H Spectra of (*S*)-Methyl-2-(N-((*S*)-2-(2-(N-((*S*)-2-(tert-butoxycarbonylamino)-3-phenylpropyl)-4-methylphenyl-sulfonamido)phenylamino)-3-phenylpropyl)-4-methylphenylsulfonamido)-4-methylpentanoate **(16b).**

Fig. S-138: ^{13}C Spectra of (*S*)-Methyl-2-(N-((*S*)-2-(2-(N-((*S*)-2-(tert-butoxycarbonylamino)-3-phenylpropyl)-4-methylphenyl-sulfonamido)phenylamino)-3-phenylpropyl)-4-methylphenylsulfonamido)-4-methylpentanoate **(16b).**

Fig. S-139: ^{1}H Spectra of (*S*)-Methyl-3-methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methyl-N-((*S*)-2-(4-methylphenylsulfonamido)-3-phenylpropyl)phenylsulfonamido)phenylamino)-3-phenylpropyl)phenylsulfonamido)butanoate **(18a).**

Fig. S-140: ^{13}C Spectra of (*S*)-Methyl-3-methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methyl-N-((*S*)-2-(4-methylphenylsulfonamido)-3-phenylpropyl)phenylsulfonamido)phenylamino)-3-phenylpropyl)phenylsulfonamido)butanoate **(18a).**

Fig. S-141: ^{1}H Spectra of (*S*)-Methyl-4-methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methyl-N-((*S*)-2-(4-methylphenylsulfonamido)-3-phenylpropyl)phenylsulfonamido)phenylamino)-3-phenylpropyl)phenylsulfonamido)pentanoate **(18b).**

Fig. S-142: ^{13}C Spectra of (*S*)-Methyl-4-methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methyl-N-((*S*)-2-(4-methylphenylsulfonamido)-3-phenylpropyl)phenylsulfonamido)phenylamino)-3-phenylpropyl)phenylsulfonamido)pentanoate **(18b).**

Fig. S-143: ^{1}H Spectra of N-((*S*)-1-Hydroxy-3-methylbutan-2-yl)-4-methyl-N-((*S*)-2-(2-(4-methyl-N-((*S*)-2-(4-methylphenyl-sulfonamido)-3-phenylpropyl)phenylsulfonamido)phenylamino)-3-phenylpropyl)benzenesulfona-mide **(19a).**

Fig. S-144: ^{13}C Spectra of N-((*S*)-1-Hydroxy-3-methylbutan-2-yl)-4-methyl-N-((*S*)-2-(2-(4-methyl-N-((*S*)-2-(4-methylphenyl-sulfonamido)-3-phenylpropyl)phenylsulfonamido)phenylamino)-3-phenylpropyl)benzenesulfona-mide **(19a).**

Fig. S-145: ^{1}H Spectra of (3*S*,6*S*,9*S*)-3,9-Dibenzyl-6-isopropyl-1,4,7-tritosyl-1,2,3,4,5,6,7,8,9,10-decahydrobenzo[b][1,4,7,10]- tetraaza-cyclododecine **(20a).**

Fig. S-146: ^{13}C Spectra of (3*S*,6*S*,9*S*)-3,9-Dibenzyl-6-isopropyl-1,4,7-tritosyl-1,2,3,4,5,6,7,8,9,10-decahydrobenzo[b][1,4,7,10]- tetraaza-cyclododecine **(20a).**

Fig. S-147: HPLC Spectra of (3*S*,6*S*,9*S*)-3,9-Dibenzyl-6-isopropyl-1,4,7-tritosyl-1,2,3,4,5,6,7,8,9,10-decahydrobenzo[b][1,4,7,10]- tetraaza-cyclododecine **(20a).**

Fig. S-148: ^{1}H Spectra of (3*S*,6*S*,9*S*)-3,9-Dibenzyl-6-isobutyl-1,4,7-tritosyl-1,2,3,4,5,6,7,8,9,10-decahydrobenzo[b][1,4,7,10]- tetraaza-cyclododecine **(20b).**

Fig. S-149: ^{13}C Spectra of (3*S*,6*S*,9*S*)-3,9-Dibenzyl-6-isobutyl-1,4,7-tritosyl-1,2,3,4,5,6,7,8,9,10-decahydrobenzo[b][1,4,7,10]- tetraaza-cyclododecine **(20b).**

Fig. S-150: HPLC Spectra of (3*S*,6*S*,9*S*)-3,9-Dibenzyl-6-isobutyl-1,4,7-tritosyl-1,2,3,4,5,6,7,8,9,10-decahydrobenzo[b][1,4,7,10]- tetraaza-cyclododecine **(20b).**

Fig. S-151: ^{1}H Spectra of (2*S*,5*S*,8*S*)-2,8-Dibenzyl-5-isopropyl-1,2,3,4,5,6,7,8,9,10-decahydrobenzo[b][1,4,7,10]tetraazacyclododecine **(21).**

Fig. S-152: ^{13}C Spectra of (2*S*,5*S*,8*S*)-2,8-Dibenzyl-5-isopropyl-1,2,3,4,5,6,7,8,9,10-decahydrobenzo[b][1,4,7,10]tetraazacyclododecine **(21).**

Fig. S-153: UV-Visible spectra of various cations in solution which have been used. .

Fig. S-154: UV-visible spectra of **14d** with gradual addition of Co^{2+} solution. Figure depicts the different kinds of response on addition the same cation.

Fig. S-155: UV-visible spectra of **14e** with gradual addition of Co^{2+} solution. Figure depicts the different kinds of response on addition the same cation.

Fig. S-156: UV-visible spectra of **14a** with gradual addition of Co^{2+} solution. Figure depicts the different kinds of response on addition the same cation.

Fig. S-157: UV-visible spectra of **14b** with gradual addition of Co^{2+} solution. Figure depicts the different kinds of response on addition the same cation.

Fig. S-158: UV-visible spectra of **14c** with gradual addition of Co^{2+} solution. Figure depicts the different kinds of response on addition the same cation

Fig. S-159: UV-visible spectra of **14d** with gradual addition of Ni^{2+} solution.

Fig. S-160: UV-visible spectra of **14e** with gradual addition of Ni^{2+} solution.

Fig. S-161: UV-visible spectra of **14a** with gradual addition of Ni^{2+} solution.

Fig. S-162: UV-visible spectra of **21** in acetonitrile.

Fig. S-163: (a)**14d** optimised in PCM mode (Acetonitrile) (b) gaseous phase.

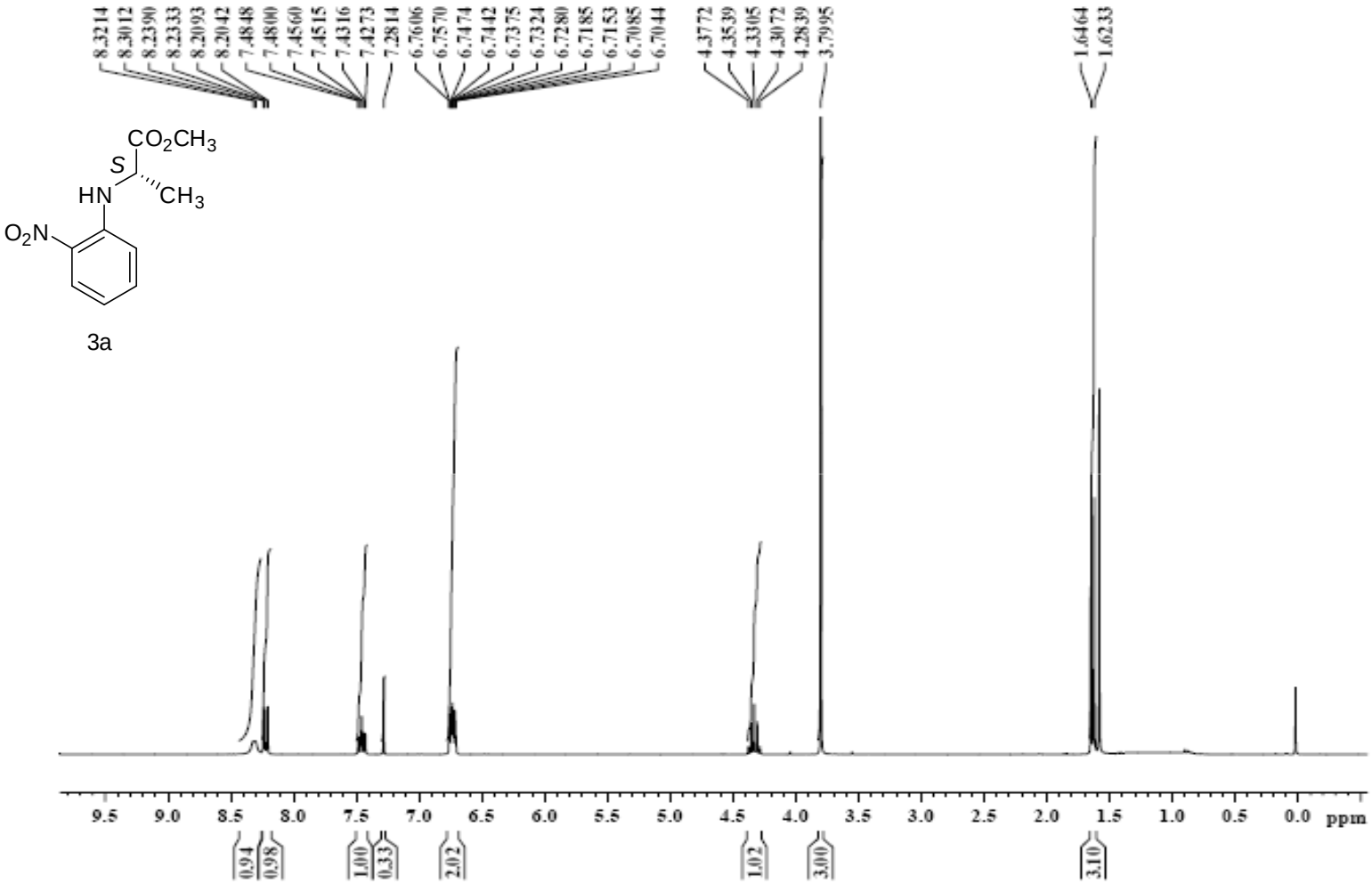
Fig. S-164: Comparisons of Energies, selected bond angles and dihedral angles of **14d** calculated by DFT in PCM mode and gaseous phase.

Fig. S-165: (a)**14c** optimised in PCM mode (Acetonitrile) (b) gaseous phase.

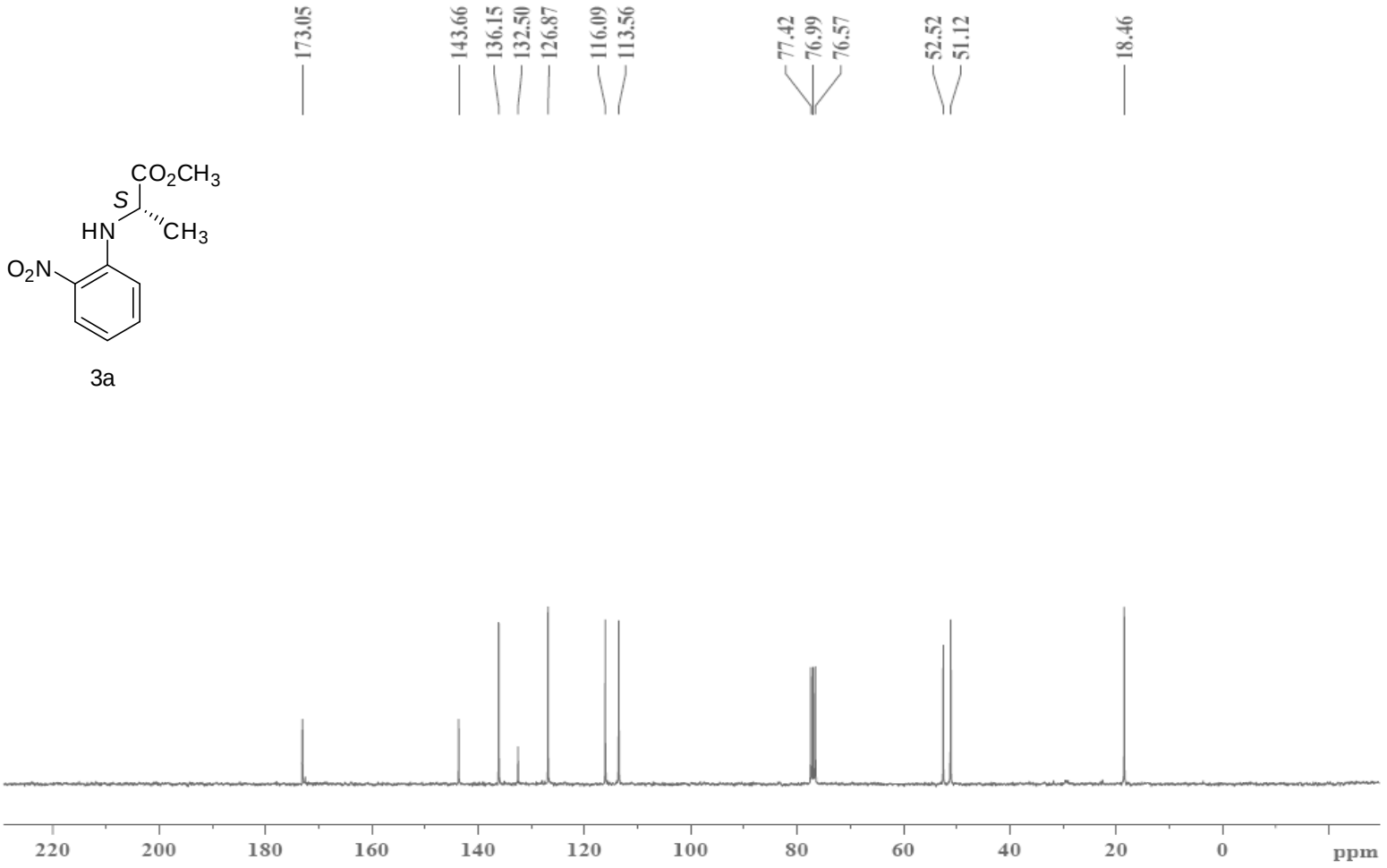
Fig. S-166: Comparisons of Energies, selected bond angles and dihedral angles of **14c** calculated by DFT in PCM mode and gaseous phase.

Fig. S-167: UV Visible spectra of **14d** in different solvents (THF= Tetra hydro furan, MeOH= Methanol, ACN=Acetonitrile, EtoAc= Ethyl acetate).

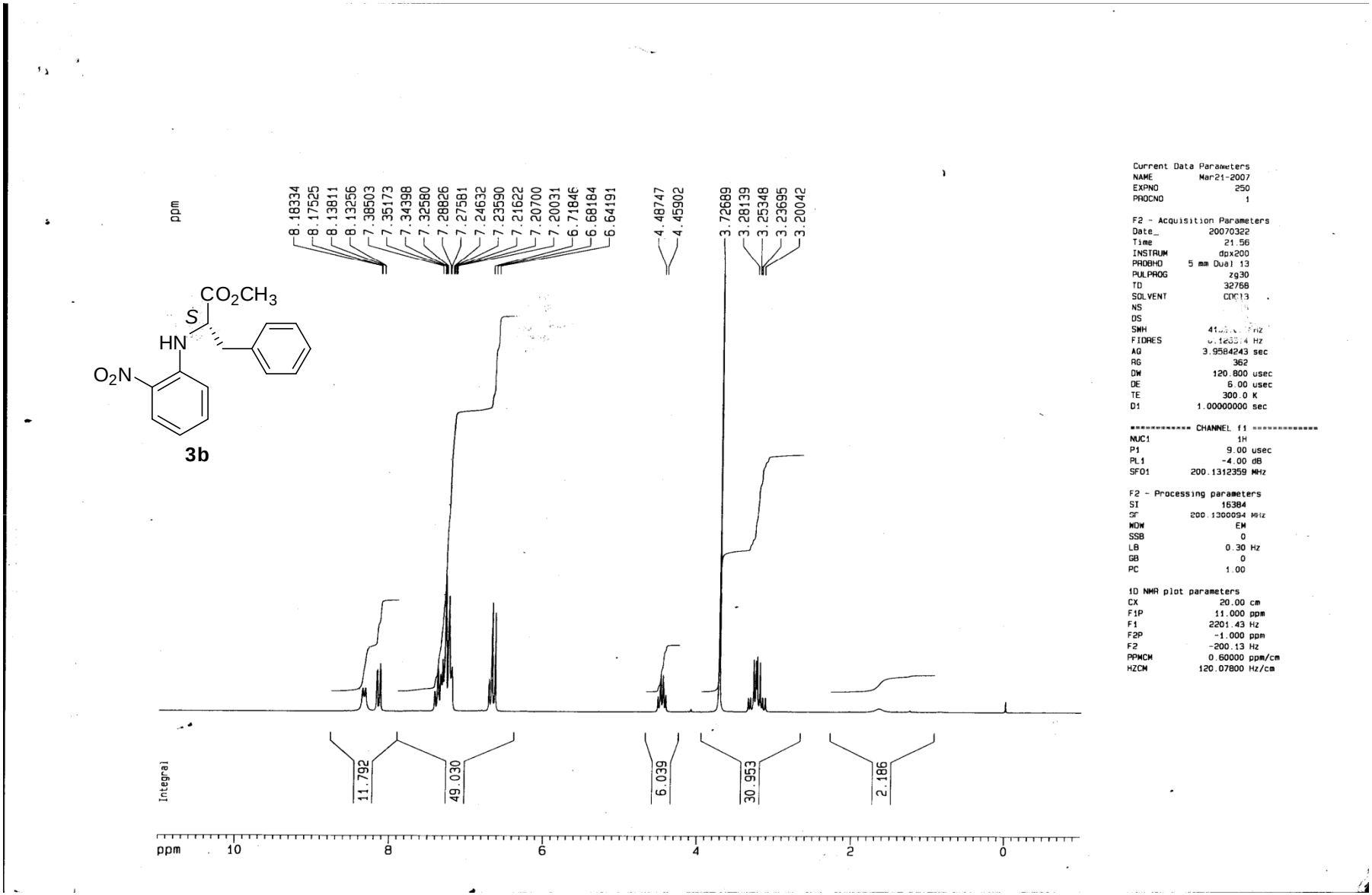
Fig. S-168: UV Visible spectra of **14c** in different solvents (THF= Tetra hydro furan, MeOH= Methanol, ACN=Acetonitrile, EtoAc= Ethyl acetate)



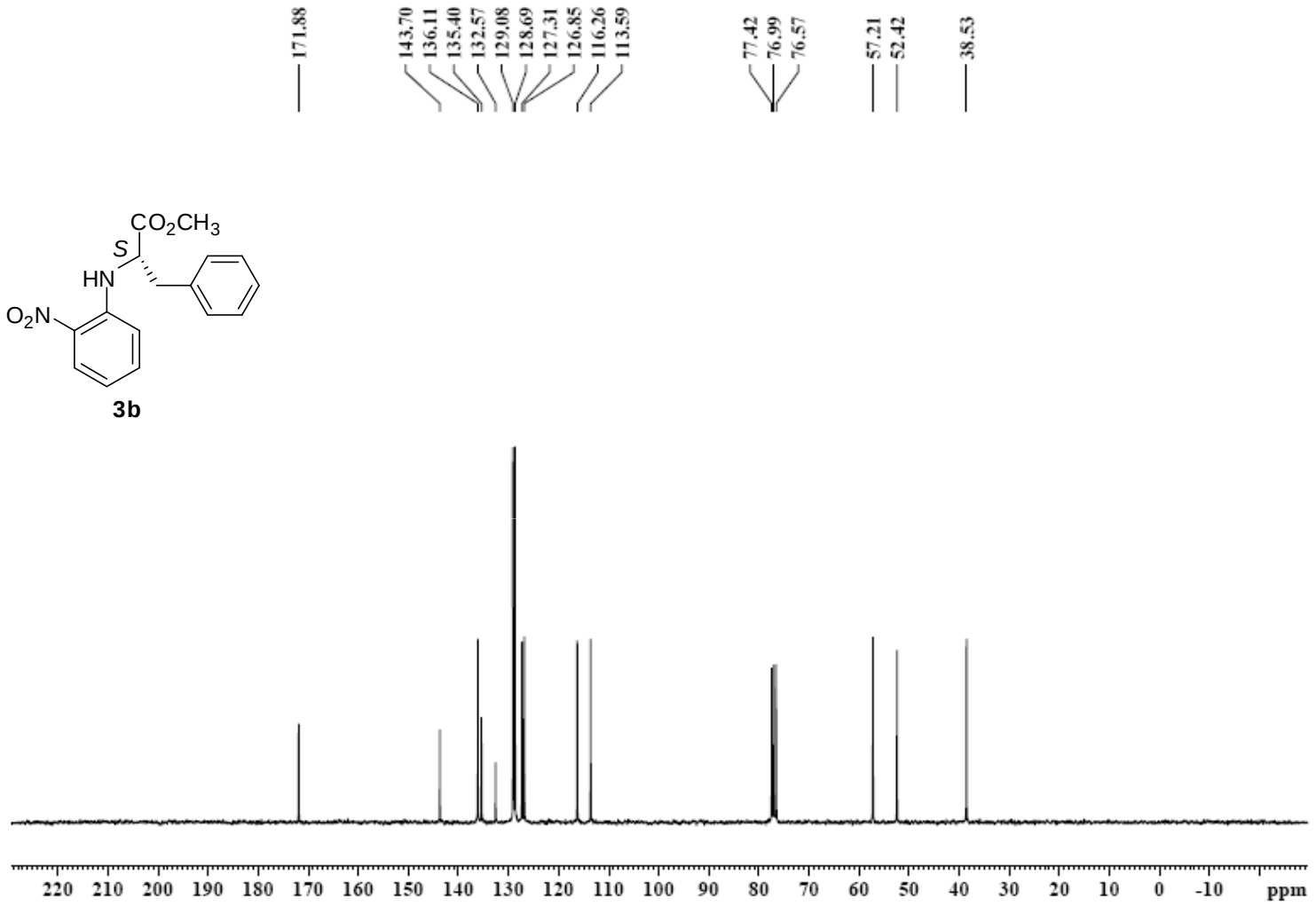
FigureS-1: ^{1}H spectrum(300 MHz, $CDCl_3$) of **3a**



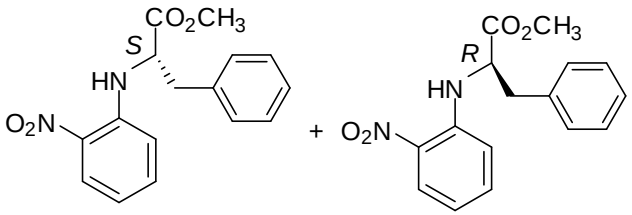
FigureS-2: ^{13}C spectrum (75MHz, $CDCl_3$) of **3a**



FigureS-3: ^{1}H spectrum(200 MHz, $CDCl_3$) of **3b**



FigureS-4: ^{13}C spectrum (75MHz, $CDCl_3$) of **3b**

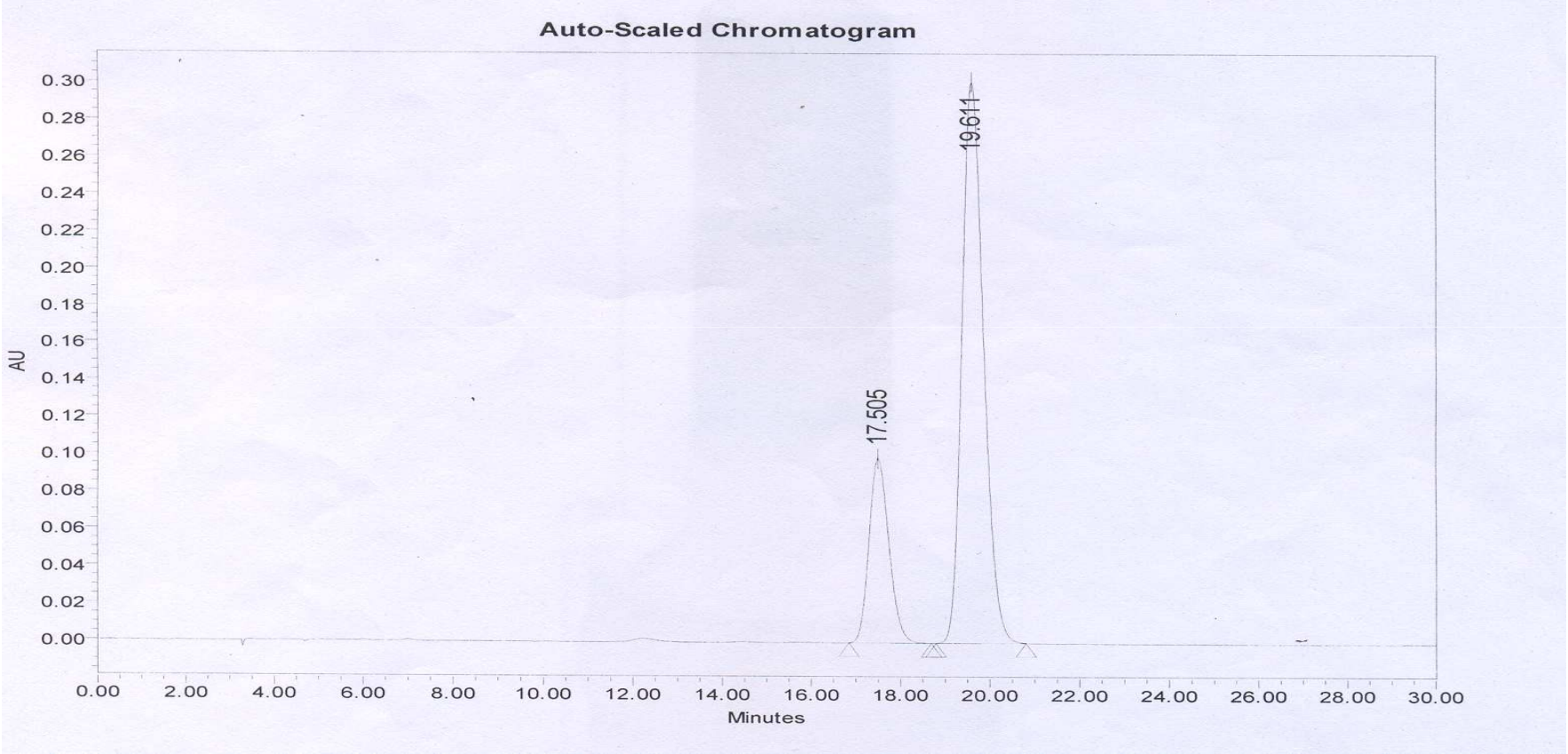


3b

+

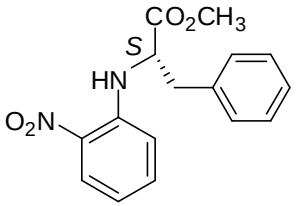
R enantiomer of **3b.**

mixture of **3b** and its enatiomer

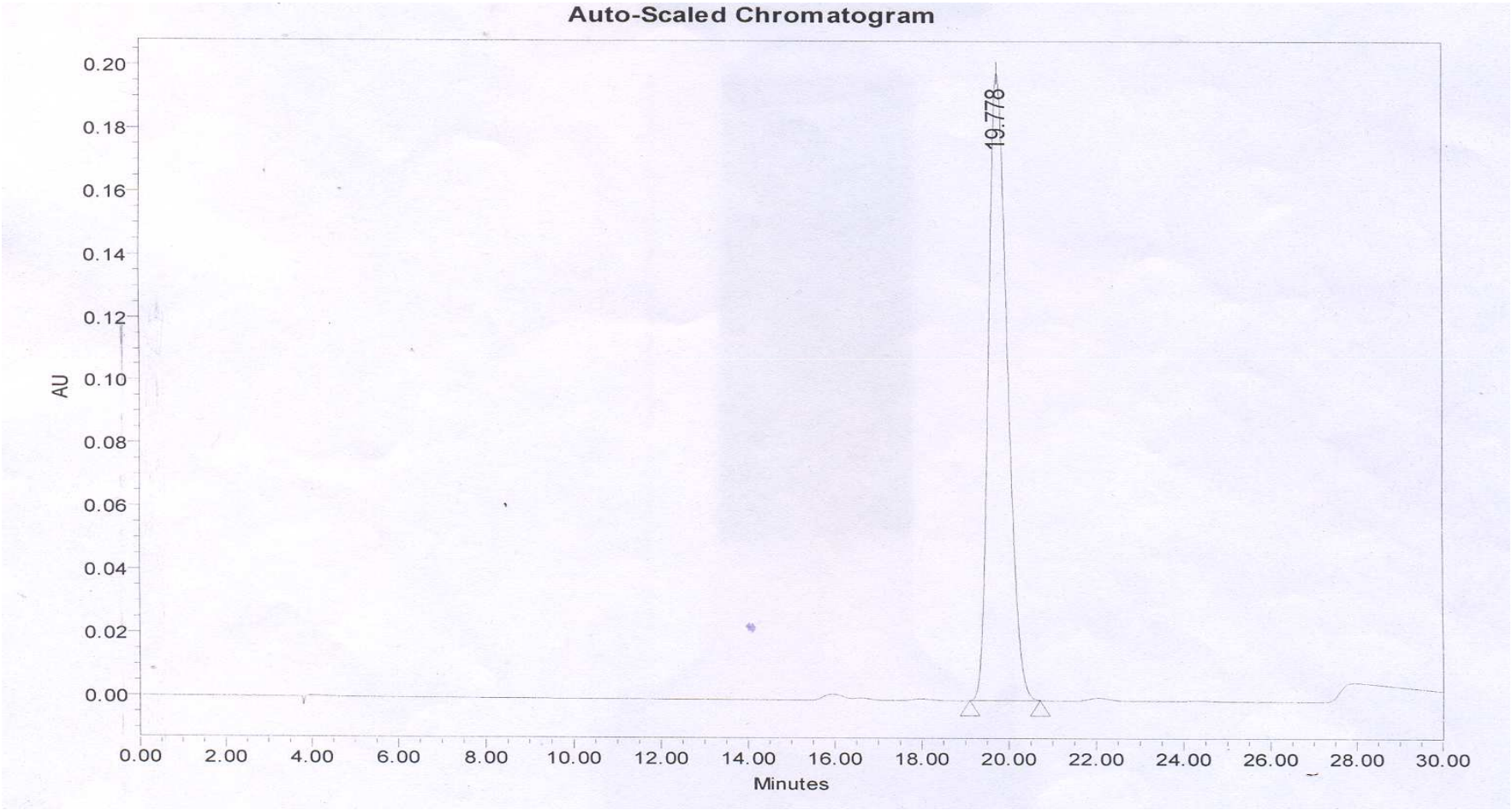


Retention time (min)

FigureS-5: HPLC spectrum of mixture of **3b** and its enatiomer.

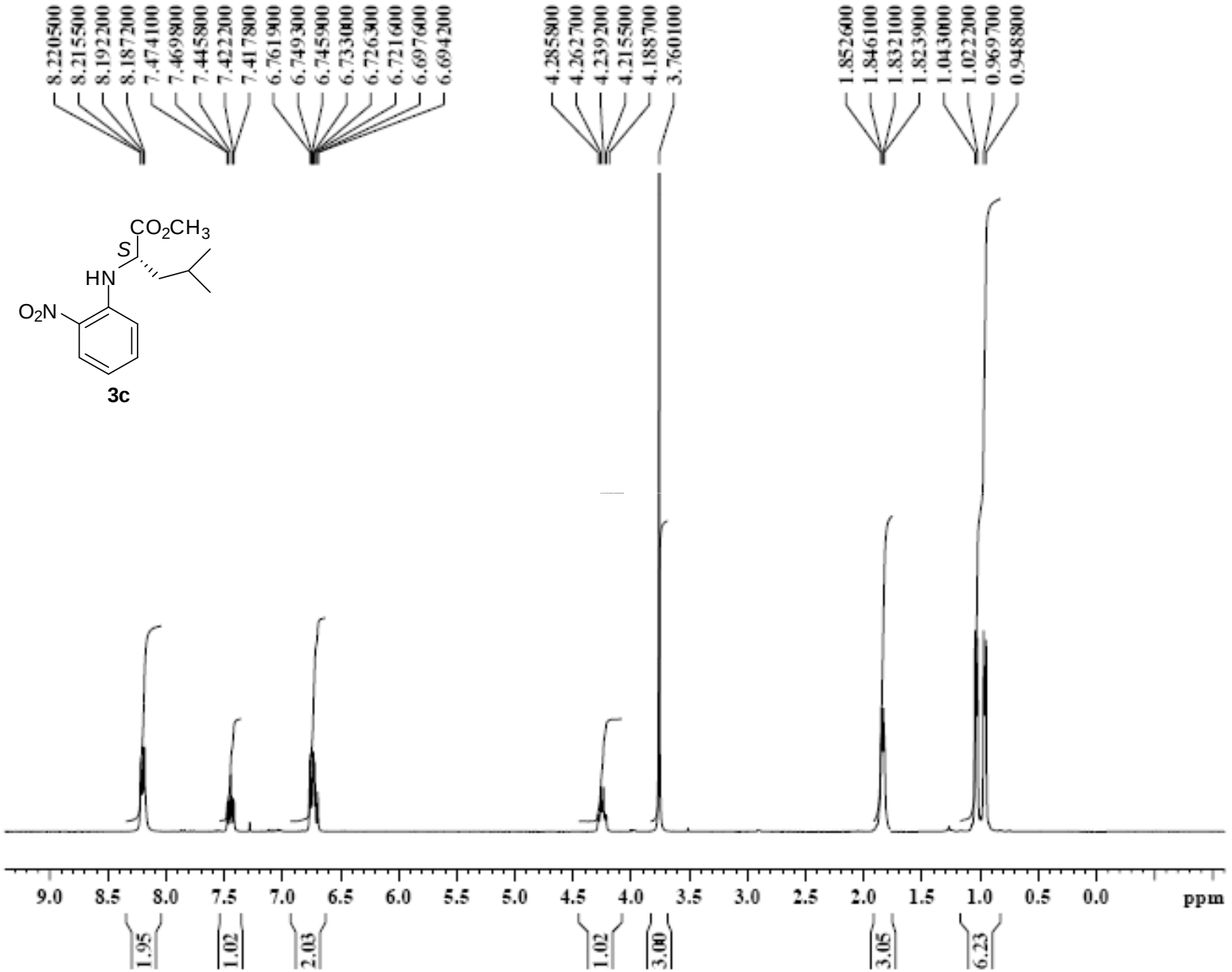


3b

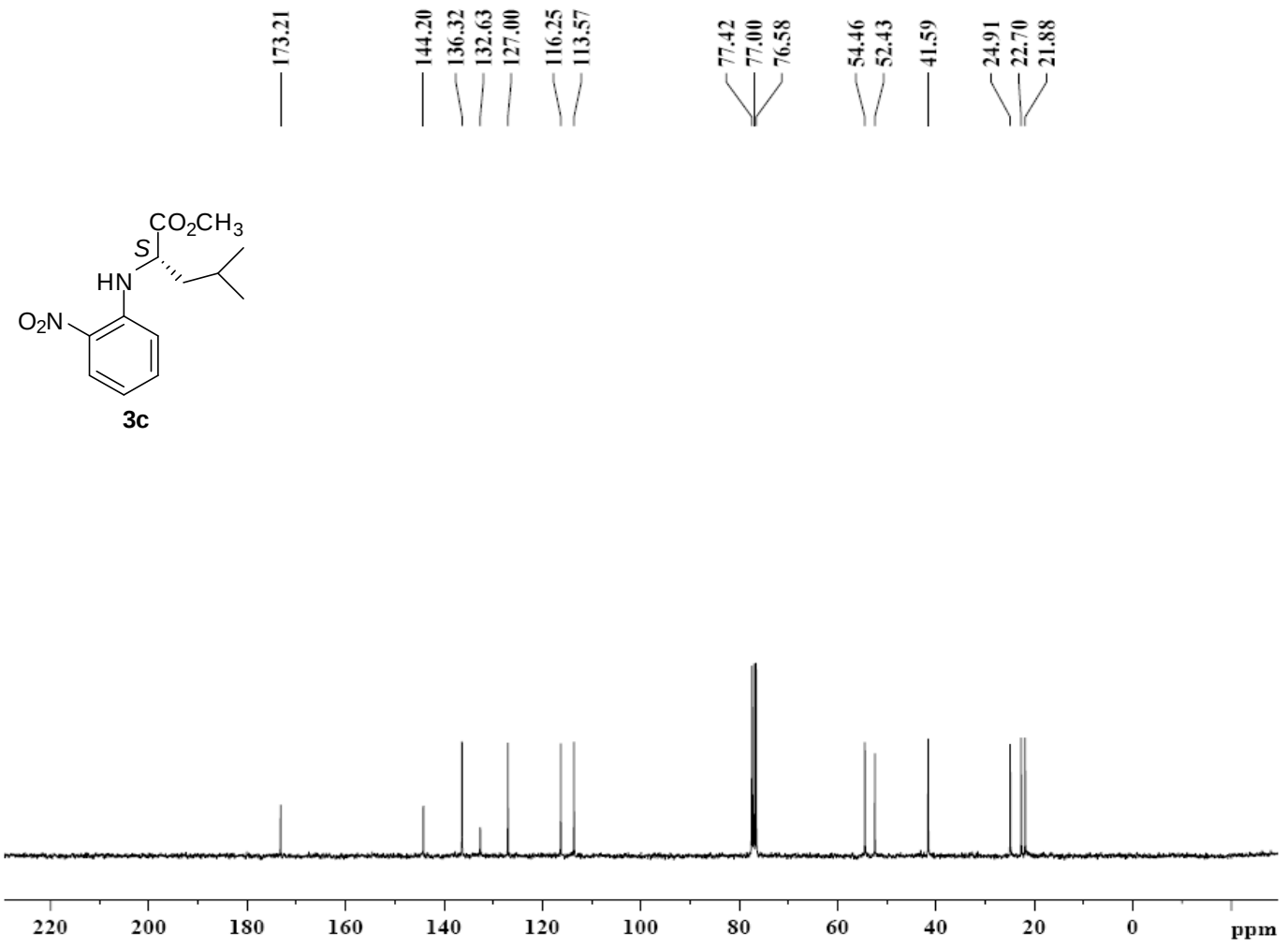


Retention time (min)

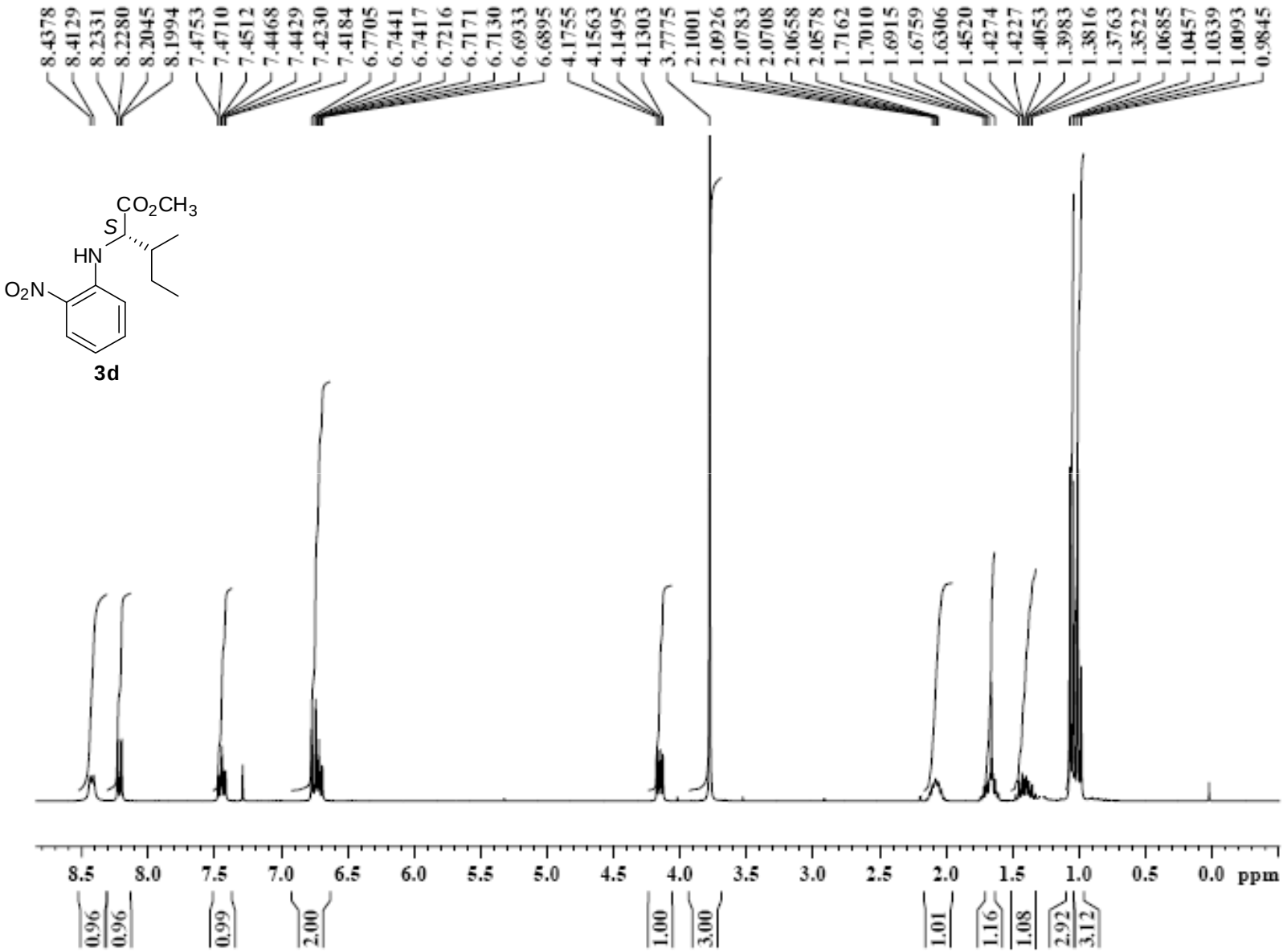
FigureS-6: HPLC spectrum of **3b.**



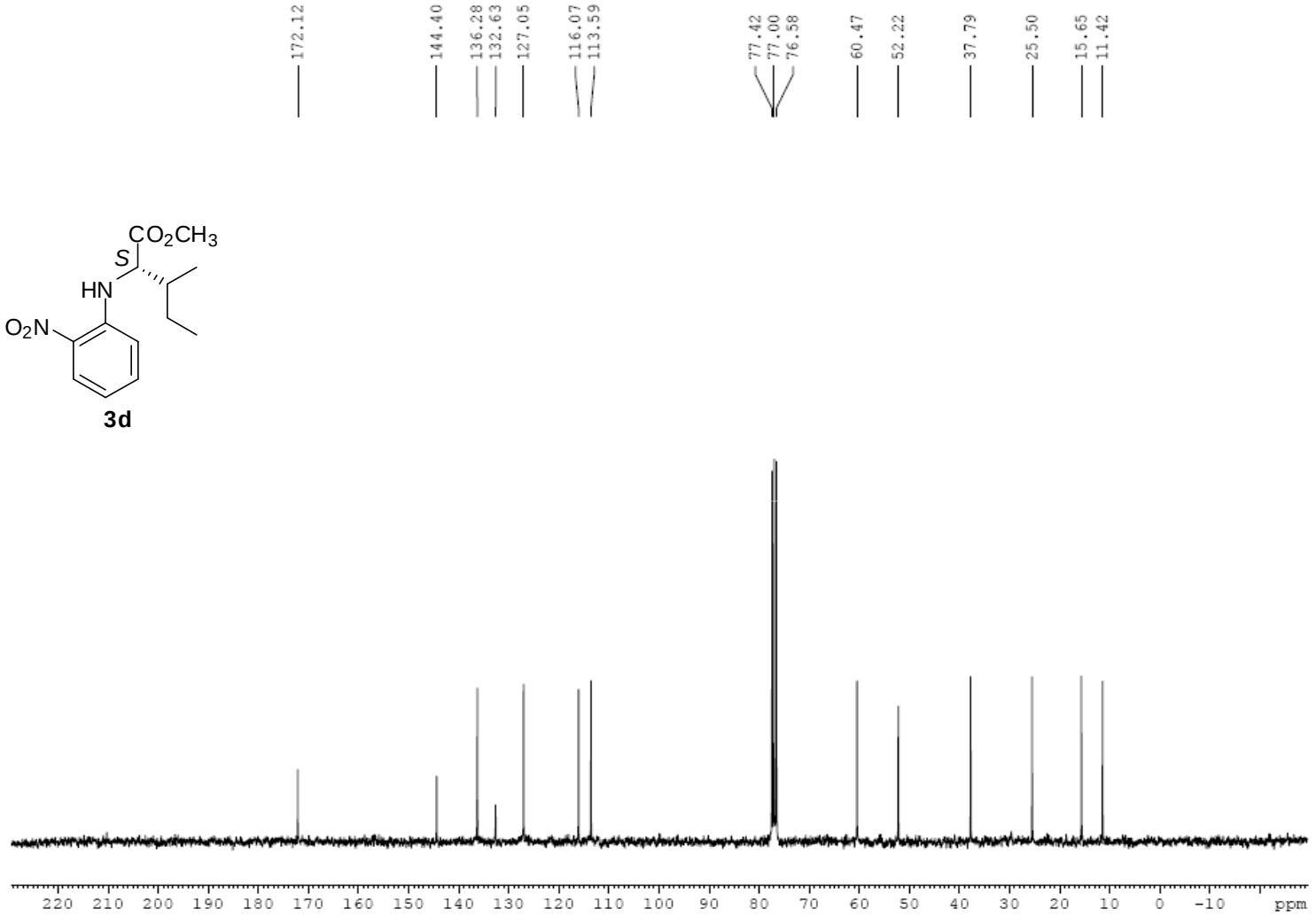
FigureS- 7: ^{1}H spectrum (300MHz, $CDCl_3$) of **3c**.



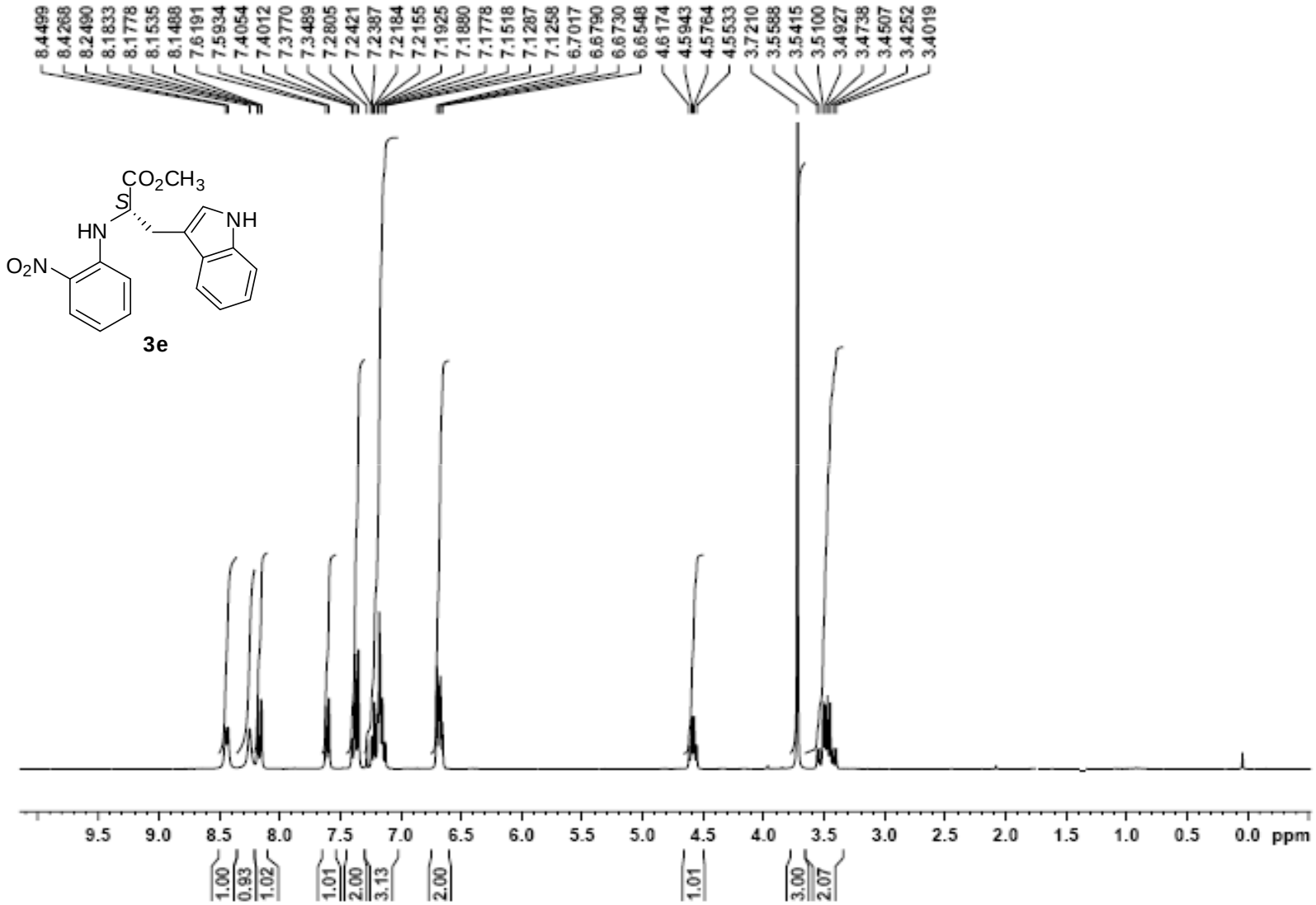
FigureS -8: ^{13}C spectrum (75MHz, $CDCl_3$) **3c**.



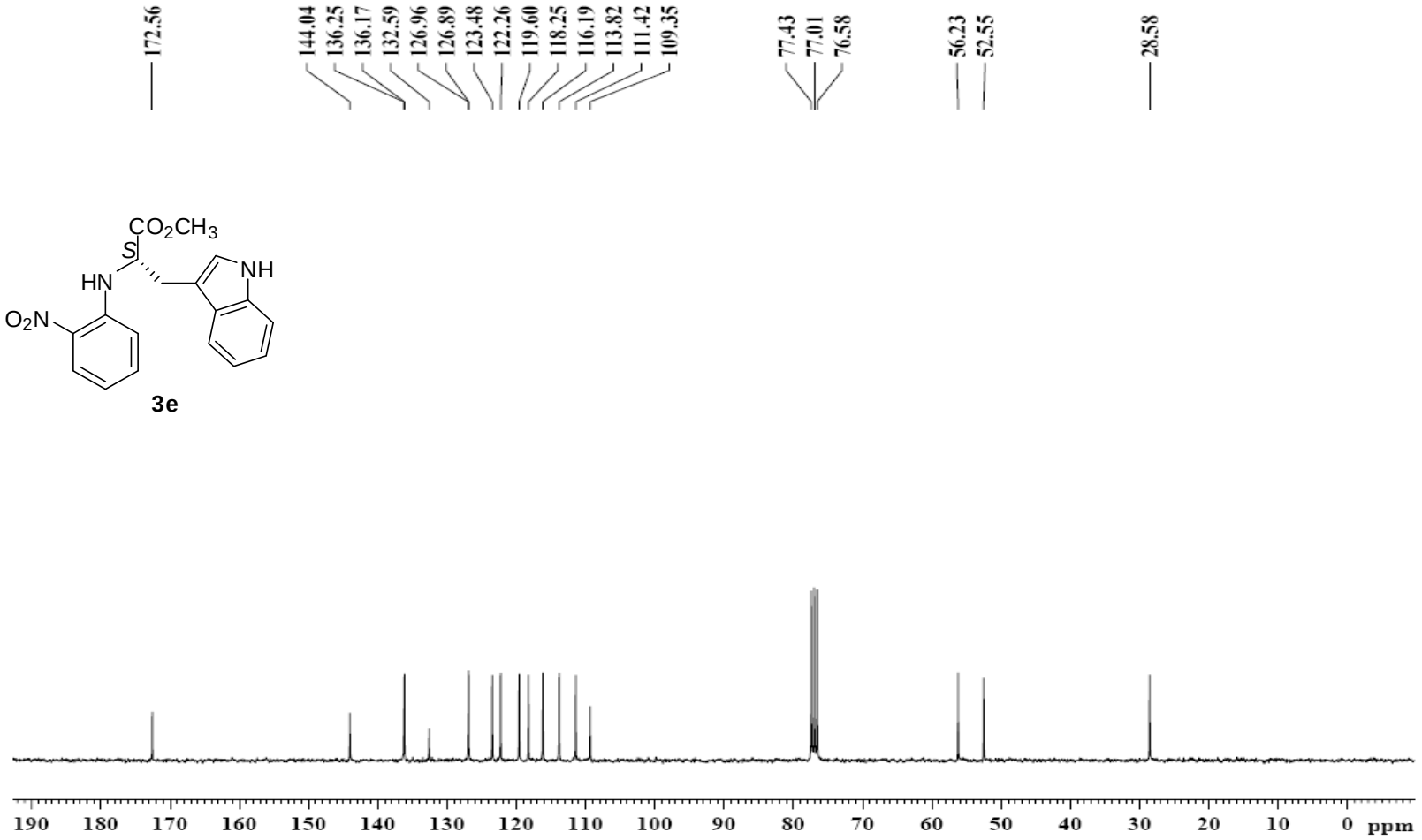
FigureS-9: ^{1}H spectrum (300MHz, $CDCl_3$) **3d**.



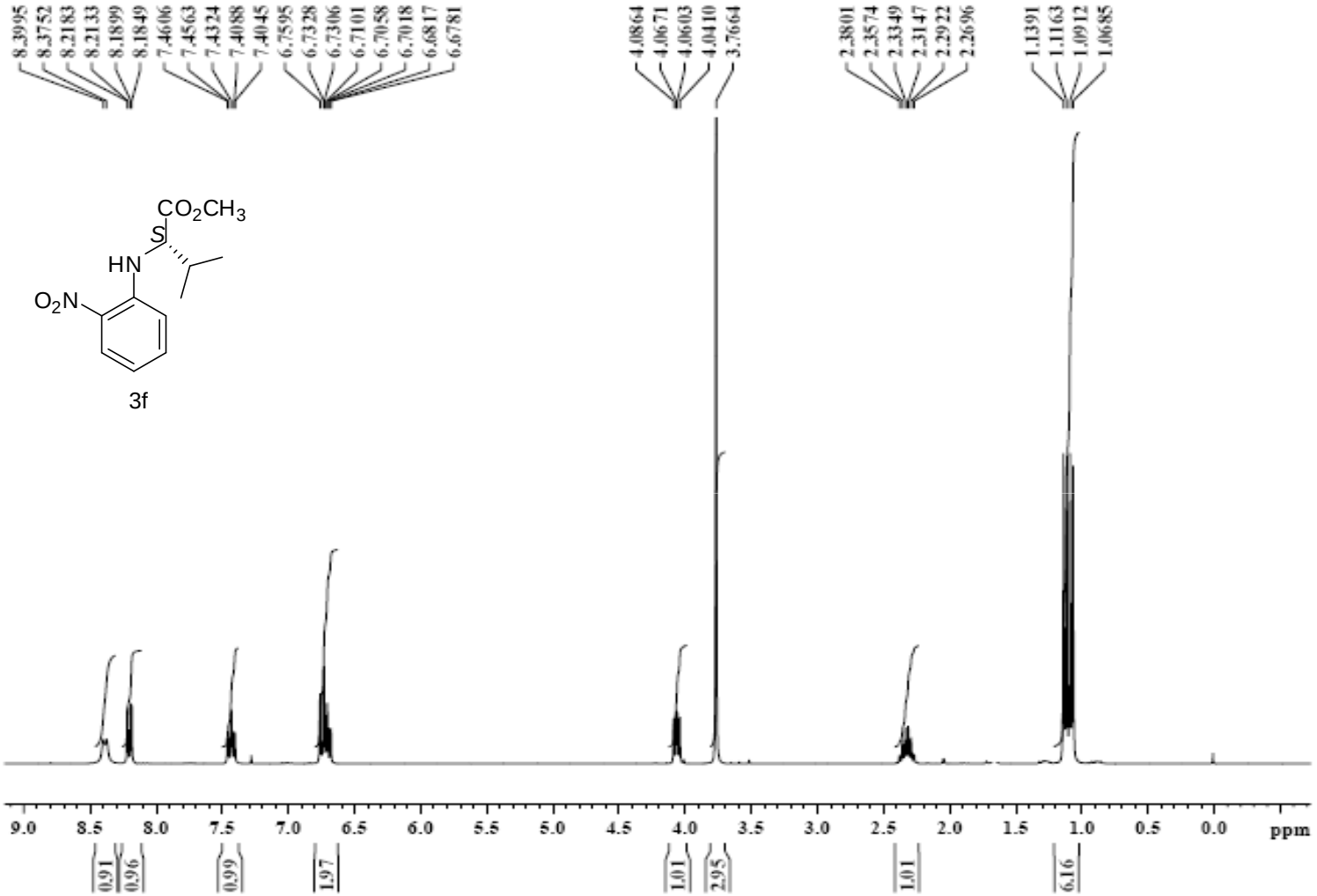
FigureS-10: ^{13}C spectrum (75MHz, $CDCl_3$) **3d**.



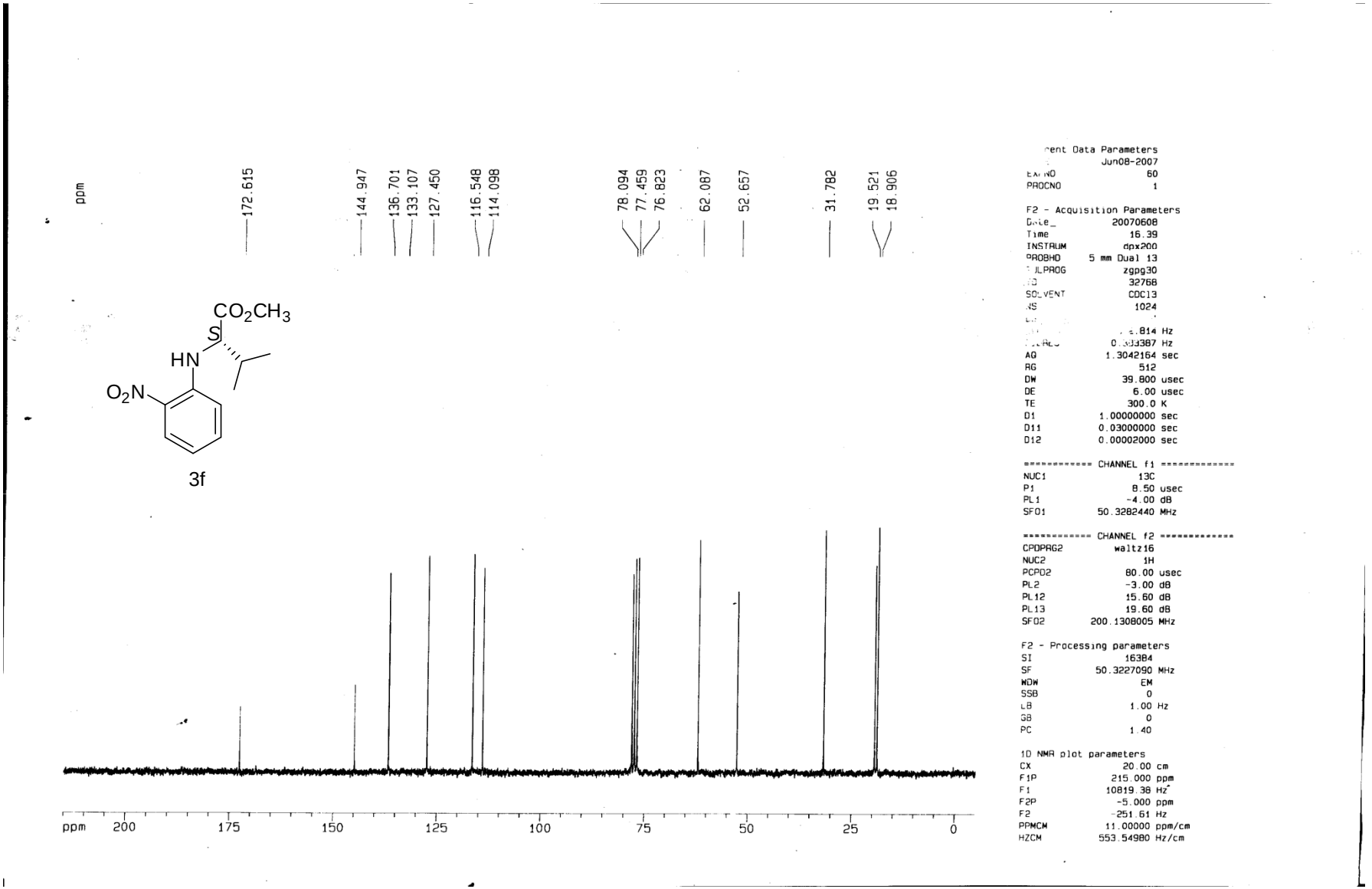
FigureS-11: ^{1}H spectrum (300MHz, $CDCl_3$) **3e**.



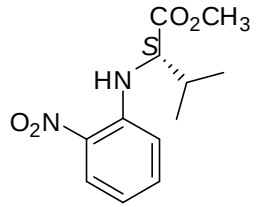
FigureS-12: ^{13}C spectrum (75MHz, $CDCl_3$) **3e**.



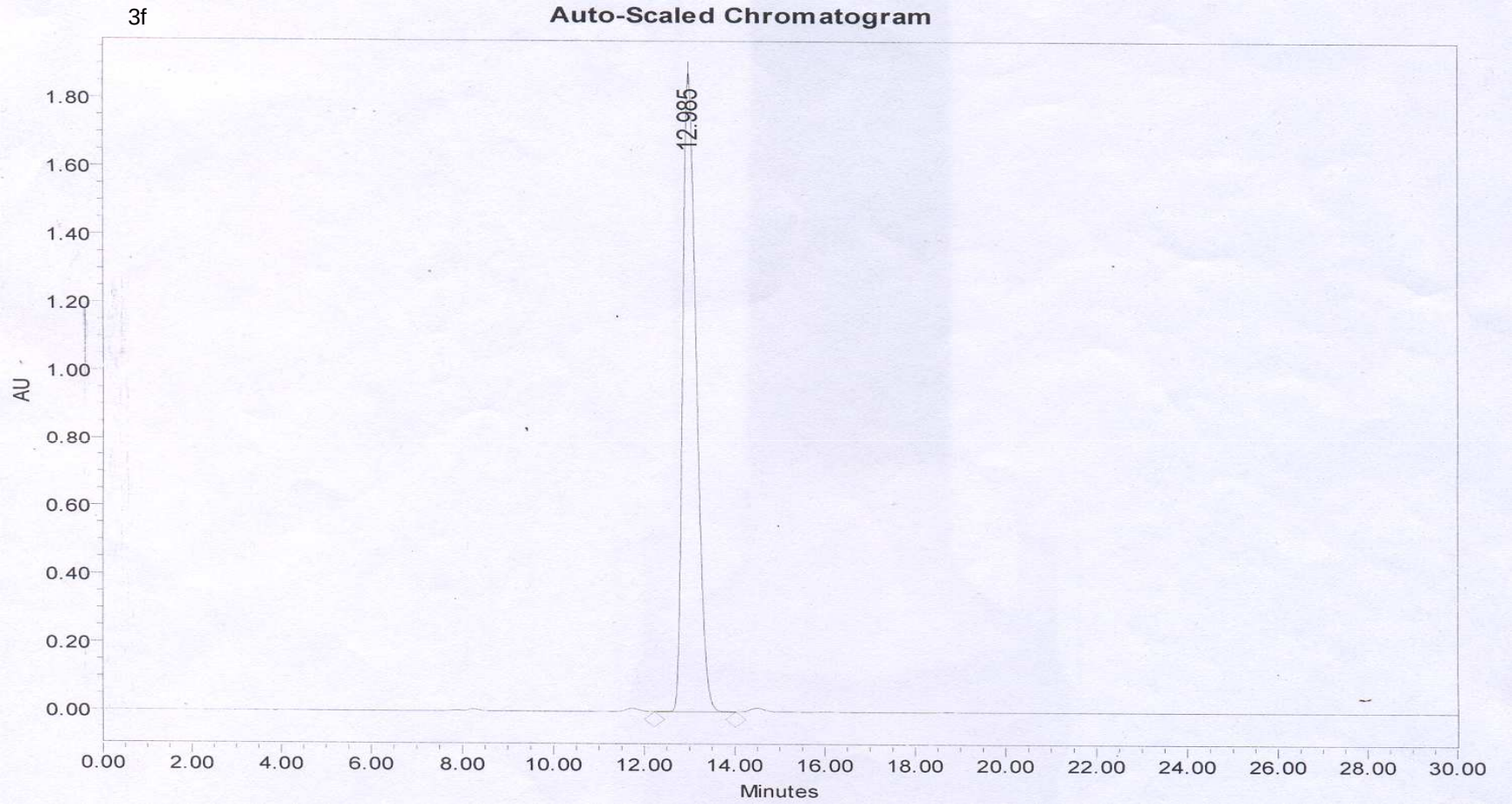
FigureS-13: ^{1}H spectrum (300MHz, $CDCl_3$) **3f.**



FigureS-14: ^{13}C spectrum (50 MHz, $CDCl_3$) **3f**.

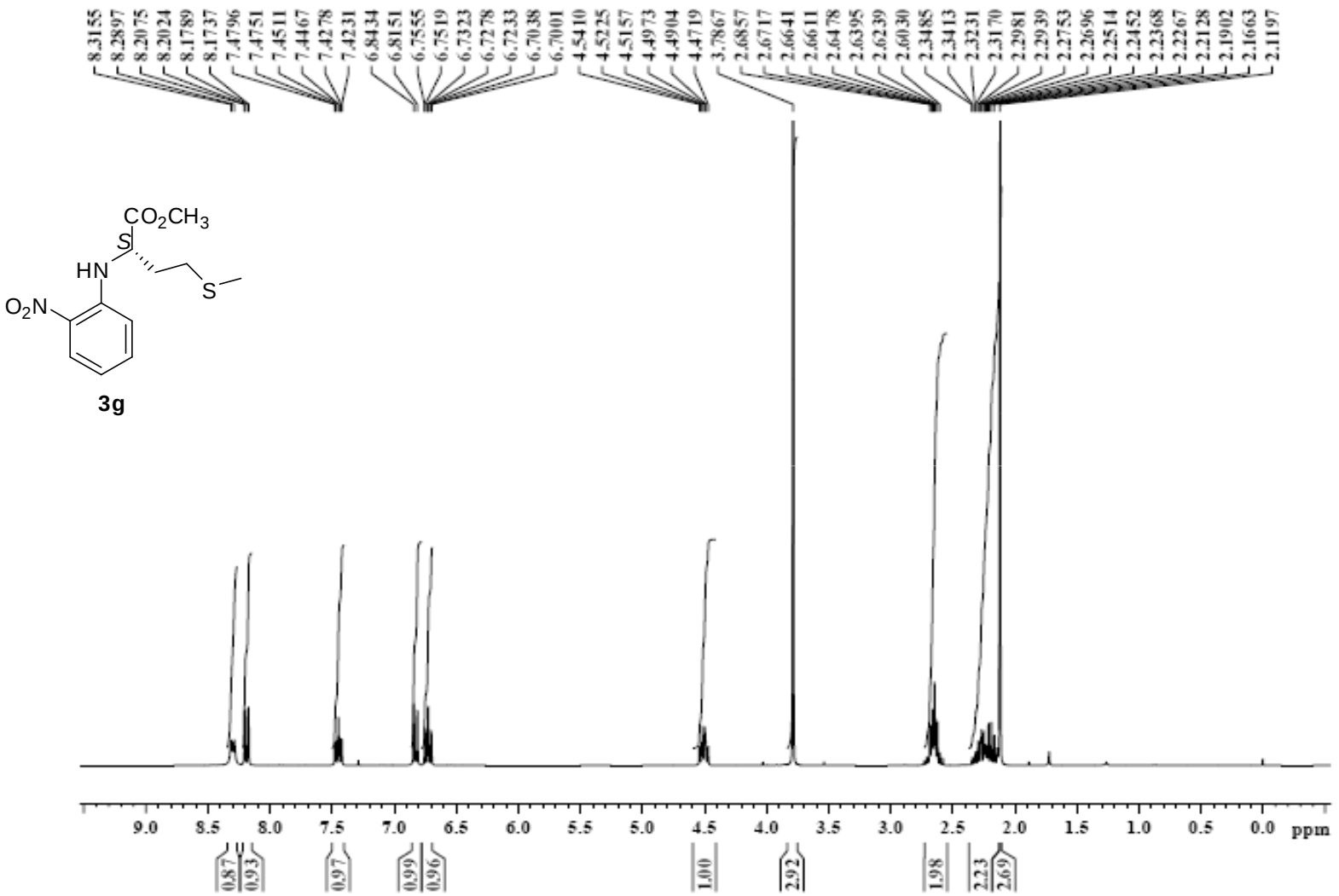


3f

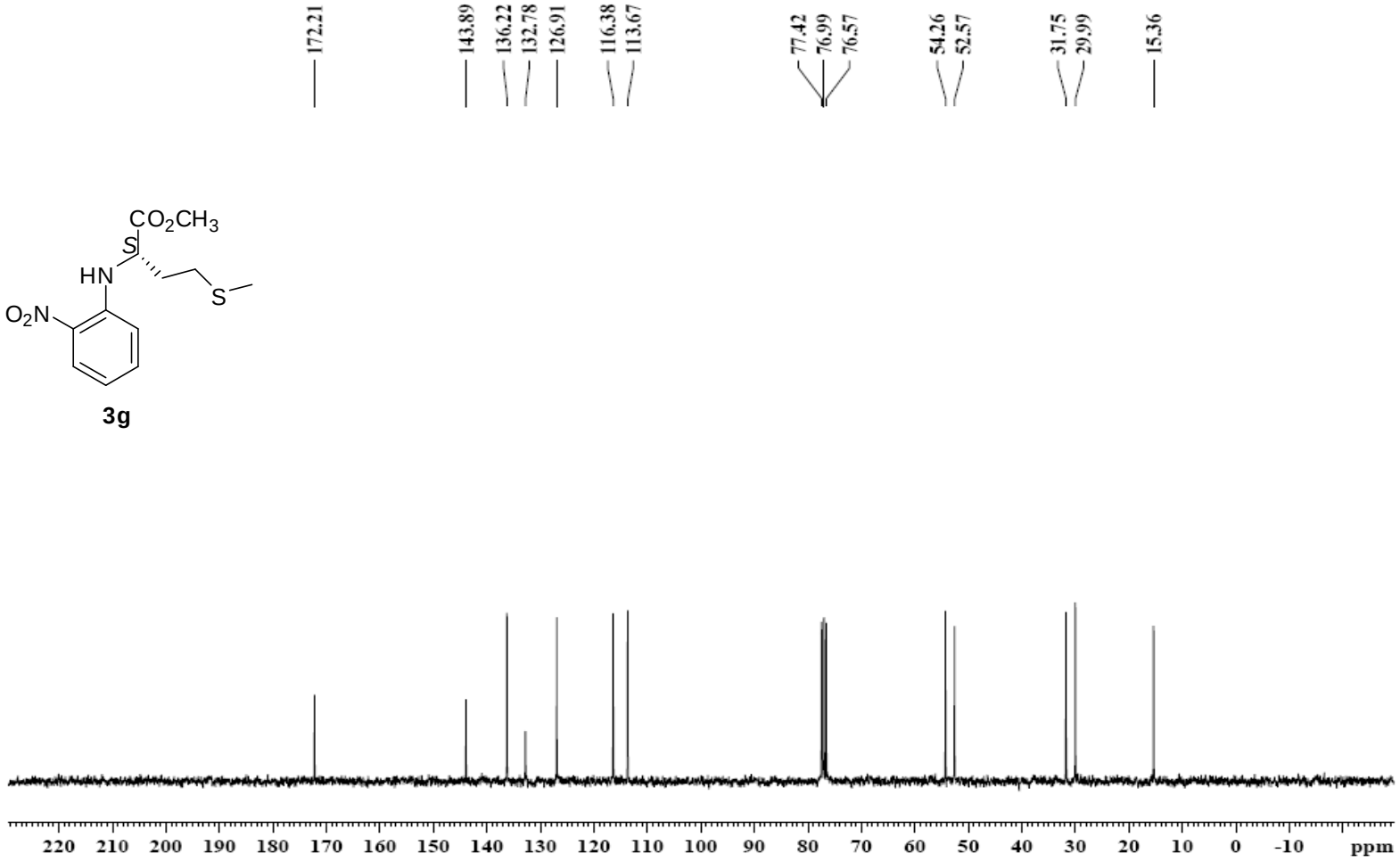


Retention time (min)

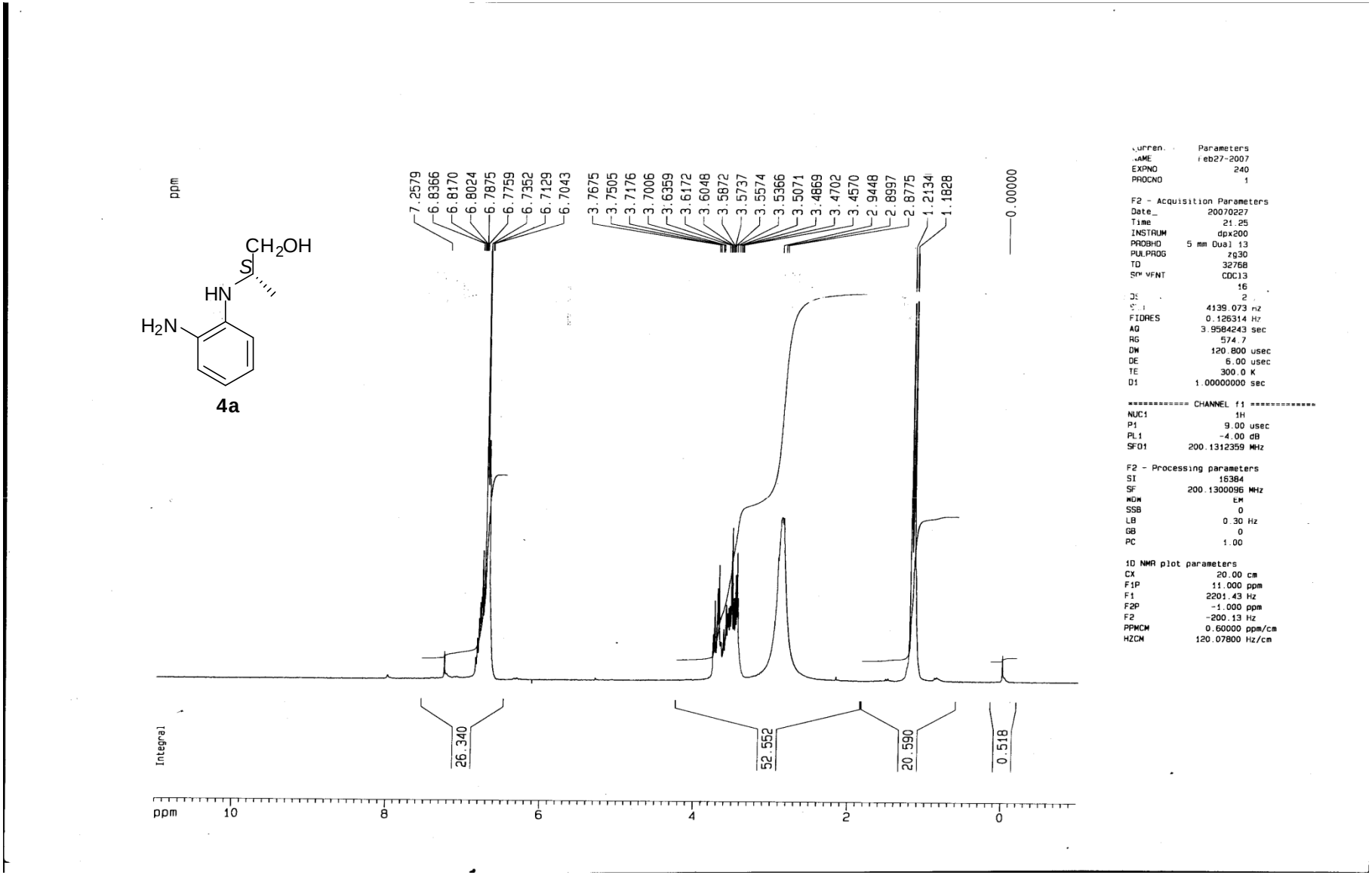
FigureS-15: HPLC spectrum of **3f.**



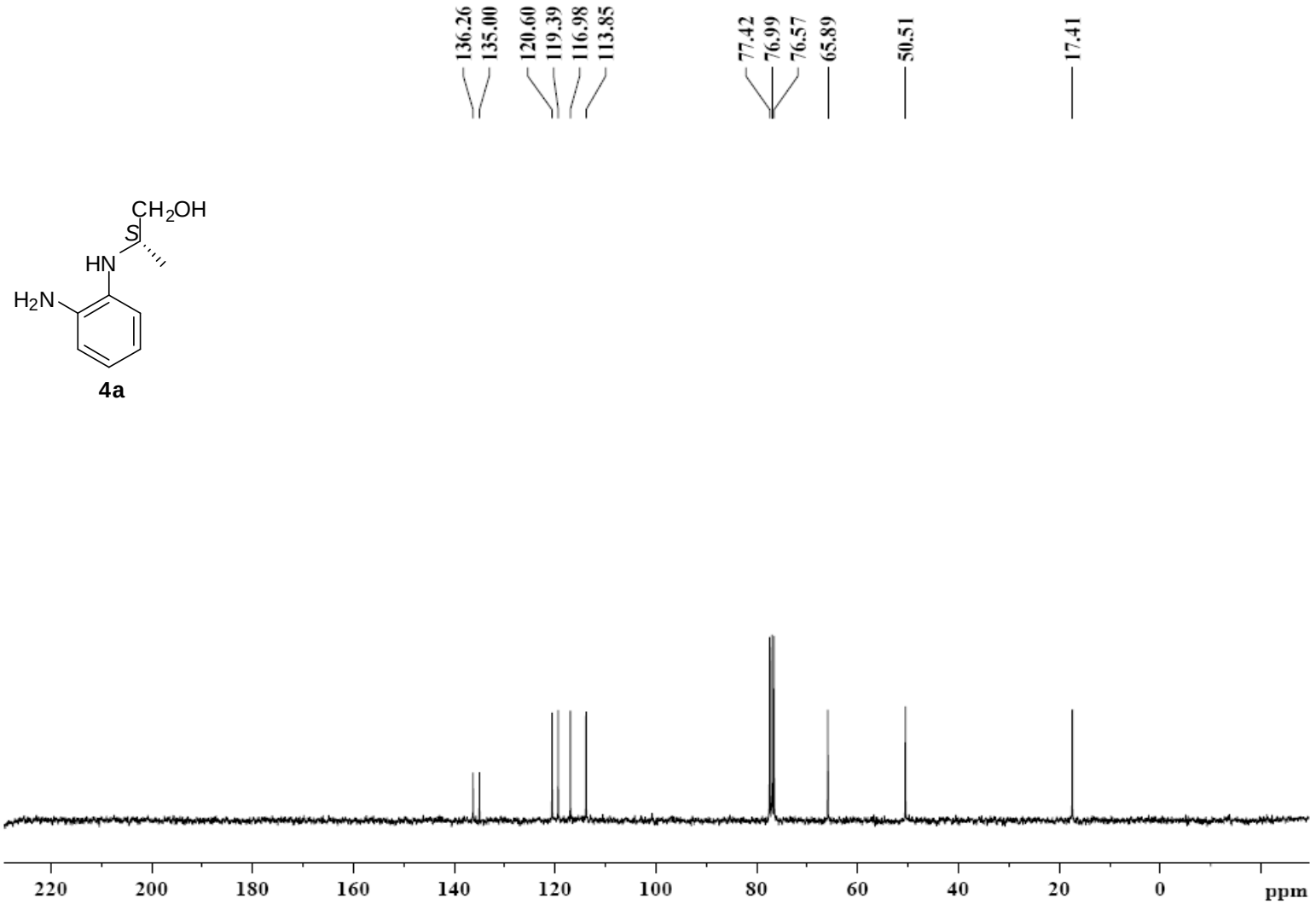
FigureS-16: ^{1}H spectrum (300 MHz, $CDCl_3$) **3g**.



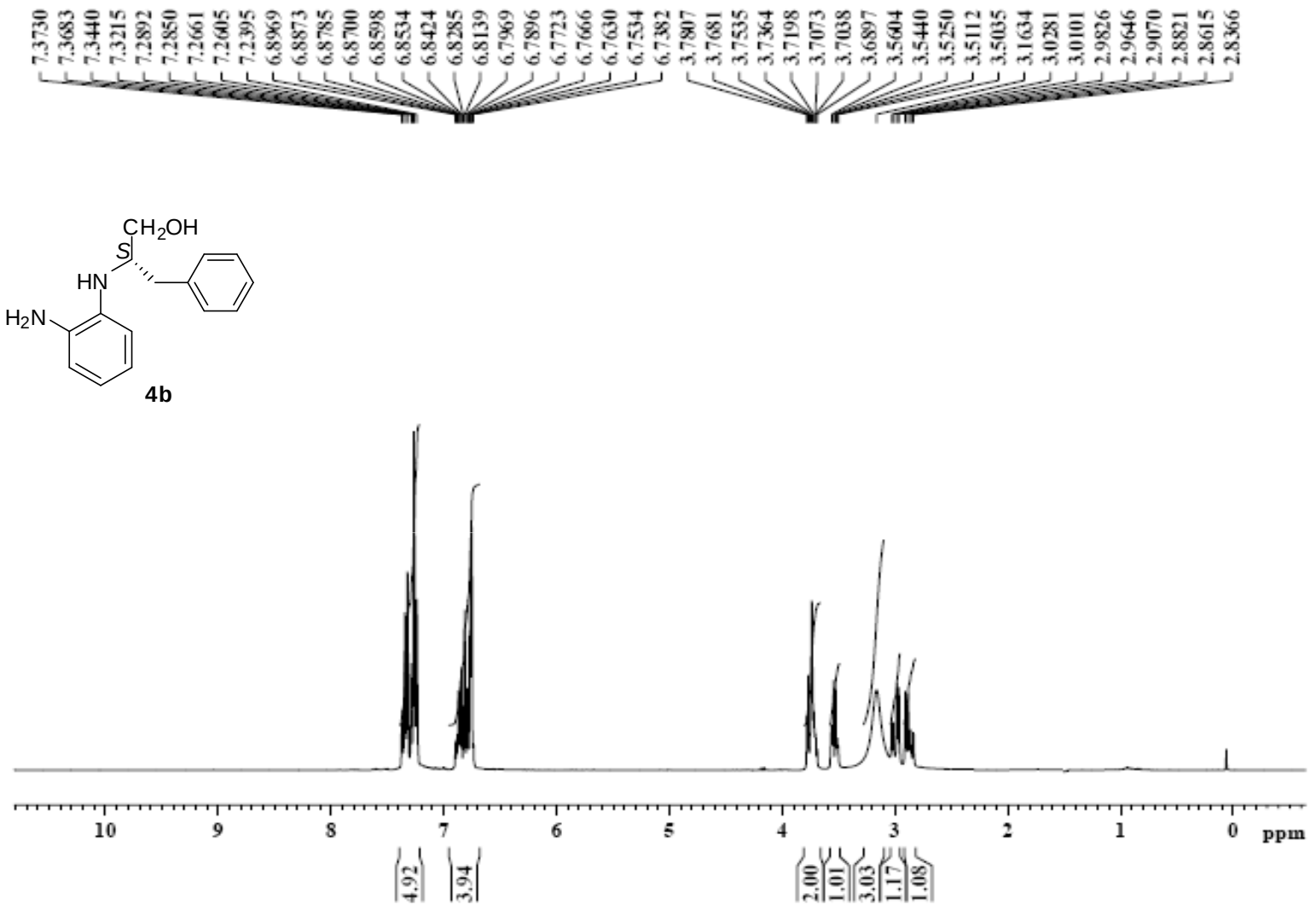
FigureS-17: ^{13}C spectrum (75MHz, $CDCl_3$) **3g**.



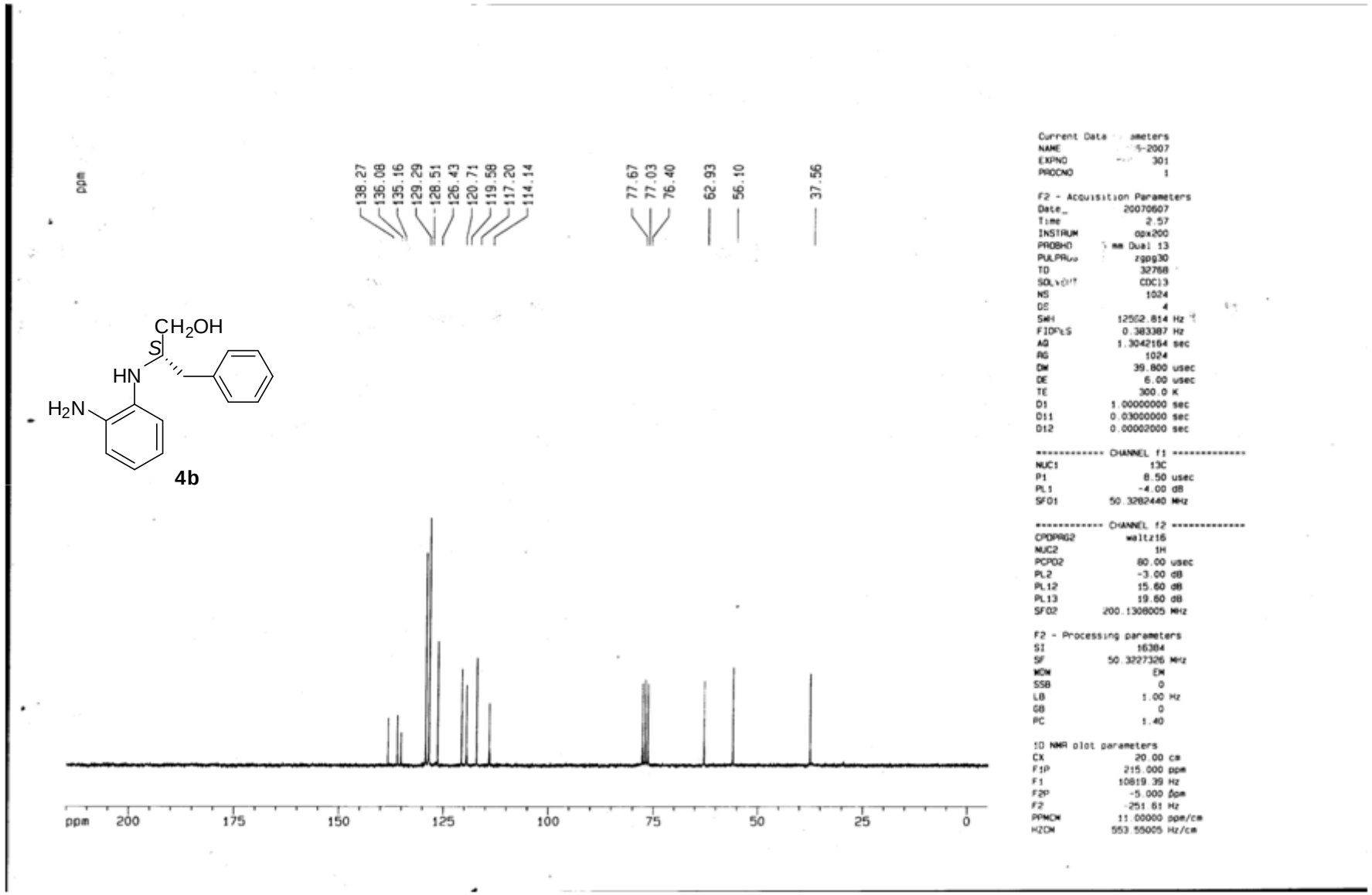
FigureS-18: ^{1}H spectrum (300MHz, $CDCl_3$) **4a**.



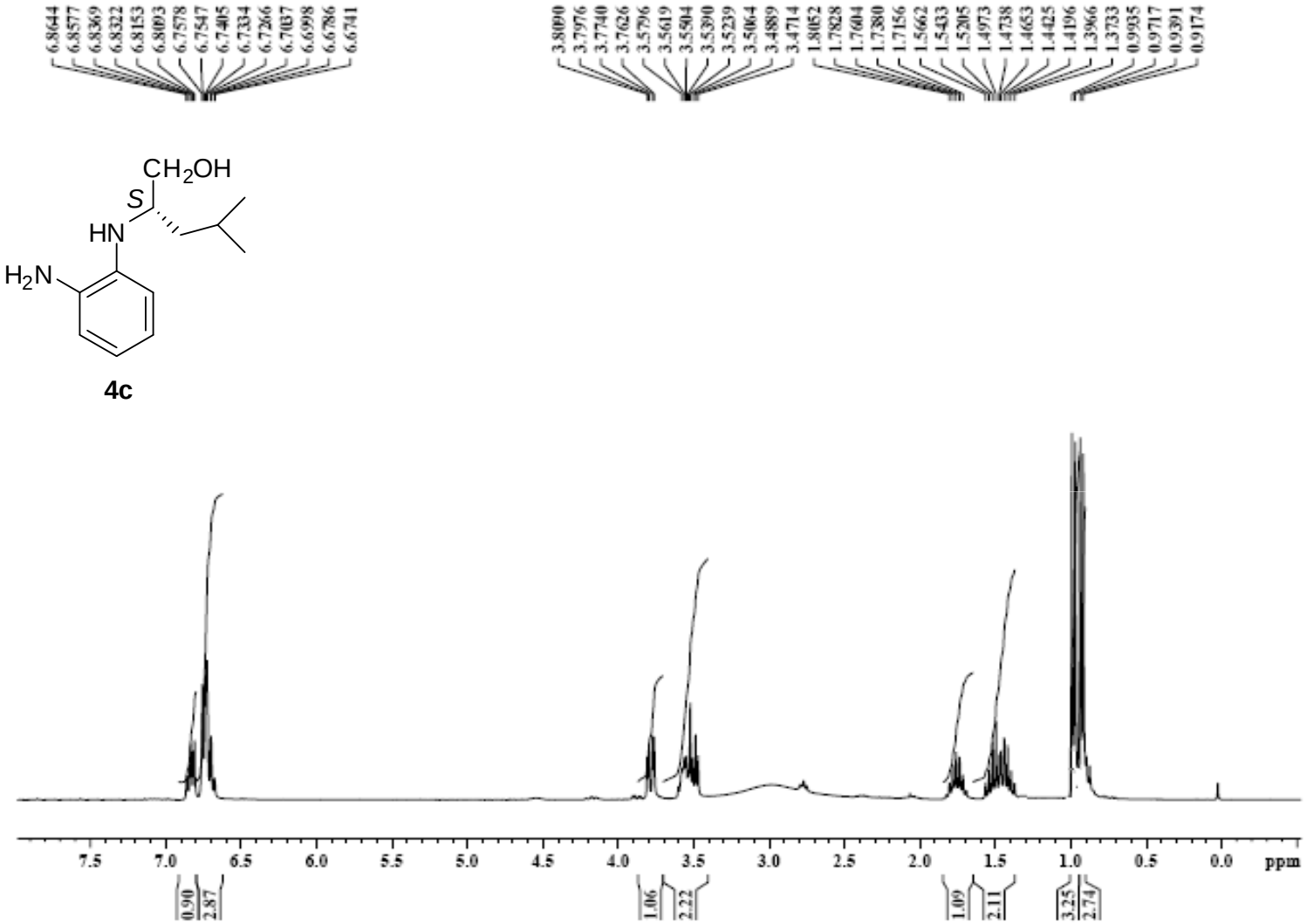
FigureS-19: ^{13}C spectrum (75MHz, $CDCl_3$) **4a**.



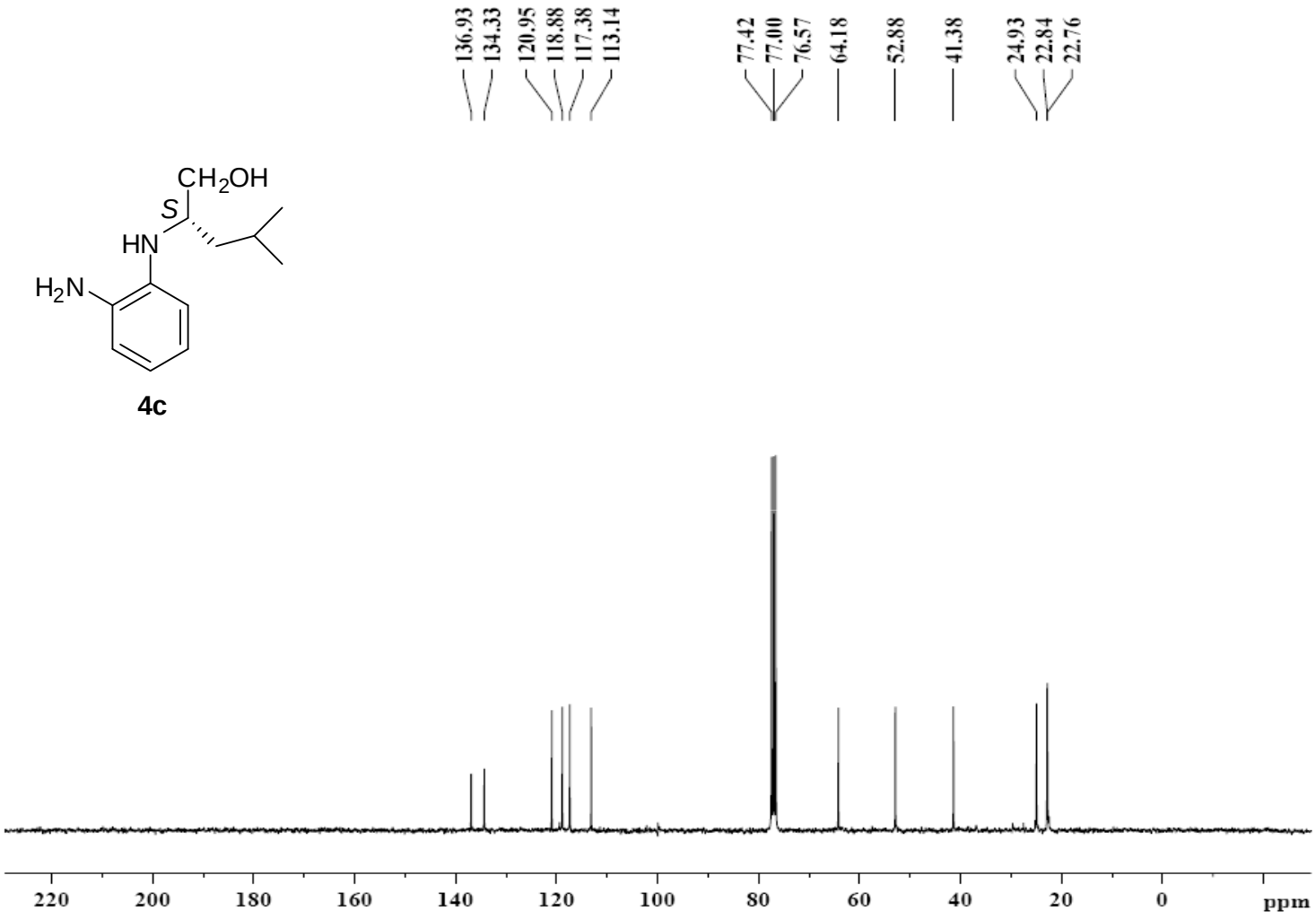
FigureS-20: ^{1}H spectrum (300MHz, $CDCl_3$) **4b**.



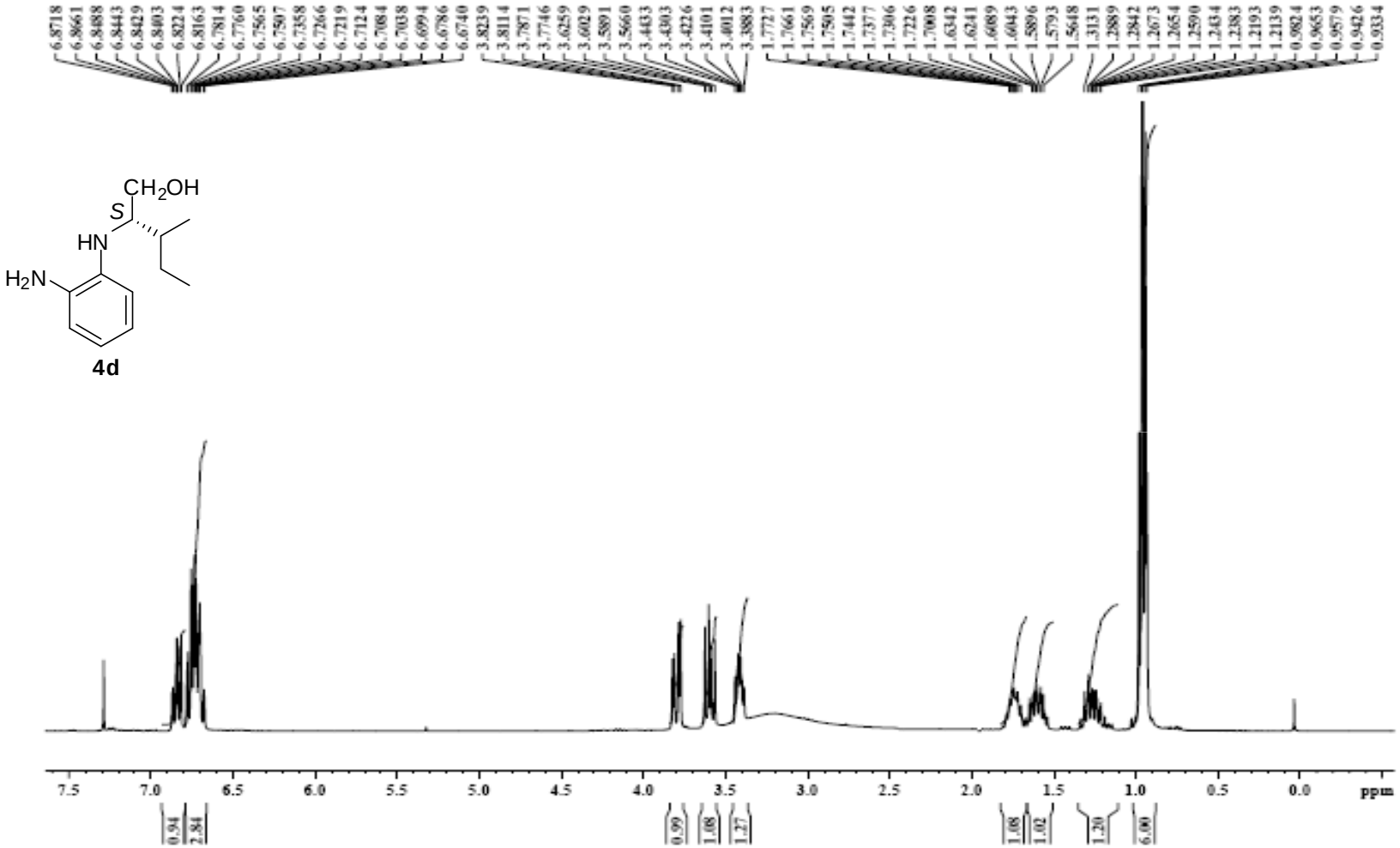
FigureS-21: ^{13}C spectrum (50 MHz, $CDCl_3$) **4b.**



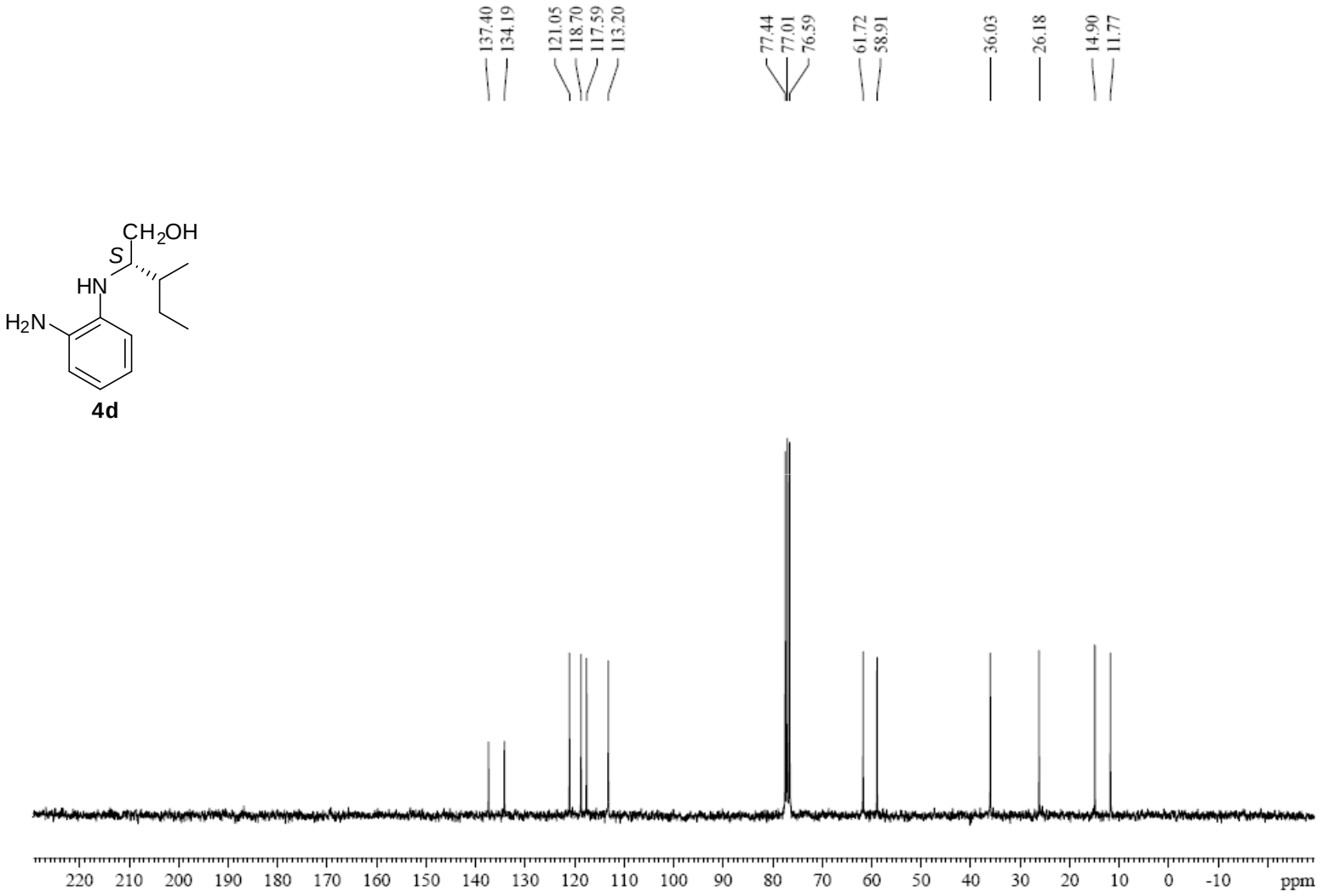
FigureS-22: ^{1}H spectrum (3OOMHz, $CDCl_3$) **4c**.



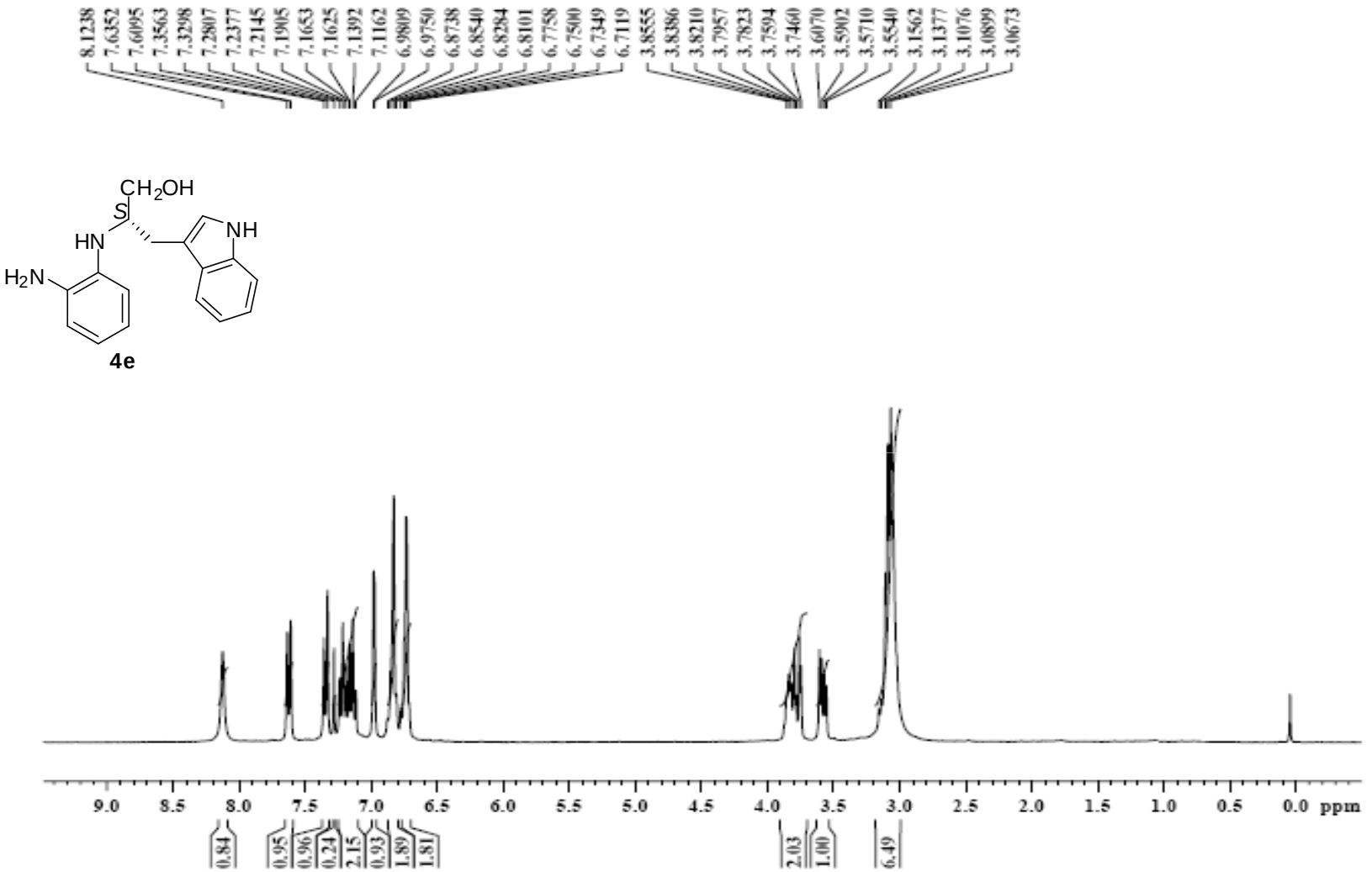
FigureS-23: ^{13}C spectrum (75MHz, $CDCl_3$) **4c**.



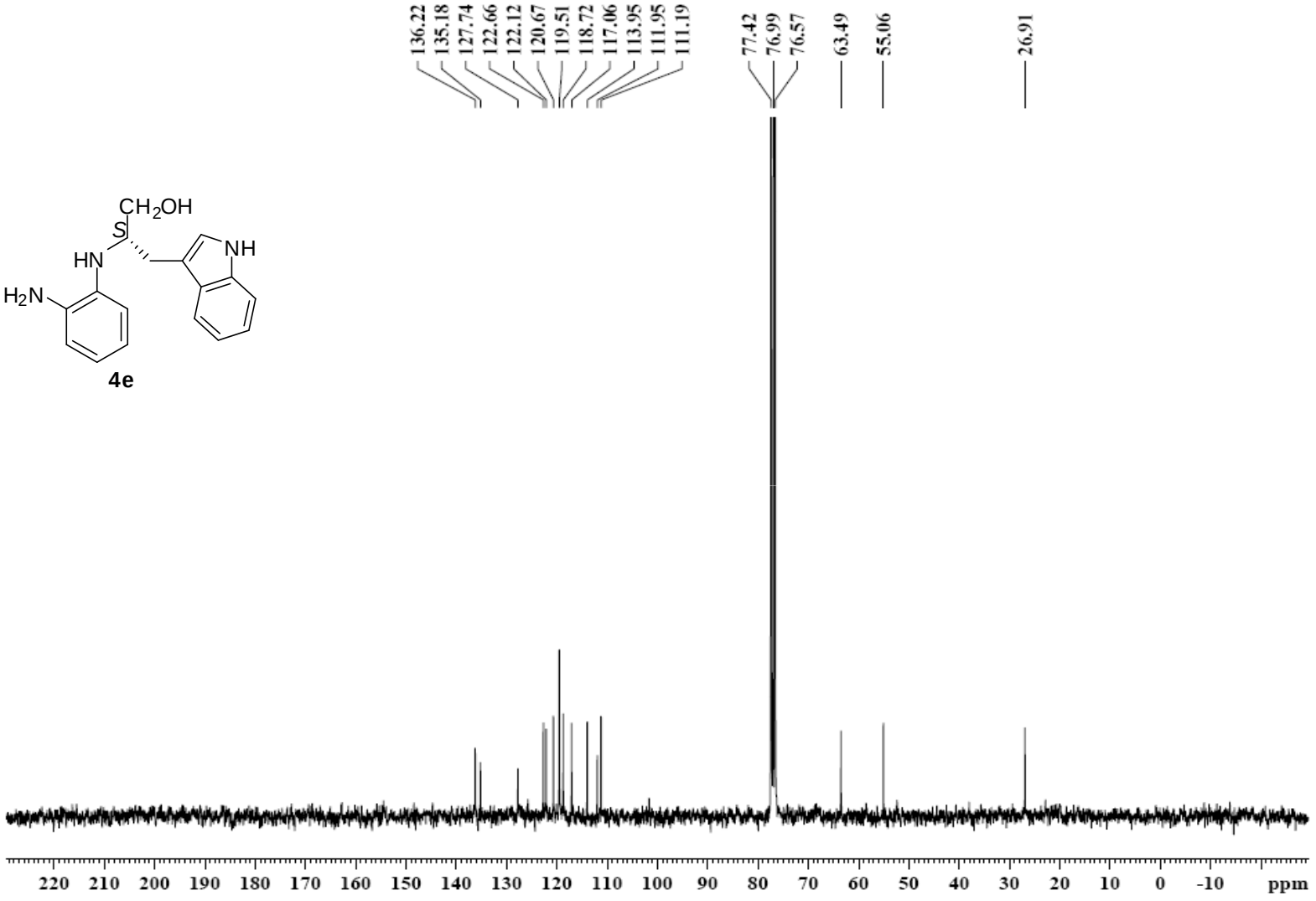
FigureS-24: ^{1}H spectrum (300MHz, $CDCl_3$) **4d**.



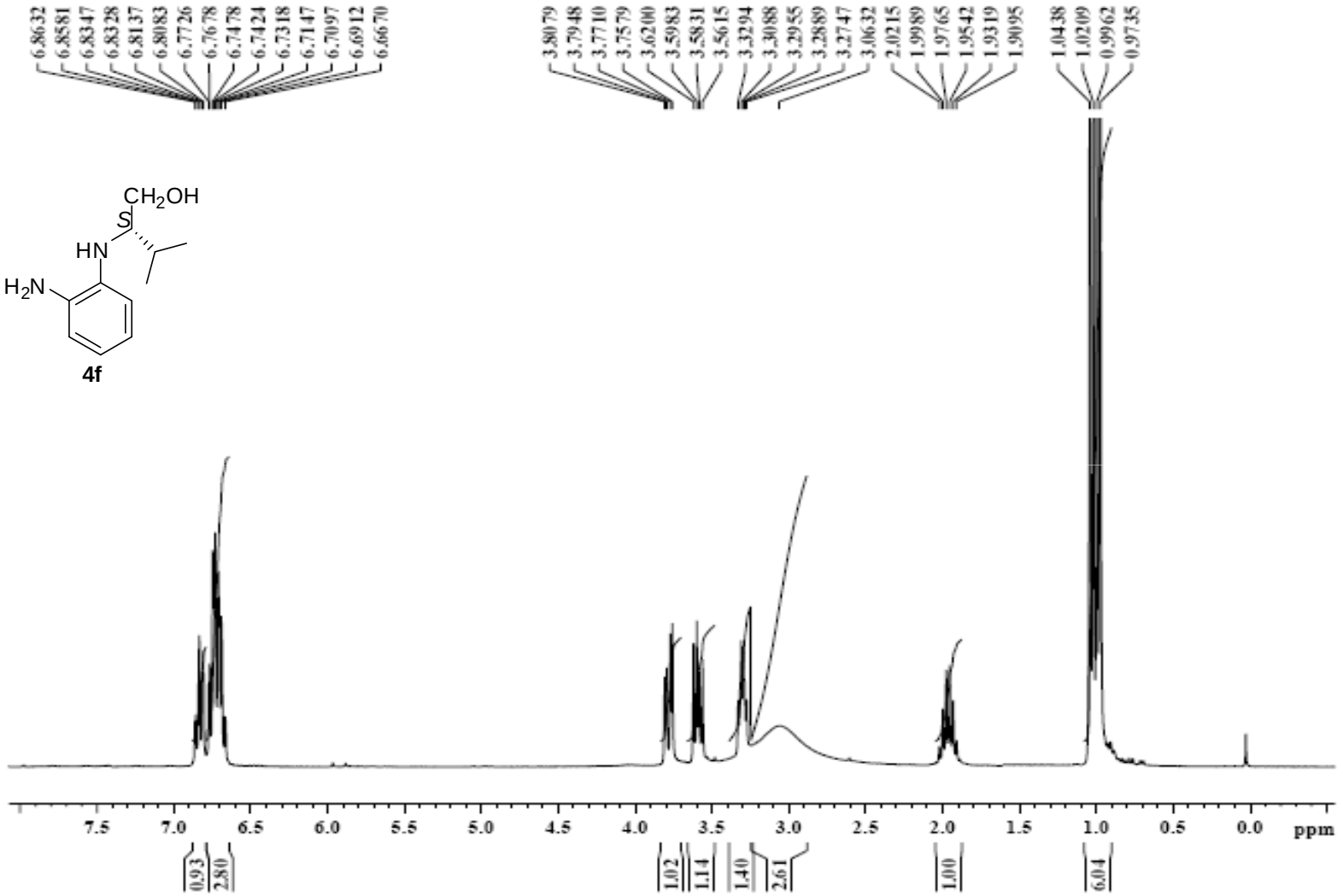
FigureS-25: ^{13}C spectrum (75MHz, $CDCl_3$) **4d**.



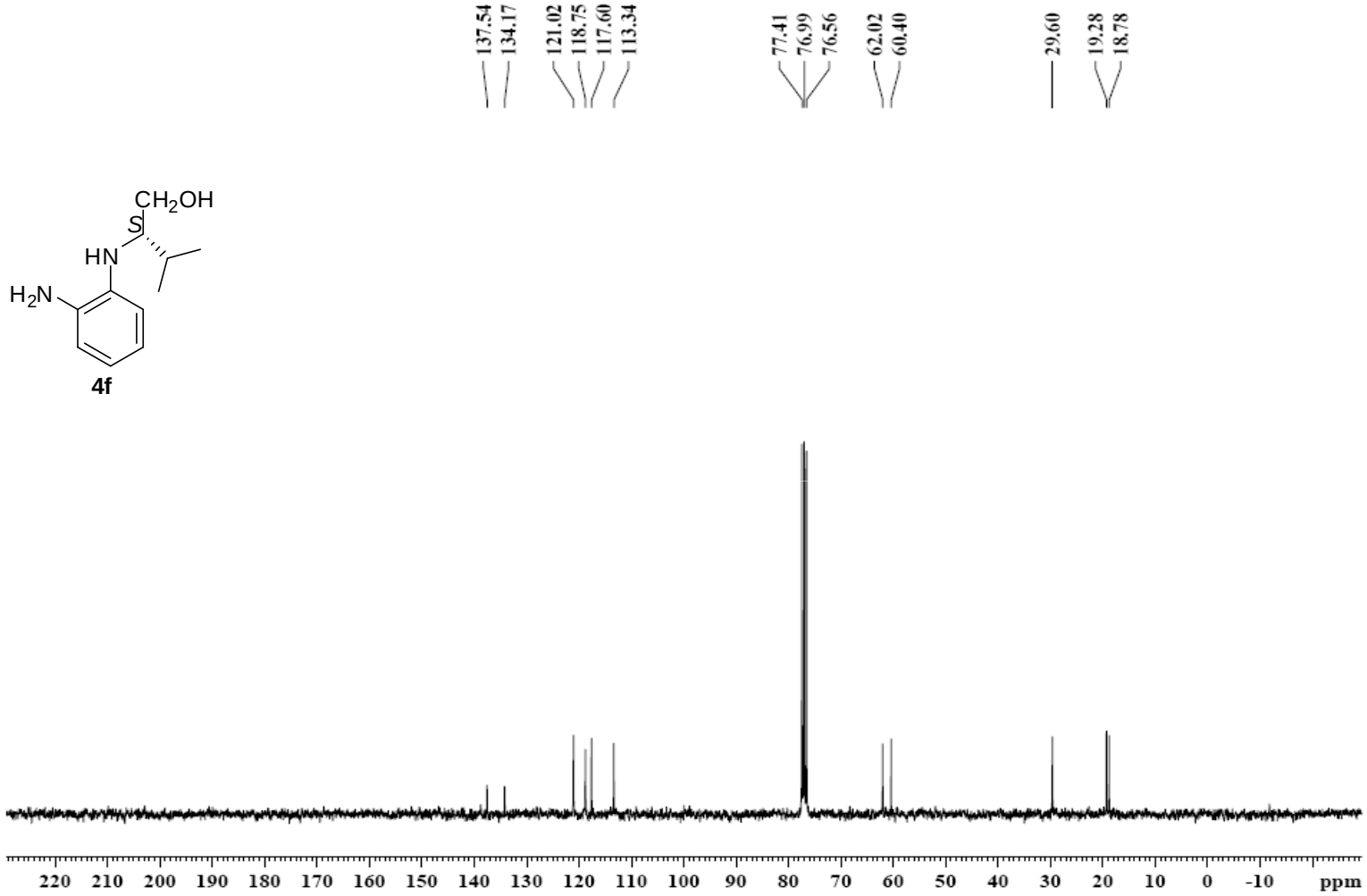
FigureS-26: ^{1}H spectrum (300MHz, $CDCl_3$) **4e**.



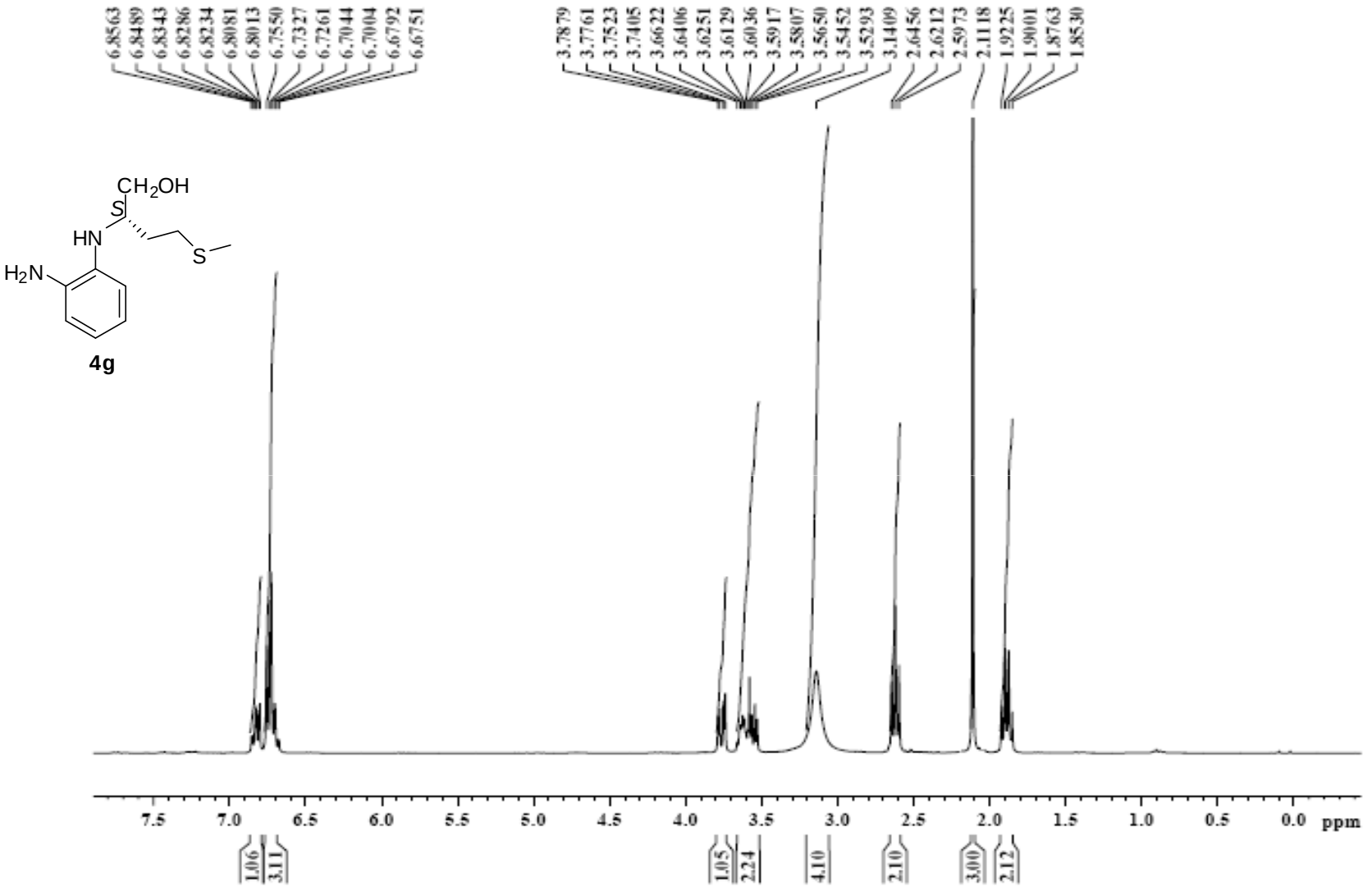
FigureS-27: ^{13}C spectrum (75MHz, $CDCl_3$) **4e**.



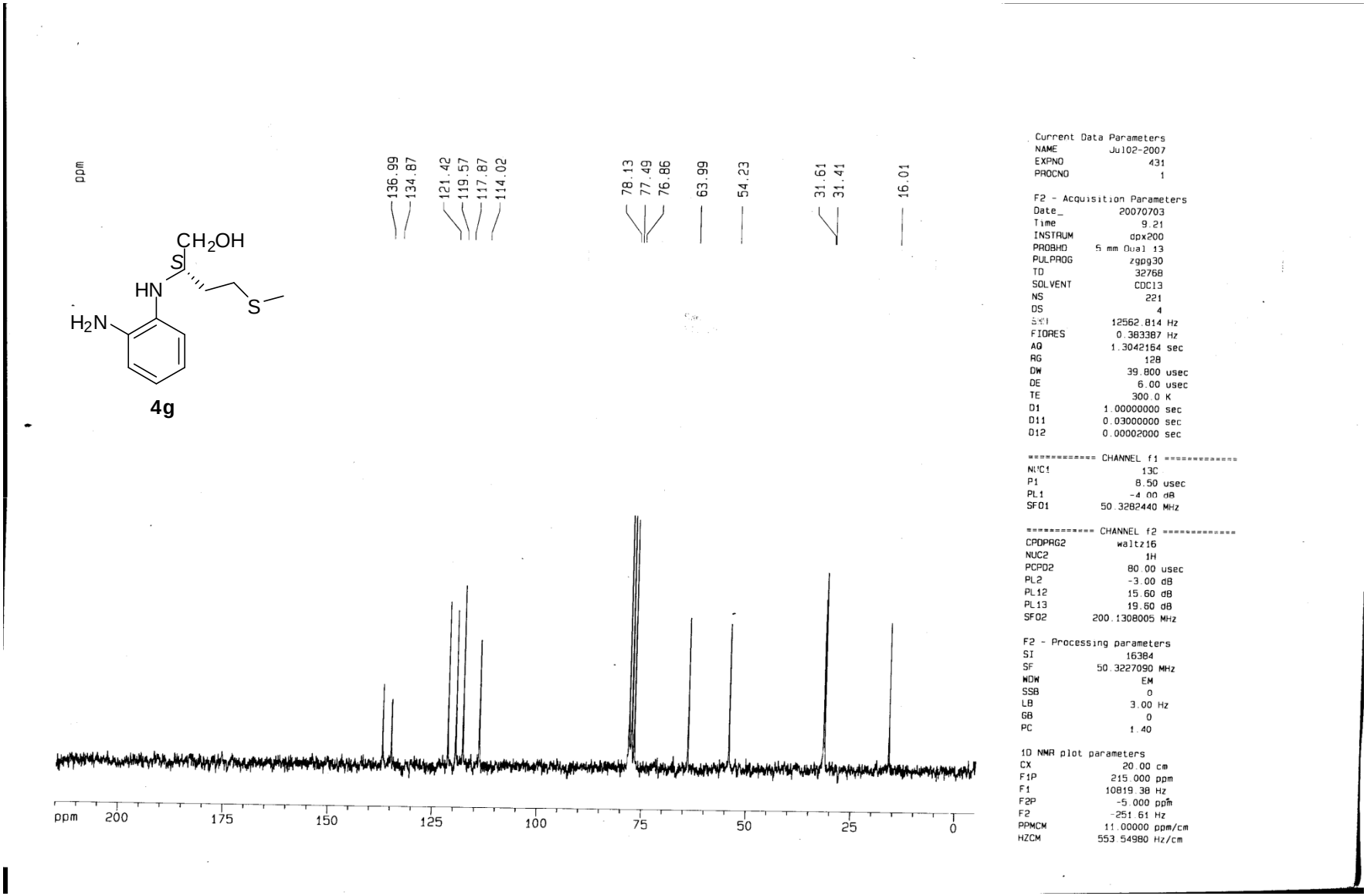
FigureS-28: ^{1}H spectrum (300MHz, $CDCl_3$) **4f**.



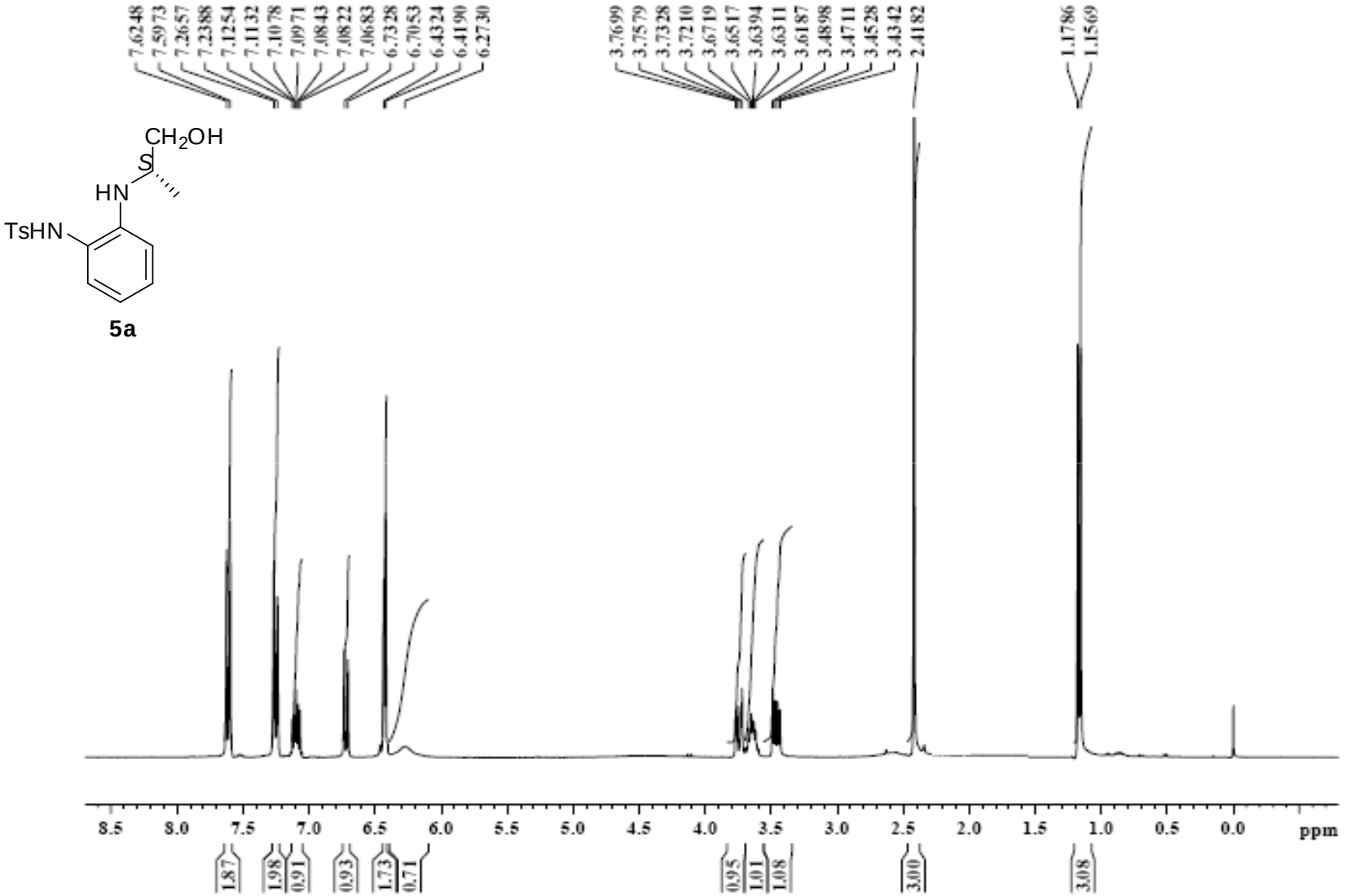
FigureS-29: ^{13}C spectrum (75MHz, $CDCl_3$) of **4f**.



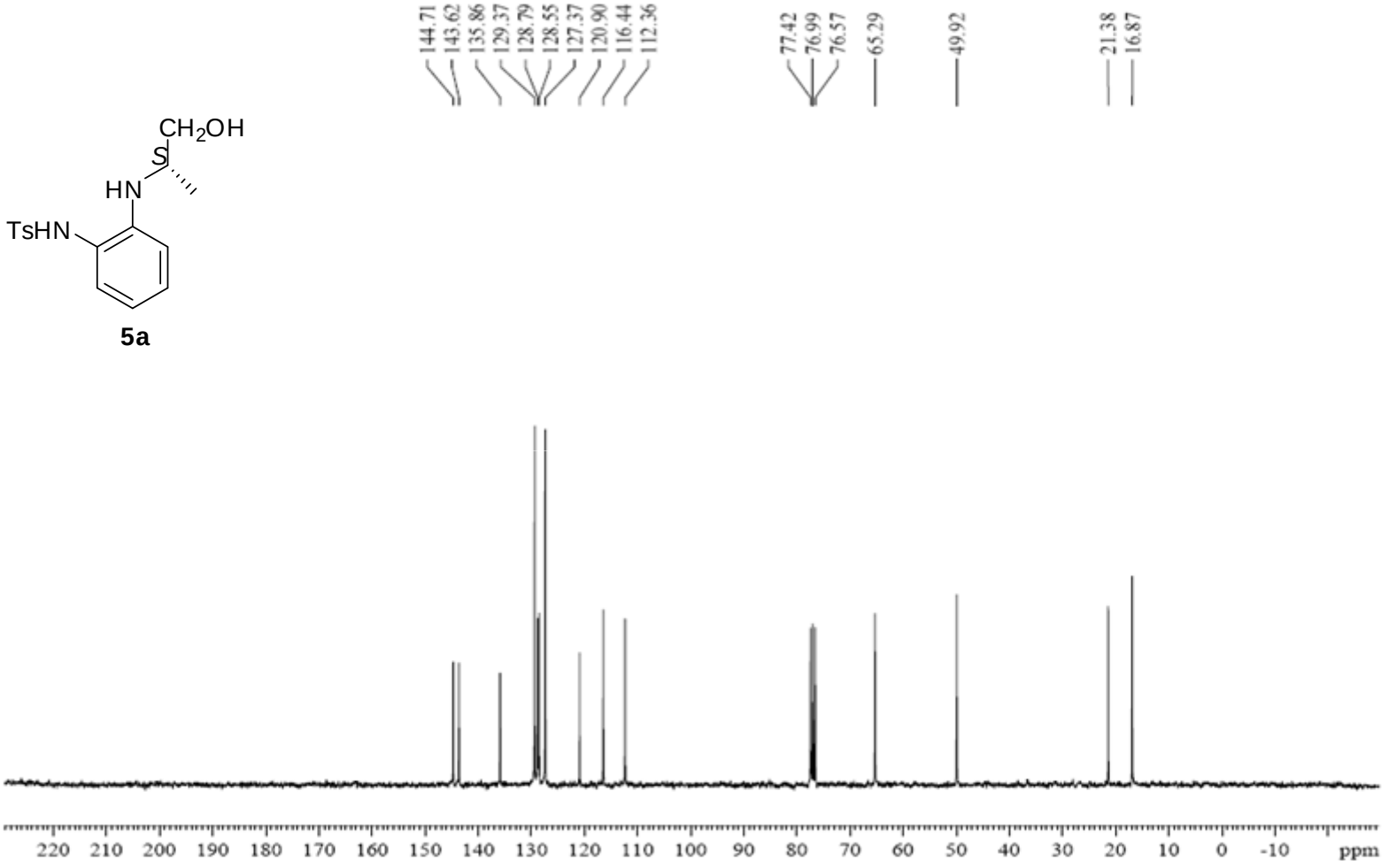
FigureS-30: ^{1}H spectrum (300MHz, $CDCl_3$) of **4g**.



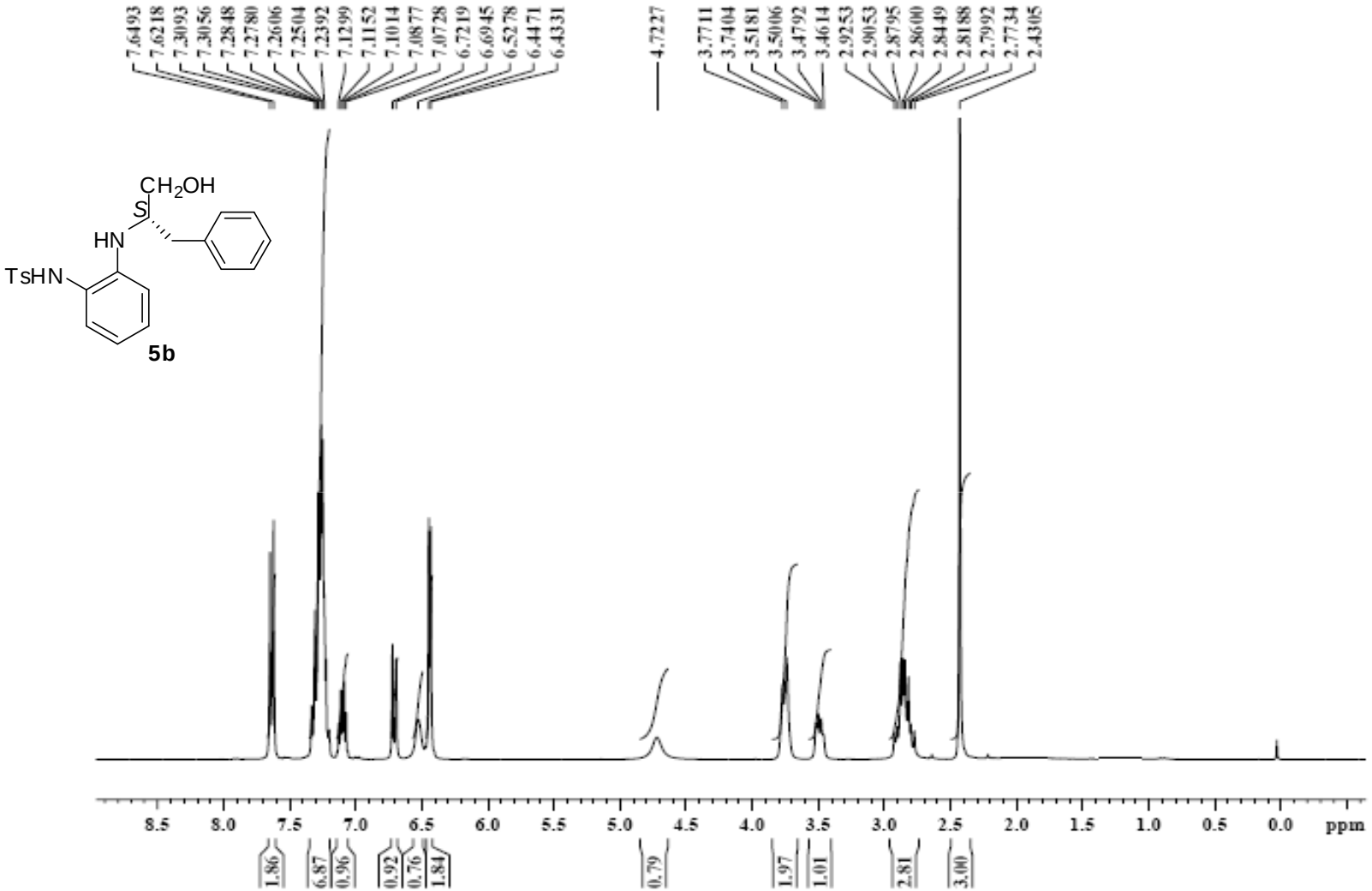
FigureS-31: ^{13}C spectrum (50 MHz, $CDCl_3$) of **4g**.



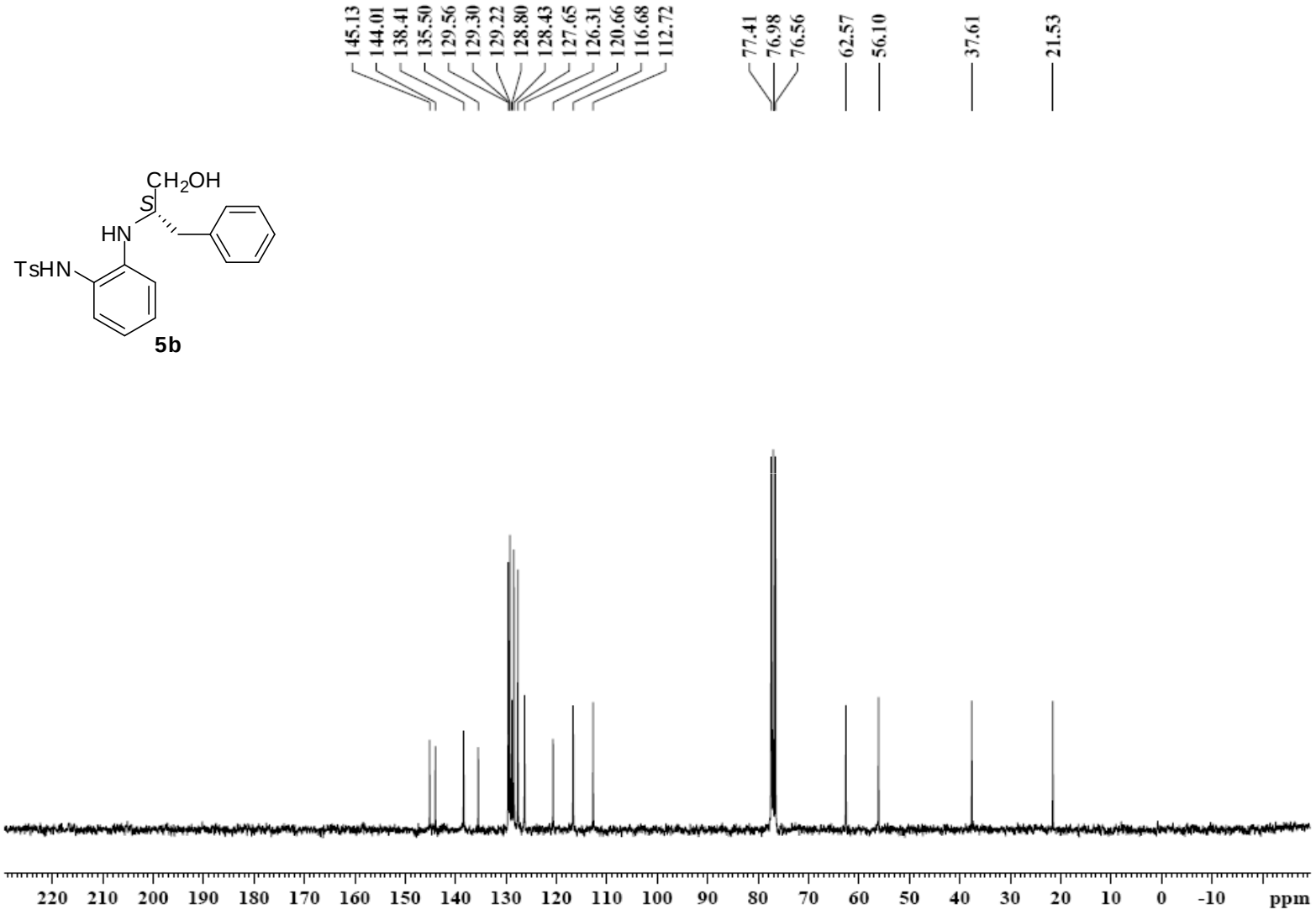
FigureS-32: ^{1}H spectrum (300MHz, $CDCl_3$) of **5a**.



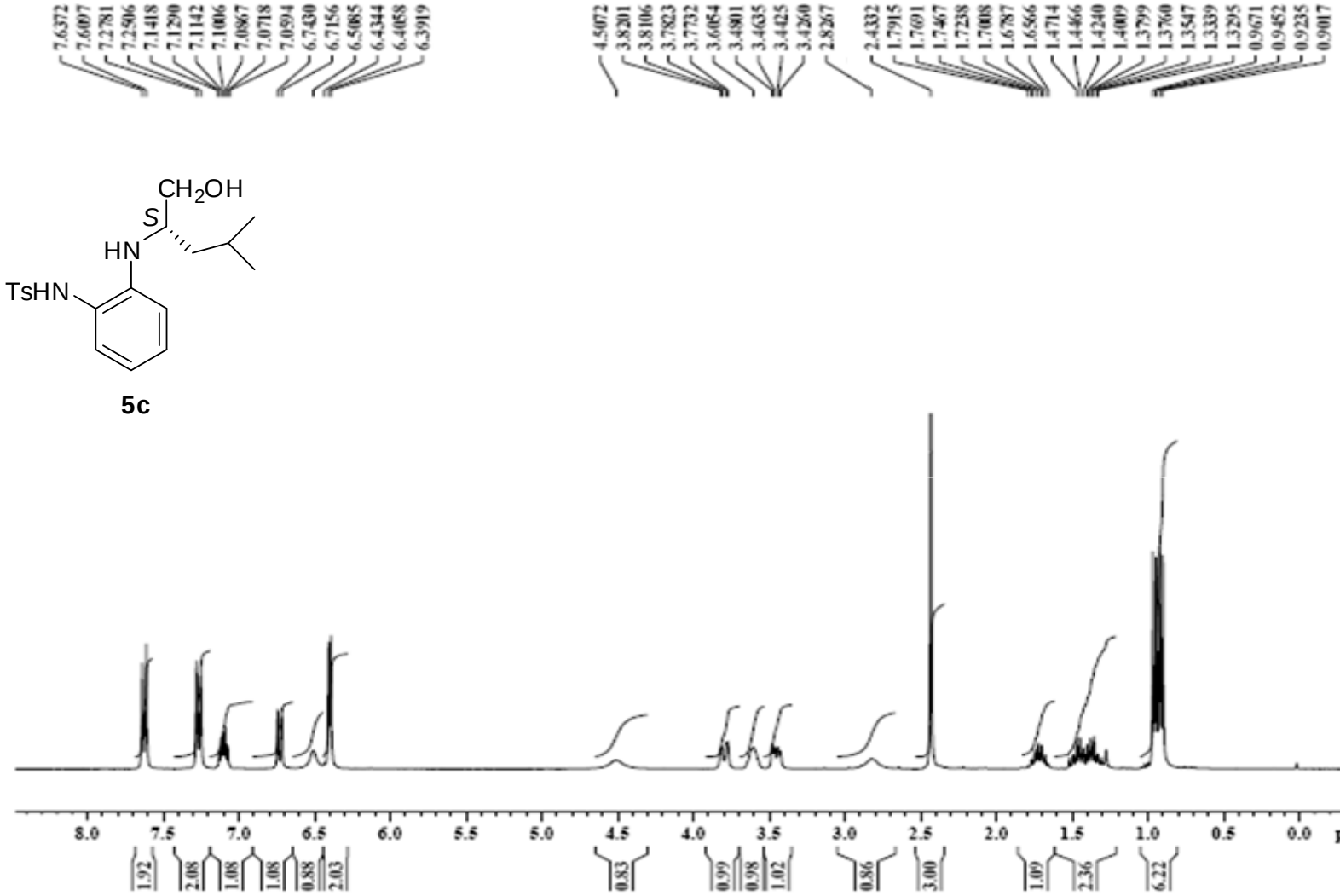
FigureS-33: ^{13}C spectrum (75MHz, $CDCl_3$) of **5a**.



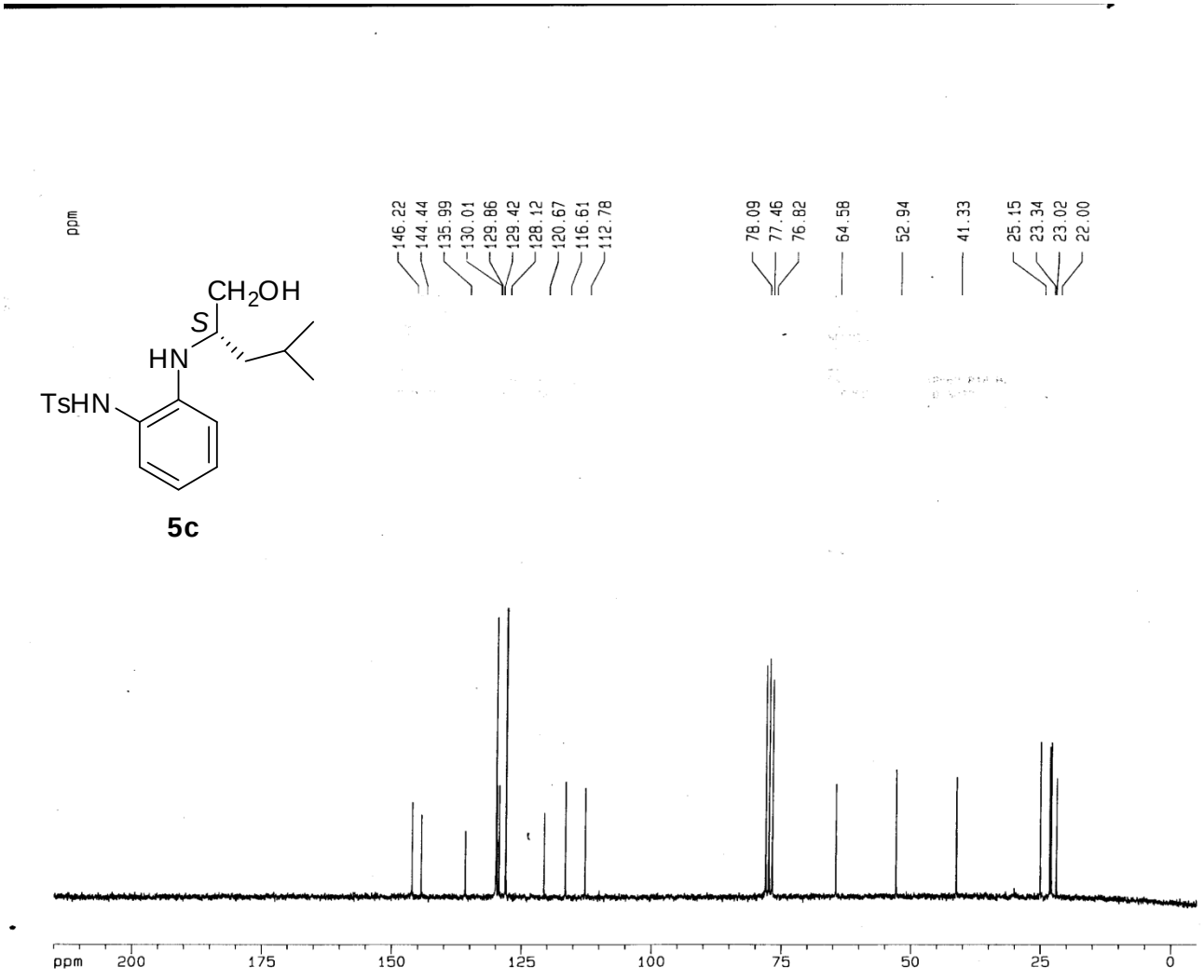
FigureS-34: ^{1}H spectrum (300MHz, $CDCl_3$) of **5b**.



FigureS-35: ^{13}C spectrum (75MHz, $CDCl_3$) of **5b**.



FigureS-36: ^{1}H spectrum (300MHz, $CDCl_3$) of **5c**.

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PROCNO                   1

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DS                     4
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FIDRES             0.383387 Hz
AQ              1.3042164 sec
RG                    64
DW                39.800 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec

========== CHANNEL f1 ==========
NUC1                  13C
P1                  8.50 usec
PL1                -4.00 dB
SFO1          50.3282440 MHz

========== CHANNEL f2 ==========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               15.60 dB
PL13               19.60 dB
SFO2         200.1308005 MHz

F2 - Processing parameters
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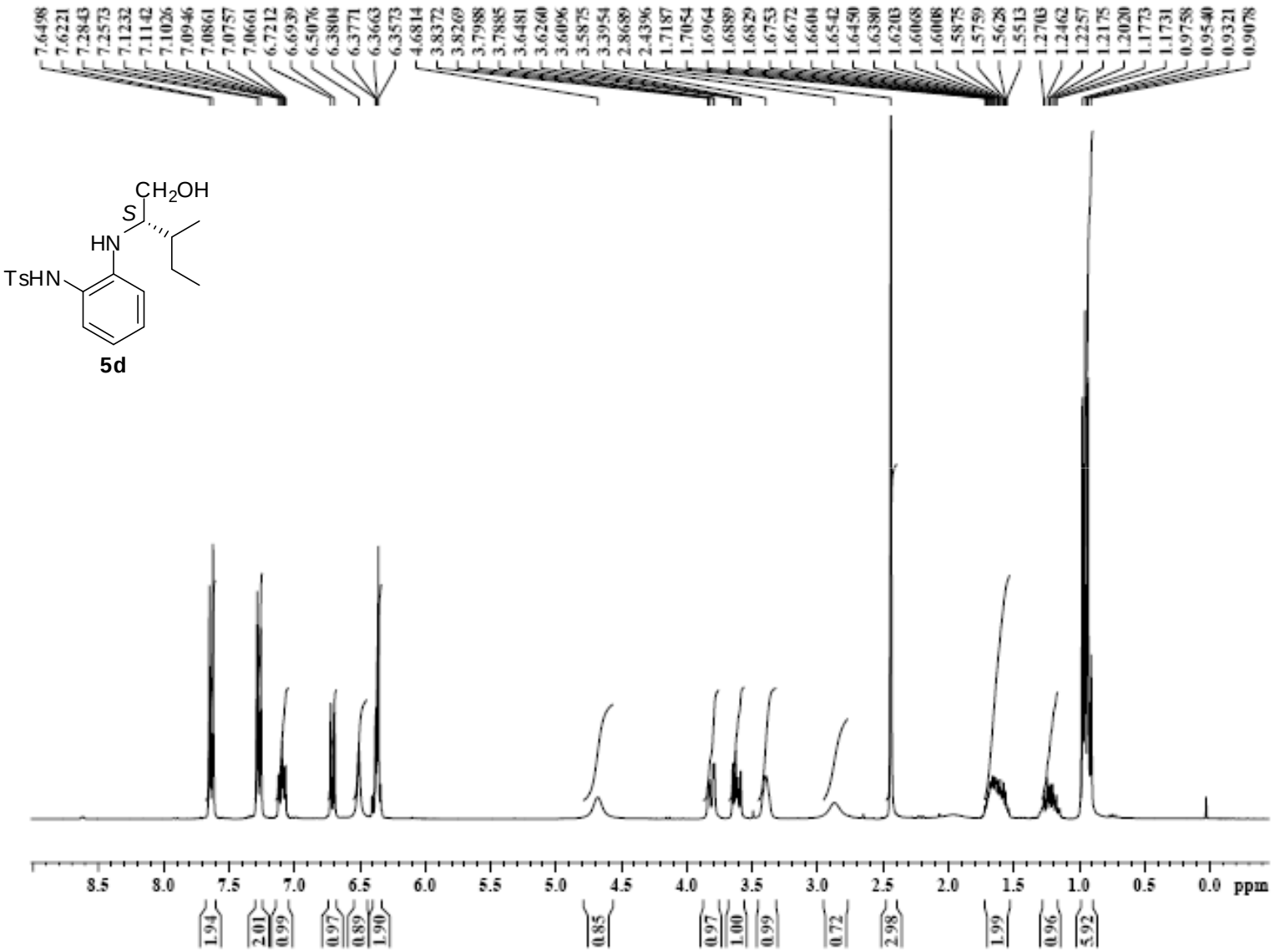
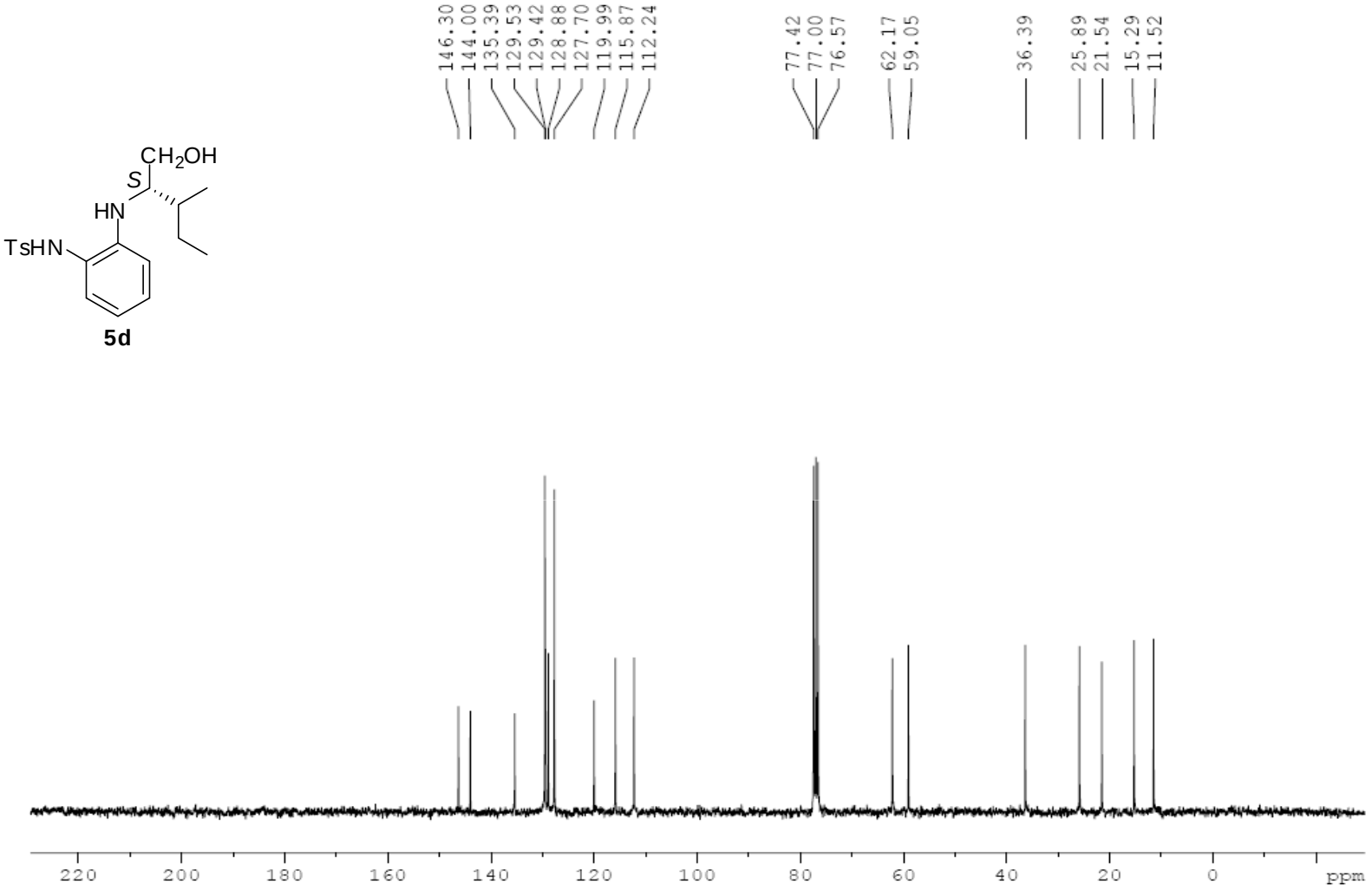
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P               215.000 ppm
F1              10819.38 Hz
F2P                -5.000 ppm
F2               -251.61 Hz
PPMCM           11.00000 ppm/cm
HZCM           553.54980 Hz/cm
```

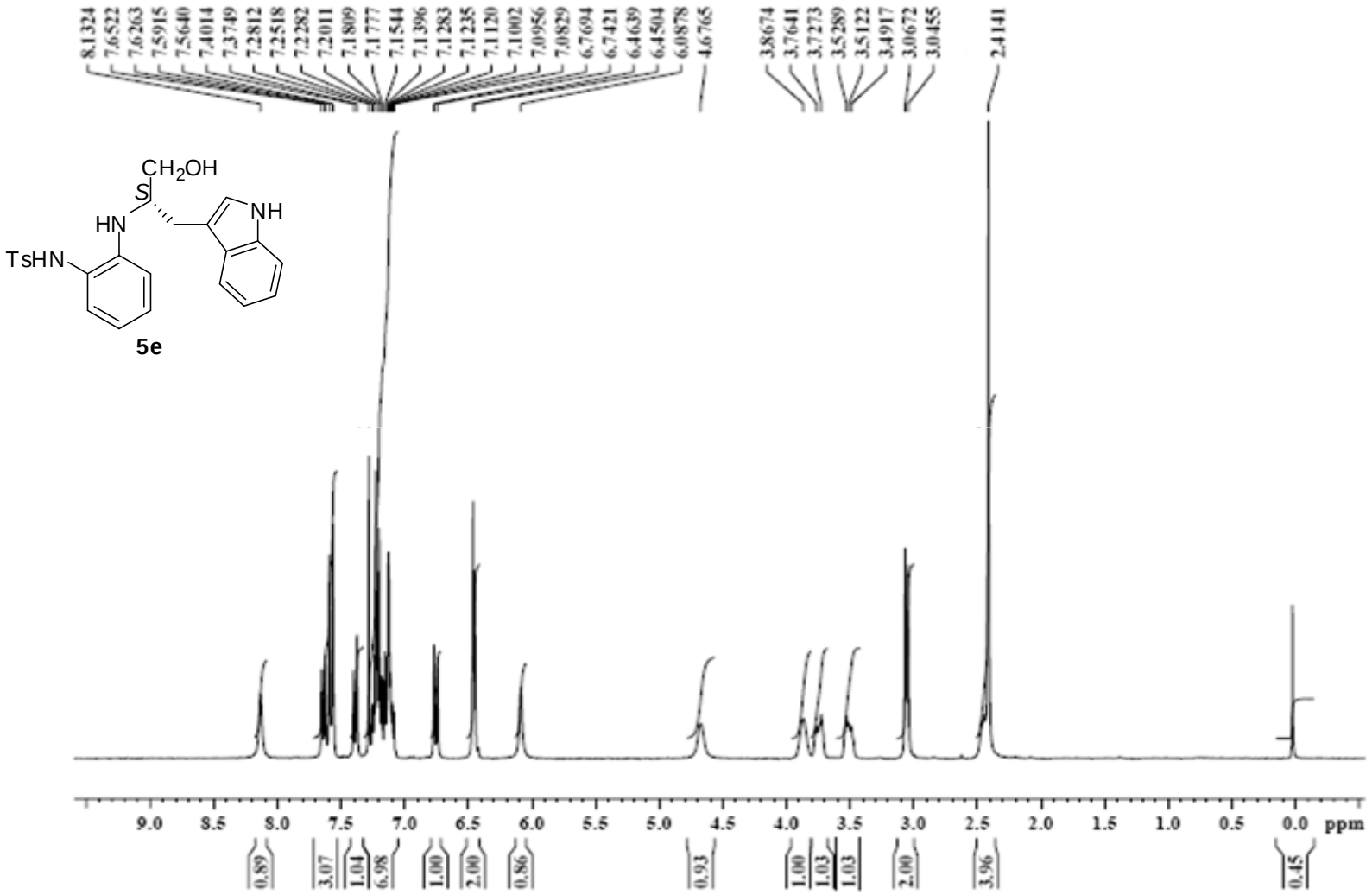
FigureS-37: ^{13}C spectrum (50 MHz, $CDCl_3$) of **5c**.



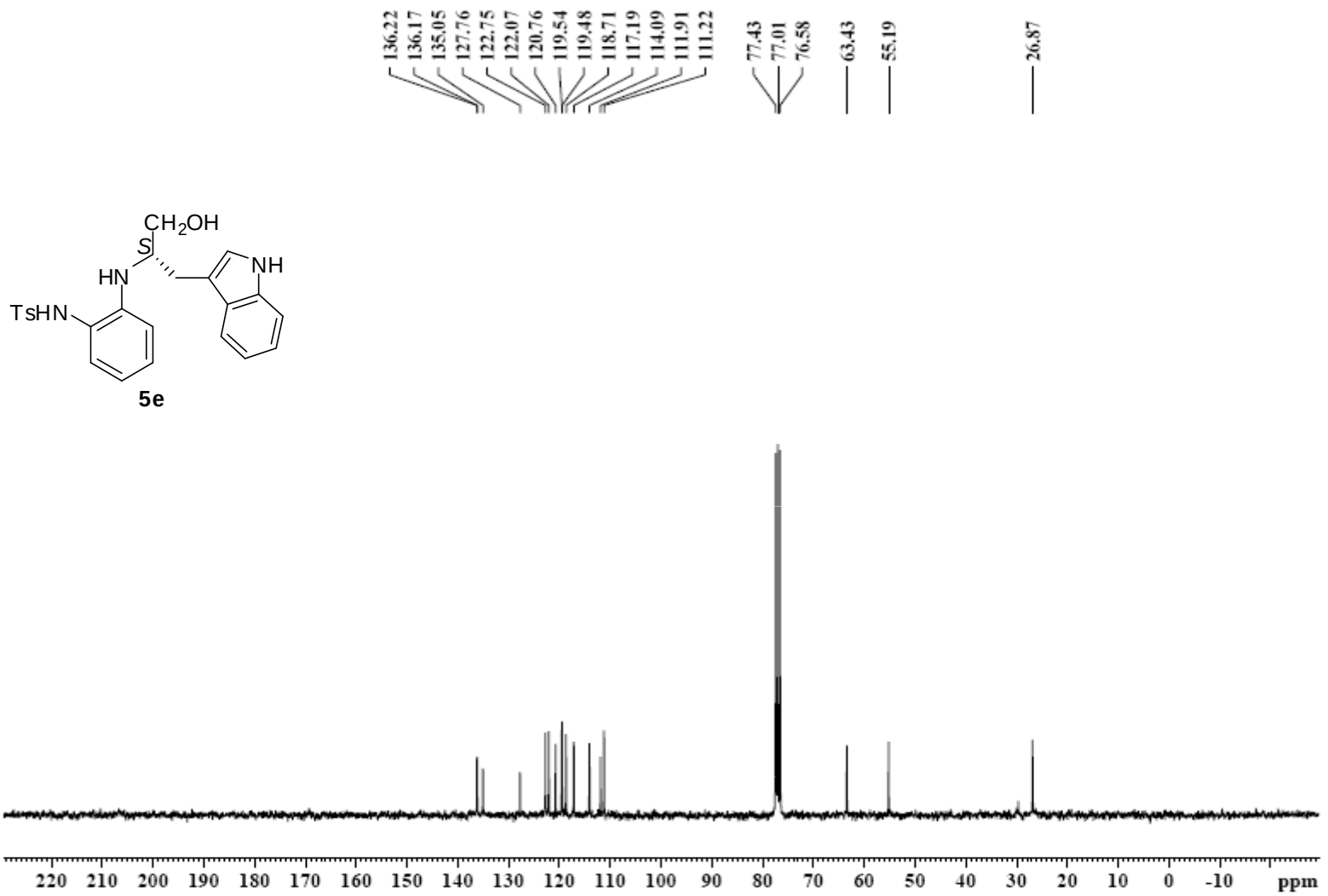
FigureS-38: ^{1}H spectrum (300MHz, $CDCl_3$) of **5d**.



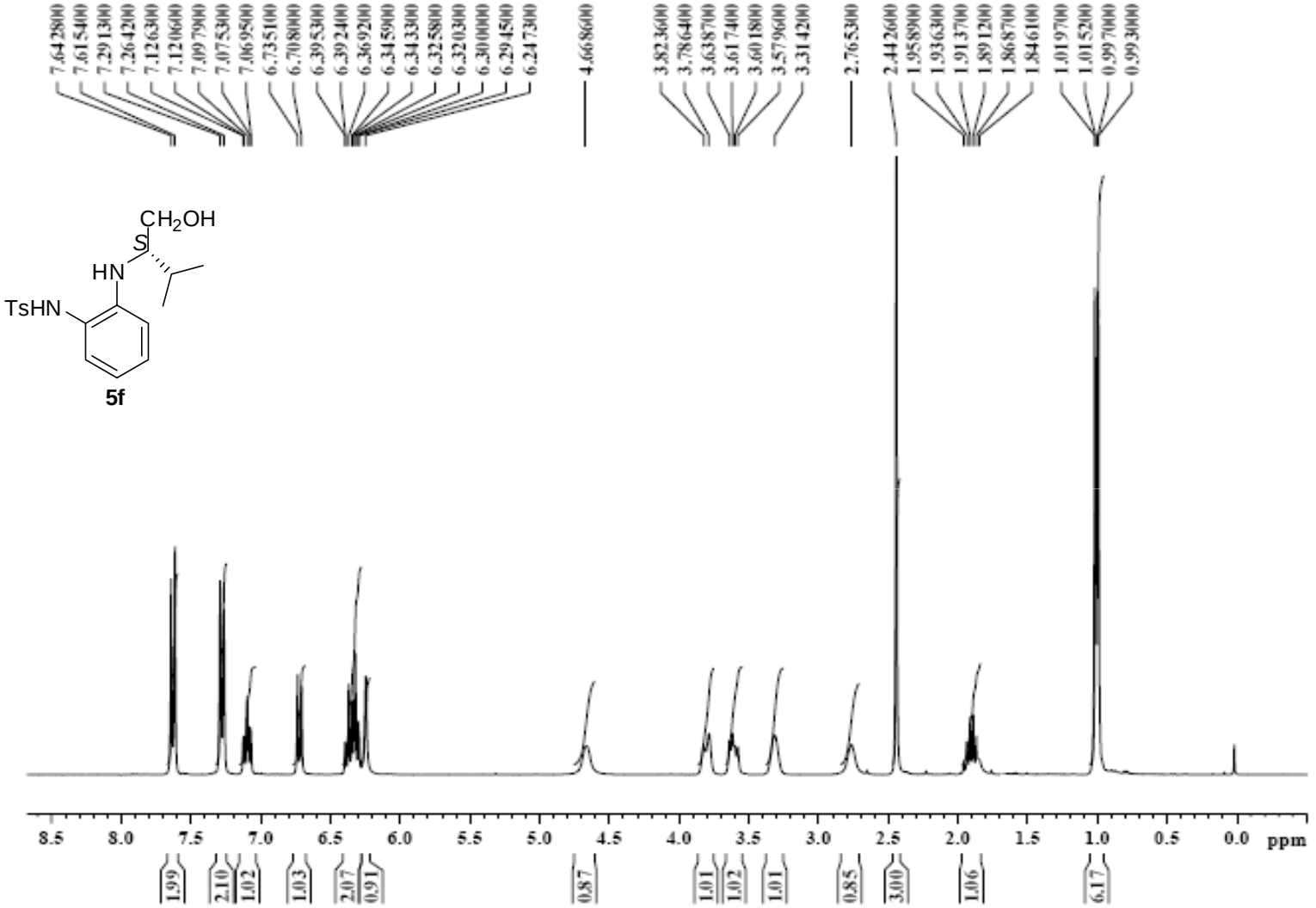
FigureS-39: ^{13}C spectrum (75MHz, $CDCl_3$) of **5d**.



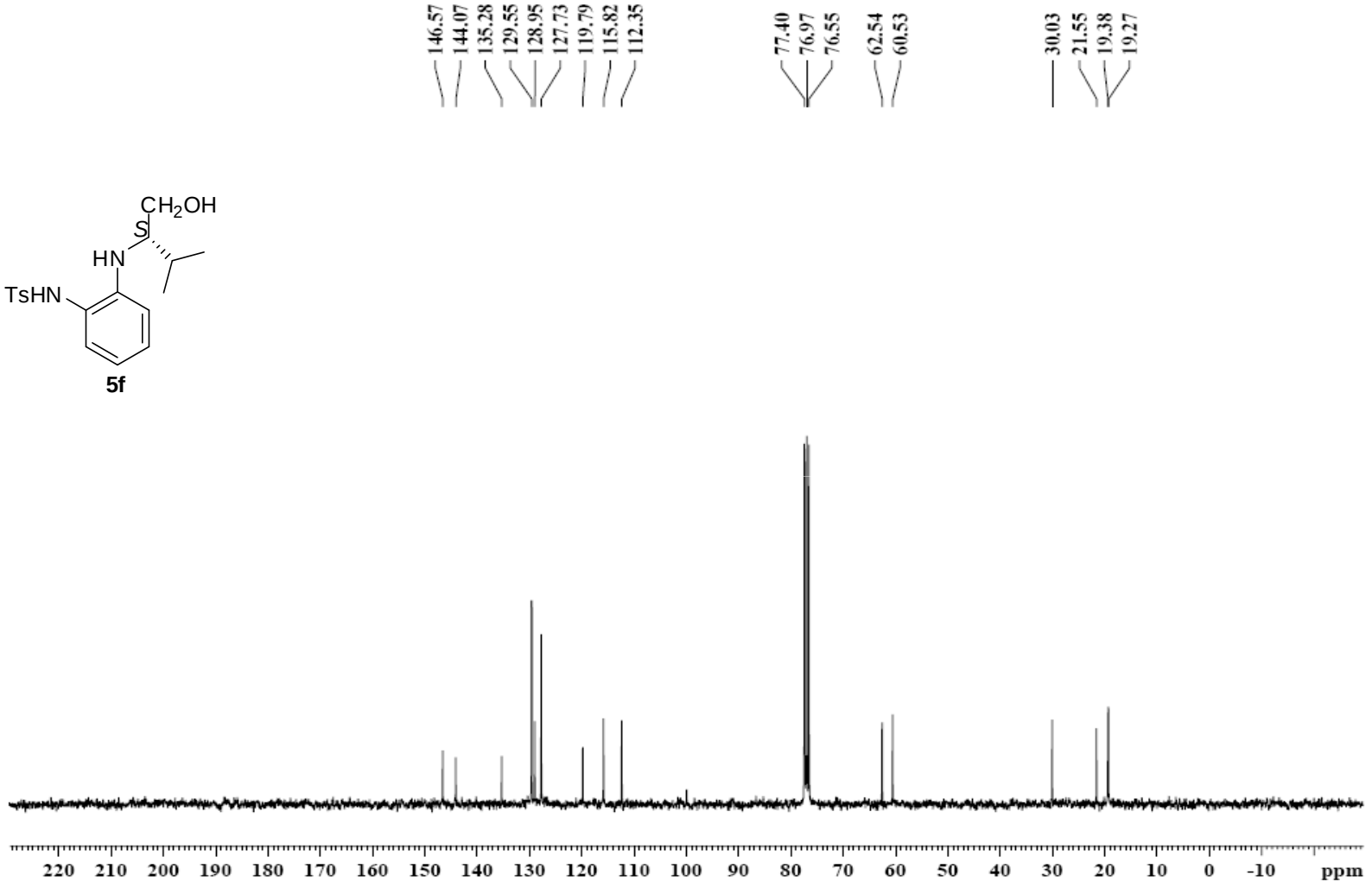
FigureS-40: ^{1}H spectrum (300MHz, $CDCl_3$) of **5e**.



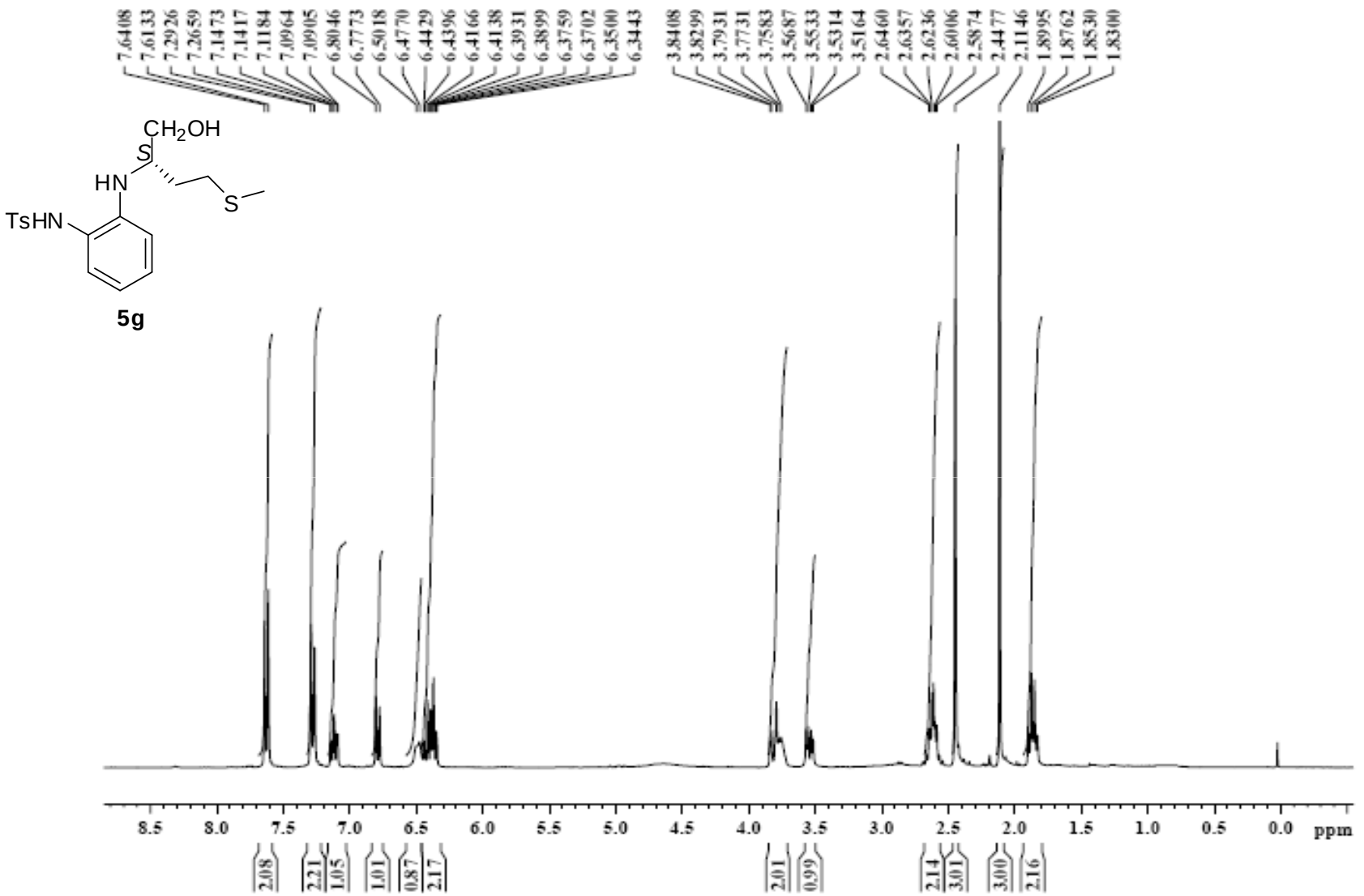
FigureS-41: ^{13}C spectrum (75MHz, $CDCl_3$) of **5e**.



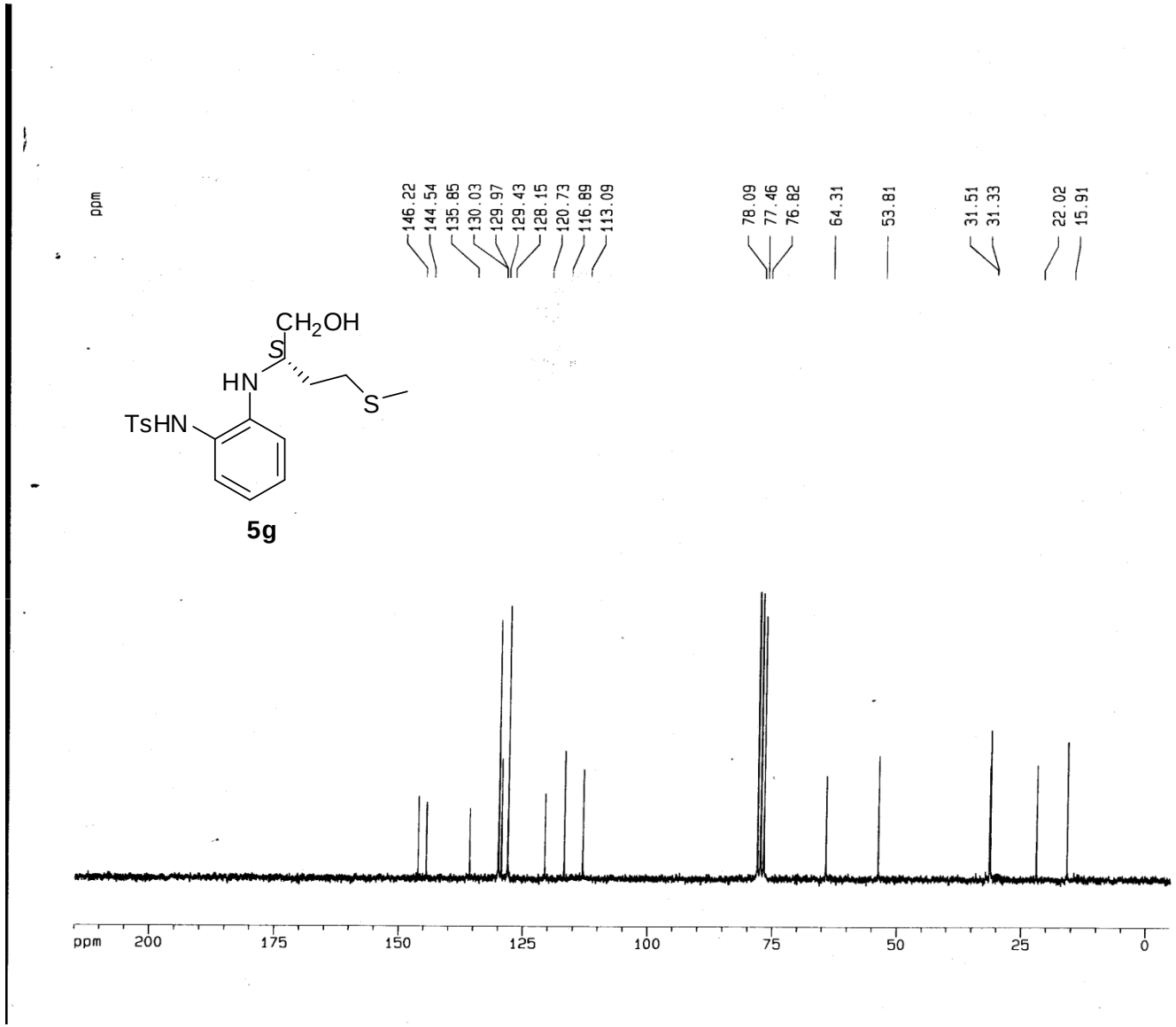
FigureS-42: ^{1}H spectrum (300MHz, $CDCl_3$) of **5f**.



FigureS-43: ^{13}C spectrum (75MHz, $CDCl_3$) of **5f**.



FigureS-44: ^{1}H spectrum (300MHz, $CDCl_3$) of **5g.**

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PROCNO                   1

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TD                 32768
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            12562.814 Hz
FIDRES         0.383387 Hz
AQ             1.3042164 sec
RG                   256
DW                39.800 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec

============ CHANNEL f1 =============
NUC1                 13C
P1                  8.50 usec
PL1                -4.00 dB
SFO1          50.3282440 MHz

============ CHANNEL f2 =============
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               15.60 dB
PL13               19.60 dB
SFO2          200.1308005 MHz

F2 - Processing parameters
SI                  16384
SF            50.3227090 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              215.000 ppm
F1             10819.38 Hz
F2P               -5.000 ppm
F2              -251.61 Hz
PPMCM          11.00000 ppm/cm
HZCM           553.54980 Hz/cm
```
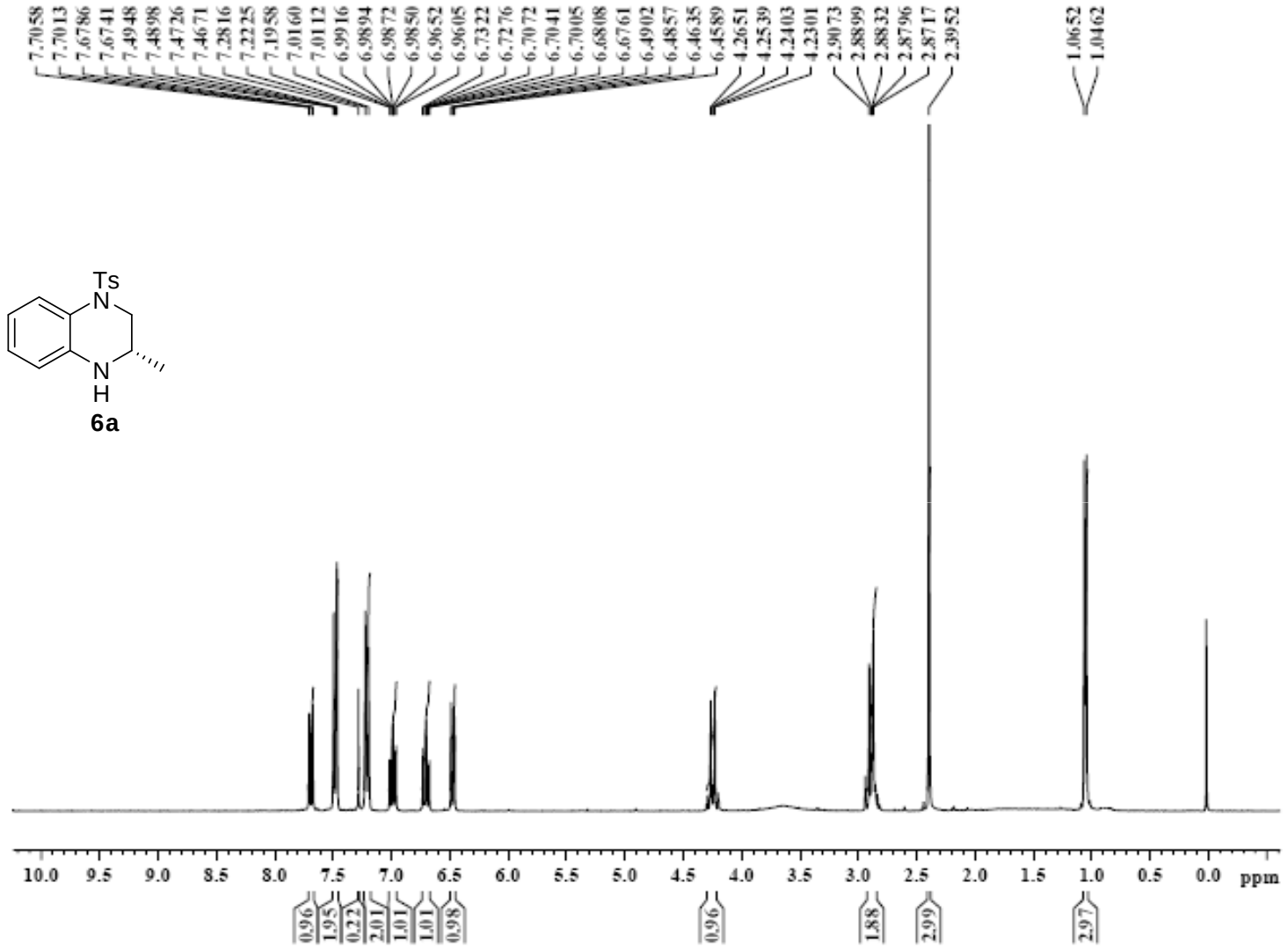
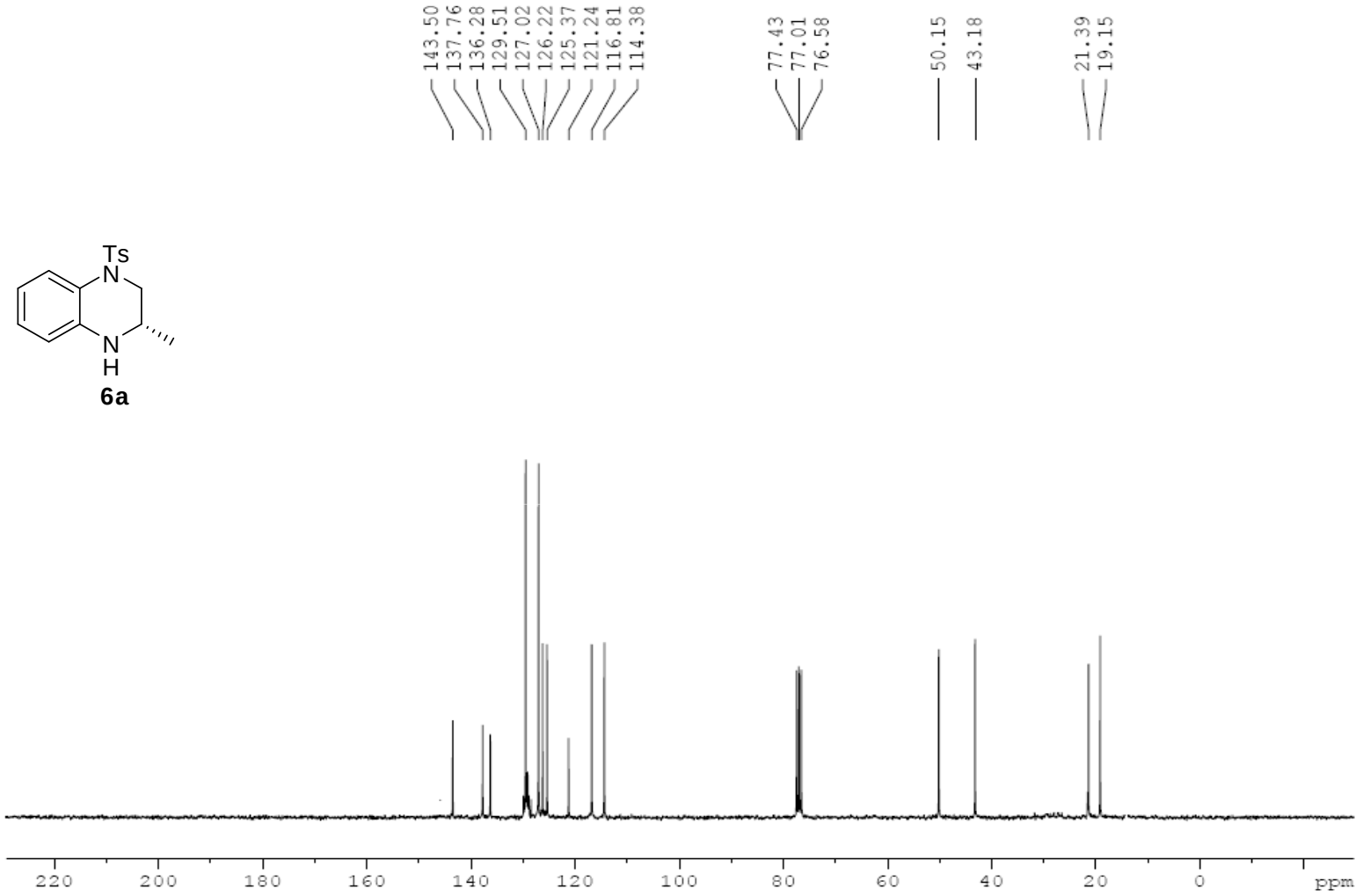
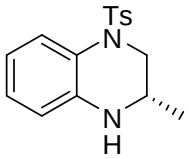

FigureS-45: ^{13}C spectrum (50 MHz, $CDCl_3$) of **5g**.



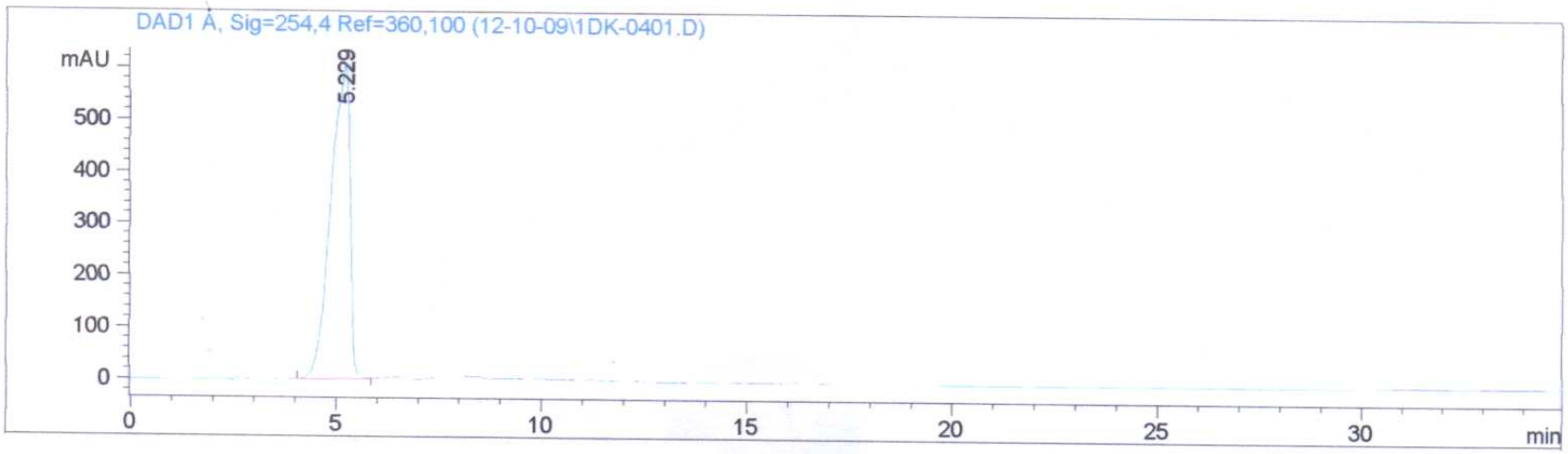
FigureS-46: ^{1}H spectrum (300MHz, $CDCl_3$) of **6a**.



FigureS-47 : ^{13}C spectrum (75MHz, $CDCl_3$) of **6a**.

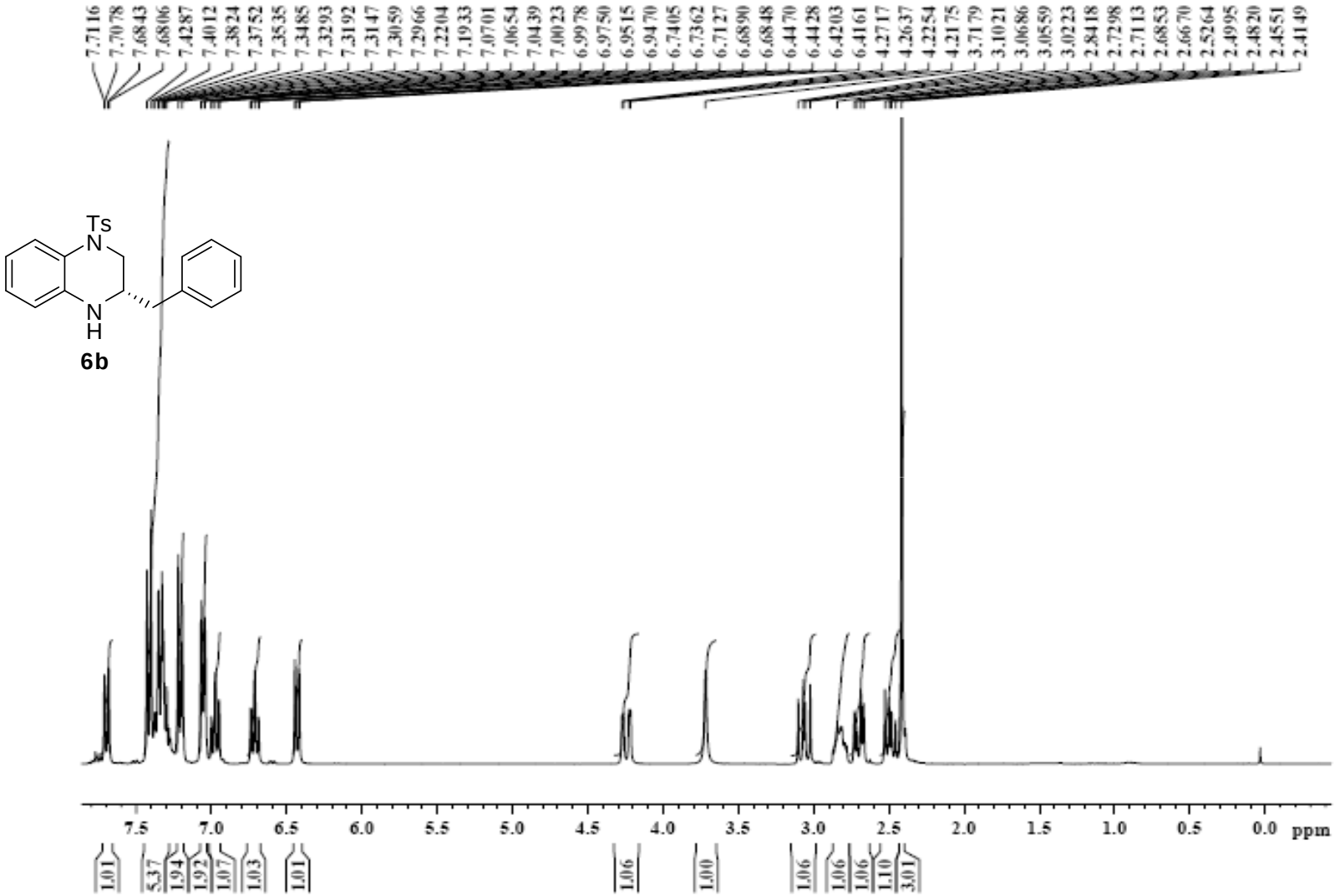


6a

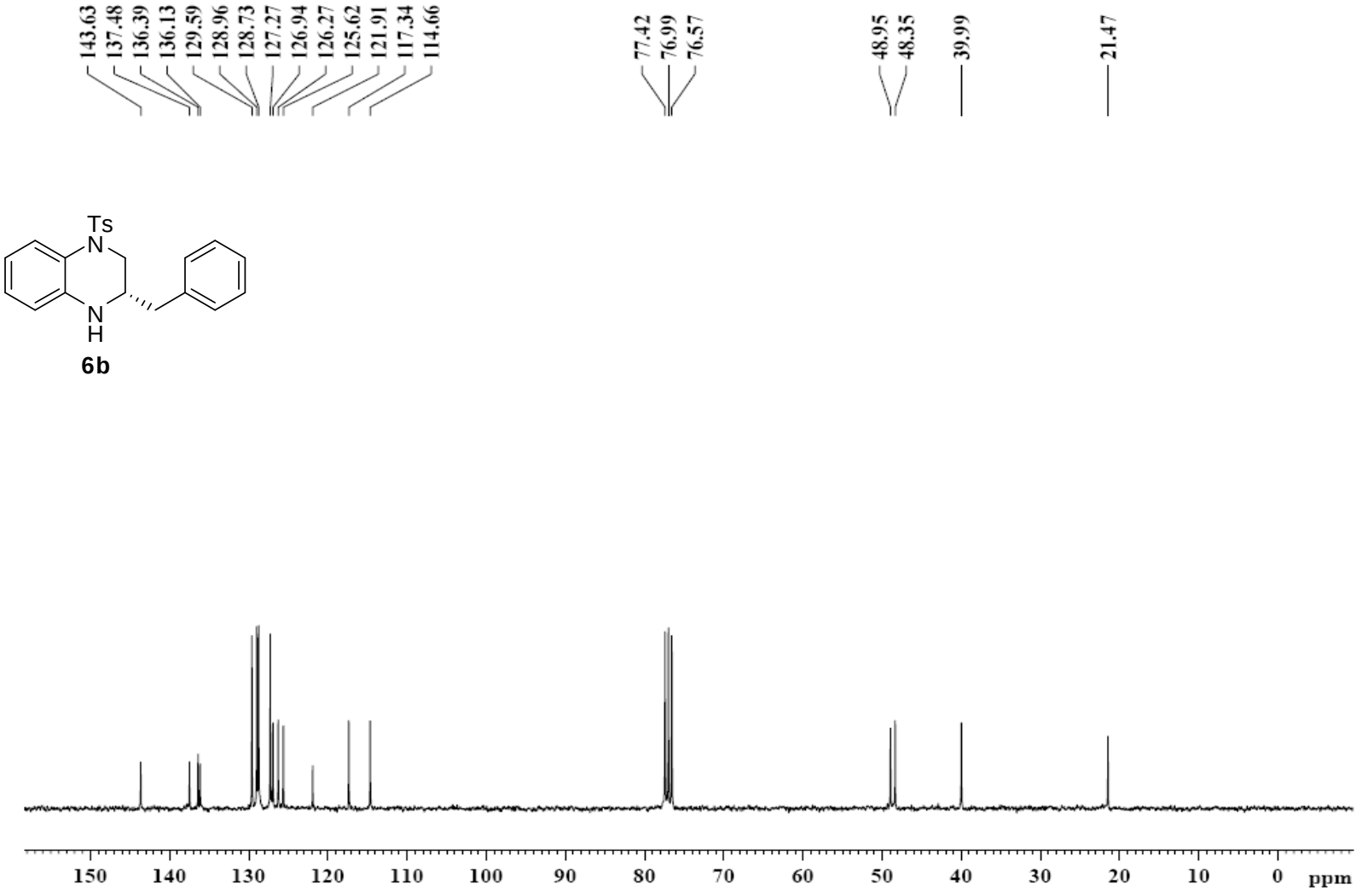


Retention time (min)

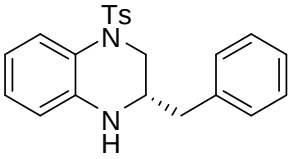
FigureS-48: HPLC spectrum of **6a**.



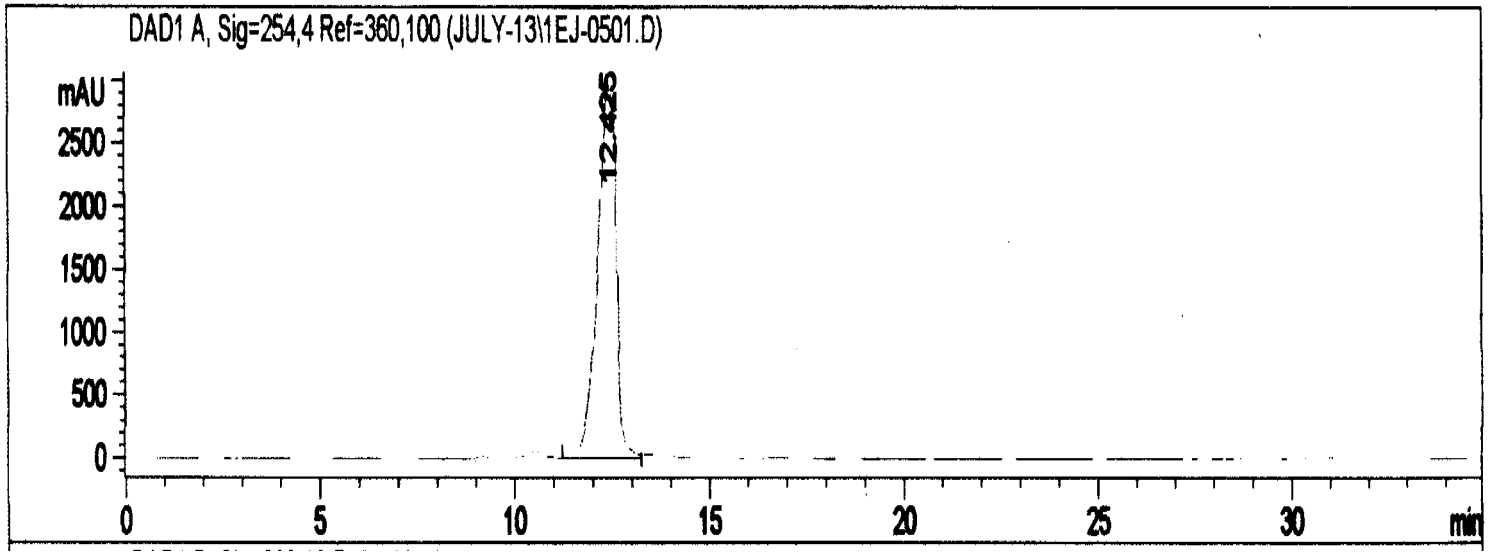
Figures-49: ^{1}H spectrum (300MHz, $CDCl_3$) of **6b**.



FigureS-50: ^{13}C spectrum (75 MHz, $CDCl_3$) of **6b**.

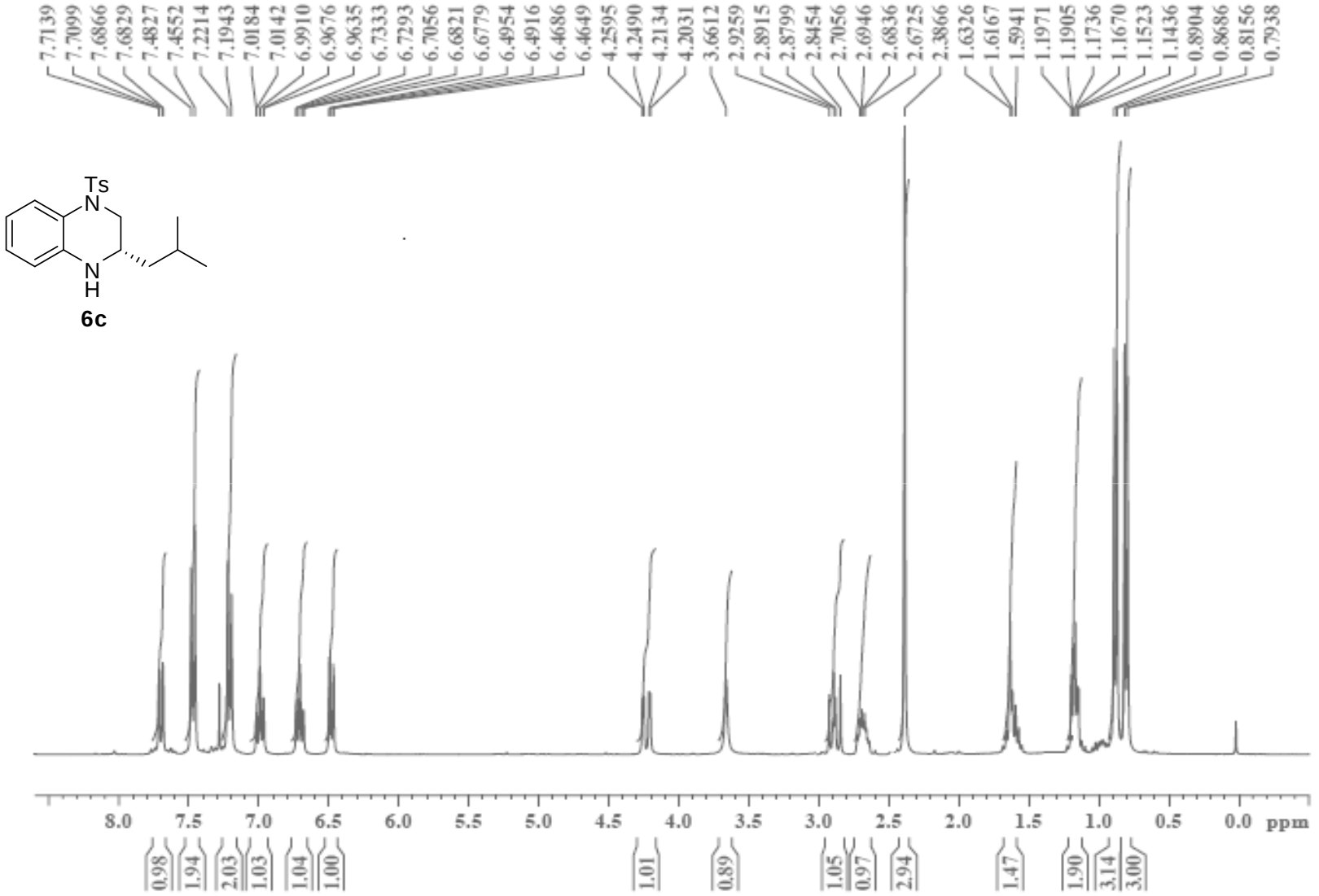


6b

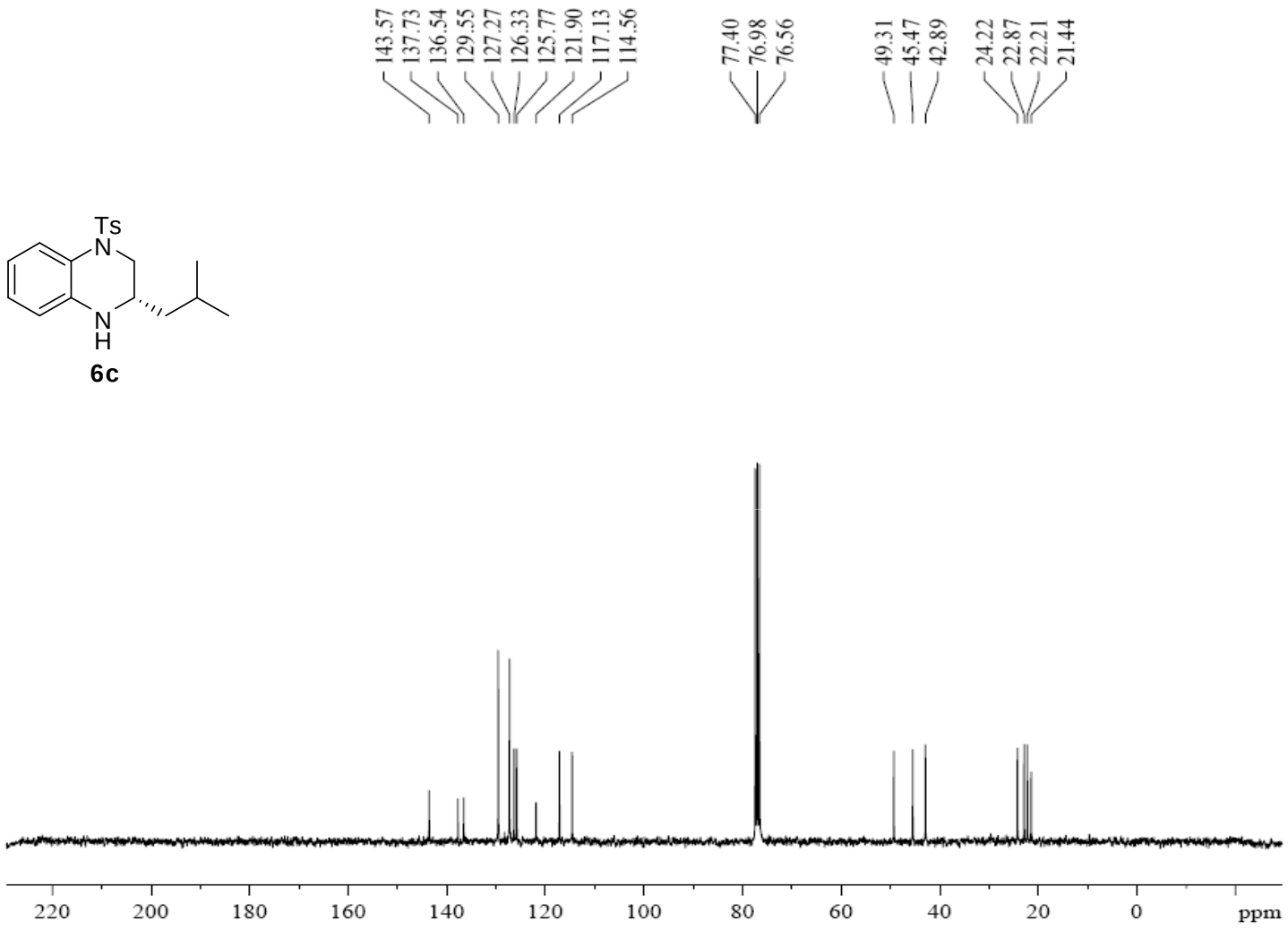


Retention time (min)

FigureS-51: HPLC graph for **6b**

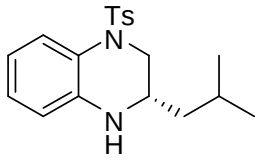


FigureS-52: ^{1}H spectrum (300MHz, $CDCl_3$) of **6c**.

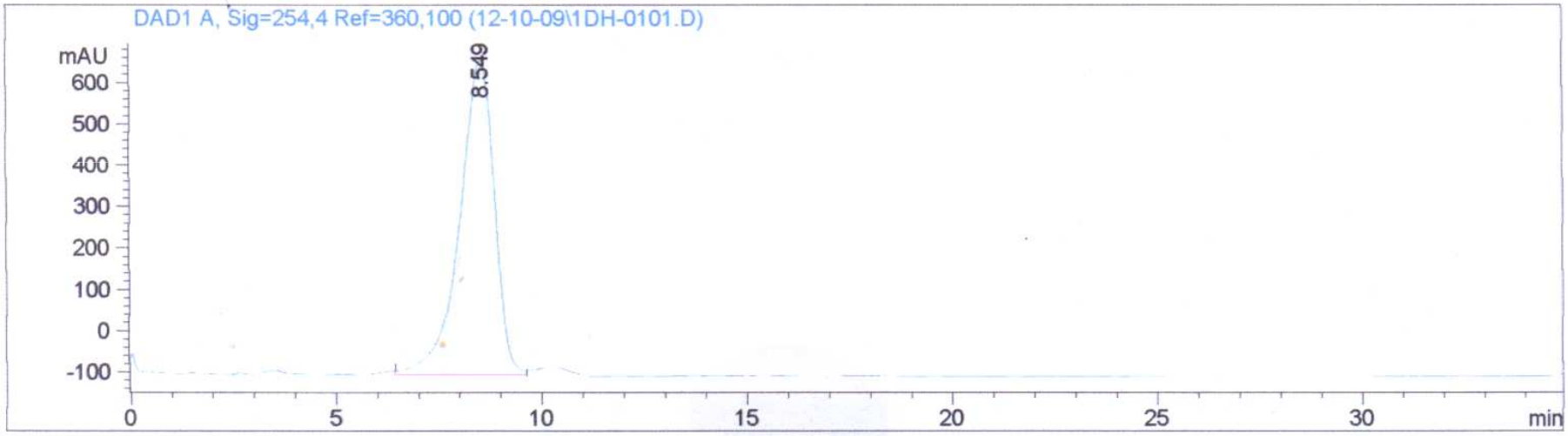


6c

FigureS-53: ^{13}C spectrum (75MHz, $CDCl_3$) of **6c**.

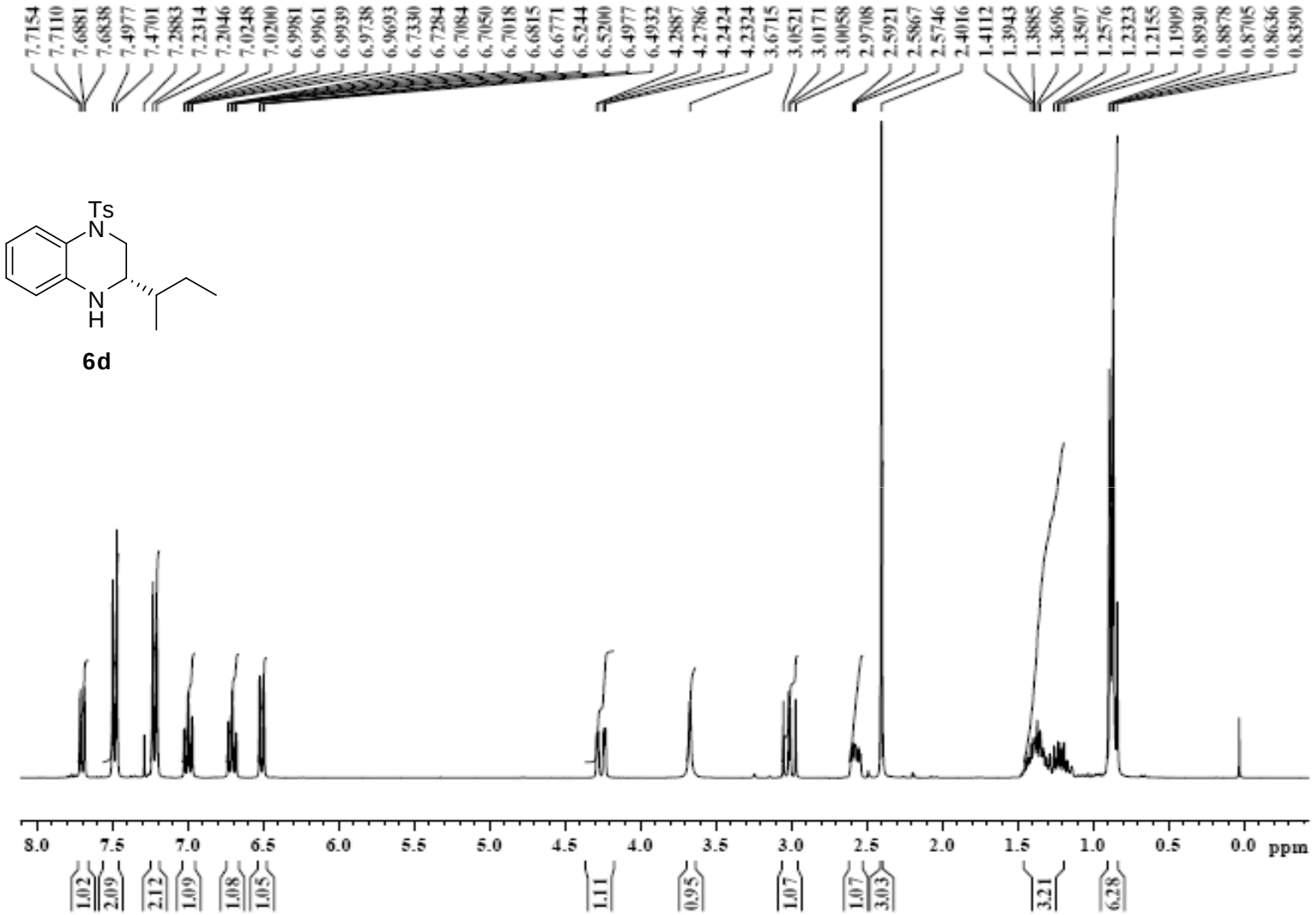


6c

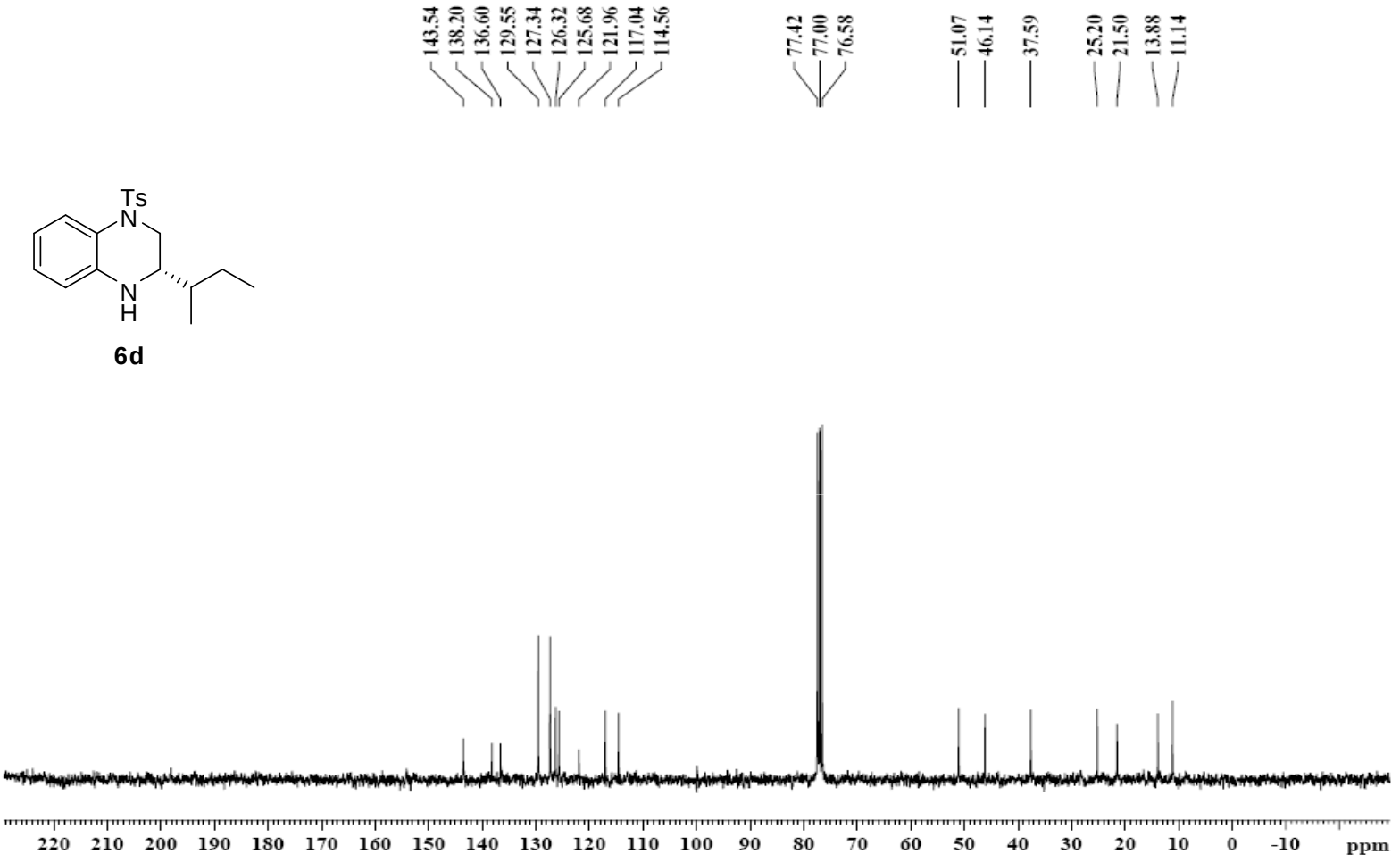


Retention time (min)

FigureS-54: HPLC graph for **6c**

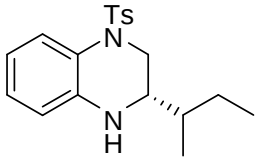


FigureS-55: ^{1}H spectrum (300MHz, $CDCl_3$) of **6d**.

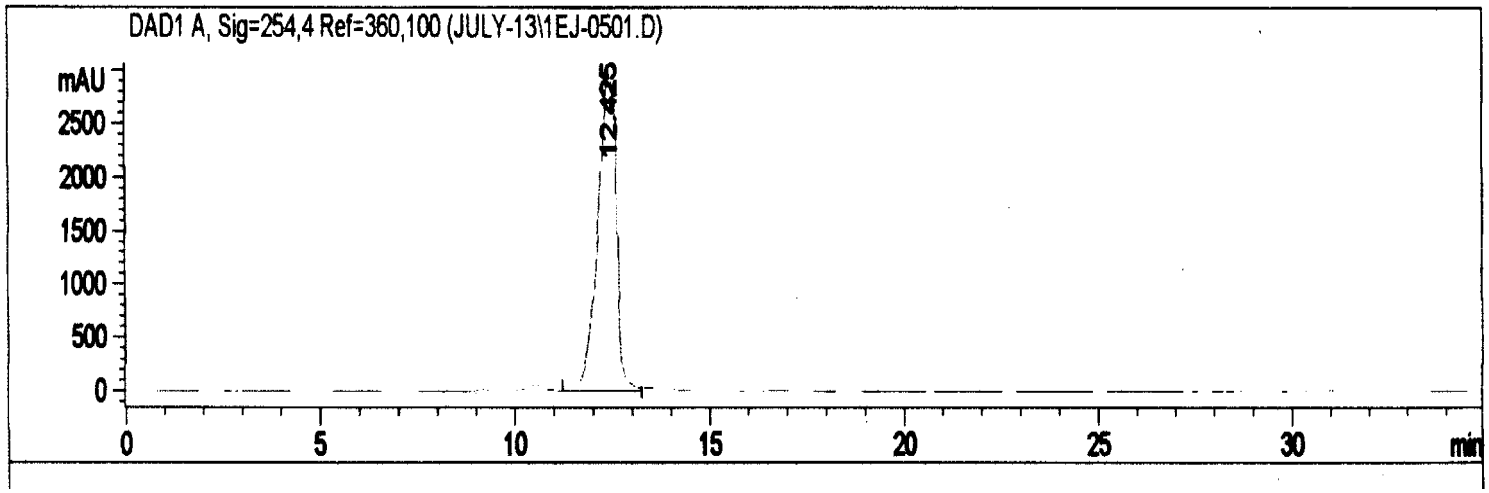


6d

FigureS-56: ^{13}C spectrum (75MHz, $CDCl_3$) of **6d**.

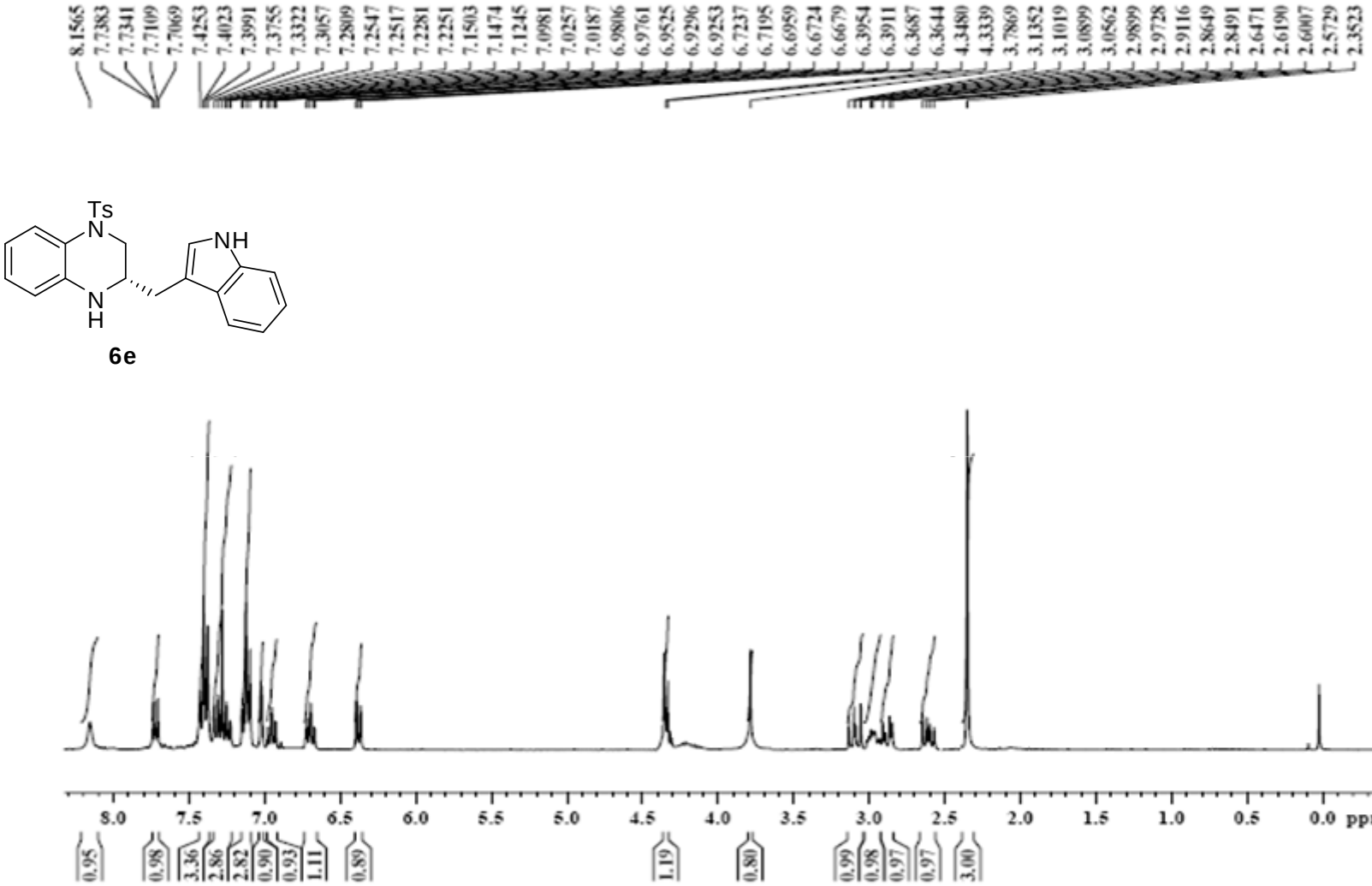


6d

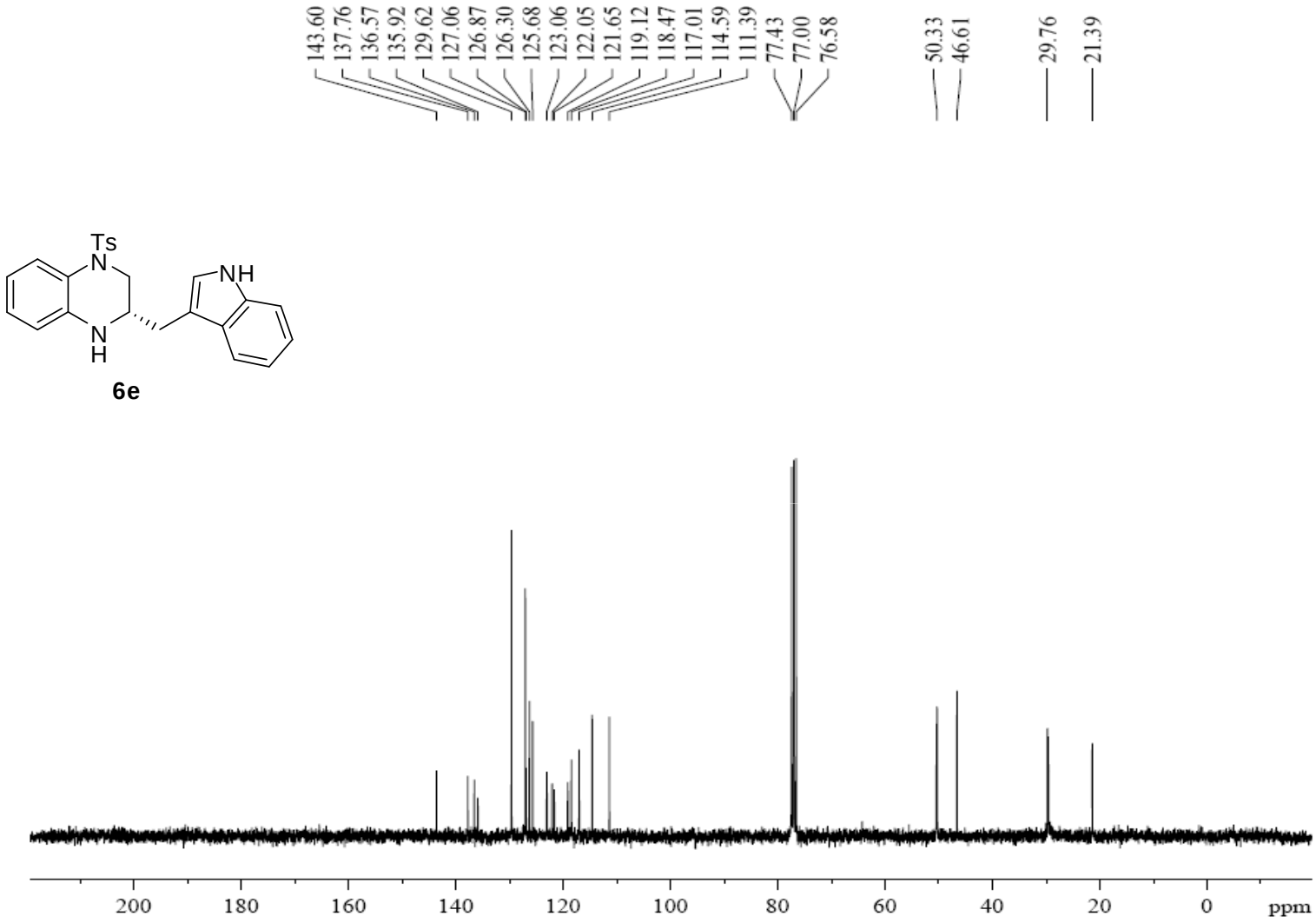


Retention time (min)

FigureS-57: HPLC graph for **6d**

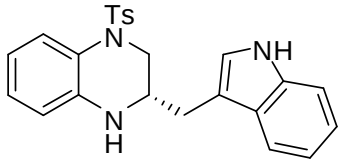


FigureS-58: ^{1}H spectrum (300MHz, $CDCl_3$) of **6e**.

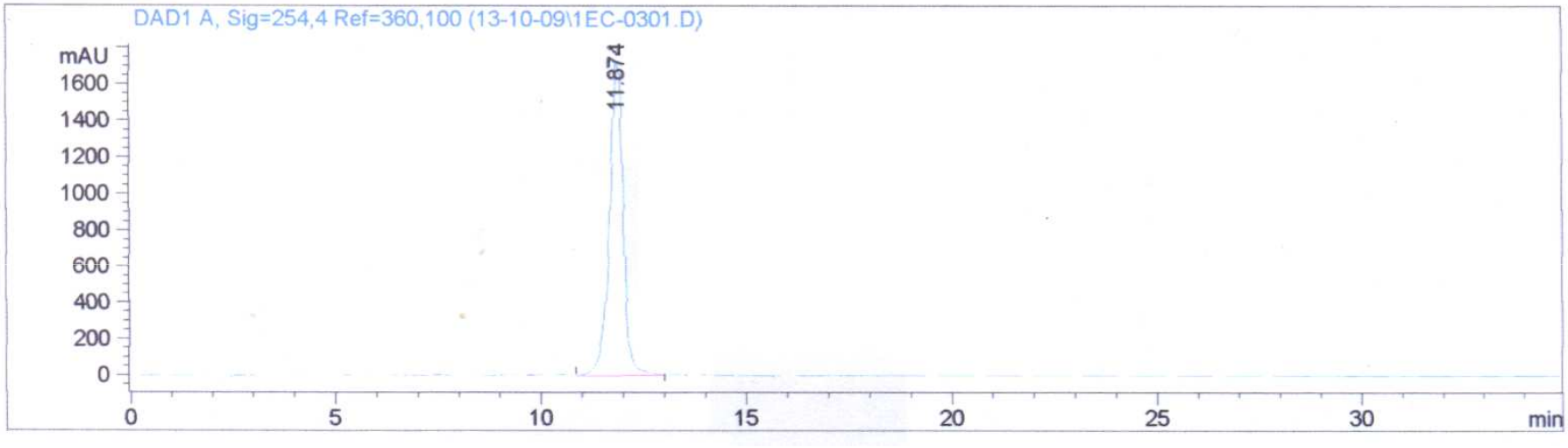


6e

FigureS-59: ^{13}C spectrum (75MHz, $CDCl_3$) of **6e**.

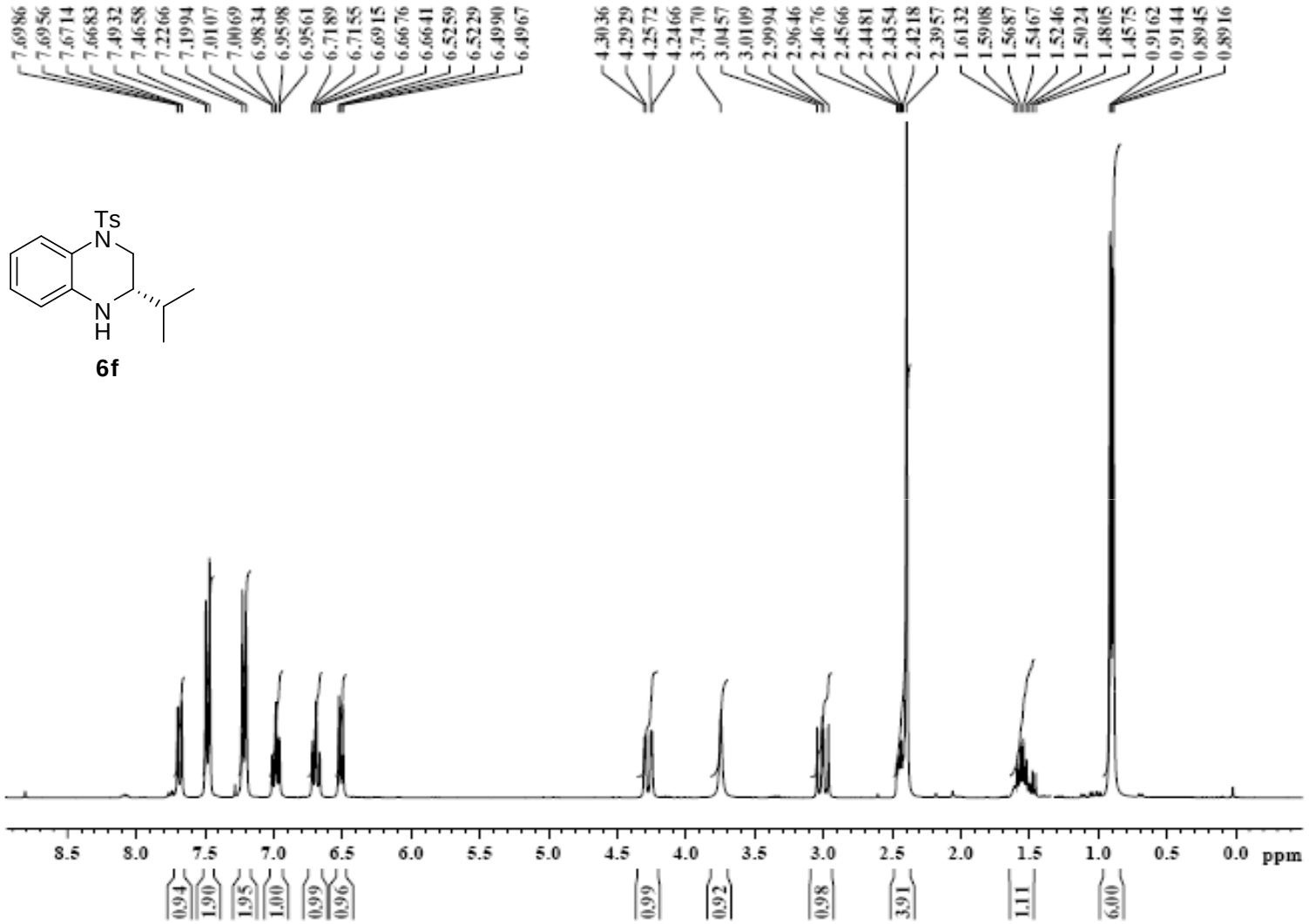


6e

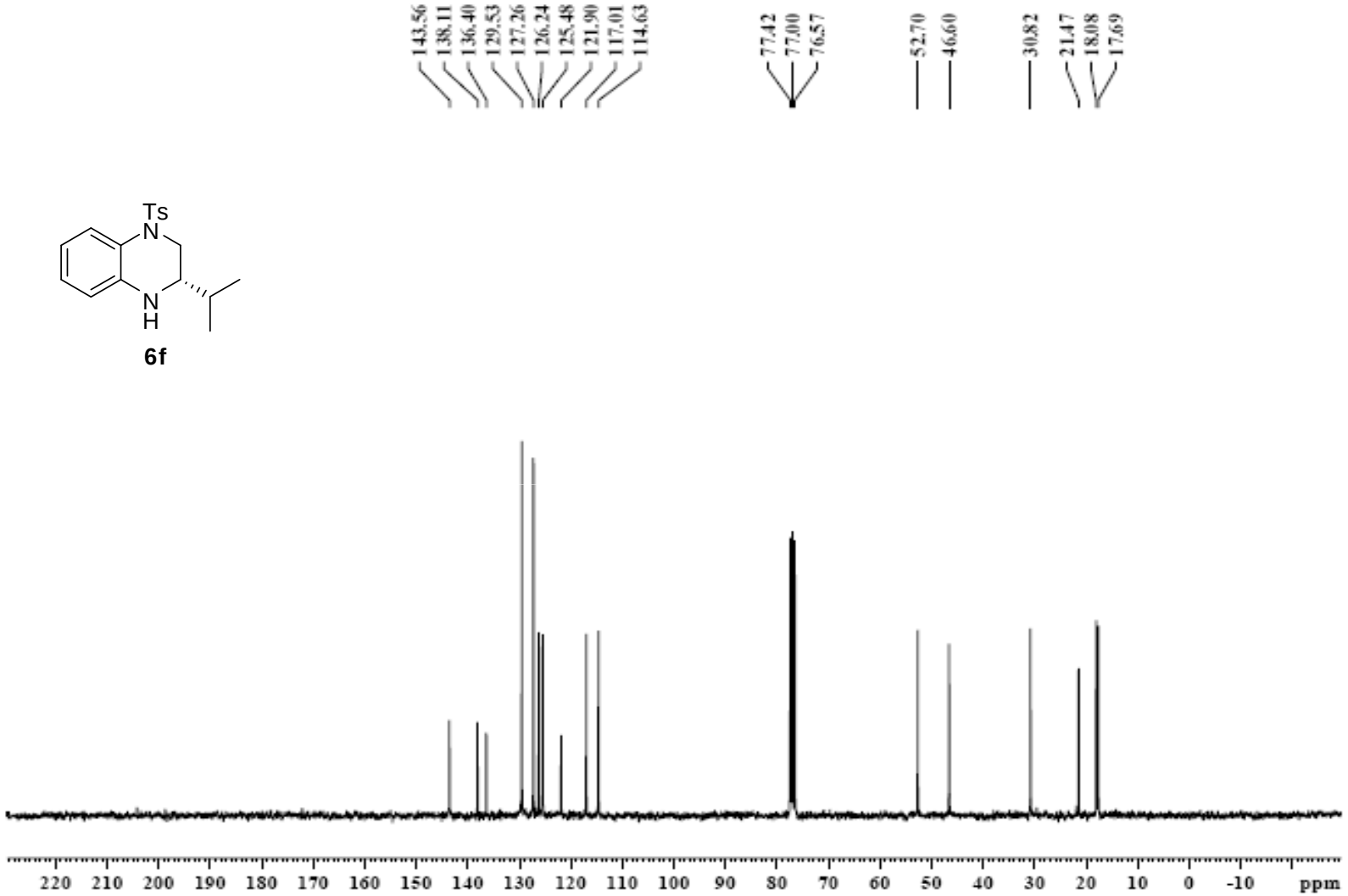


Retention time (min)

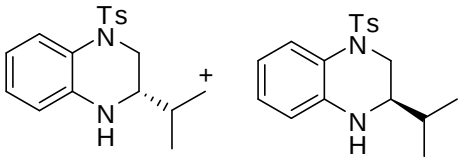
FigureS-60: HPLC graph for **6e**



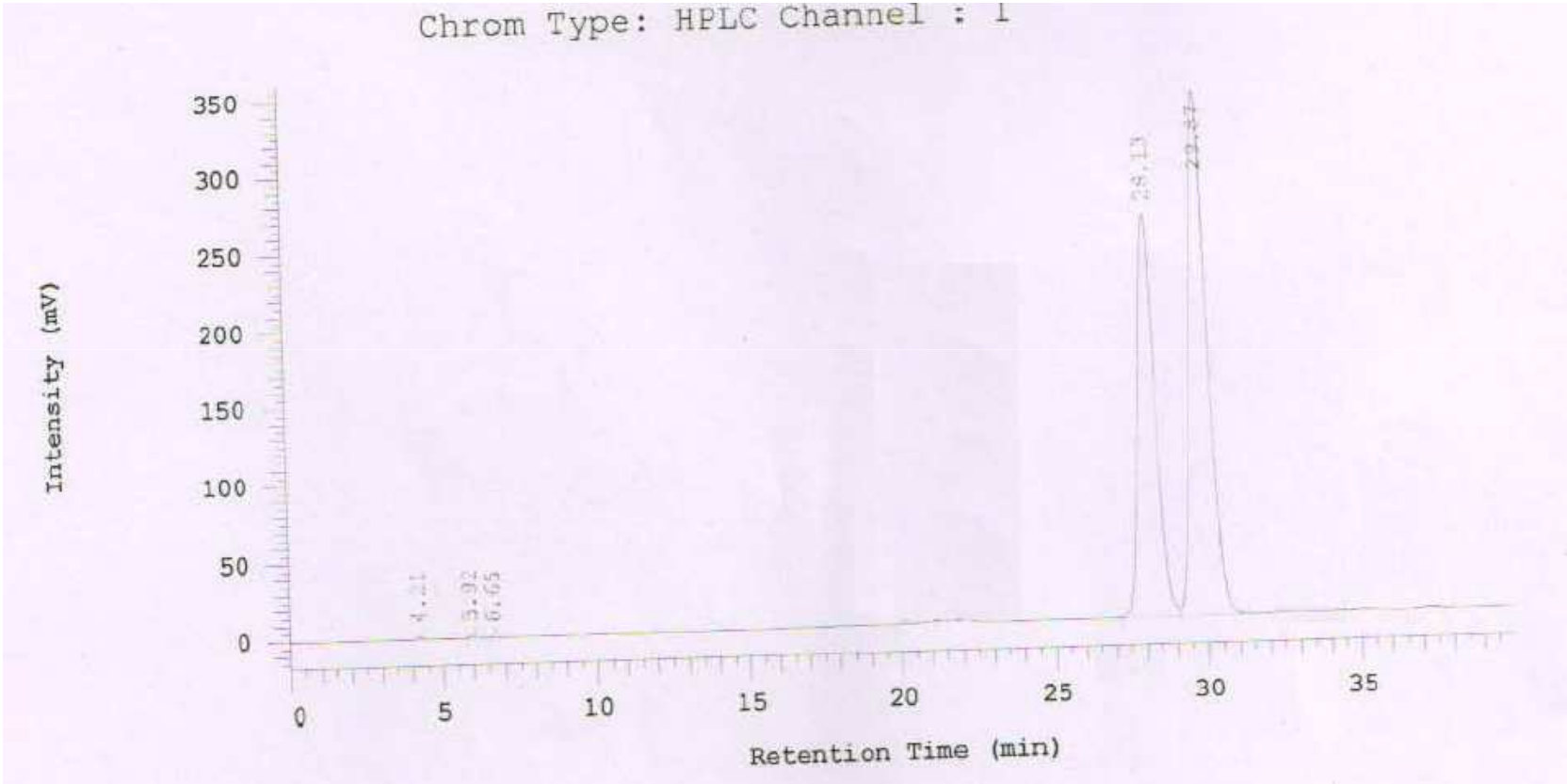
FigureS-61: ^{1}H spectrum (300MHz, $CDCl_3$) of **6f.**



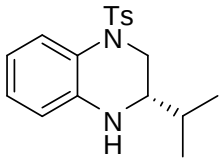
FigureS-62: ^{13}C spectrum (75MHz, $CDCl_3$) of **6f**.



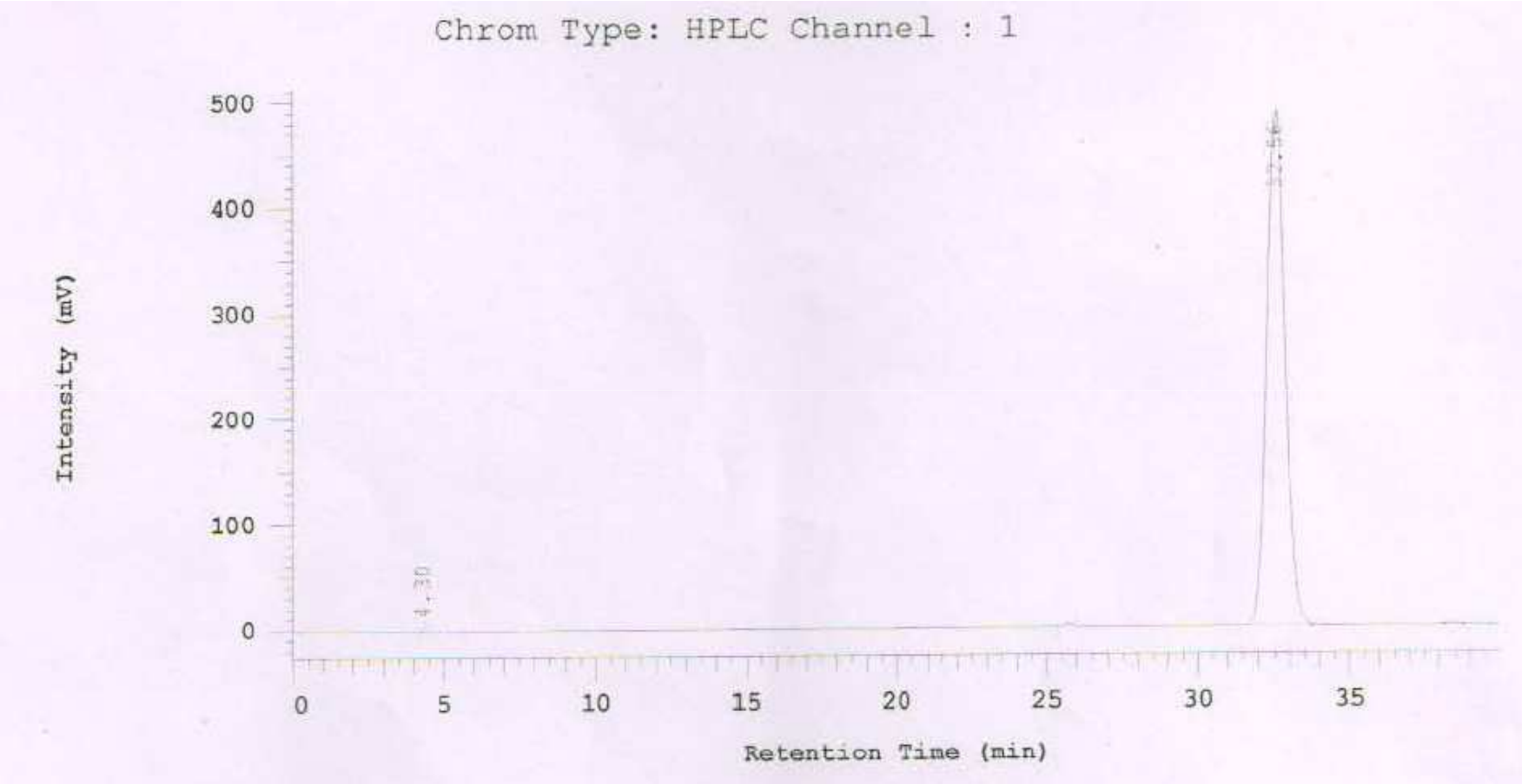
***S*-6f** **R-6f**



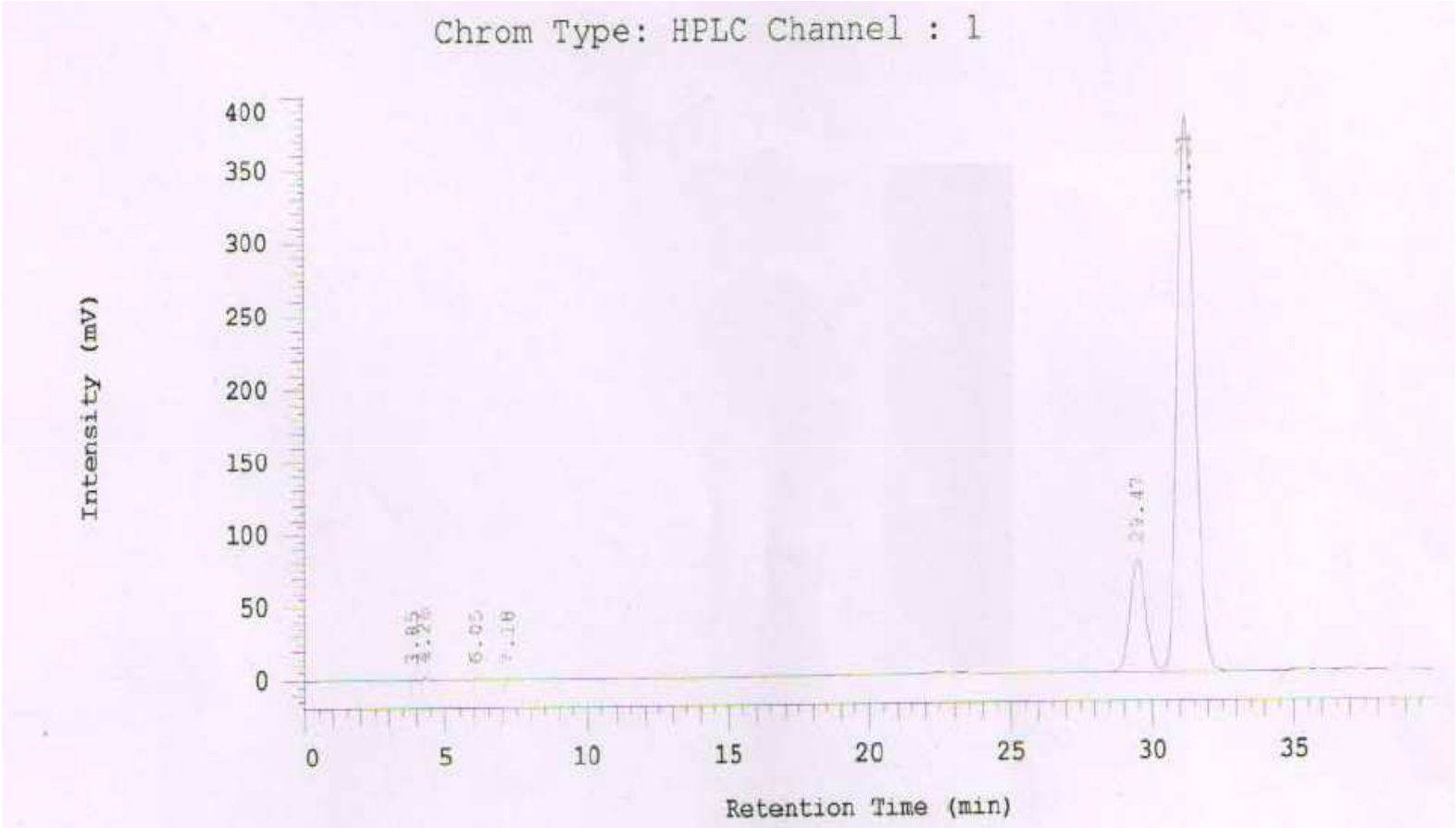
FigureS-63: HPLC graph for mixture of **6f** and its enantiomer.



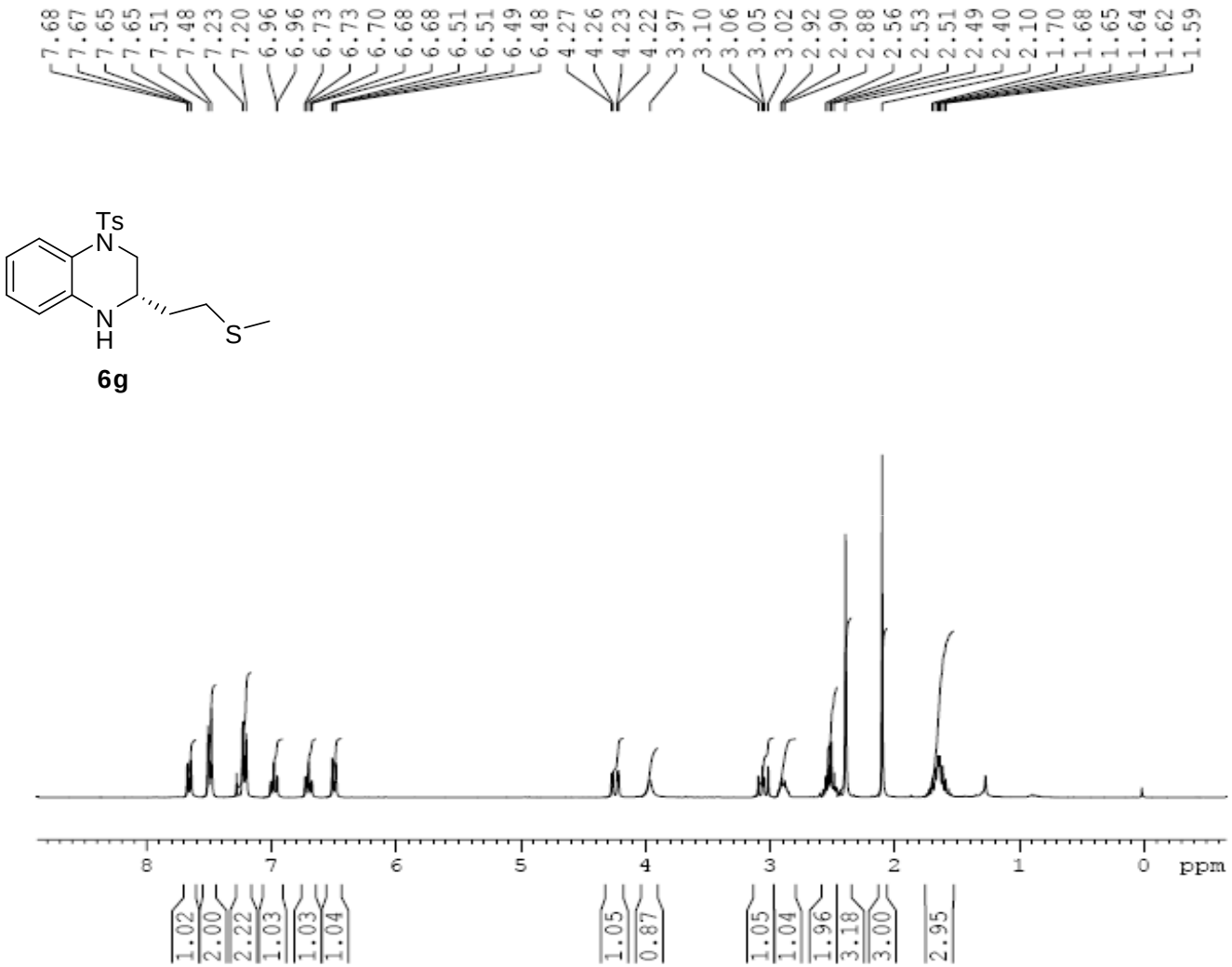
6f



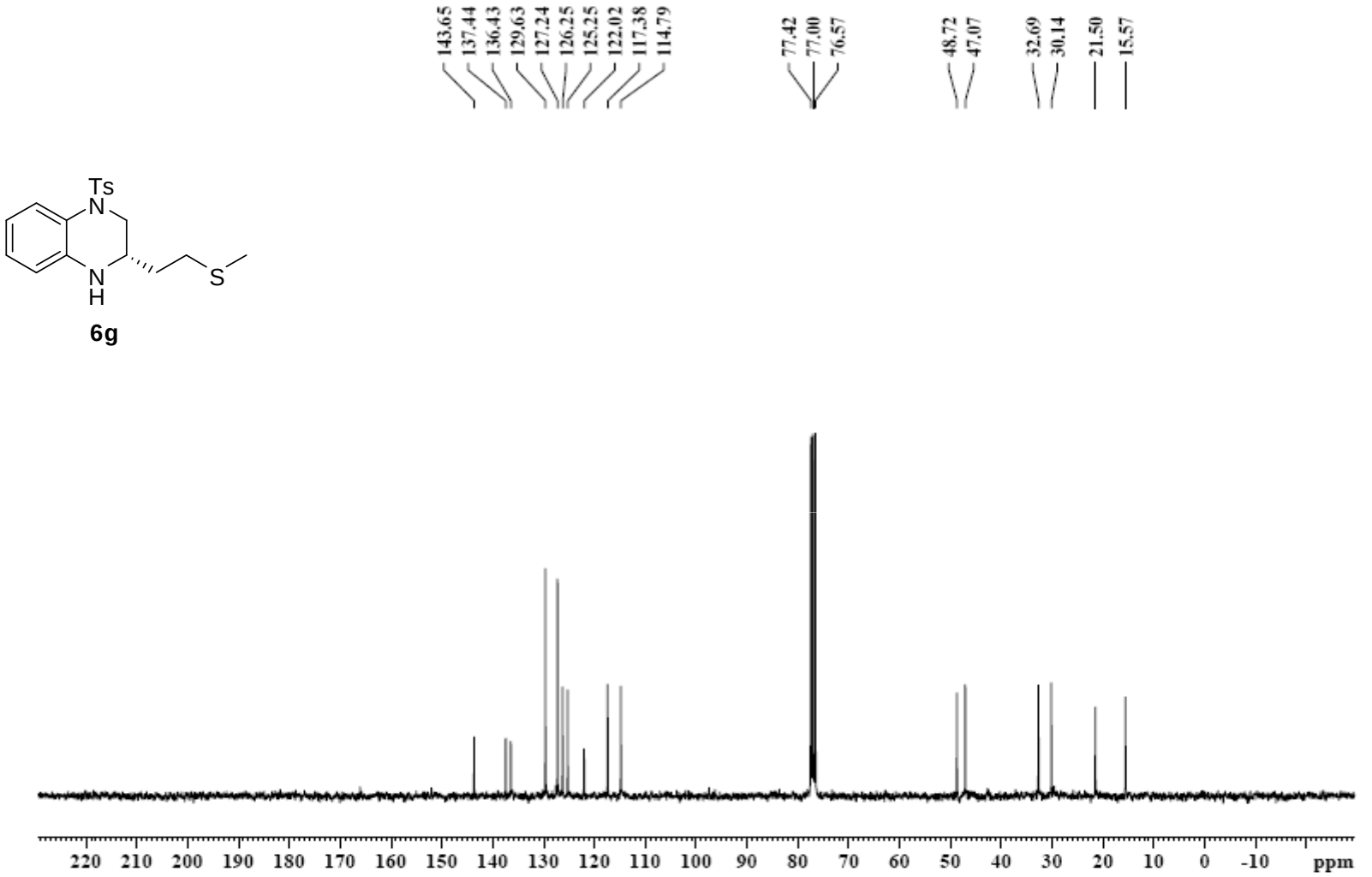
FigureS-64: HPLC graph for pure **6f**.



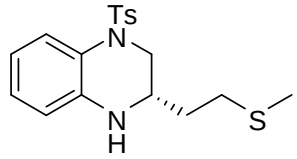
FigureS-65: HPLC graph for co-injection of racemic plus **6f.**



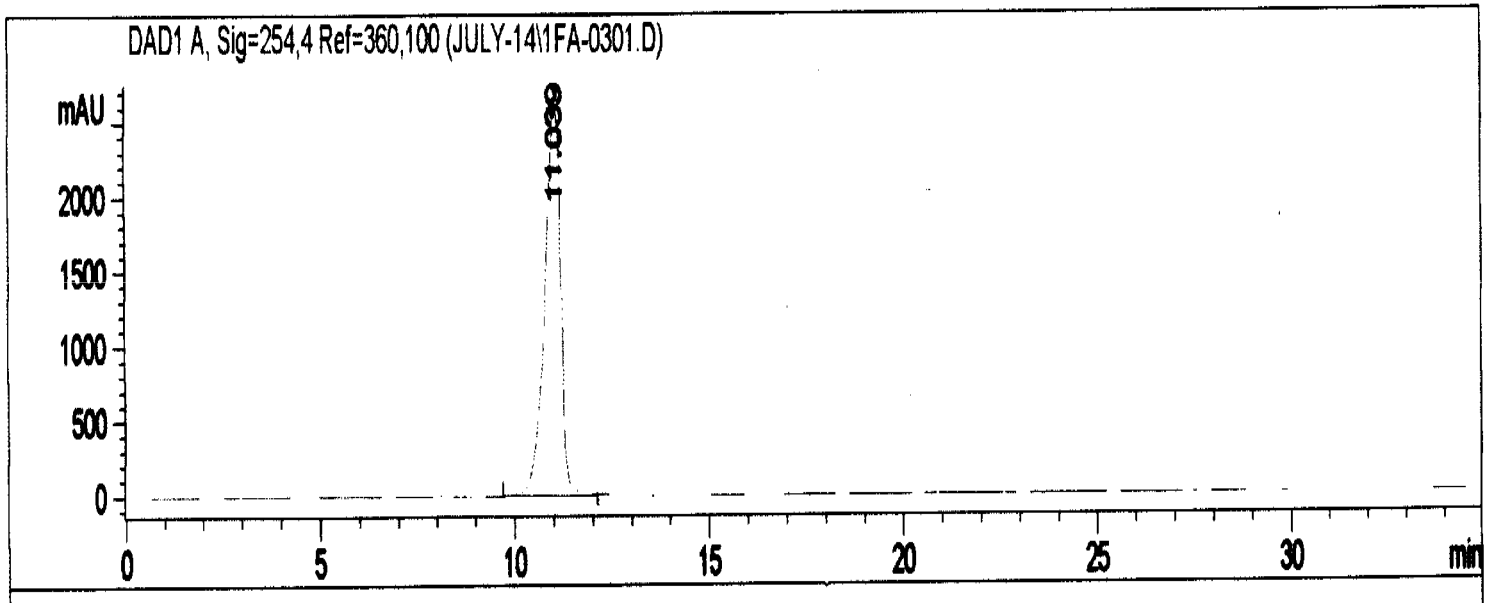
FigureS-66: ^{1}H spectrum (300MHz, $CDCl_3$) of **6g.**



FigureS-67: ^{13}C spectrum (75MHz, $CDCl_3$) of **6g**.

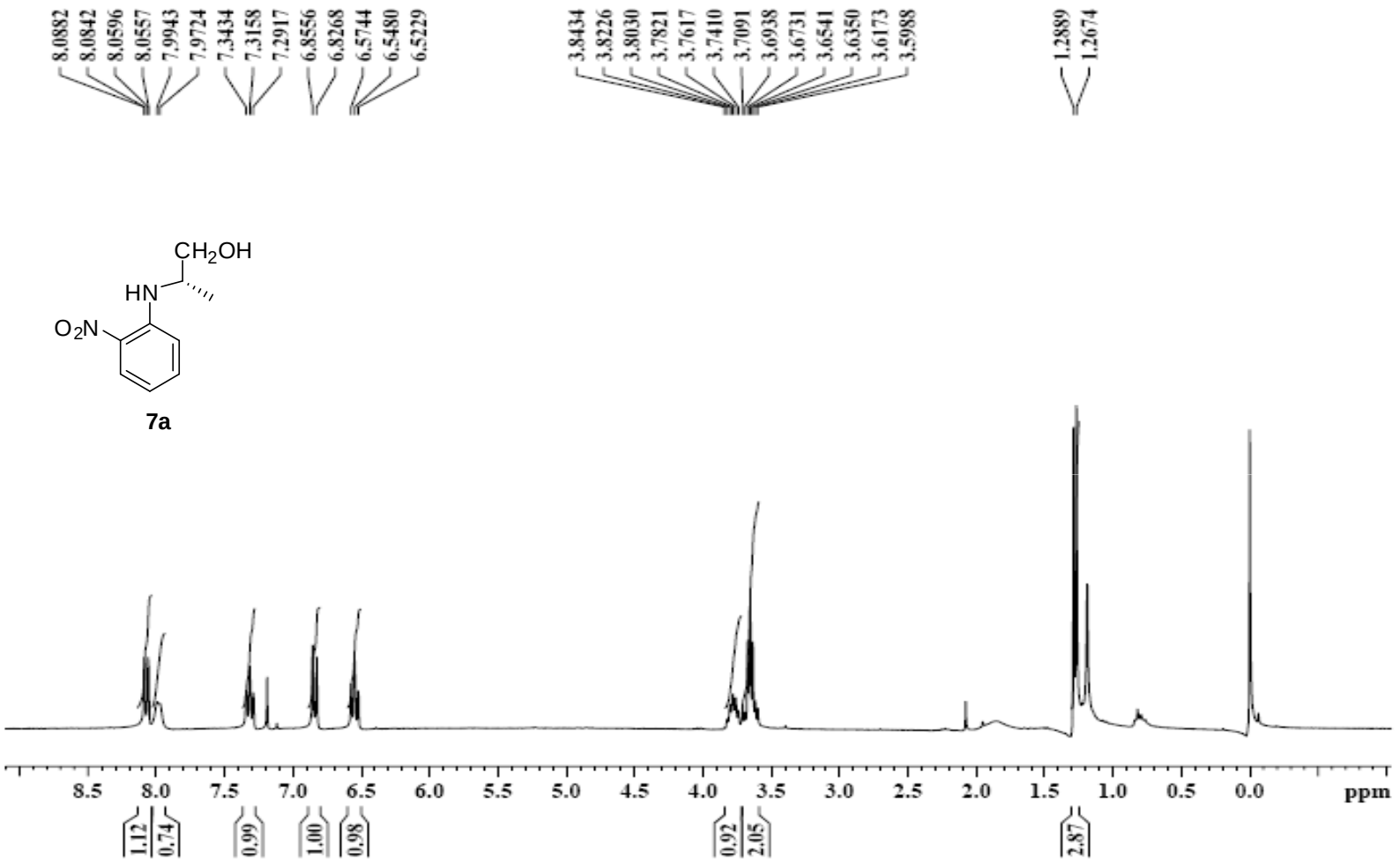


6g

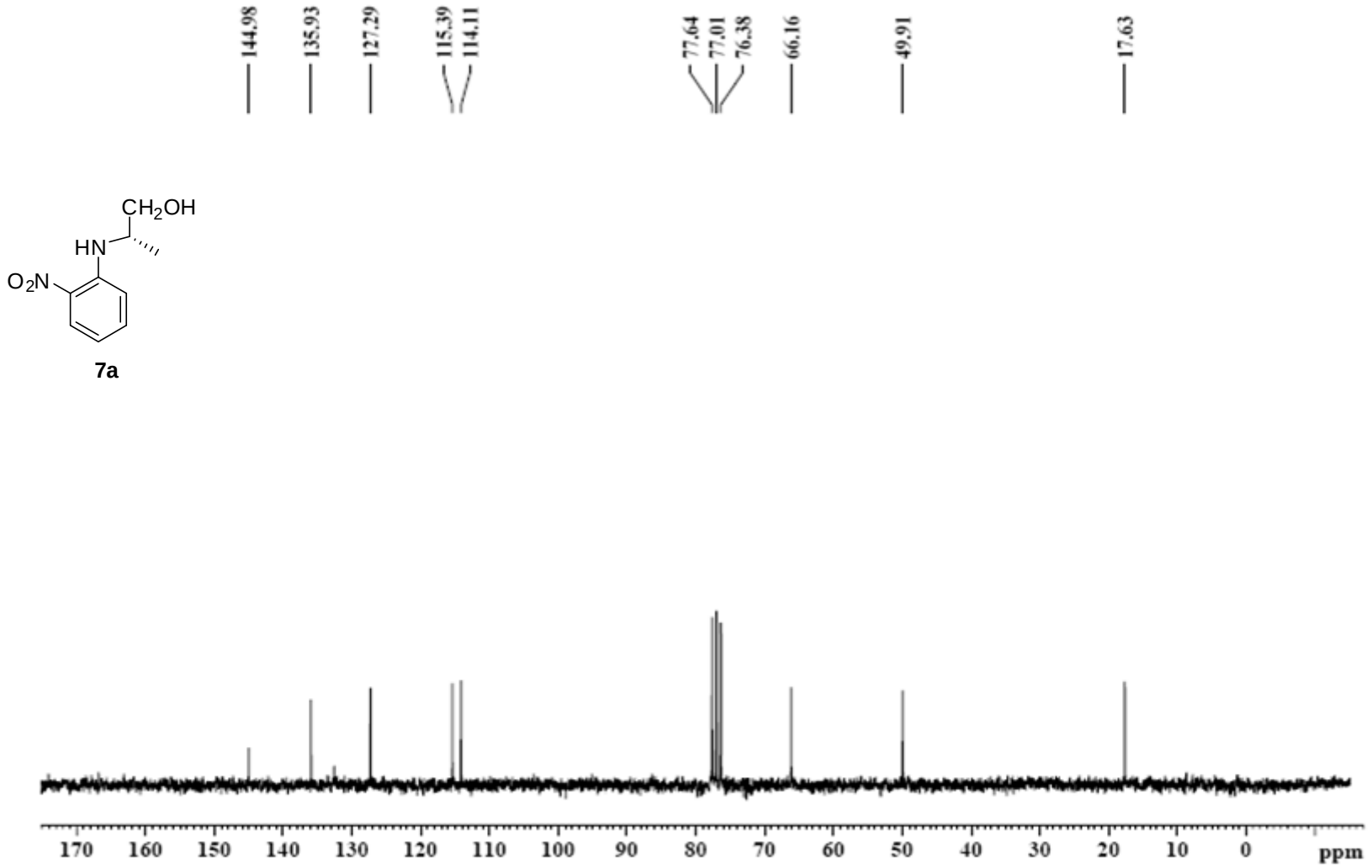


Retention time (min)

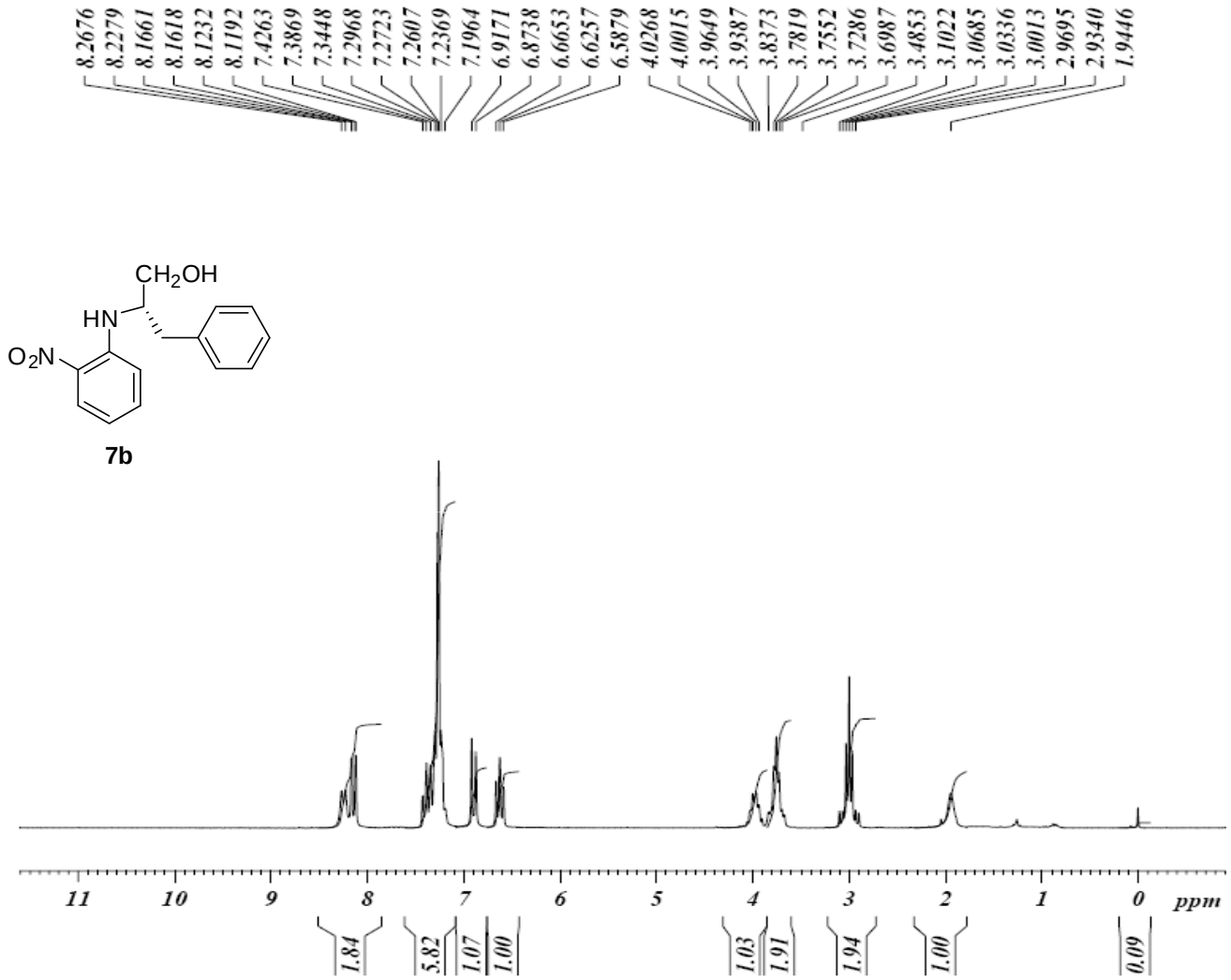
FigureS-68: HPLC graph for **6g**



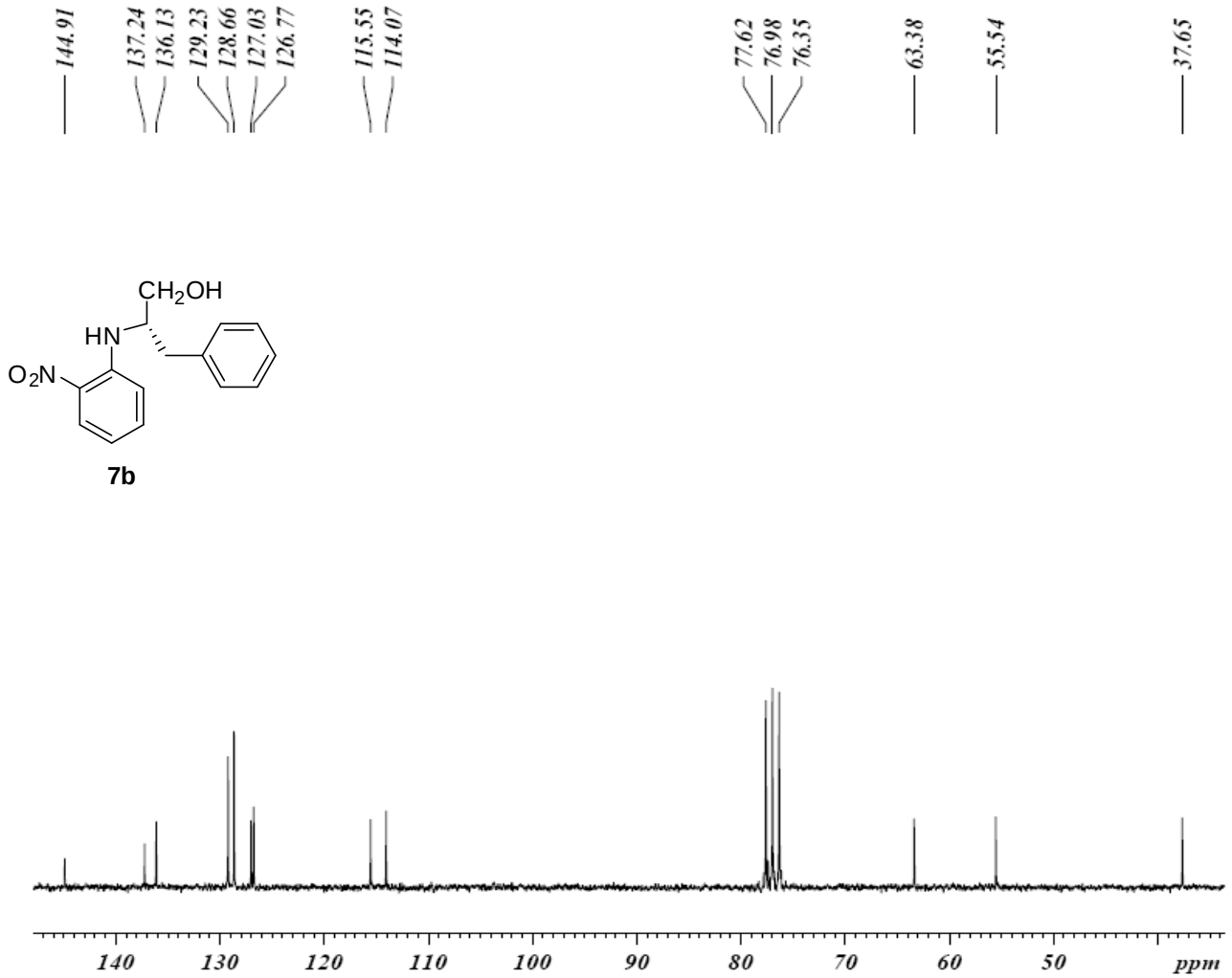
FigureS-69: ^{1}H spectrum (200MHz, $CDCl_3$) of **7a**.



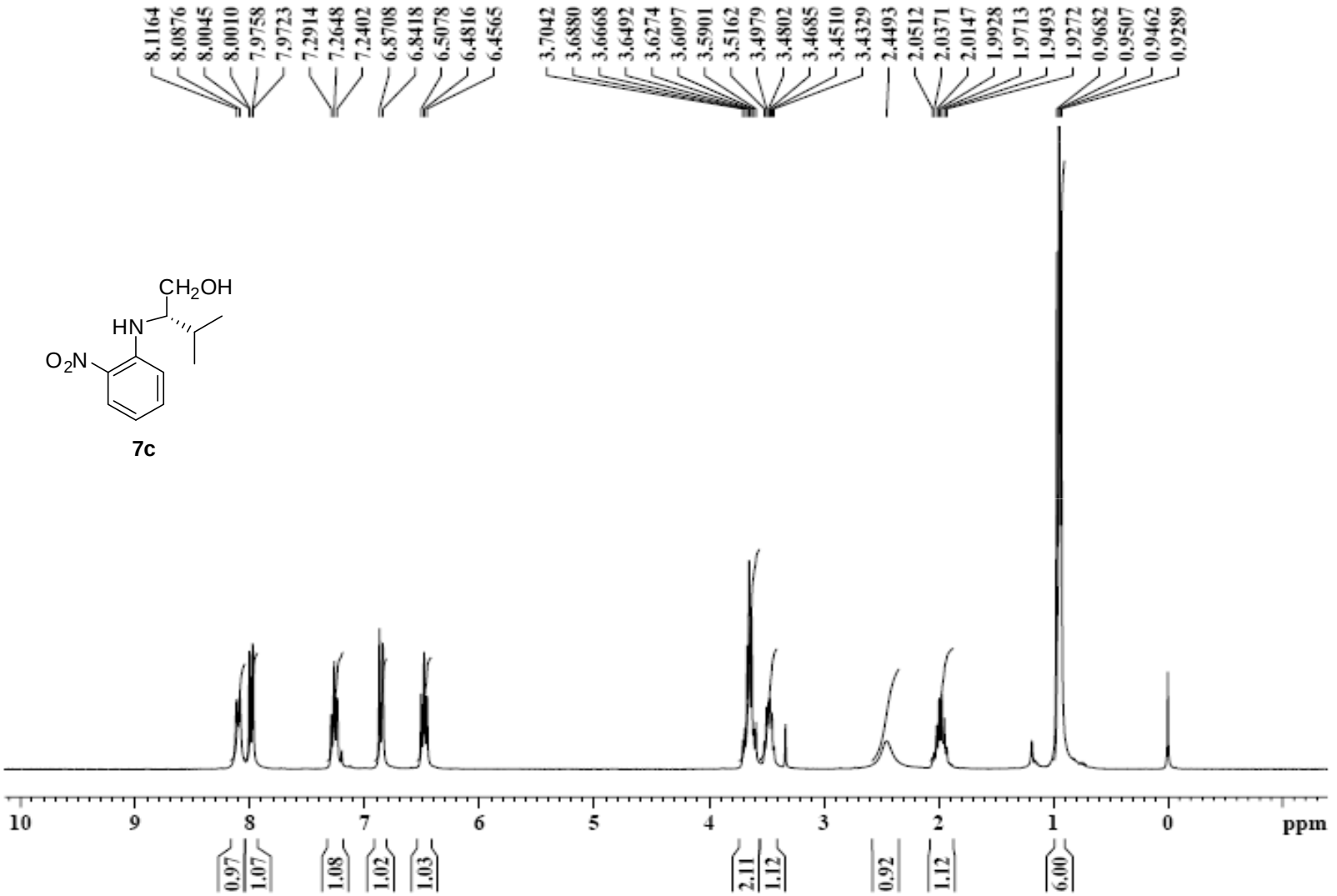
FigureS-70: ^{13}C spectrum (50MHz, $CDCl_3$) of **7a**.



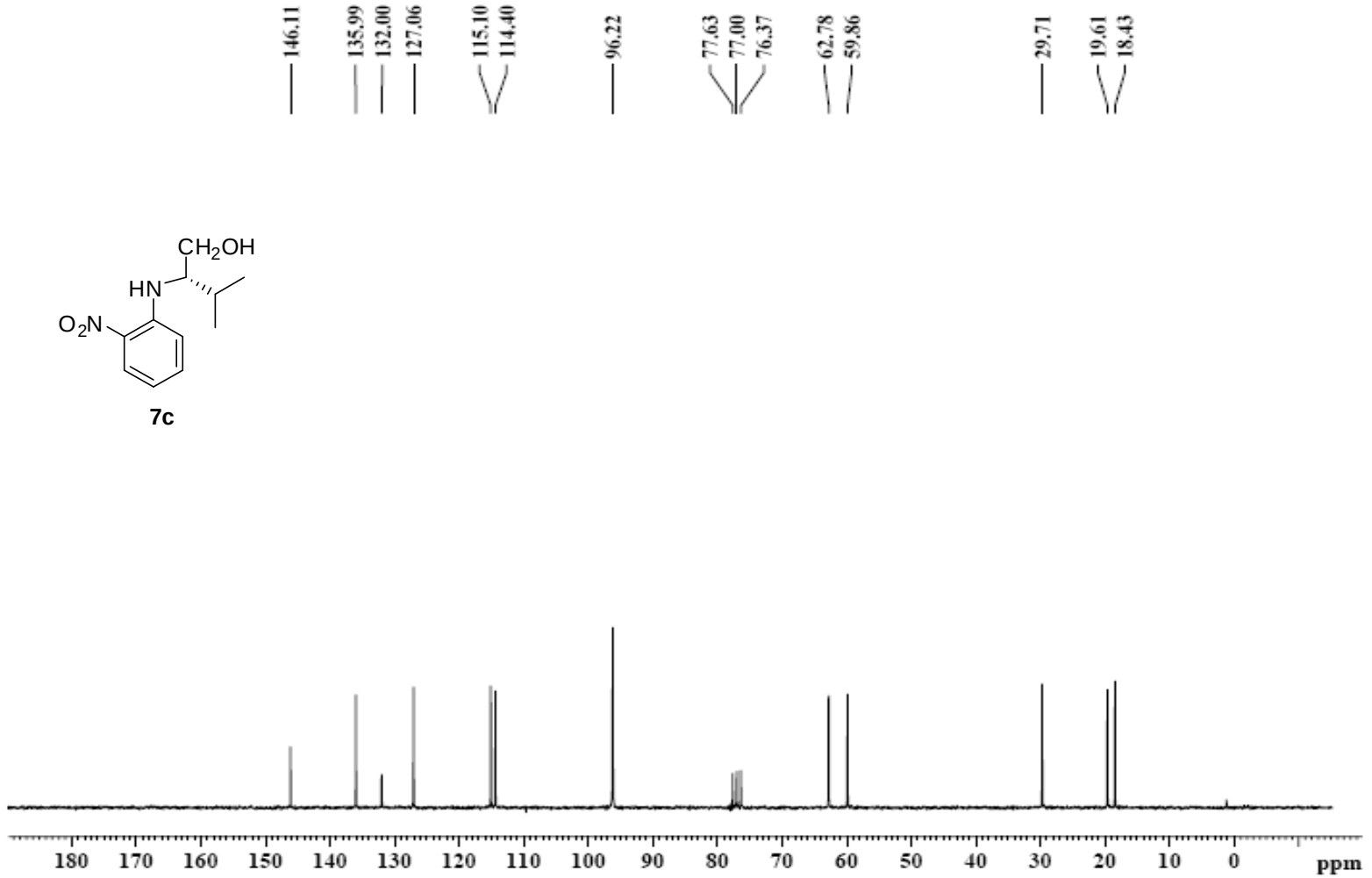
FigureS-71: ^{1}H spectrum (200MHz, $CDCl_3$) of **7b**.



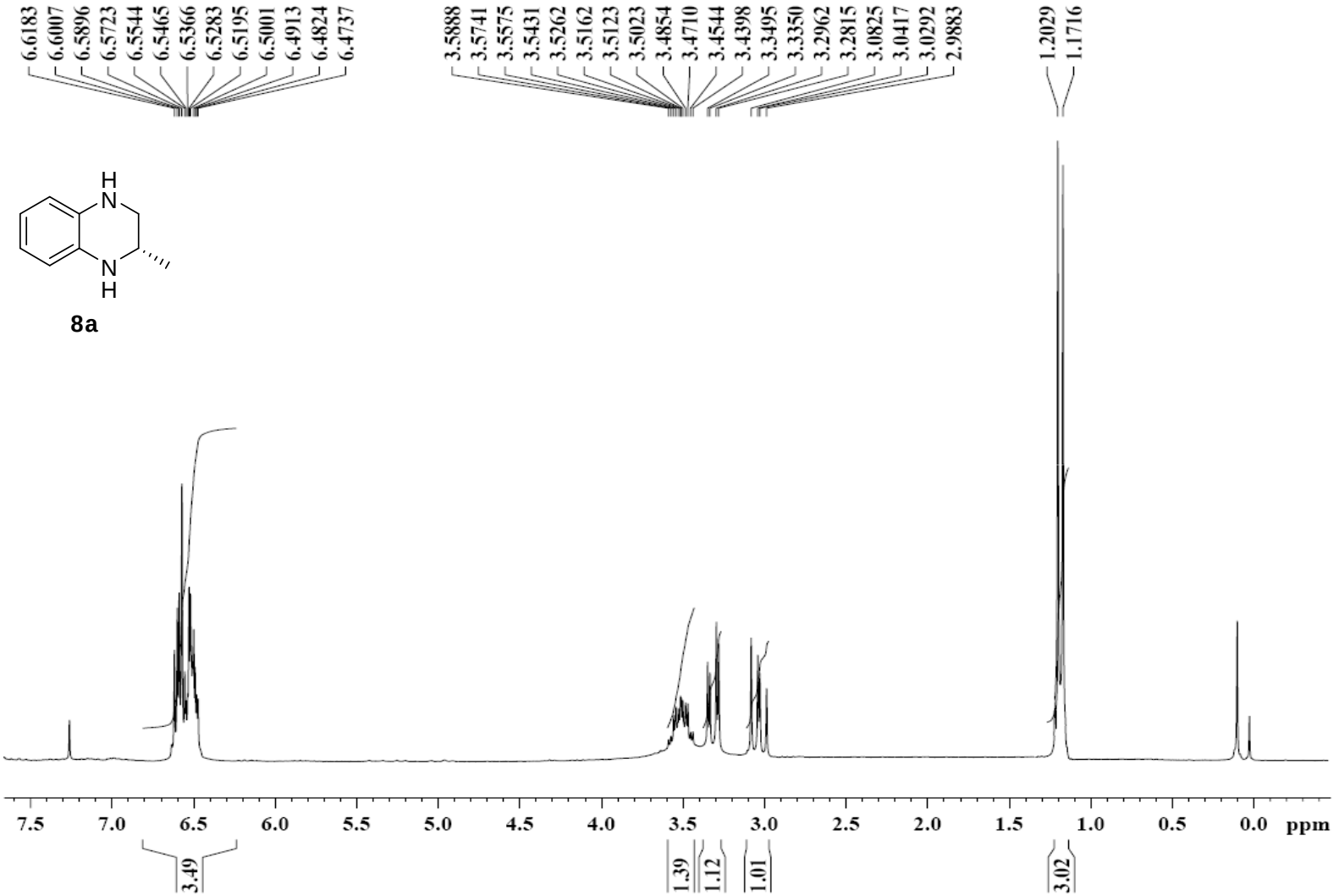
FigureS-72: ^{13}C spectrum (50MHz, $CDCl_3$) of **7b**.



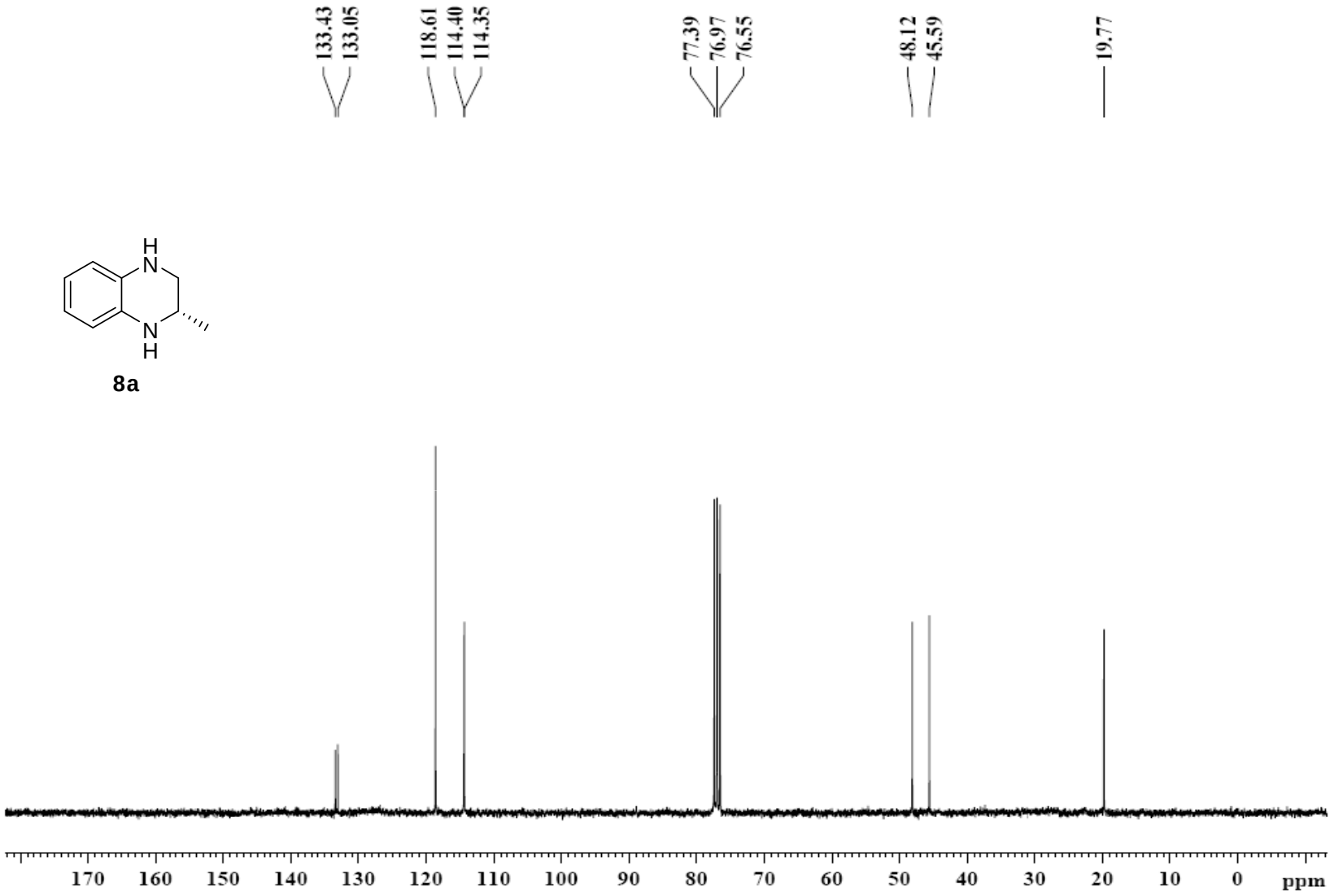
FigureS-73: ^{1}H spectrum (300MHz, $CDCl_3$ + CCl_4) **7c**.



FigureS-74: ^{13}C spectrum (50MHz, $CDCl_3$ + CCl_4) **7c.**

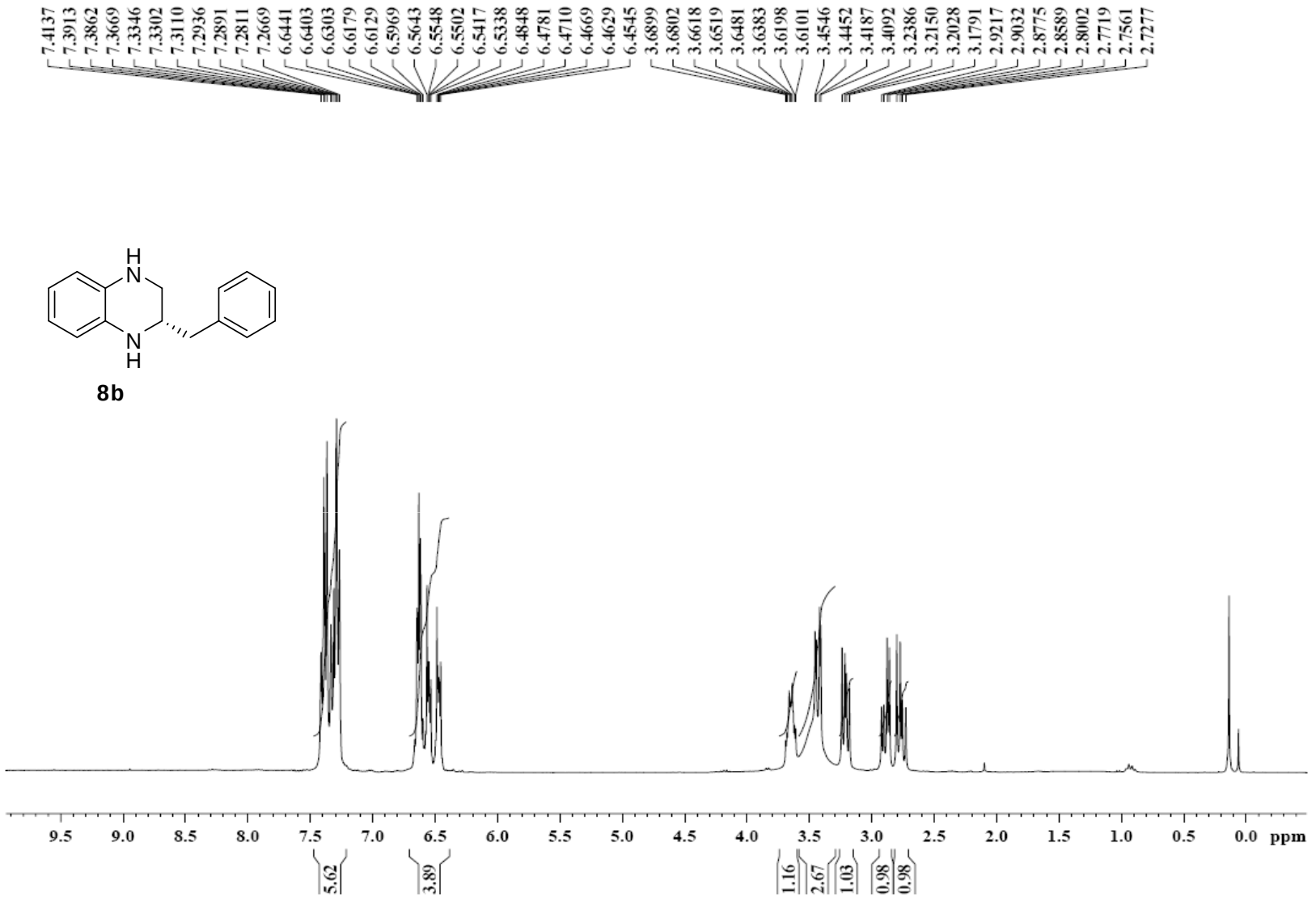


FigureS-75: ^{1}H spectrum (200MHz, $CDCl_3$) of **8a**.

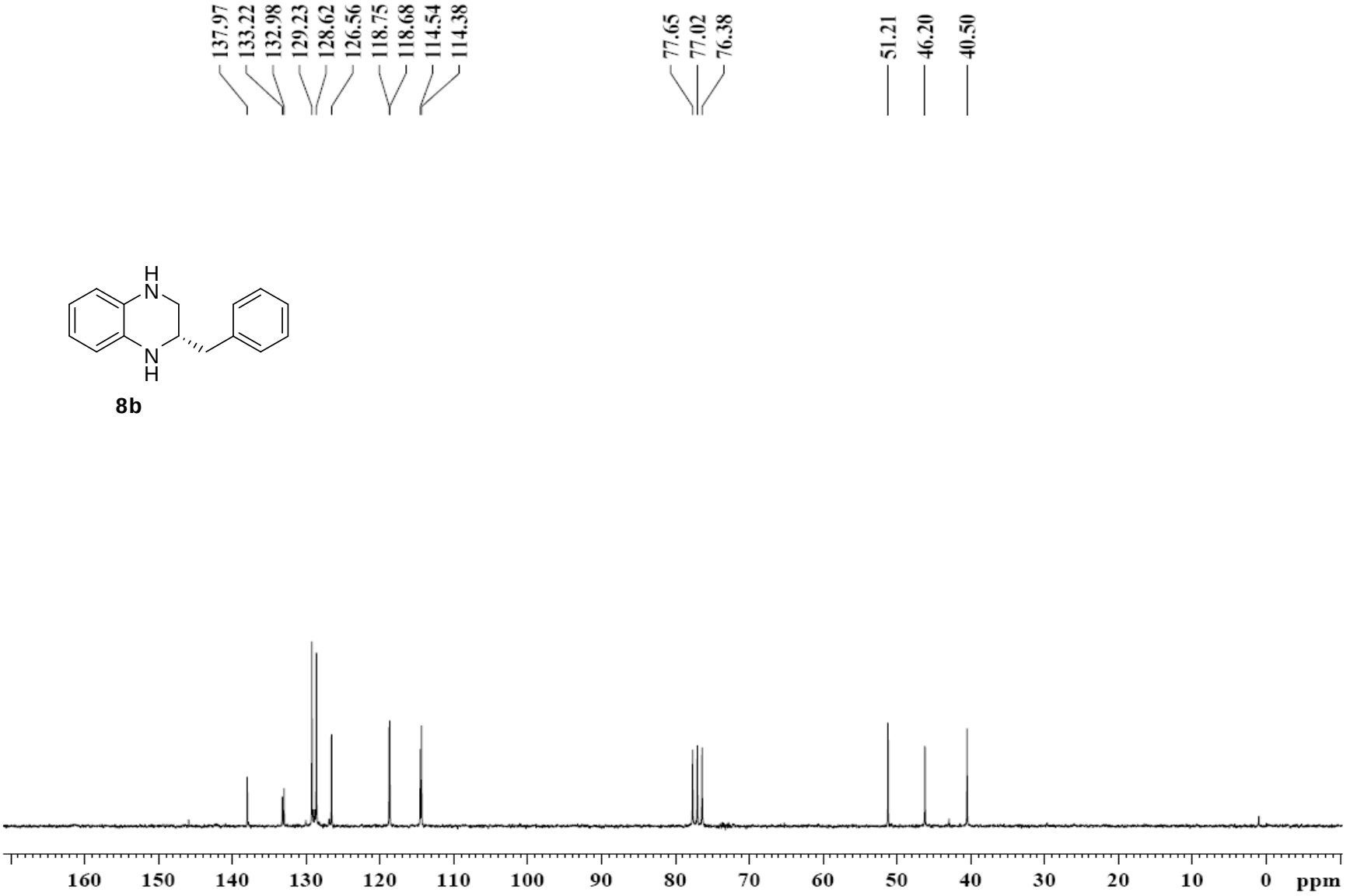


8a

FigureS-76: ^{13}C spectrum (75 MHz, $CDCl_3$) of **8a**.

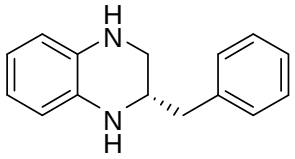


FigureS-77: ^{1}H spectrum (300MHz, $CDCl_3$) of **8b**

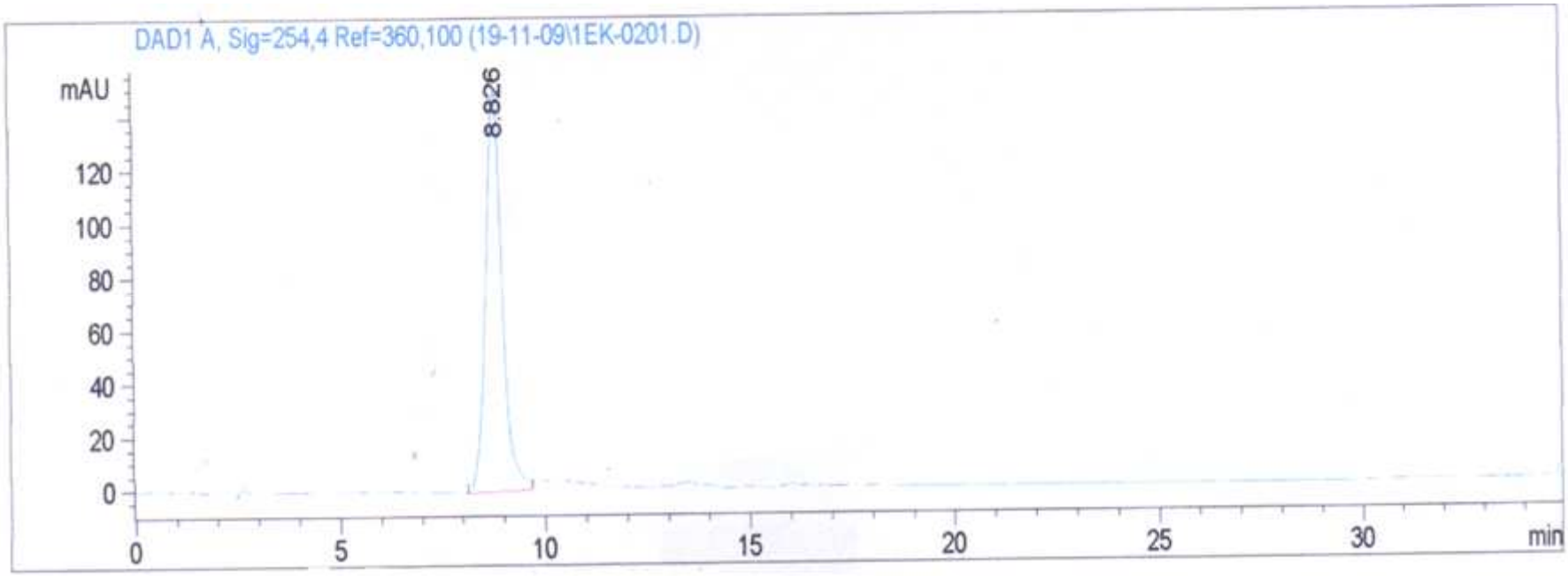


8b

FigureS-78: ^{13}C spectrum (50 MHz, $CDCl_3$) of **8b.**

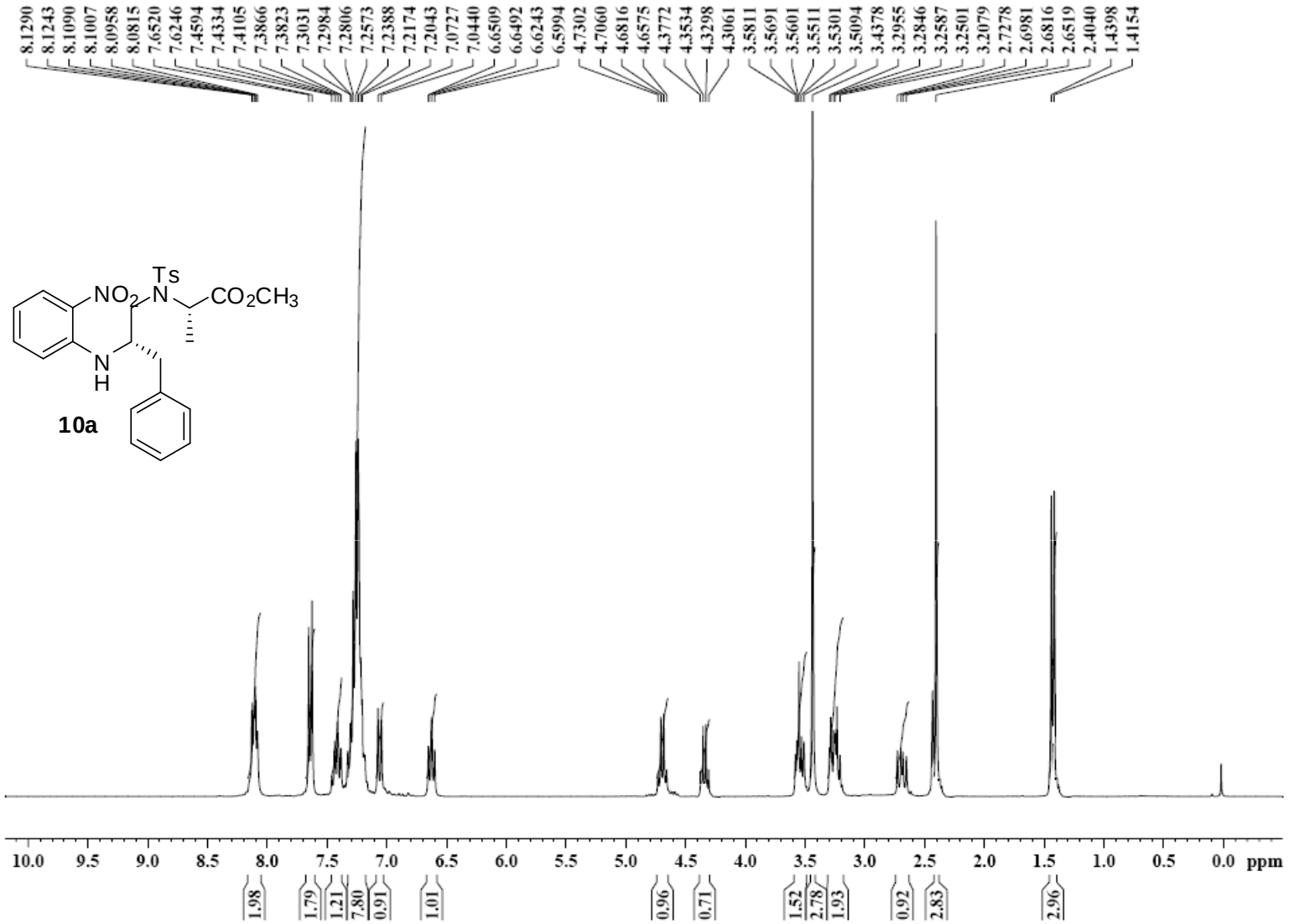


8b

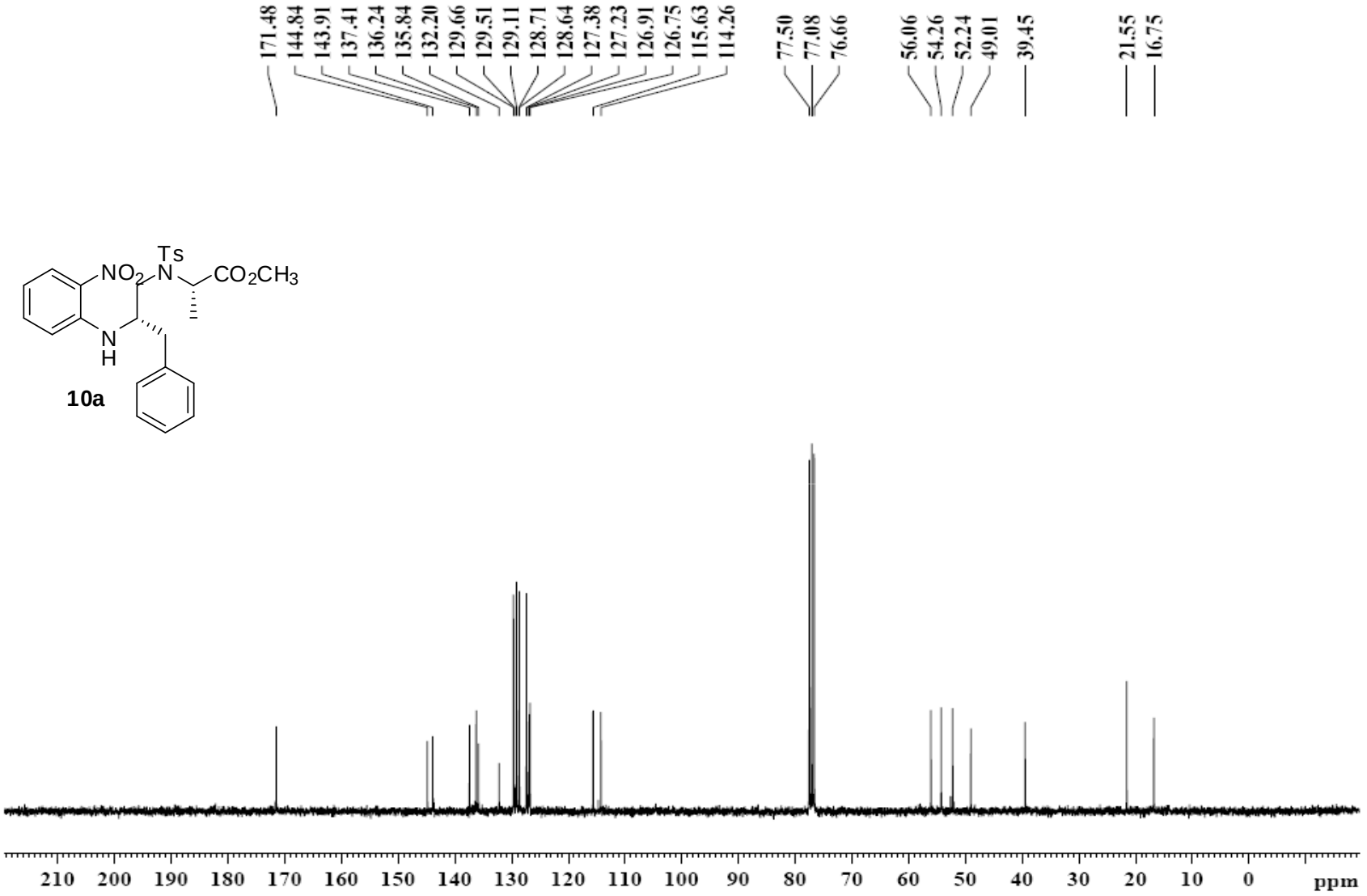


Retention time (min)

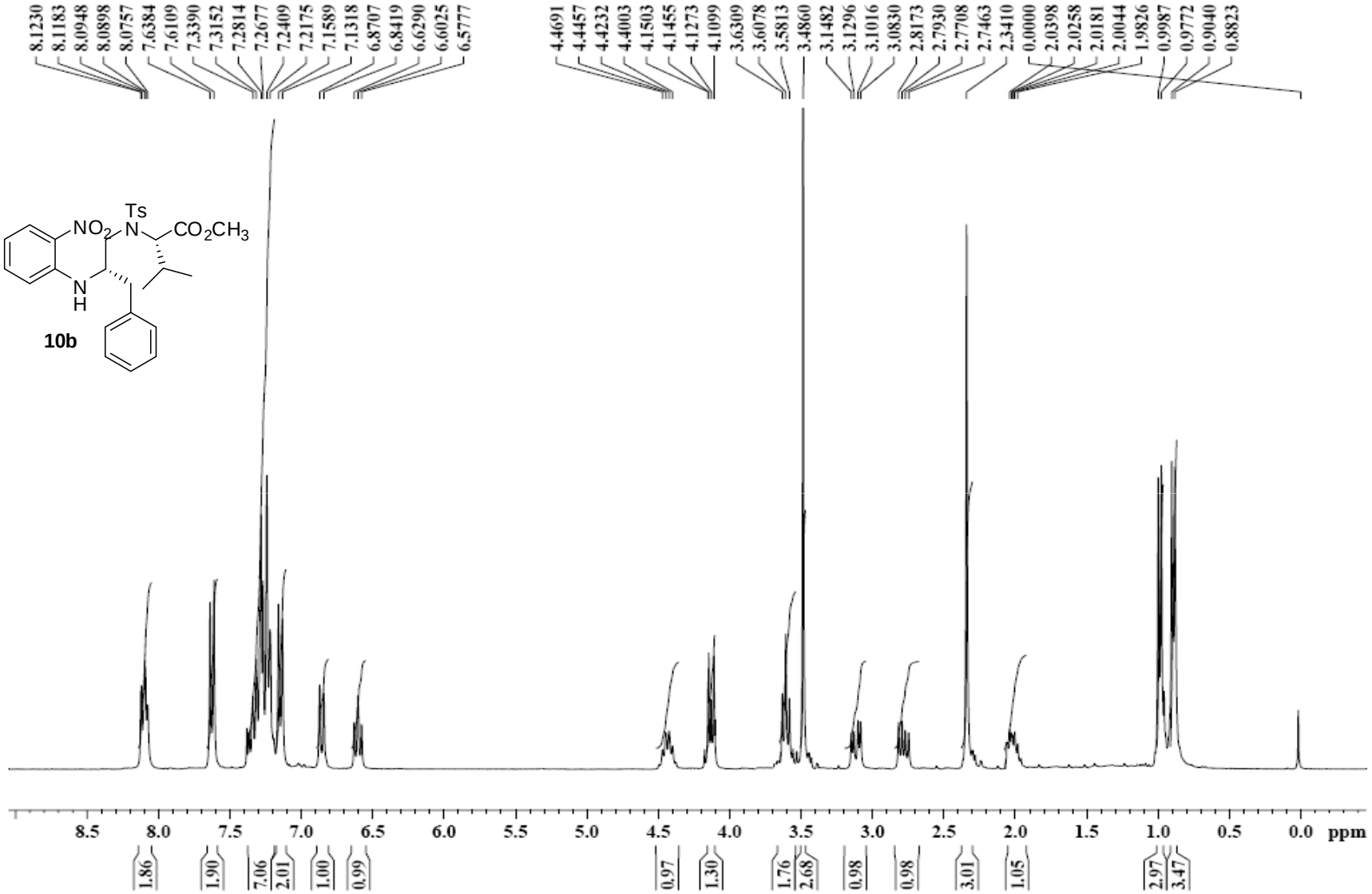
FigureS-79: HPLC graph for **8b.**



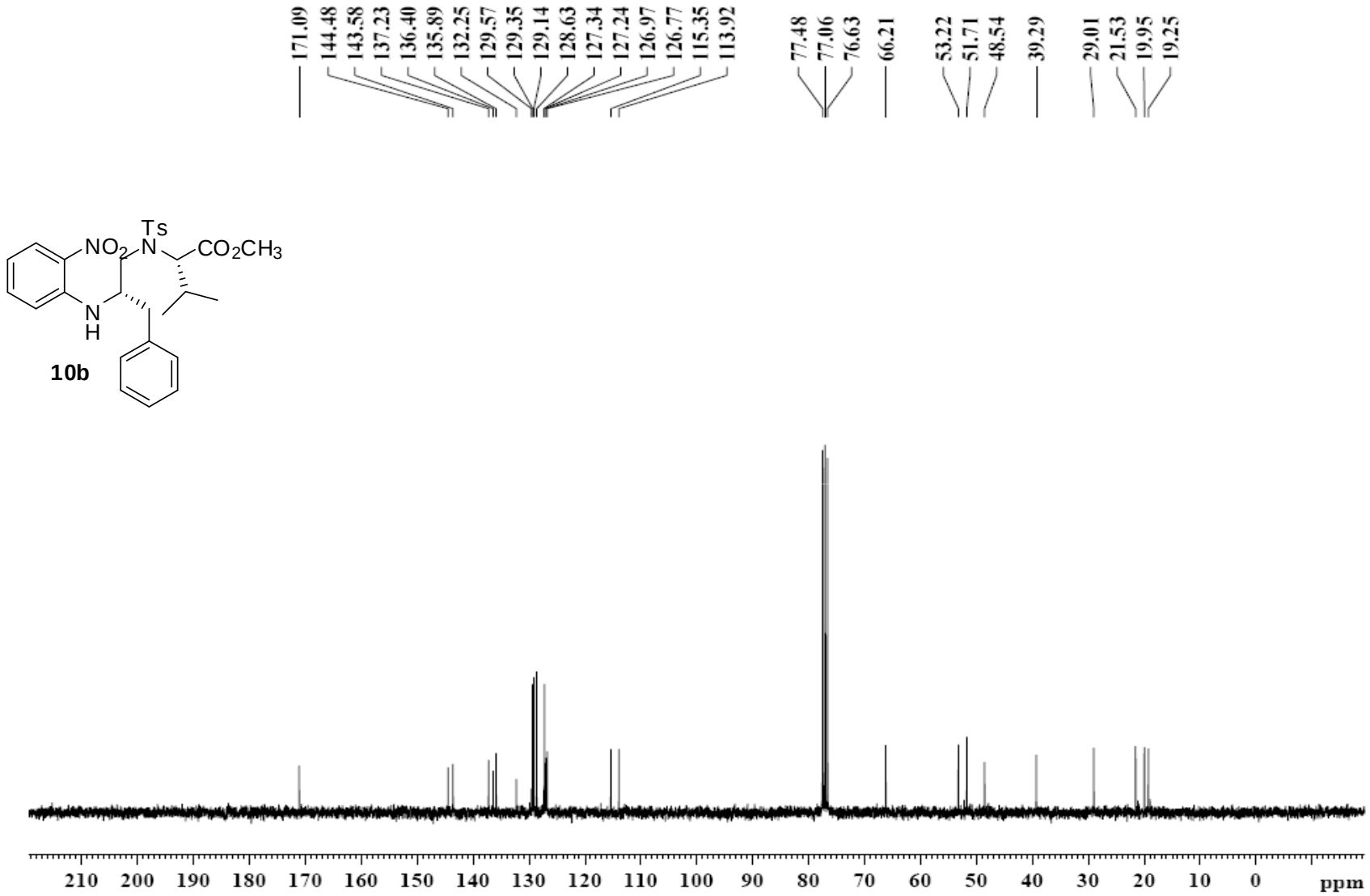
FigureS-80: ^{1}H spectrum (300MHz, $CDCl_3$) of **10a**.



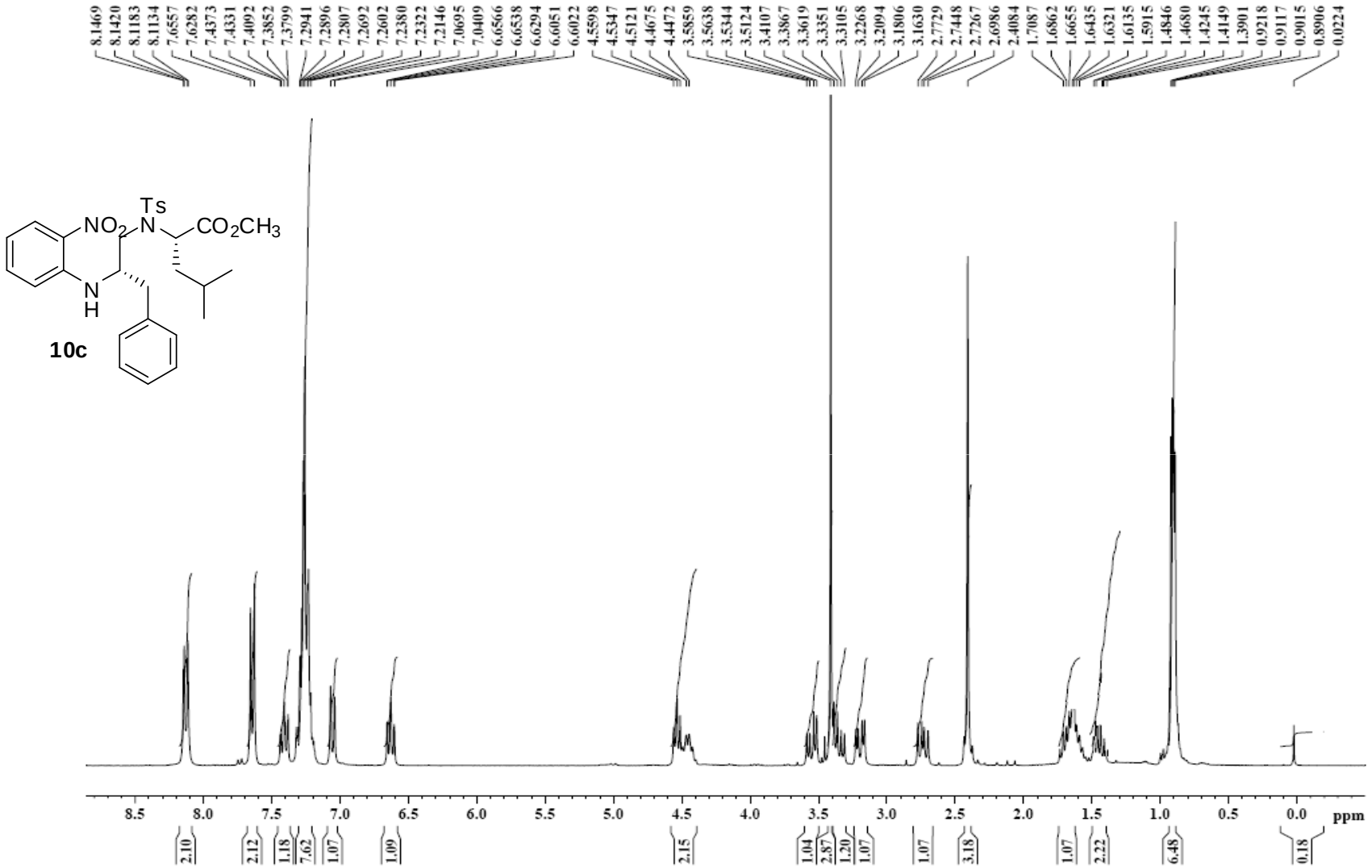
FigureS-81: ^{13}C spectrum (75MHz, $CDCl_3$) of **10a**.



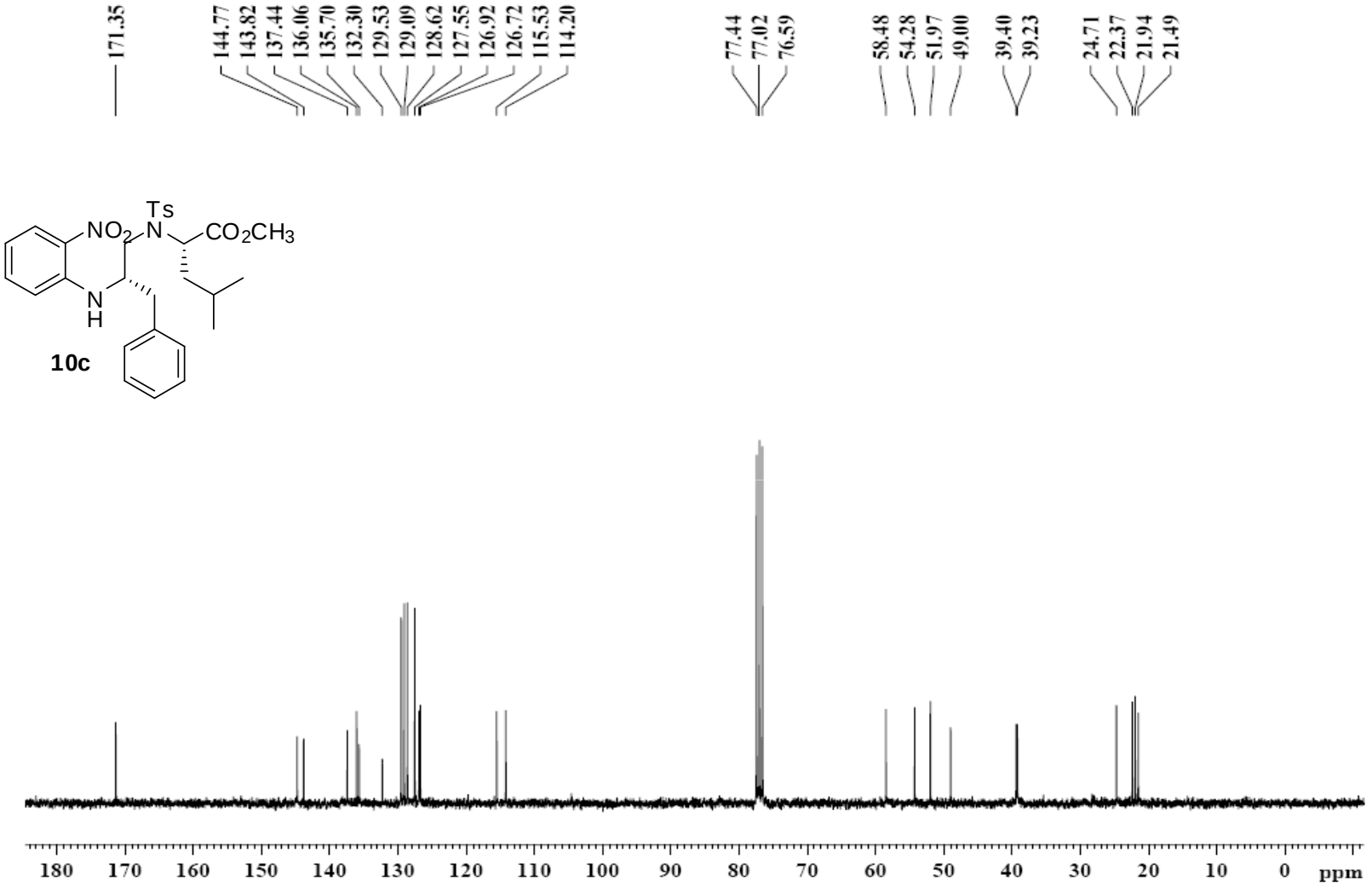
FigureS-82: ^{1}H spectrum (300MHz, $CDCl_3$) of **10b**.



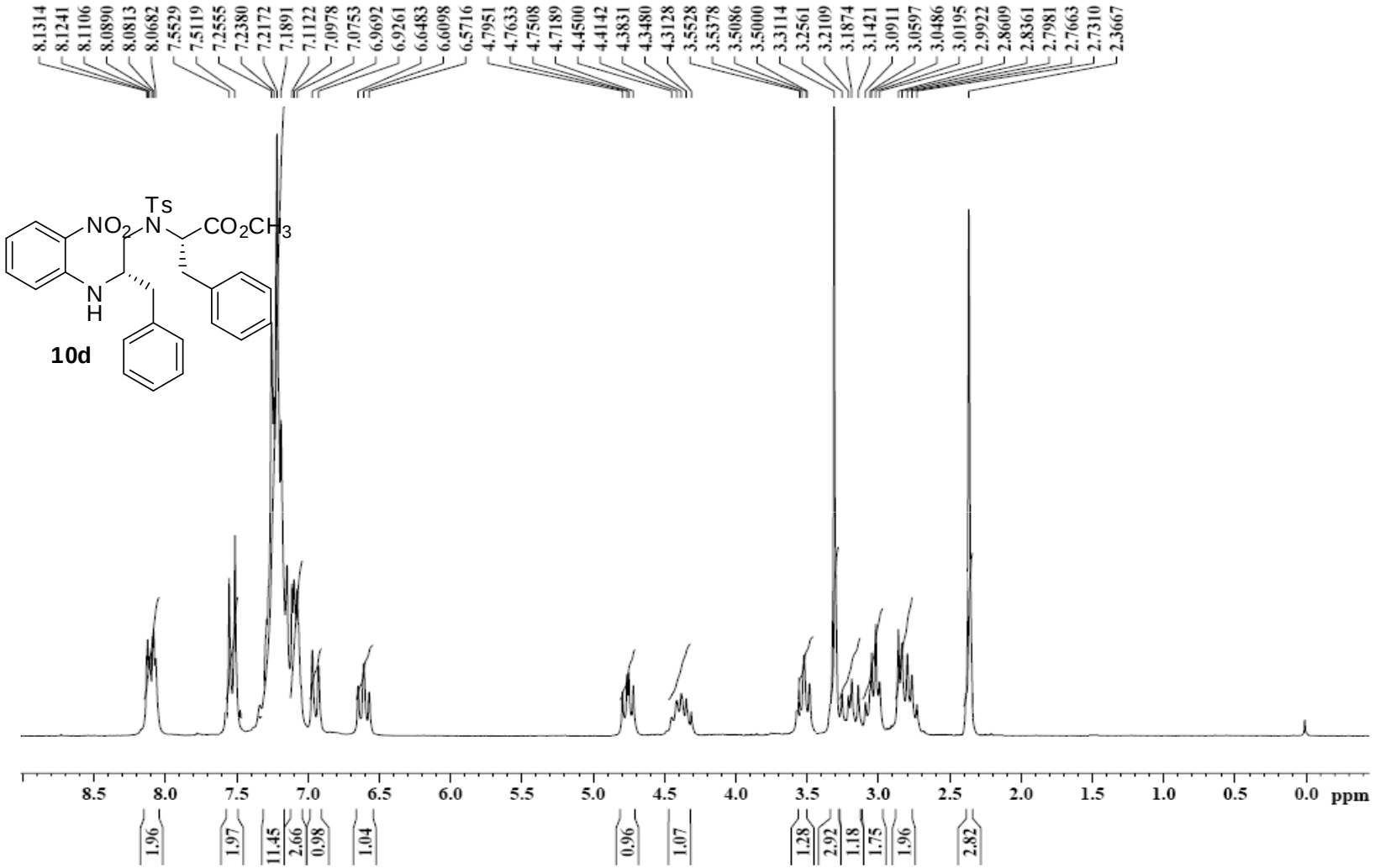
FigureS-83: ^{13}C spectrum (75MHz, $CDCl_3$) of **10b**.



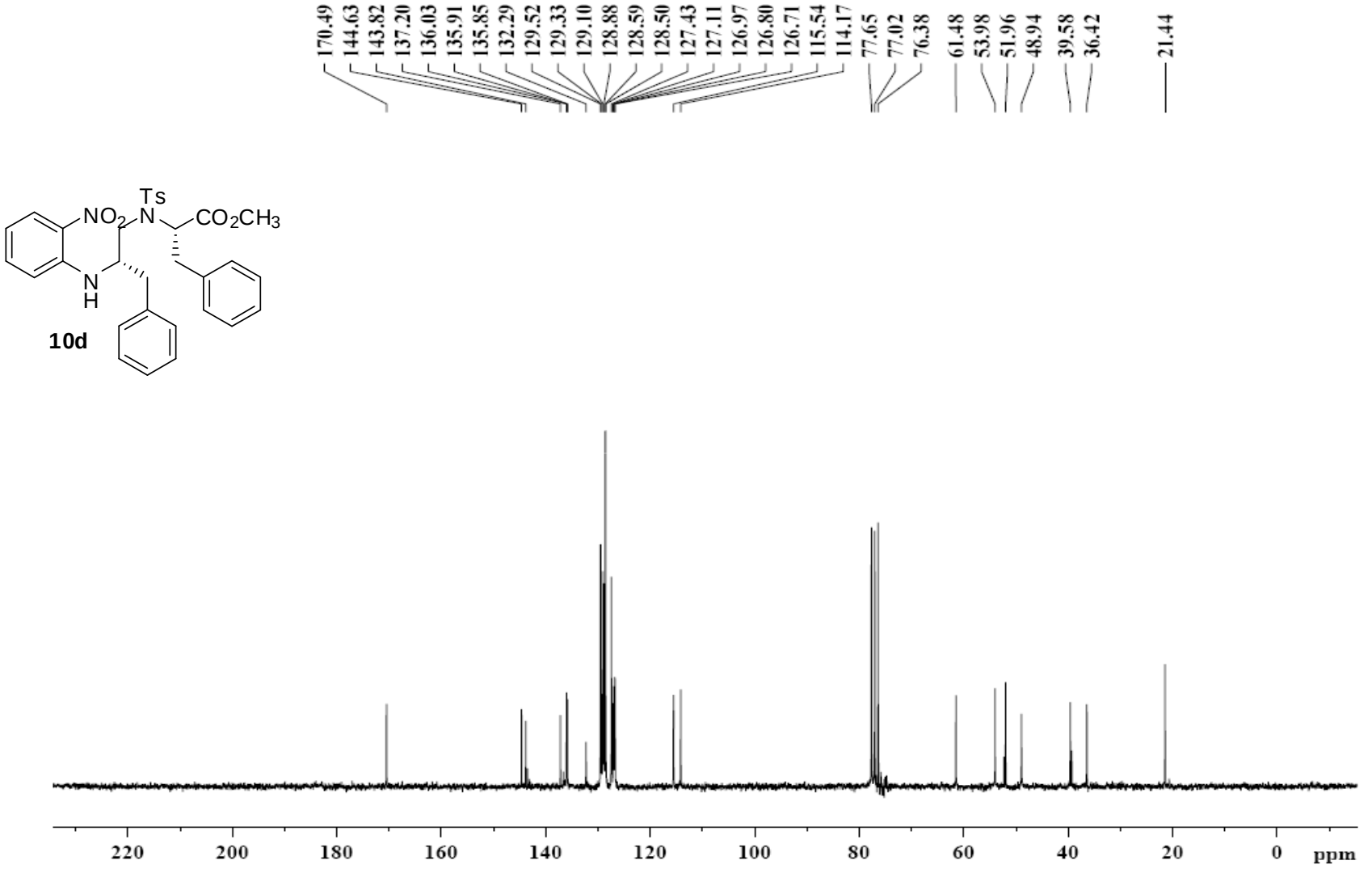
FigureS-84: ^{1}H spectrum (300MHz, $CDCl_3$) of **10c**.



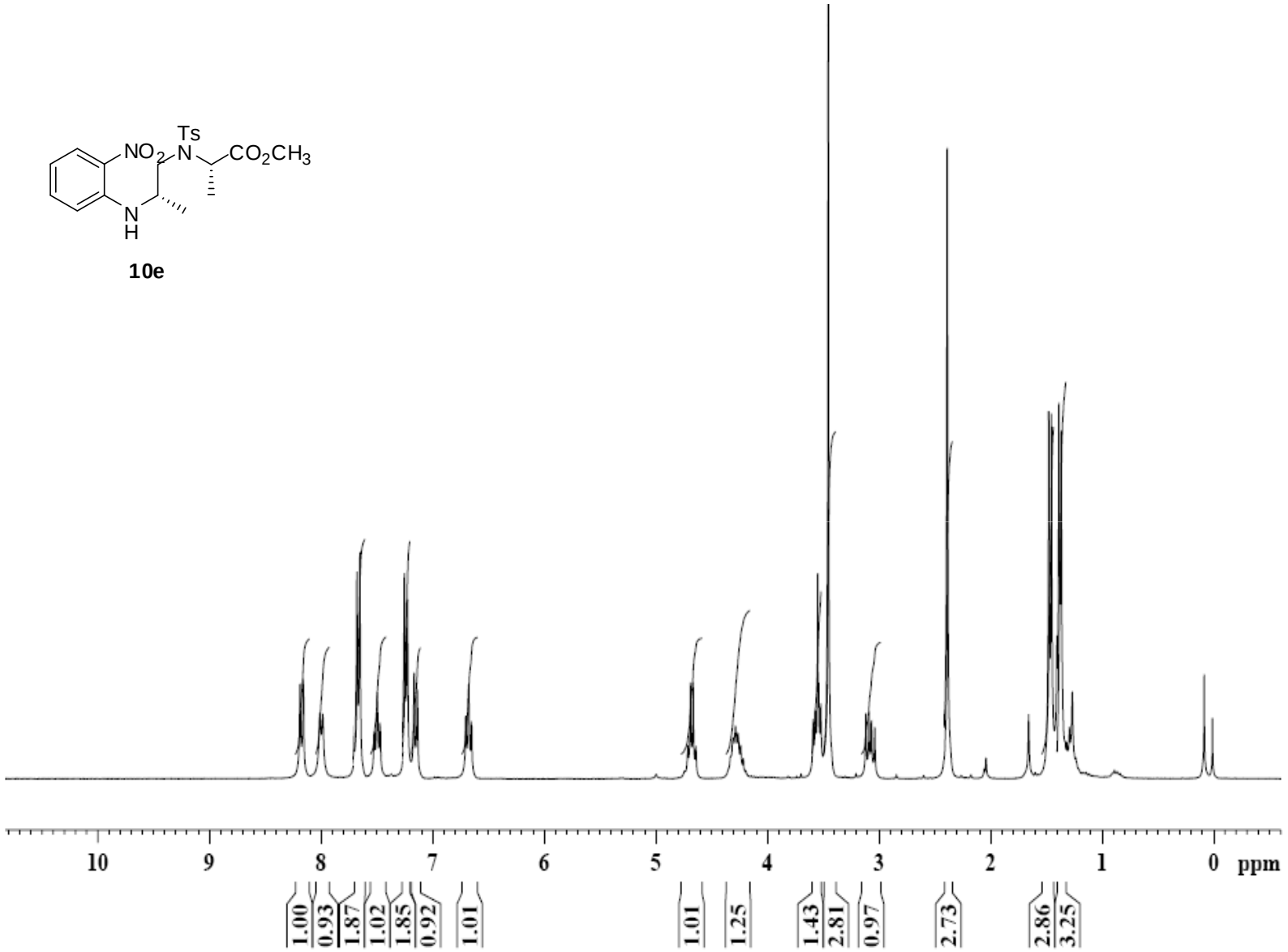
FigureS-85: ^{13}C spectrum (75MHz, $CDCl_3$) of **10c**.



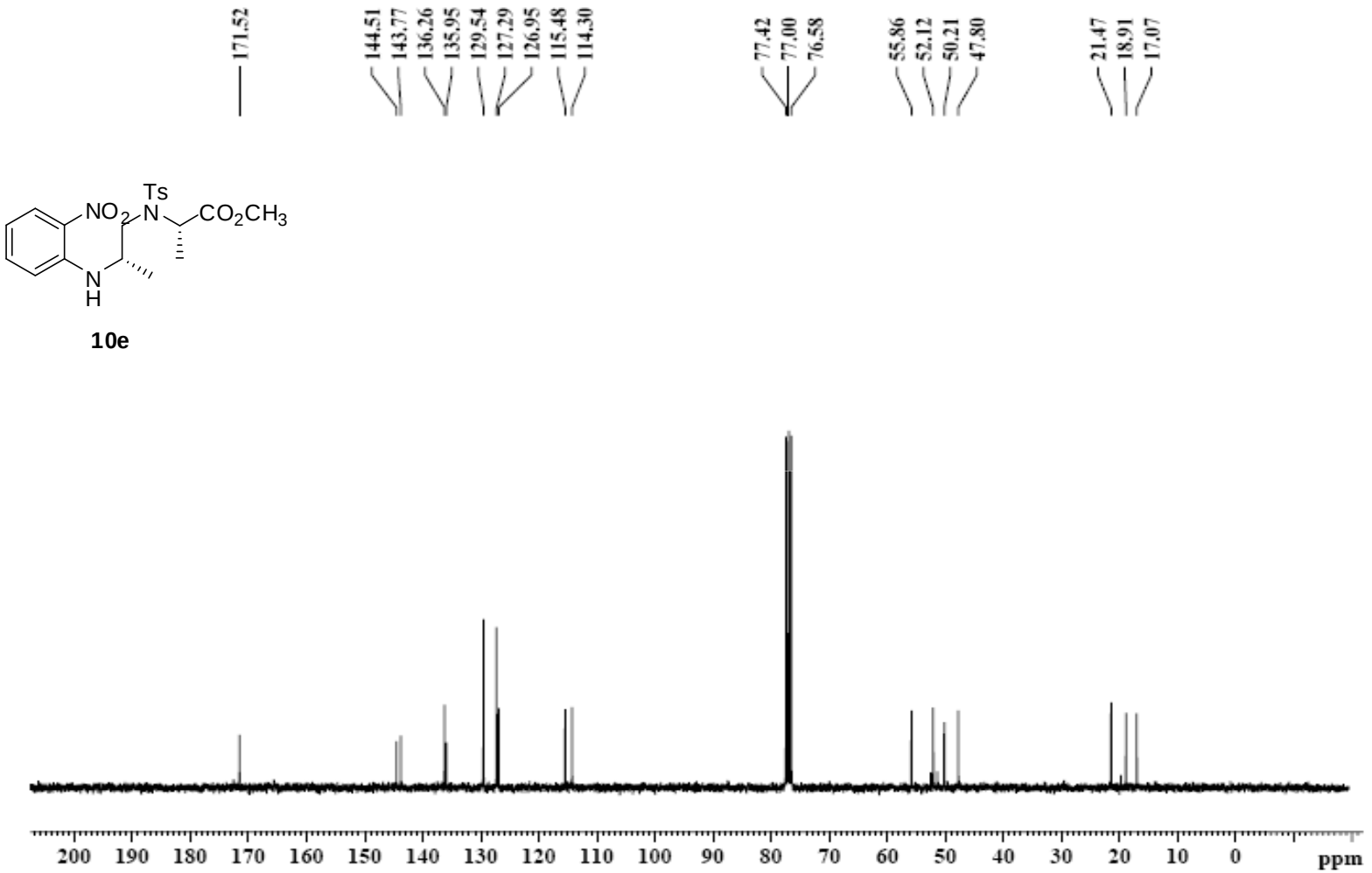
FigureS-86: ^{1}H spectrum (300MHz, $CDCl_3$) of **10d**.



FigureS-87: ^{13}C spectrum (75MHz, $CDCl_3$) of **10d**.

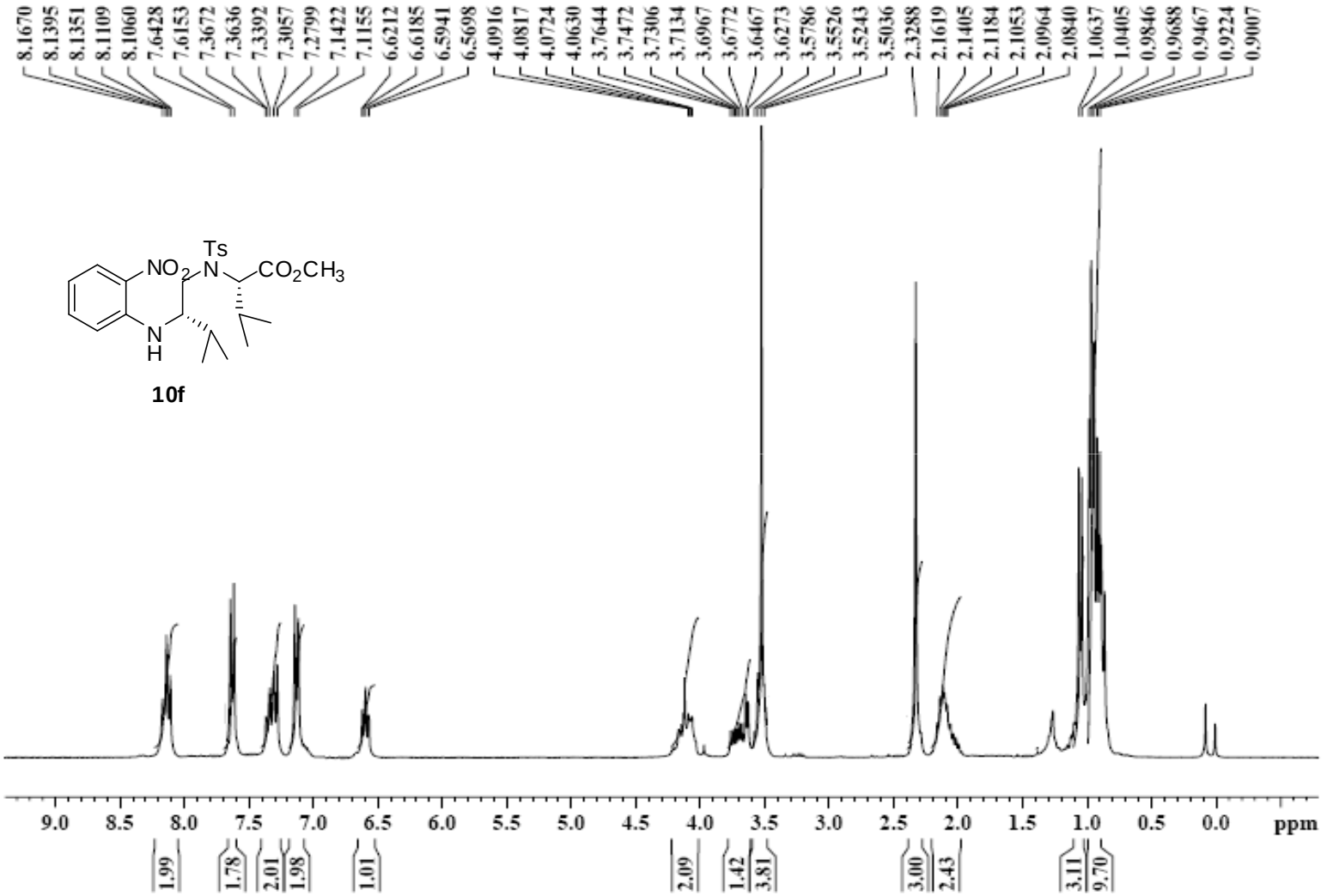


FigureS-88: ^{1}H spectrum (300MHz, $CDCl_3$) of **10e**.

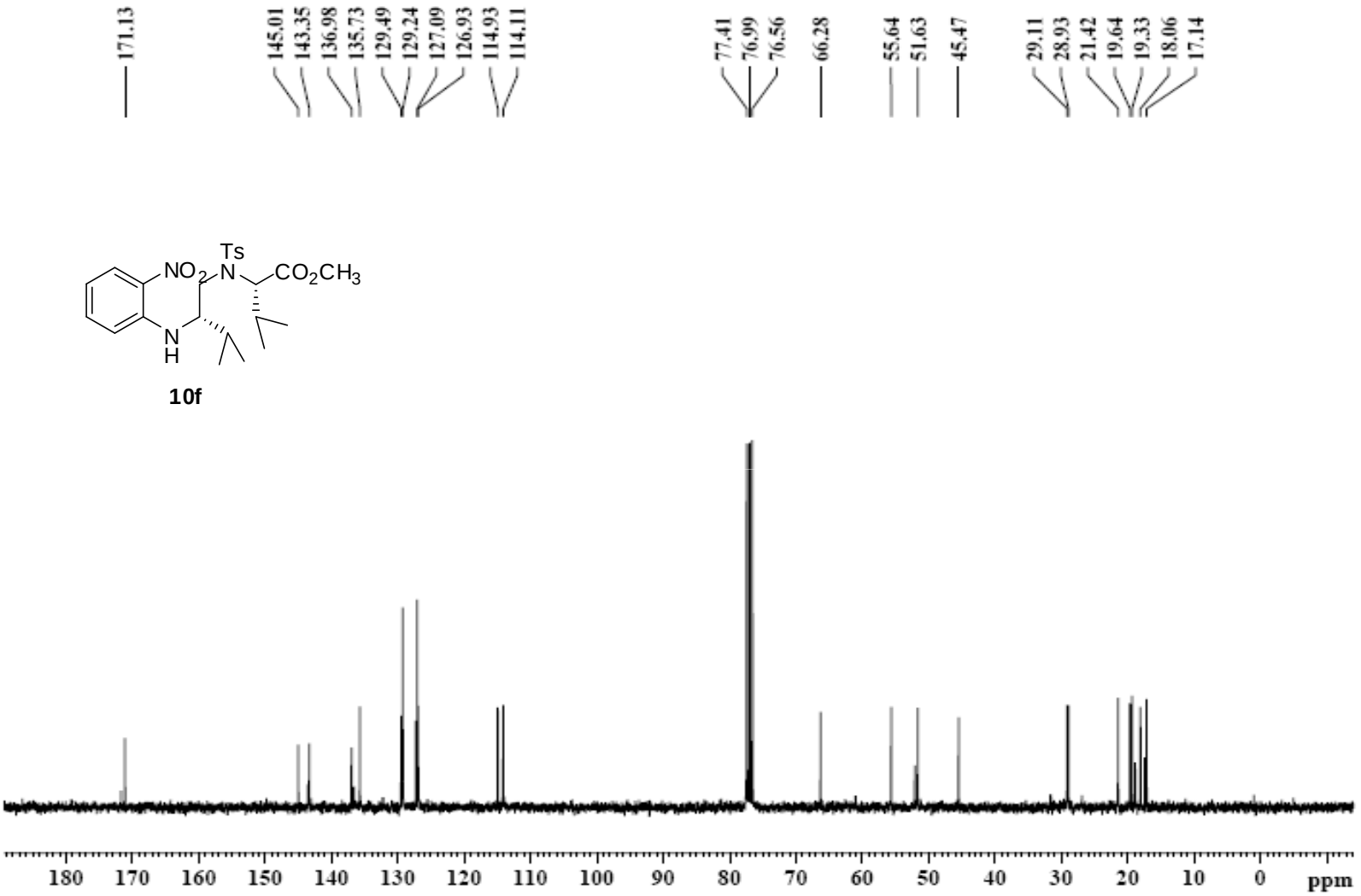


10e

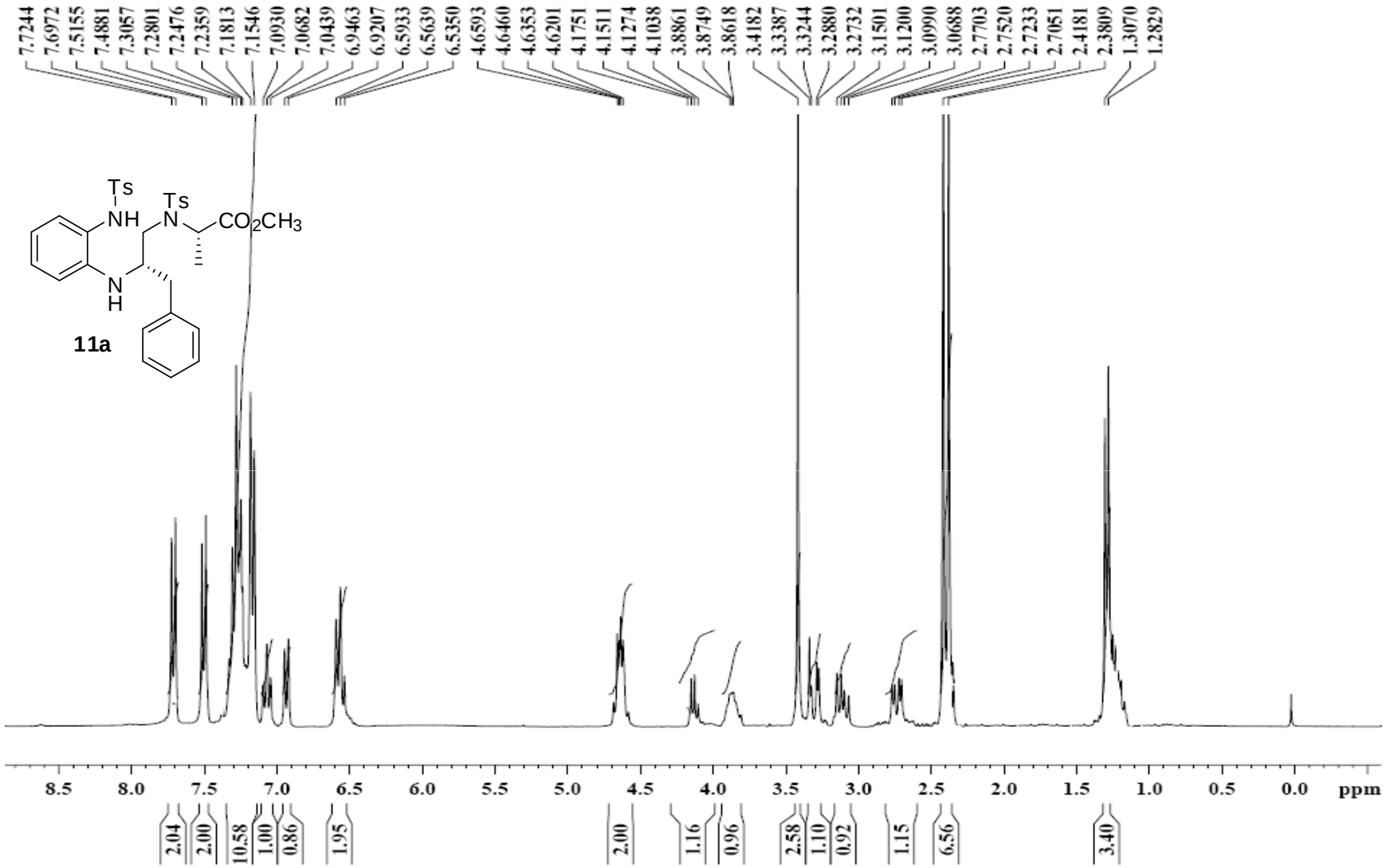
FigureS-89: ^{13}C spectrum (75MHz, $CDCl_3$) of **10e**.



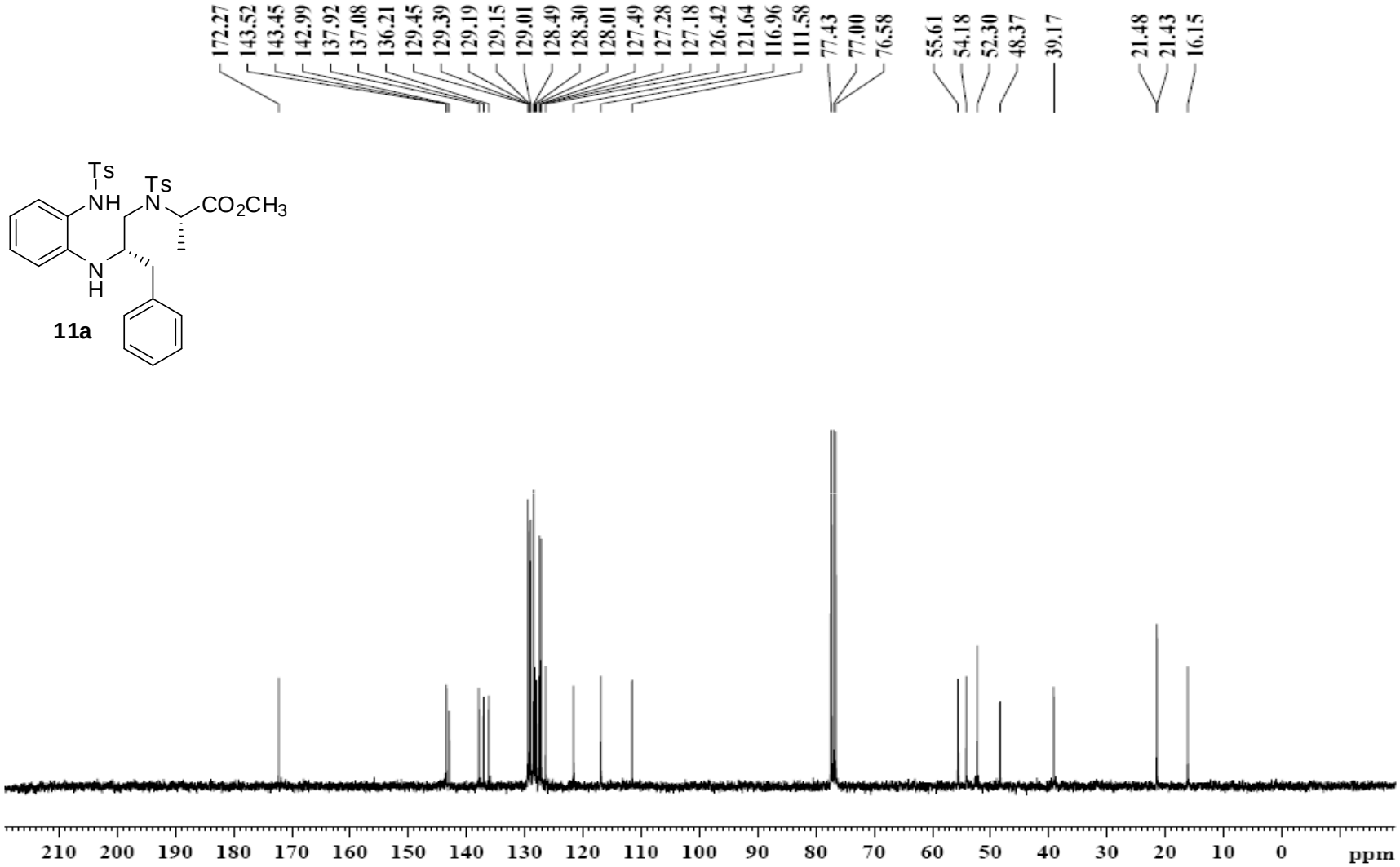
FigureS-90: ^{1}H spectrum (300MHz, $CDCl_3$) of **10f**.



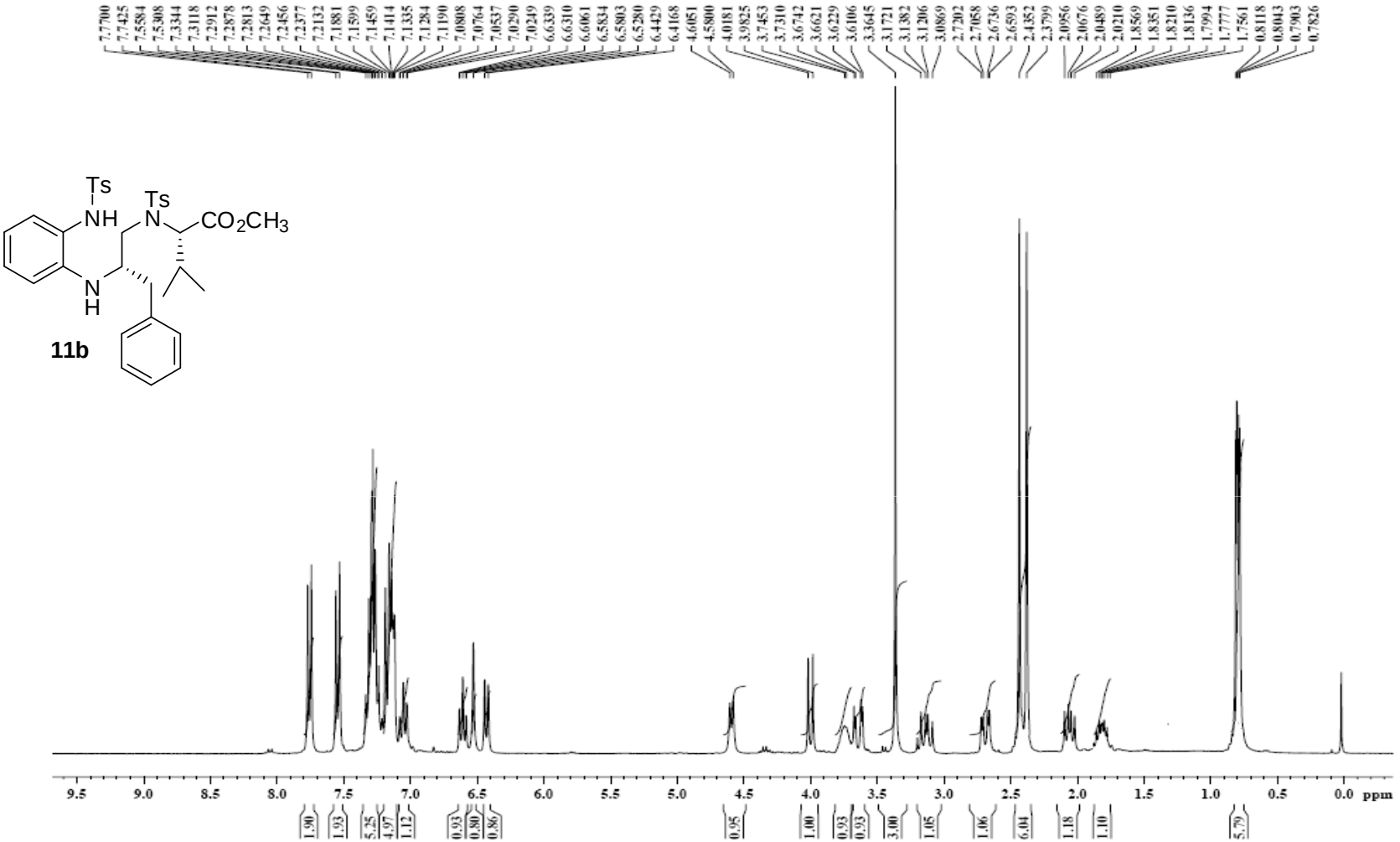
FigureS-91: ^{13}C spectrum (75MHz, $CDCl_3$) of **10f**.



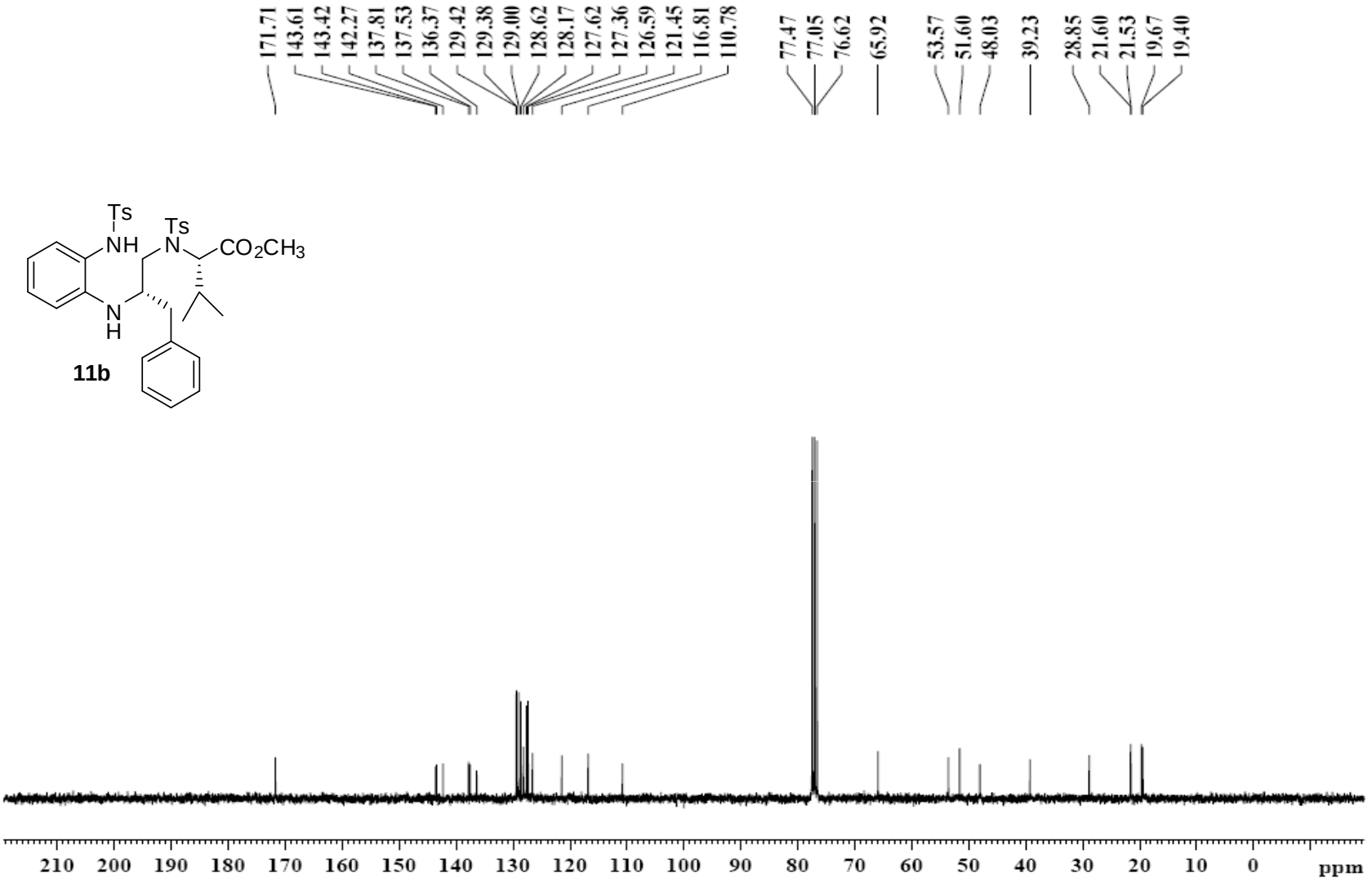
FigureS-92: ^{1}H spectrum (300MHz, $CDCl_3$) of **11a**.



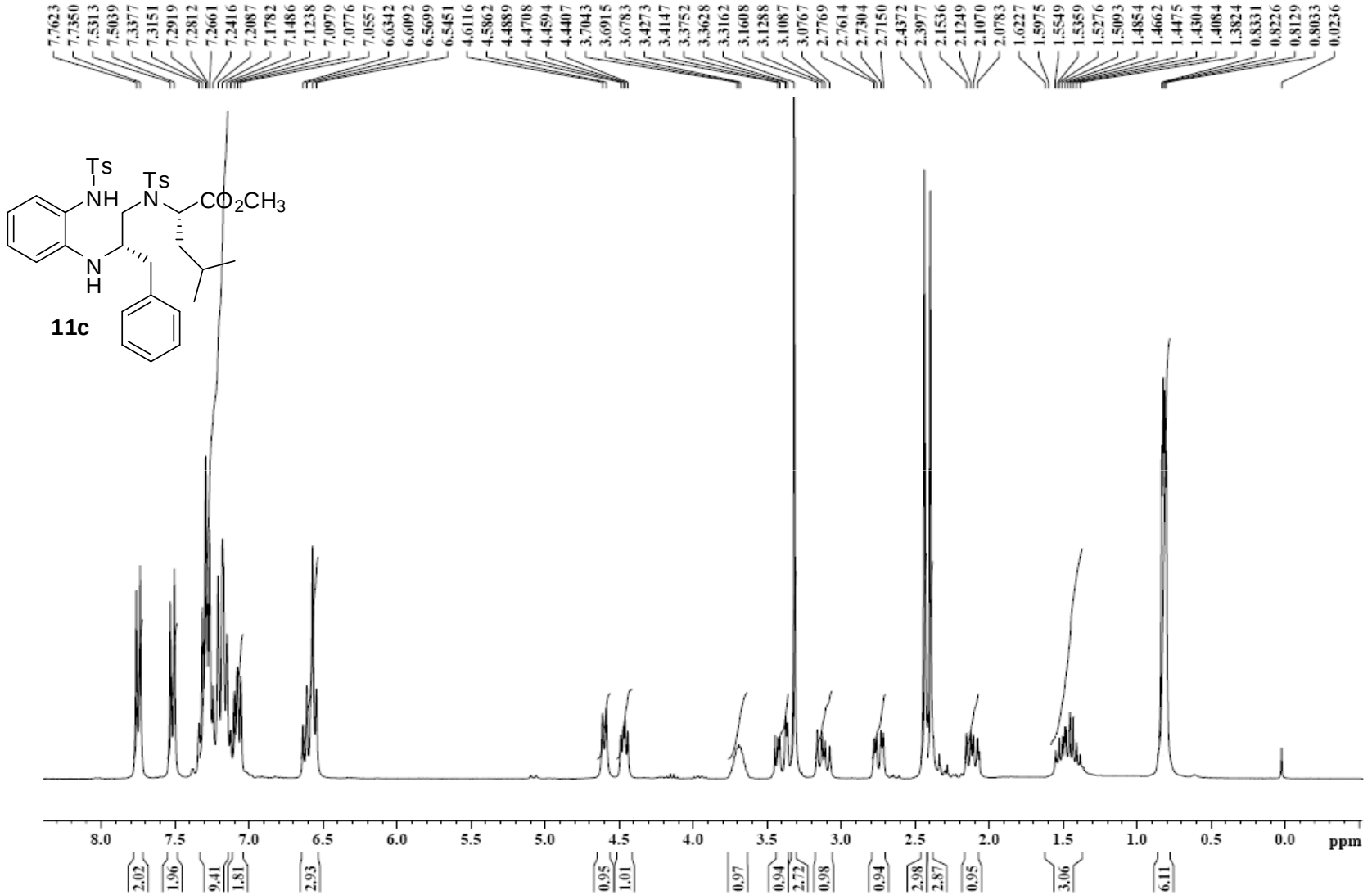
FigureS-93: ^{13}C spectrum (75MHz, $CDCl_3$) of **11a**.



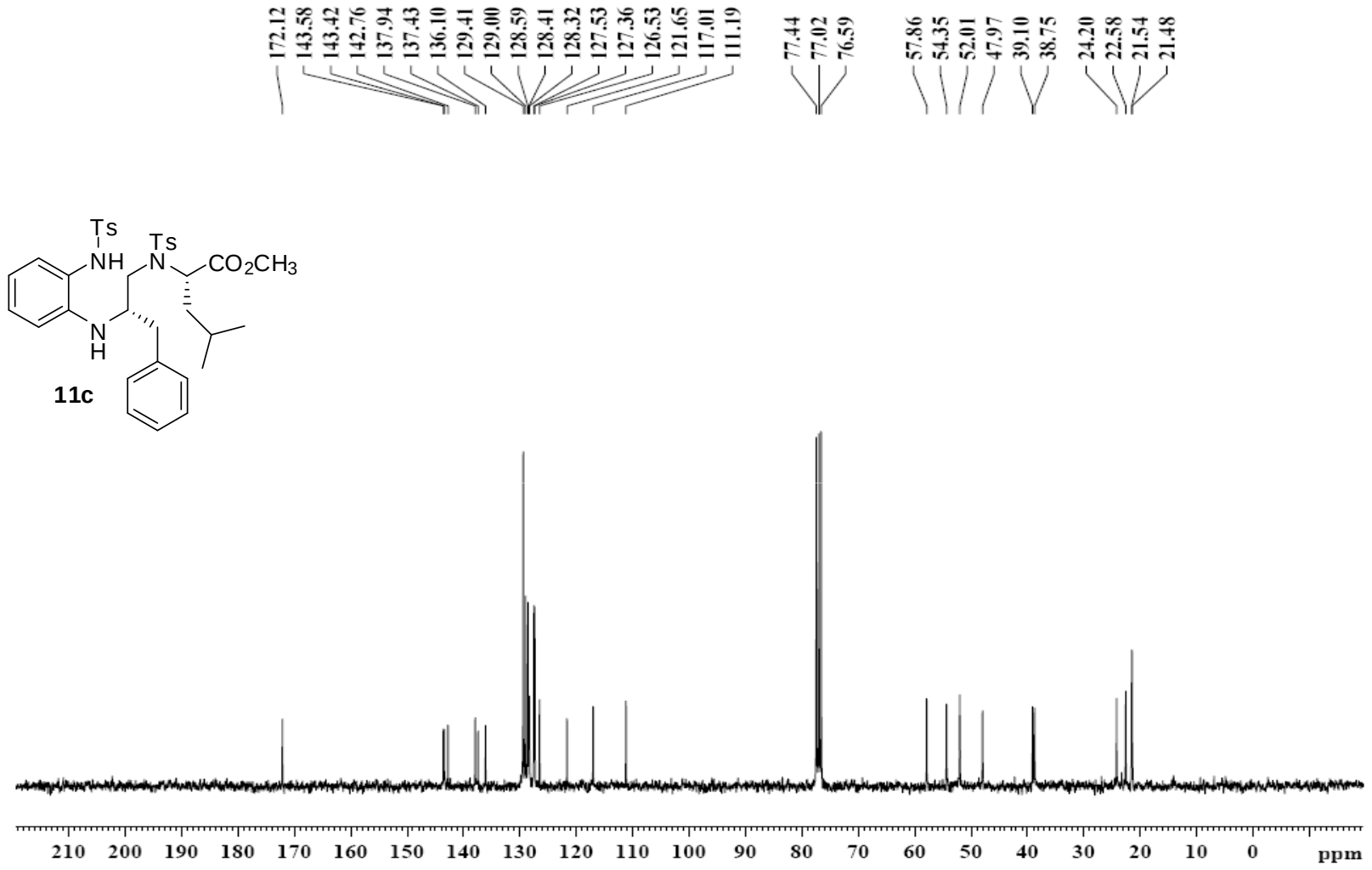
FigureS-94: ^{1}H spectrum (300MHz, $CDCl_3$) of **11b**.



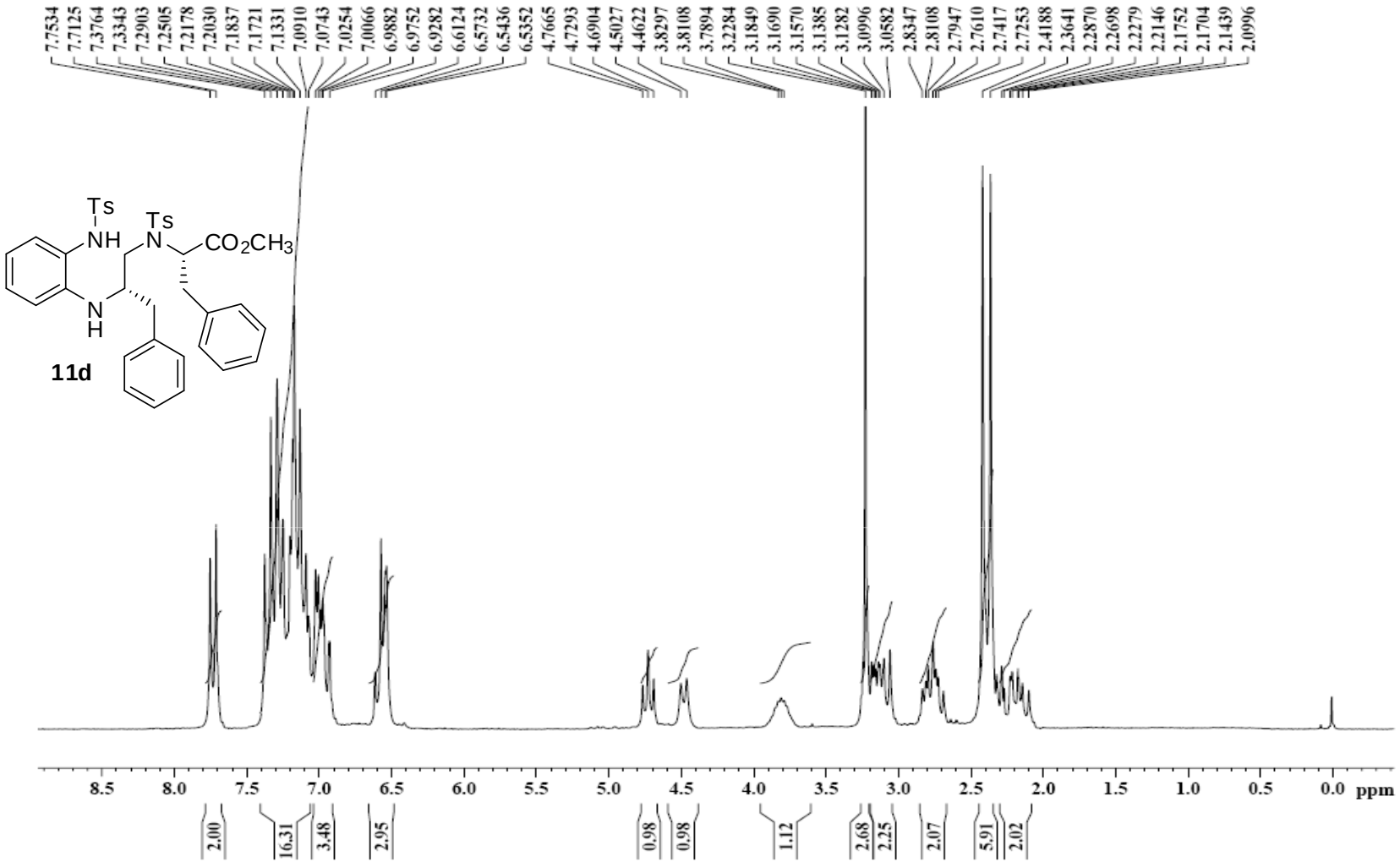
FigureS-95: ^{13}C spectrum (75MHz, $CDCl_3$) of **11b**.



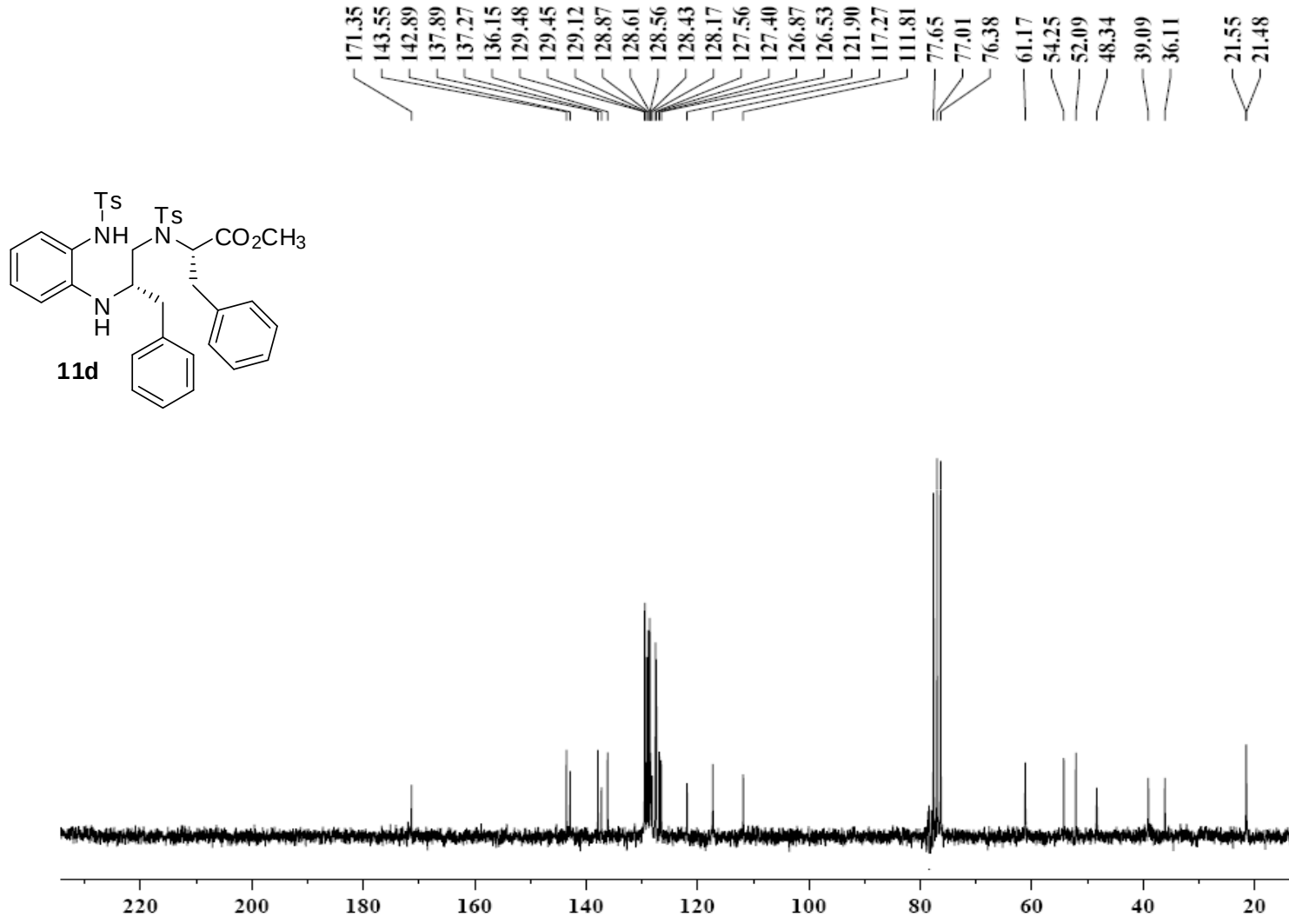
FigureS-96: ^{1}H spectrum (300MHz, $CDCl_3$) of **11c**.



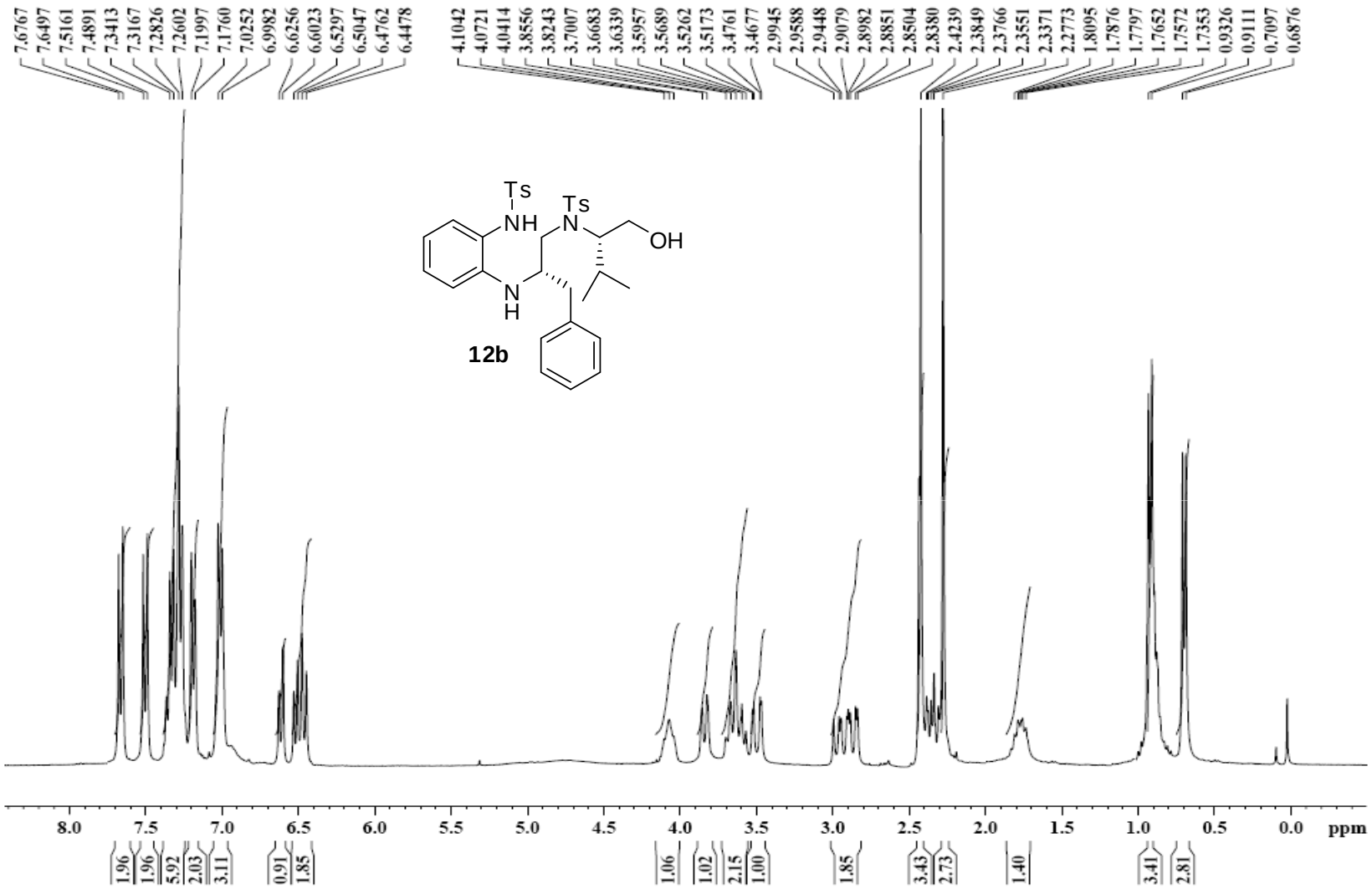
FigureS-97: ^{13}C spectrum (75MHz, $CDCl_3$) of **11c**.



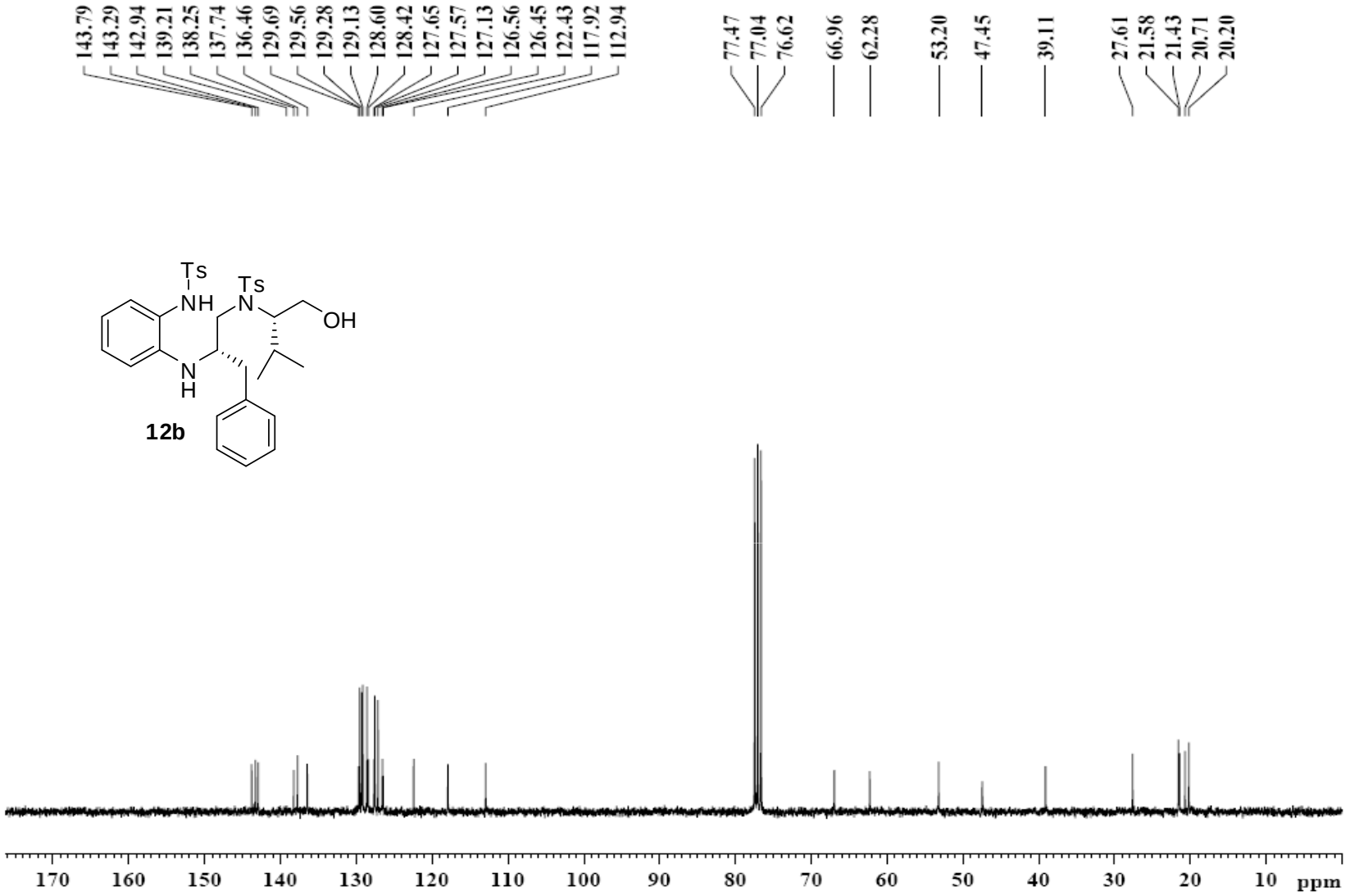
FigureS-98: ^{1}H spectrum (300MHz, $CDCl_3$) of **11d**.



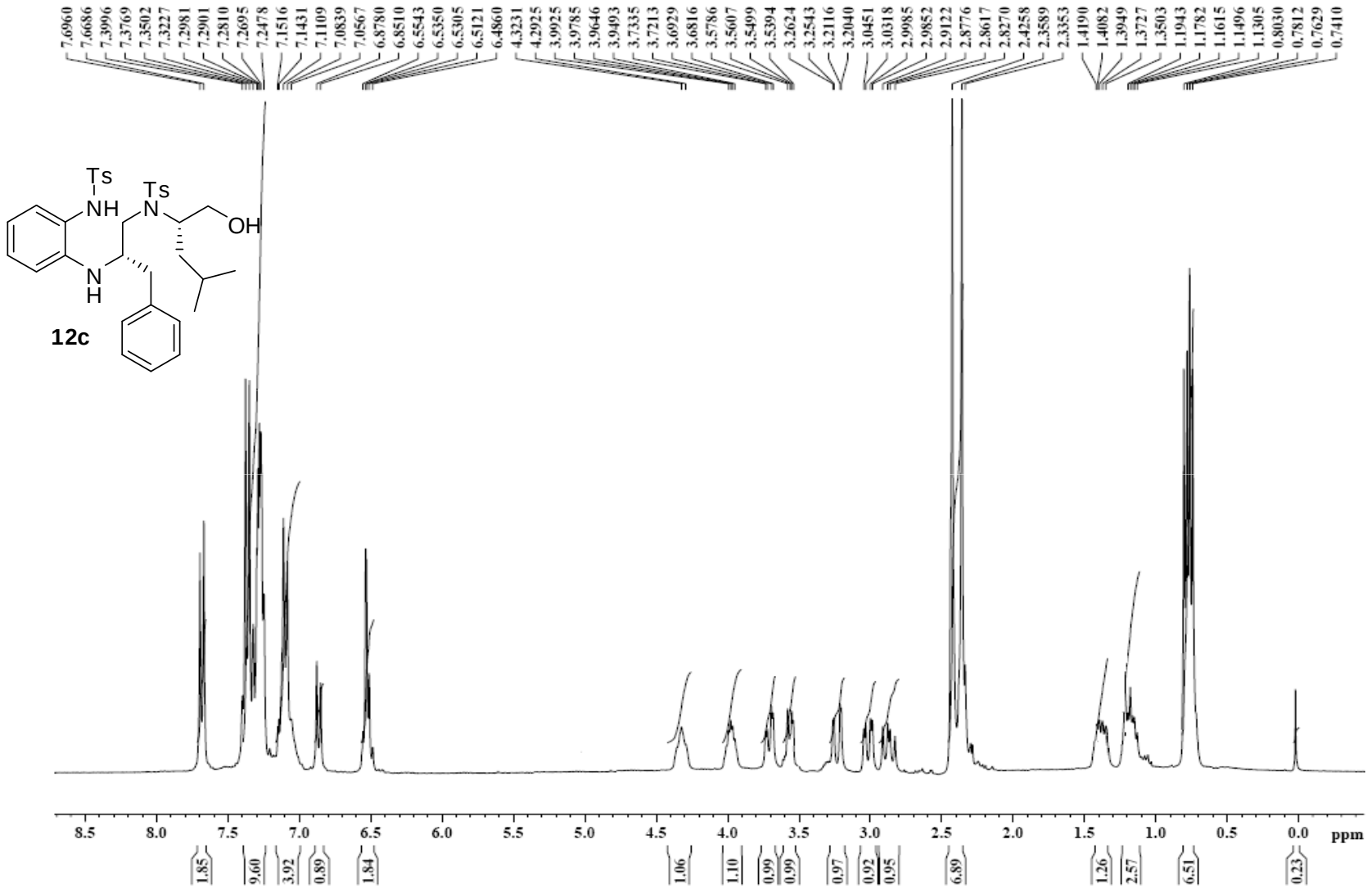
FigureS-99: ^{13}C spectrum (75 MHz, $CDCl_3$) of **11d**.



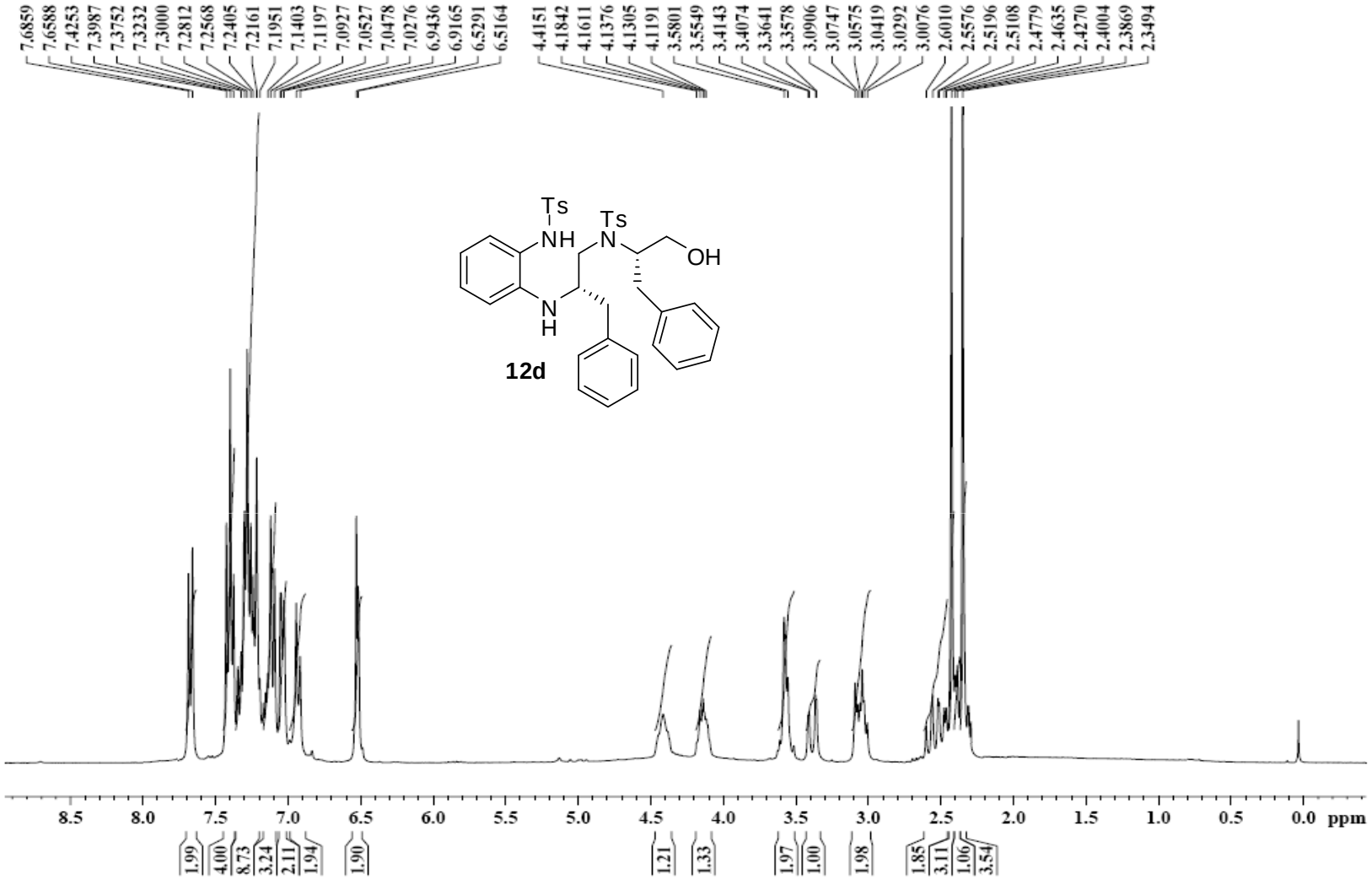
FigureS-100: ^{1}H spectrum (300MHz, $CDCl_3$) of **12b**.



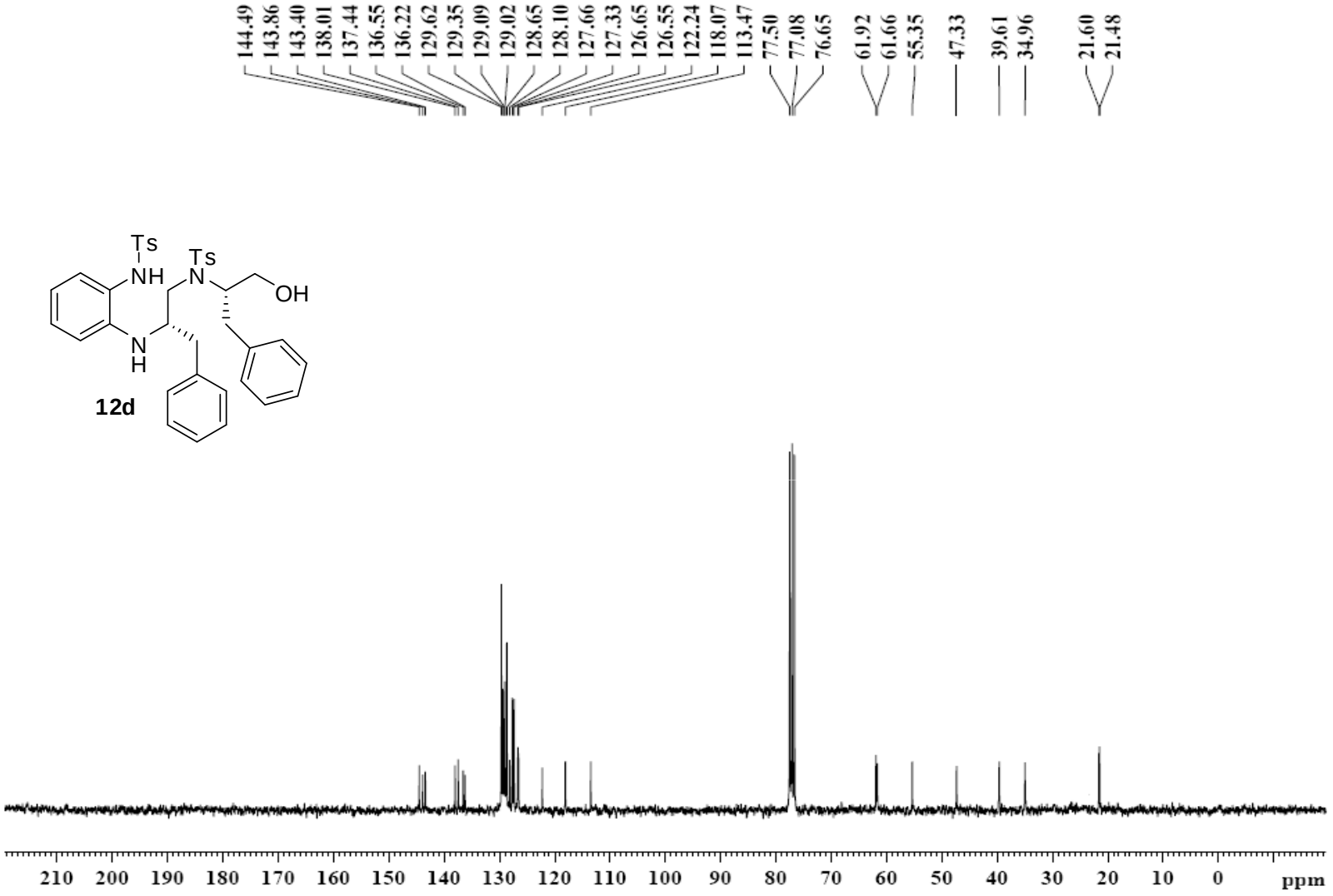
FigureS-101: ^{13}C spectrum (75 MHz, $CDCl_3$) of **12b**.



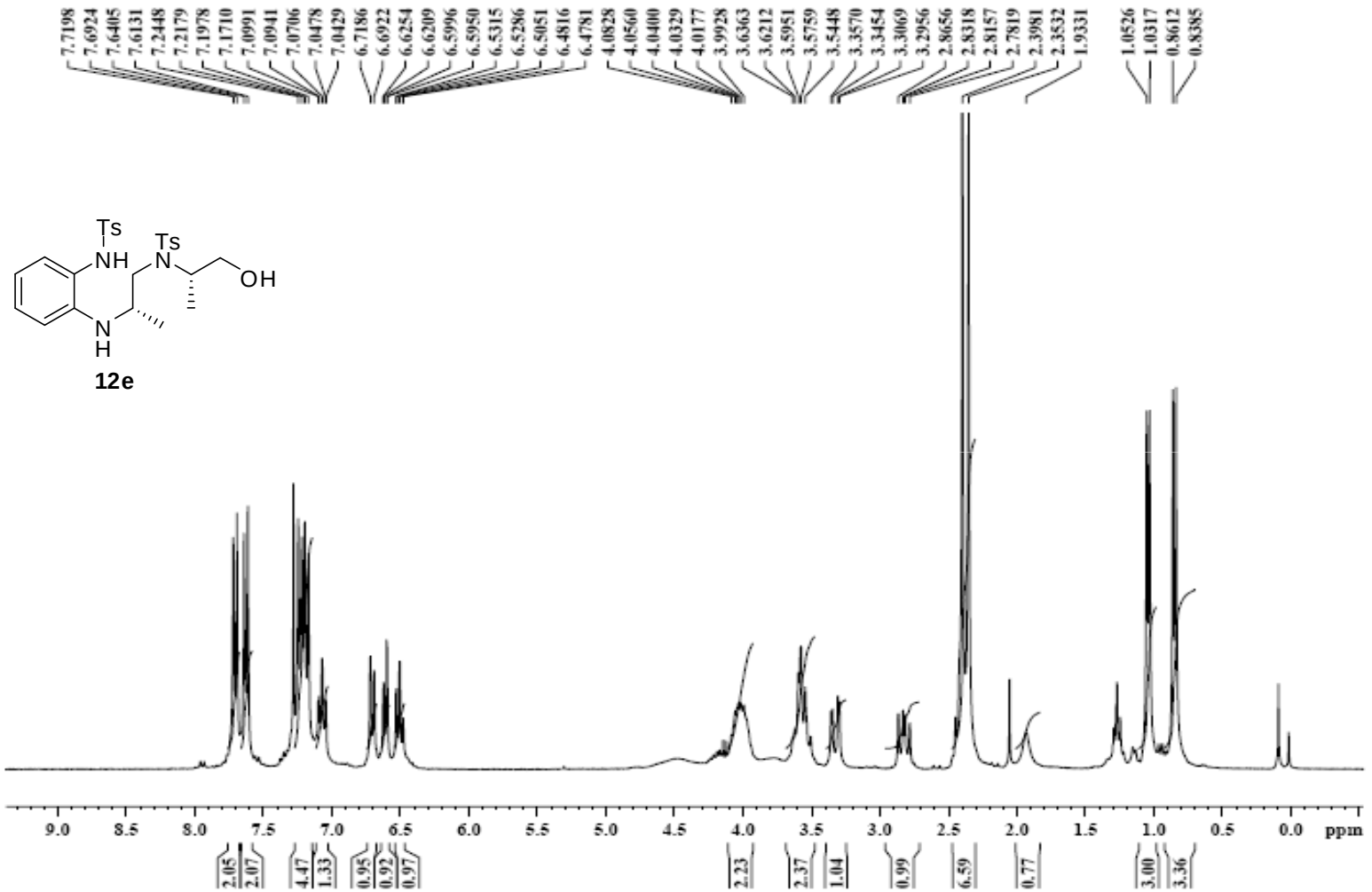
FigureS-102: ^{1}H spectrum (300MHz, $CDCl_3$) of **12c**.



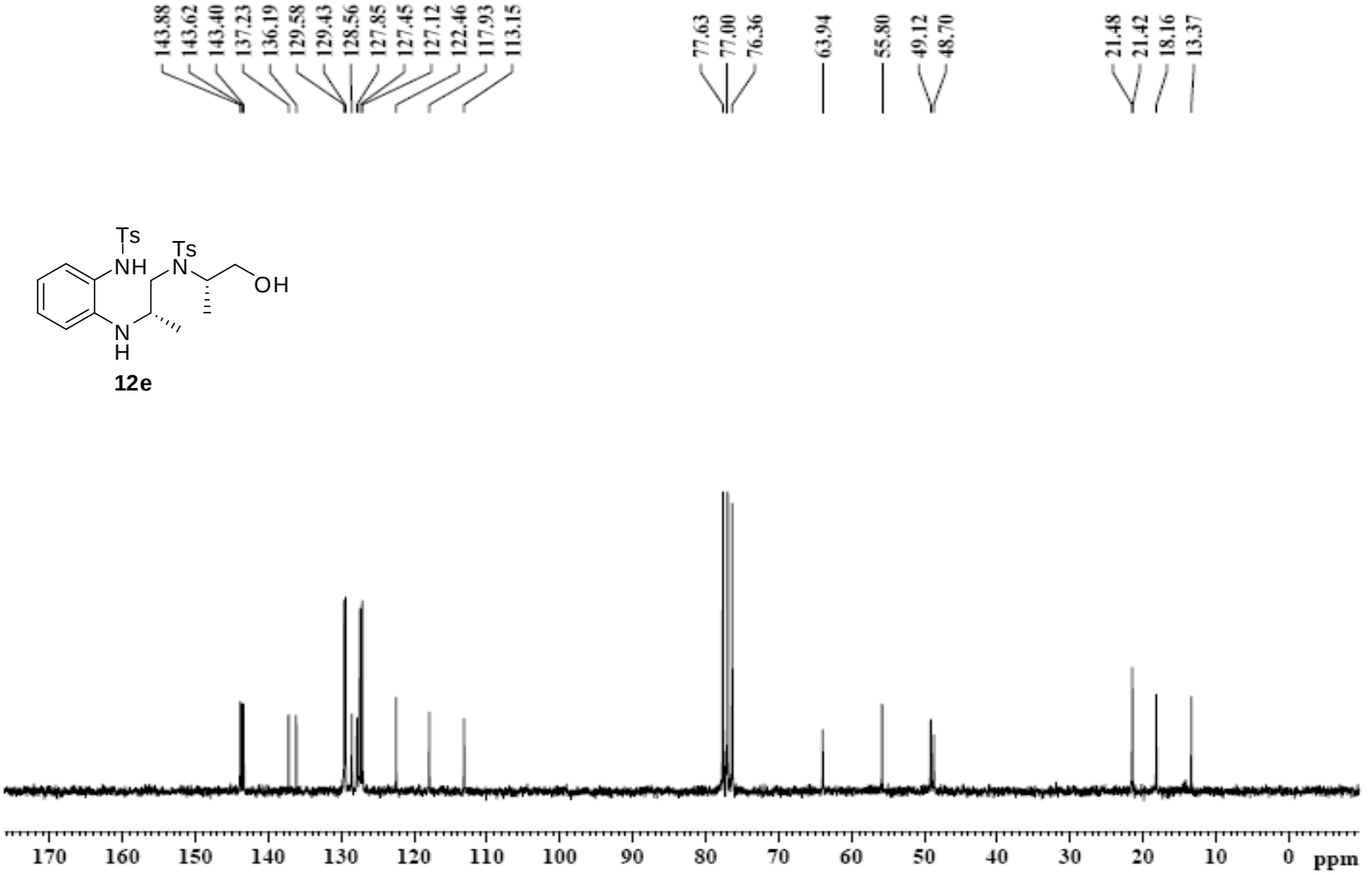
FigureS-103: ^{1}H spectrum (300MHz, $CDCl_3$) of **12d**.



FigureS-104: ^{13}C spectrum (75 MHz, $CDCl_3$) of **12d**.

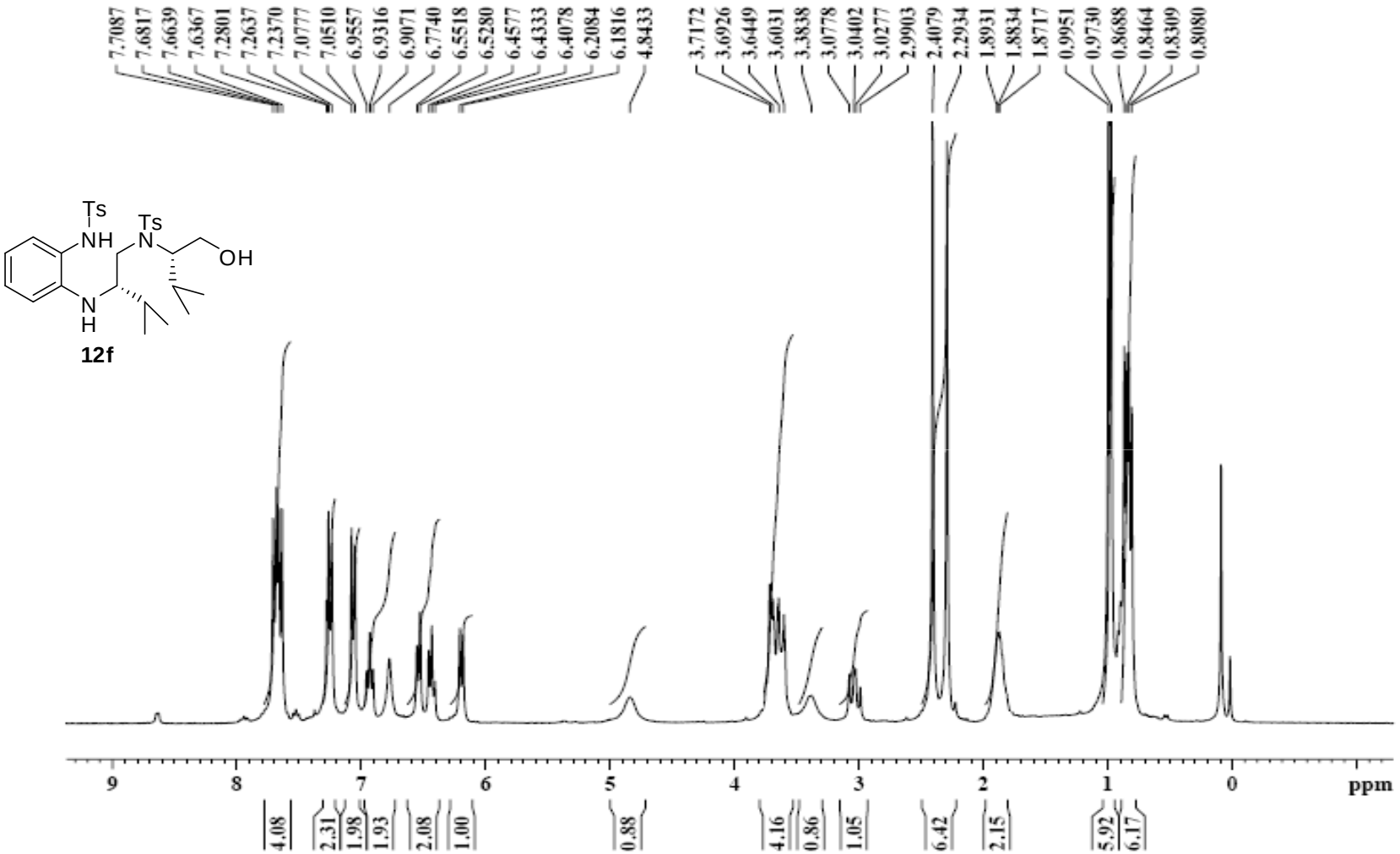


FigureS-105: ^{1}H spectrum (300MHz, $CDCl_3$) of **12e**.

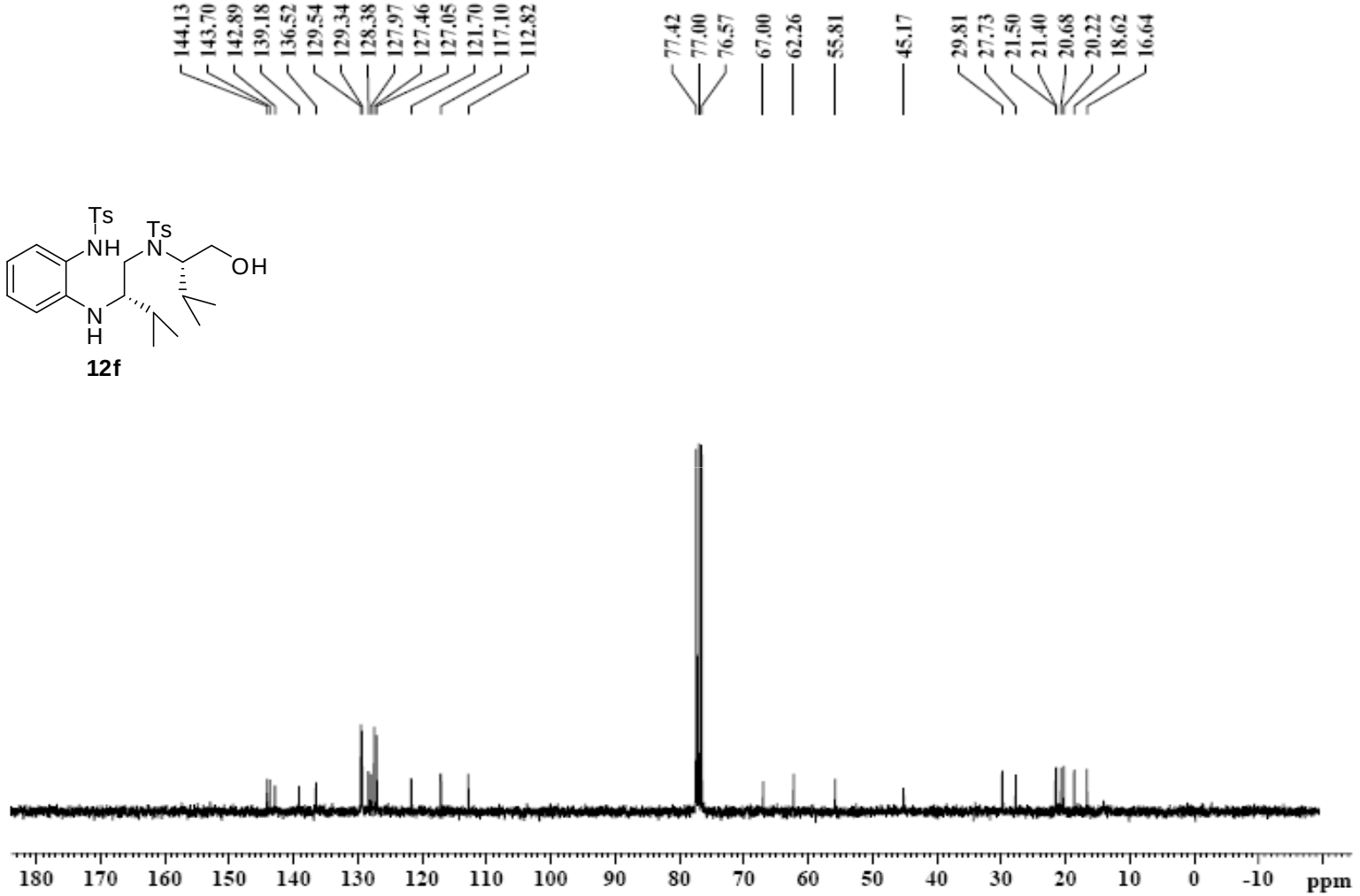


12e

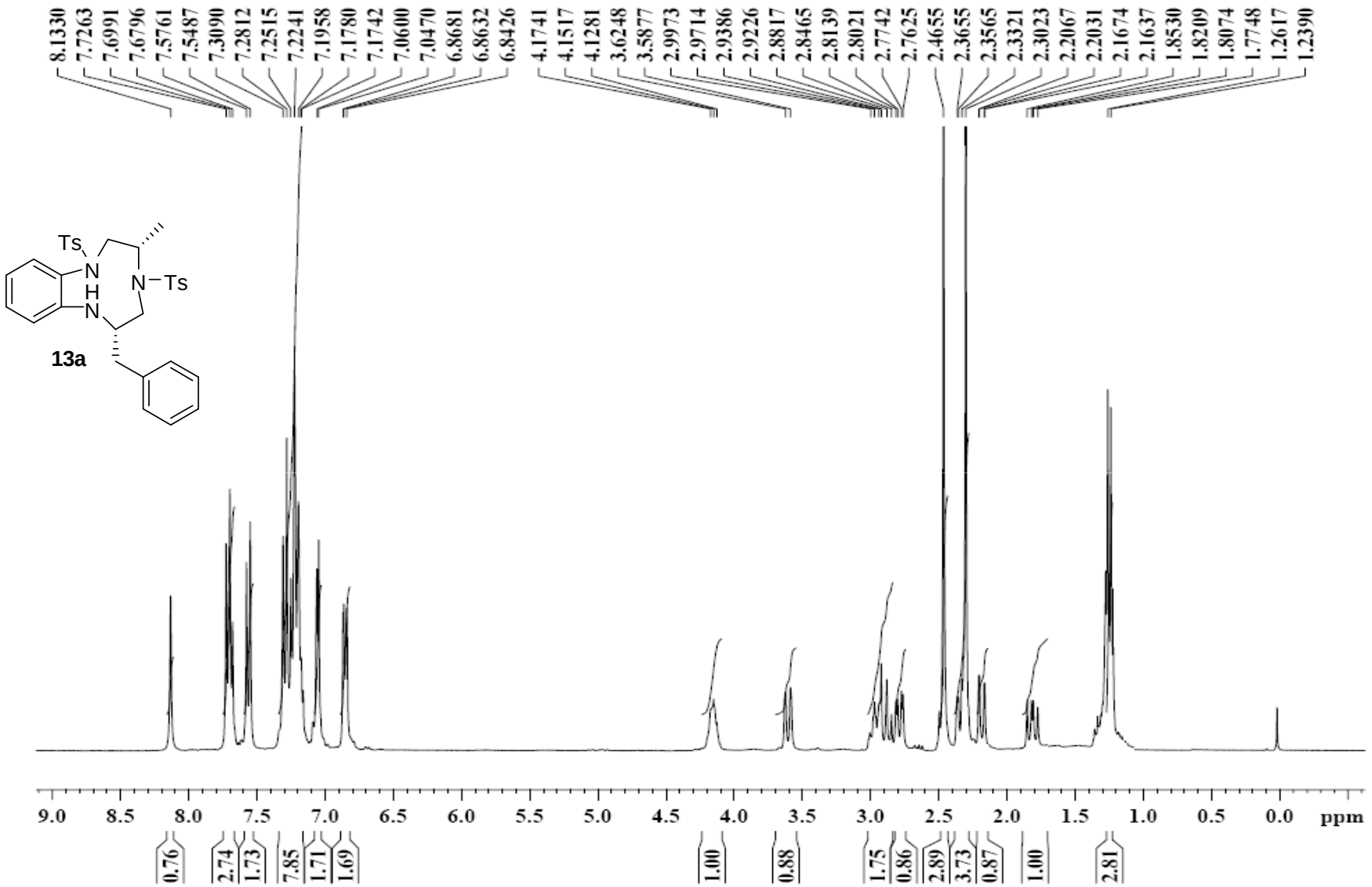
FigureS-106: ^{13}C spectrum (75 MHz, $CDCl_3$) of **12e**.



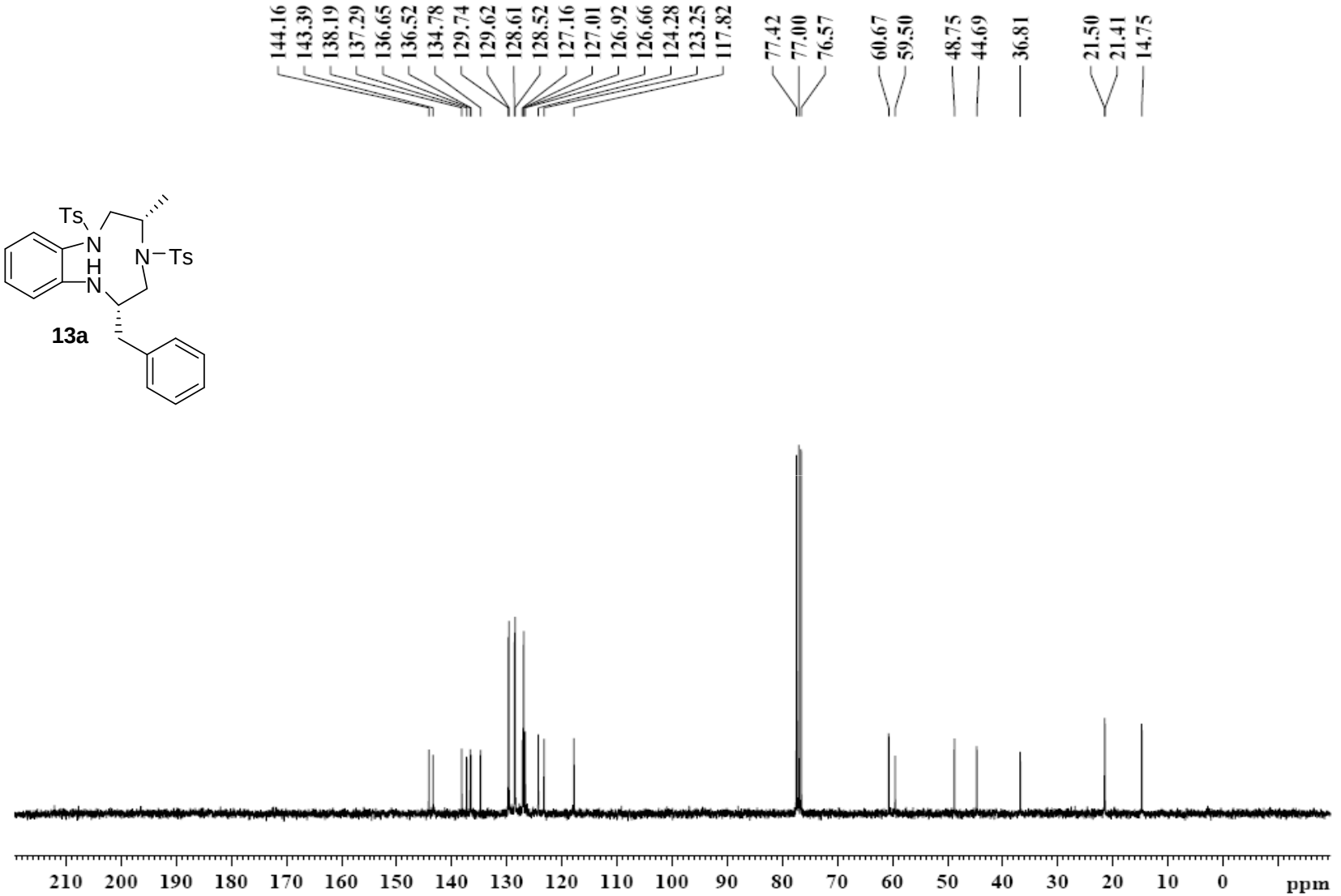
FigureS-107: ^{1}H spectrum (300MHz, $CDCl_3$) of **12f**.



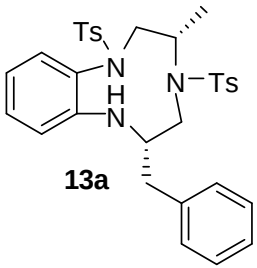
FigureS-108: ^{13}C spectrum (75 MHz, $CDCl_3$) of **12f**.



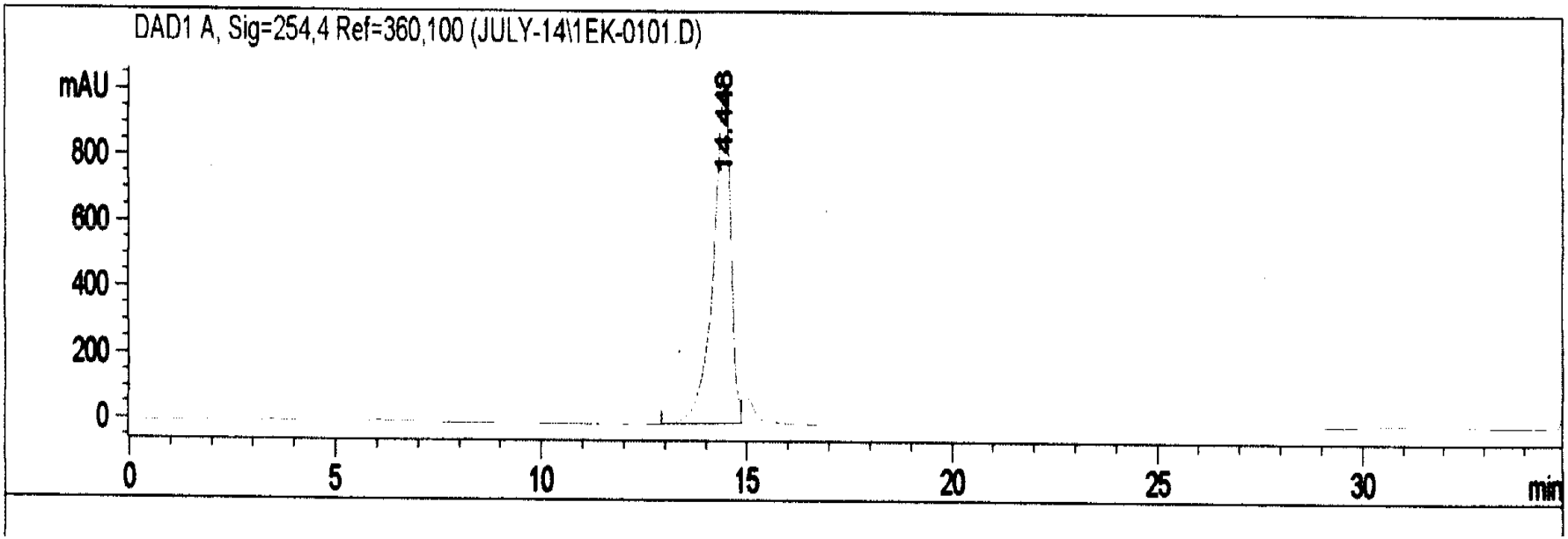
FigureS-109: ^{1}H spectrum (300MHz, $CDCl_3$) of **13a**.



FigureS-110:^{13}C spectrum (75MHz, $CDCl_3$) of **13a**.

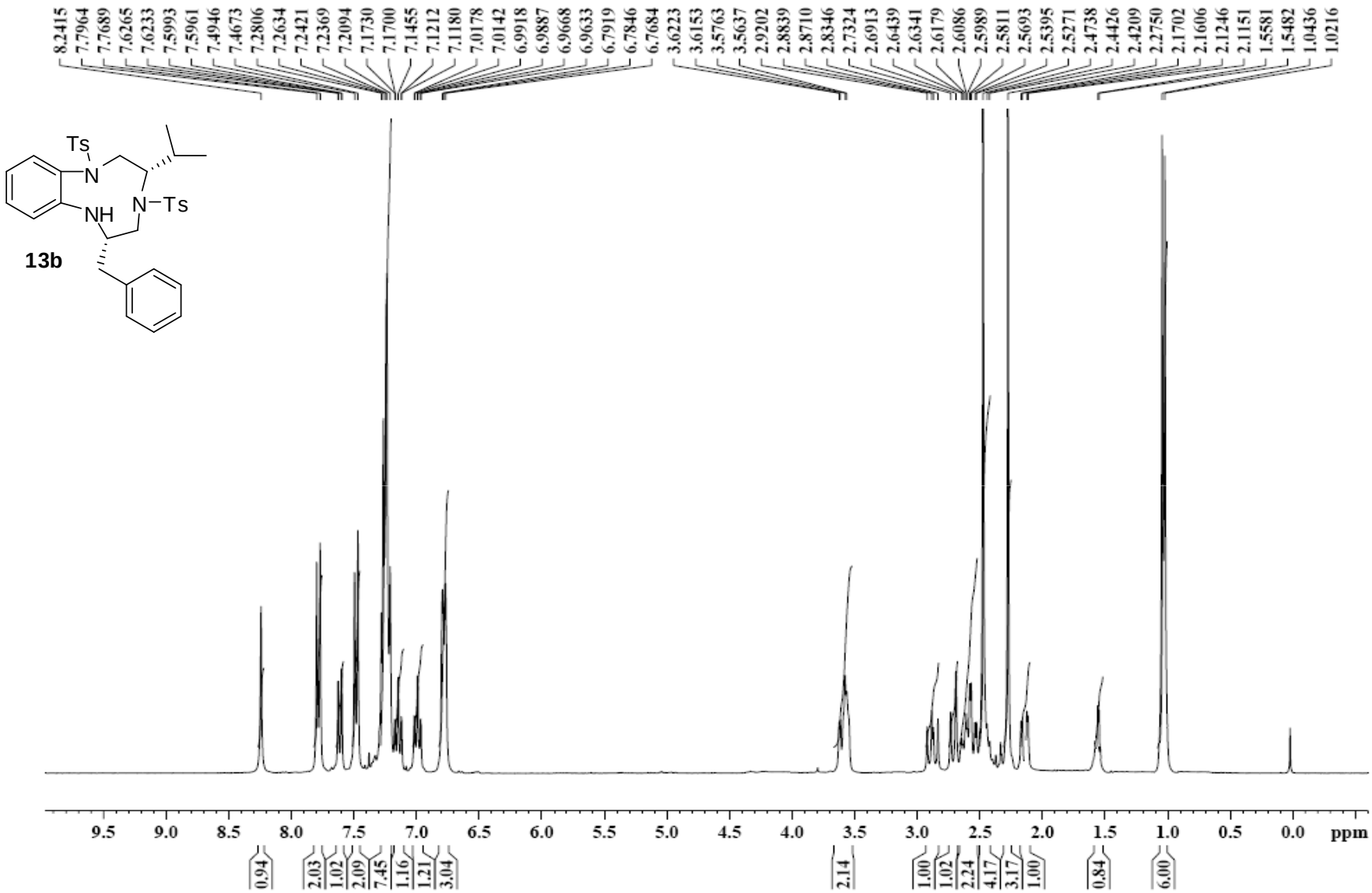


13a



Retention time (min)

FigureS-111: HPLC graph for **13a**



FigureS-112: ^{1}H spectrum (300MHz, $CDCl_3$) of **13b**.

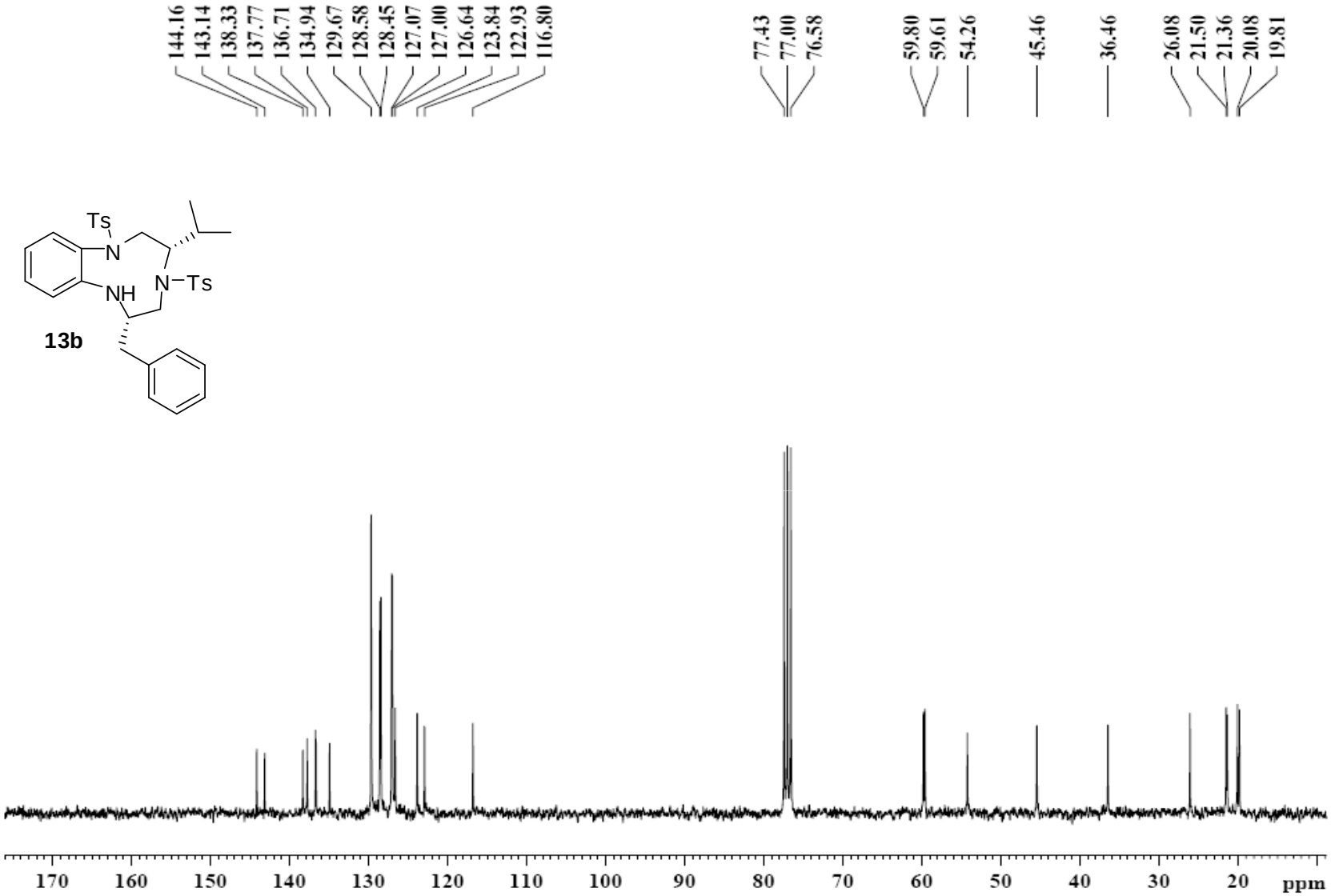
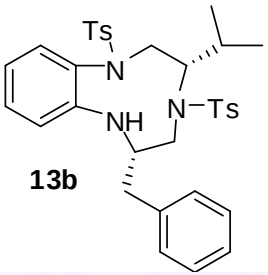
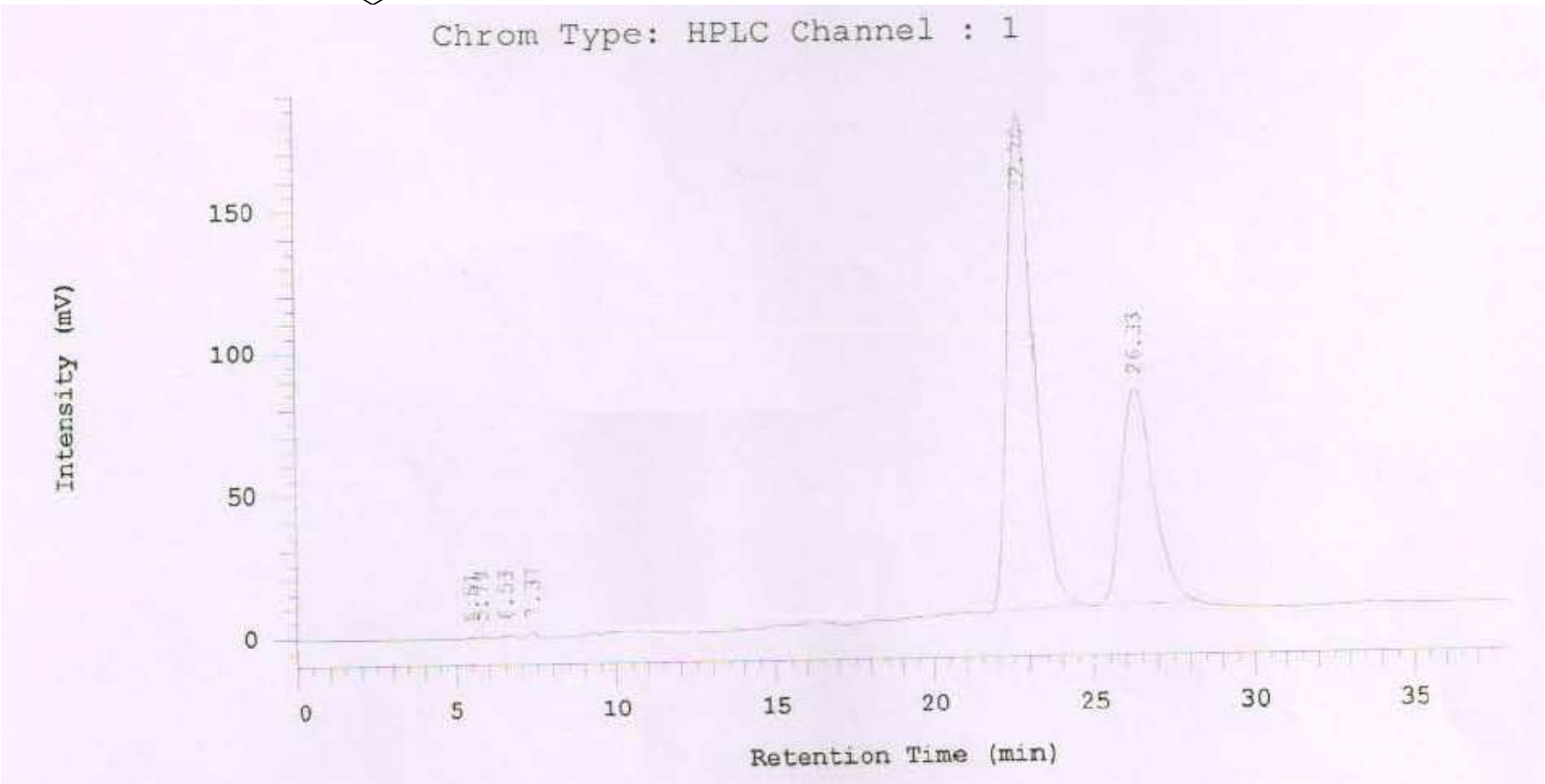


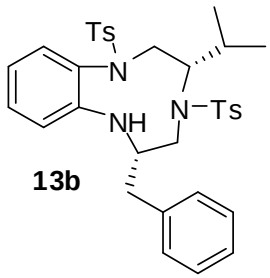
Figure S-113: ^{13}C spectrum (75MHz, $CDCl_3$) of **13b**.



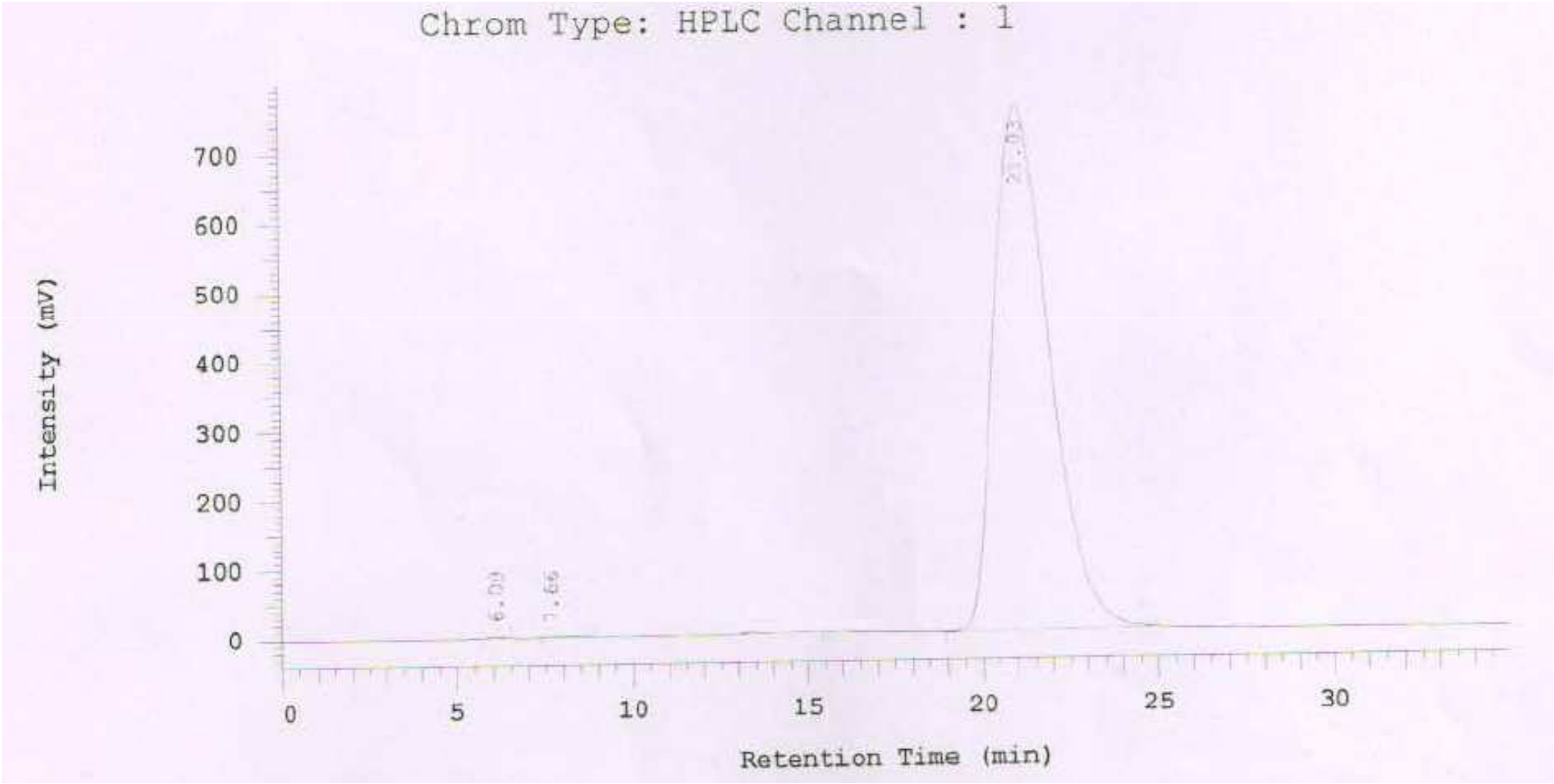
13b



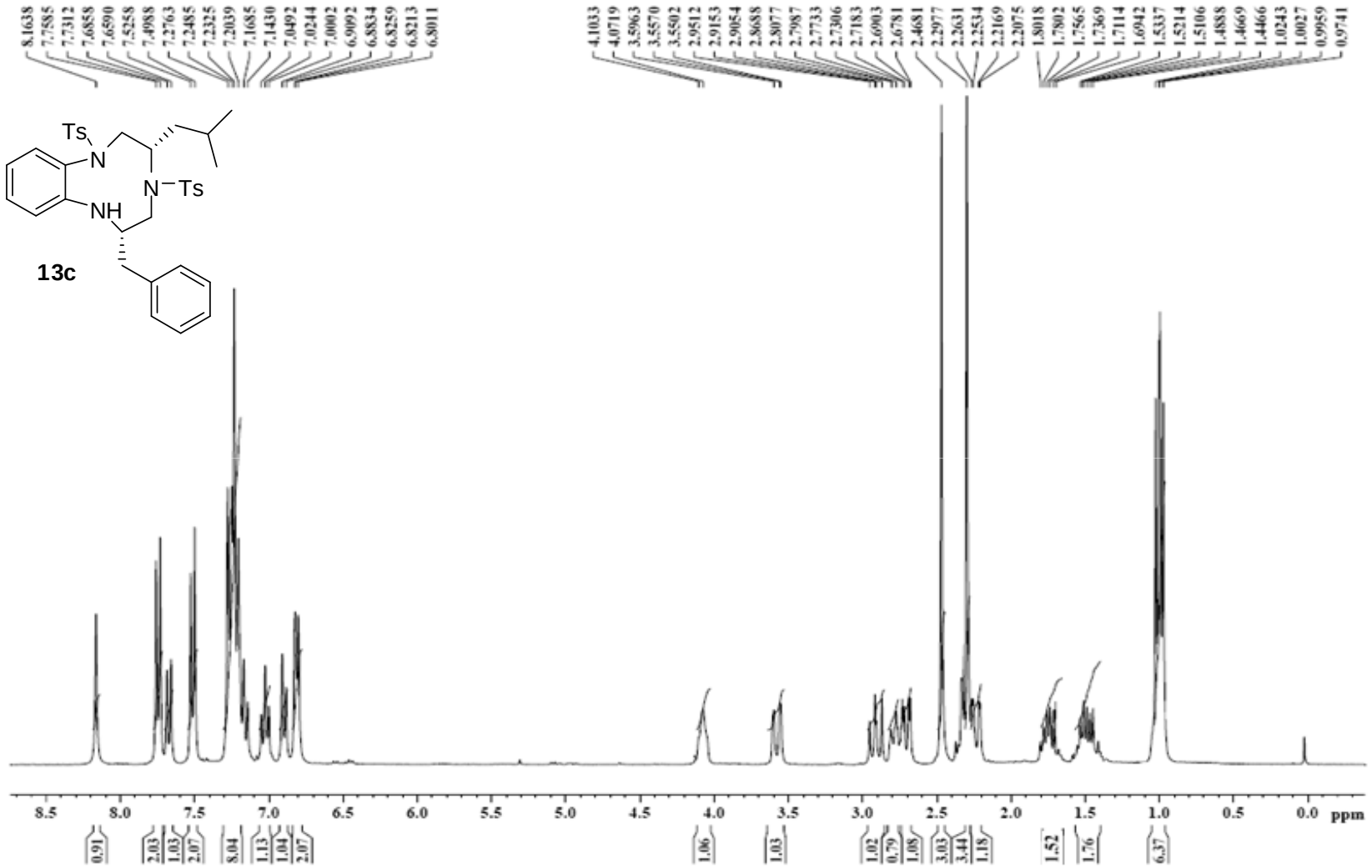
FigureS-114: HPLC graph for mixture of **13b** and its enantiomer**.**



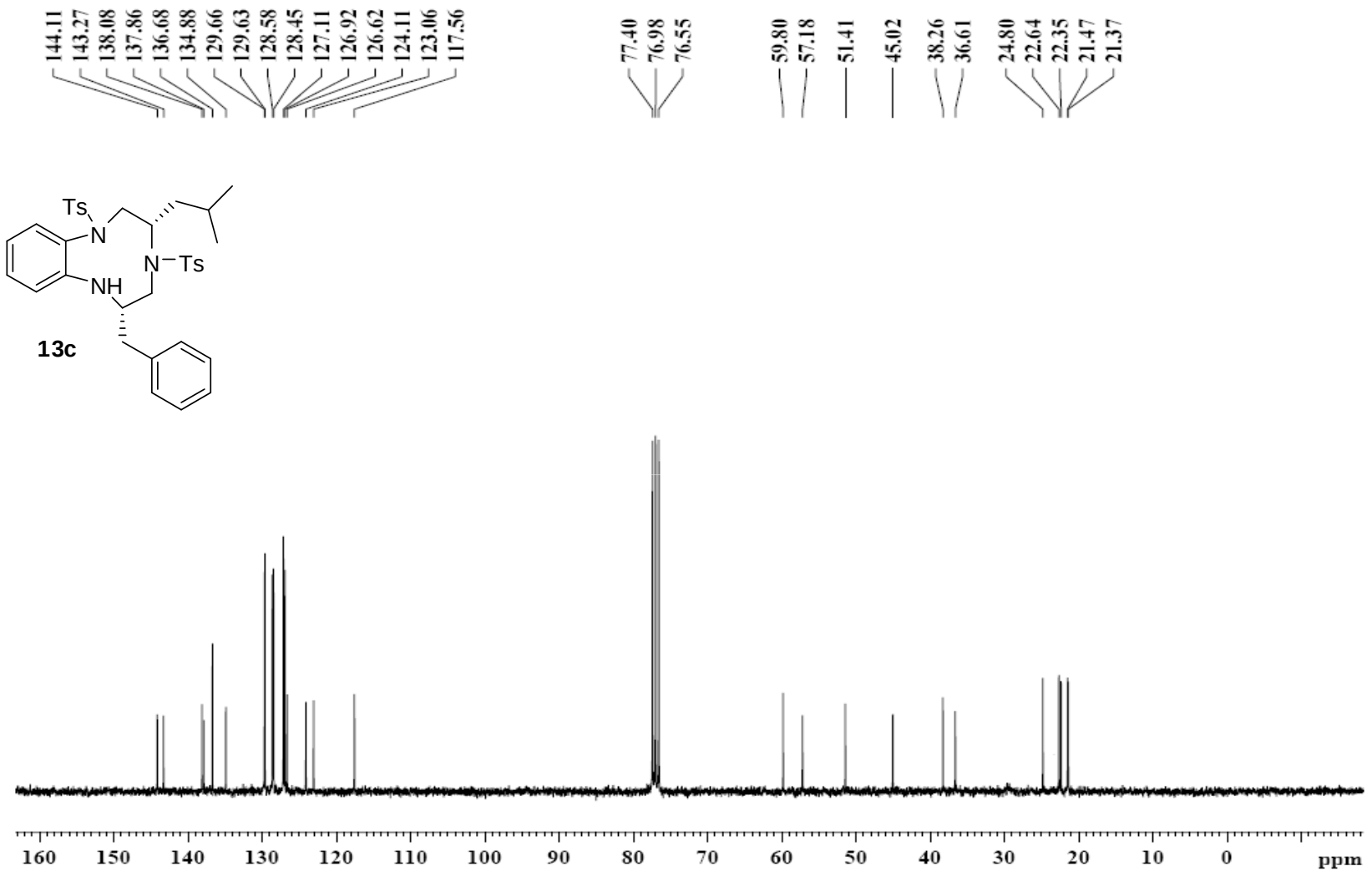
13b



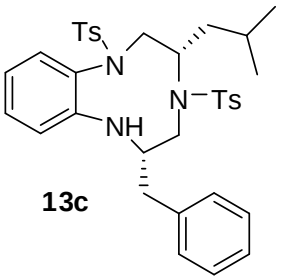
FigureS-115: HPLC graph for enantiomerically pure **13b.**



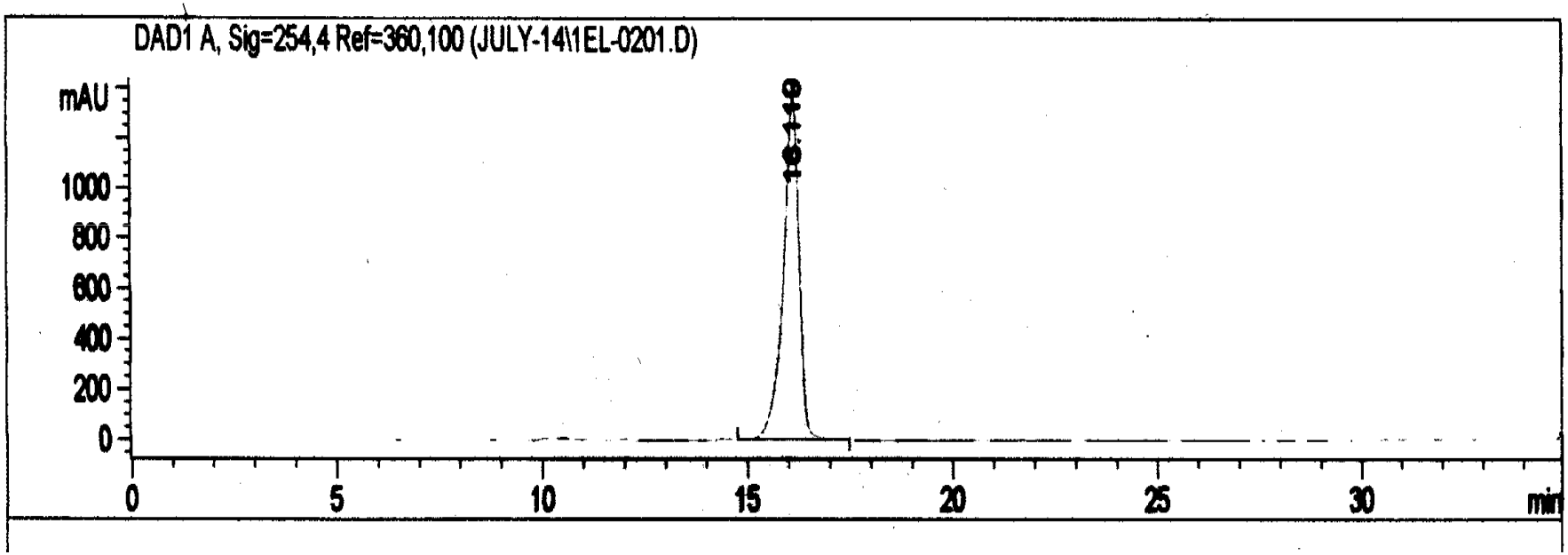
FigureS-116: ^{1}H spectrum (300MHz, $CDCl_3$) of **13c**.



FigureS-117: ^{13}C spectrum (75MHz, $CDCl_3$) of **13c**.

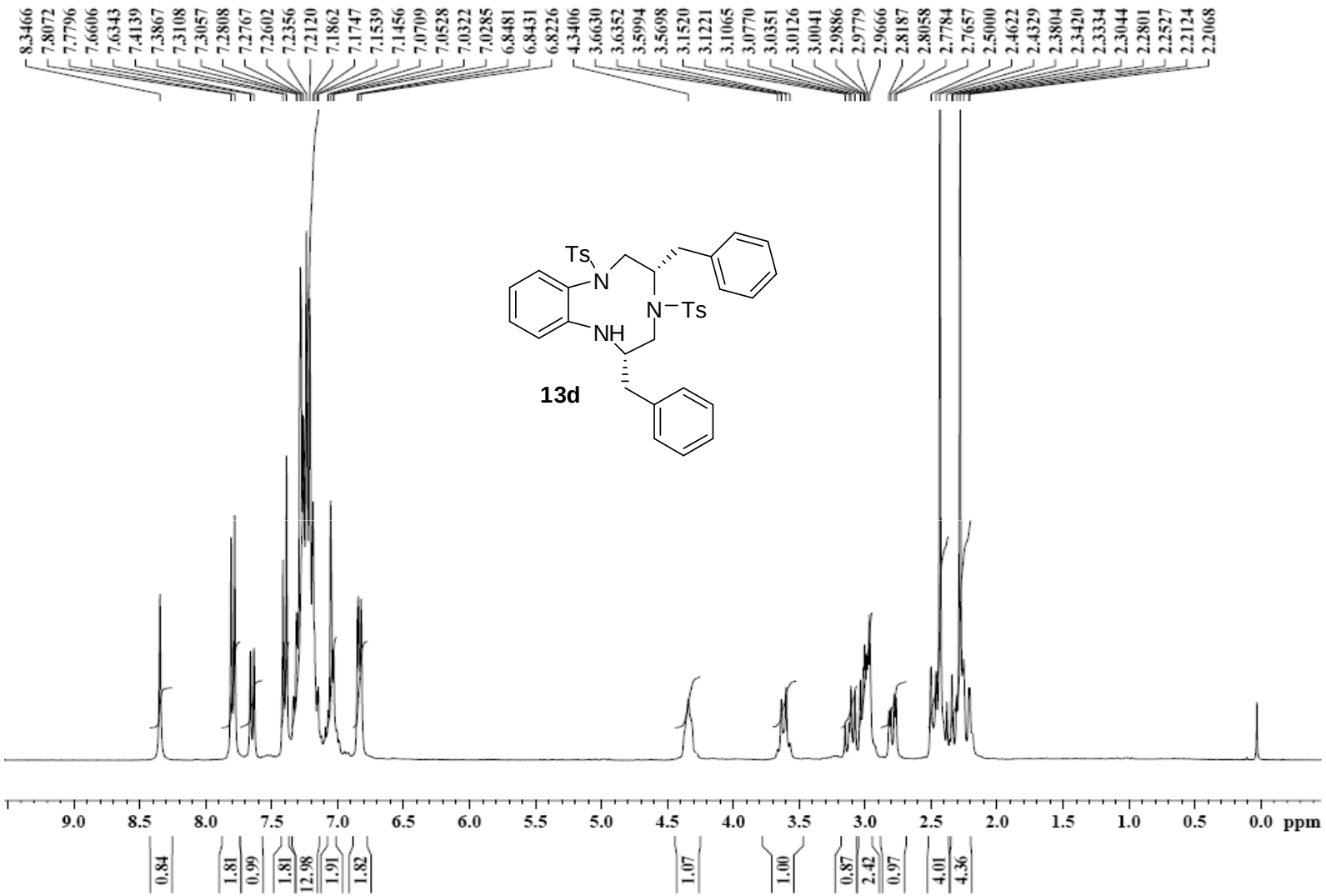


13c

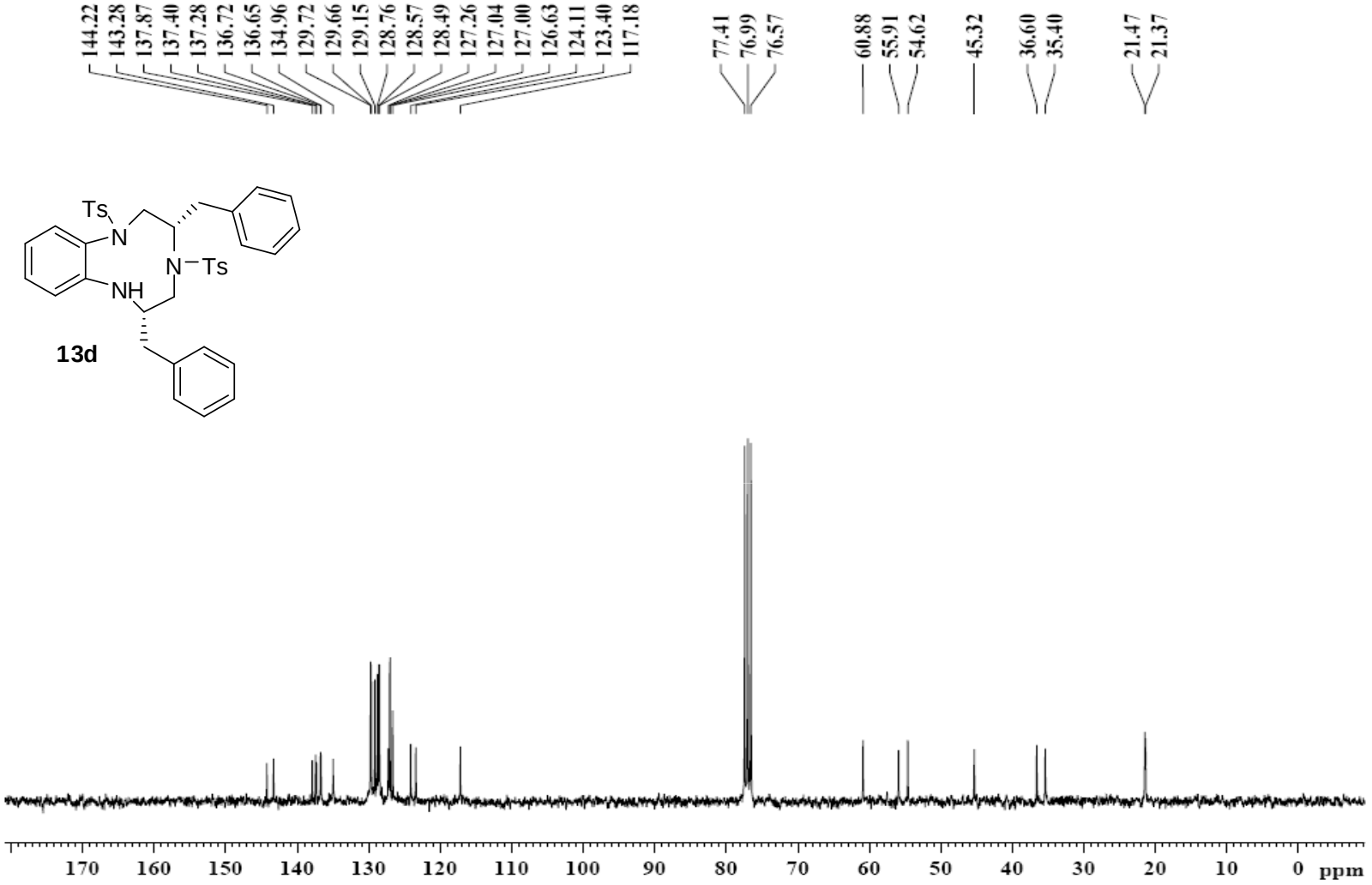


Retention time (min)

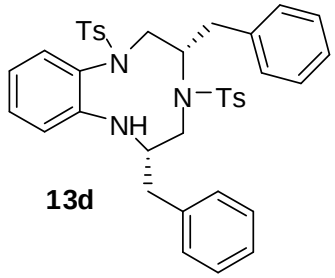
FigureS-118: HPLC graph for **13c**



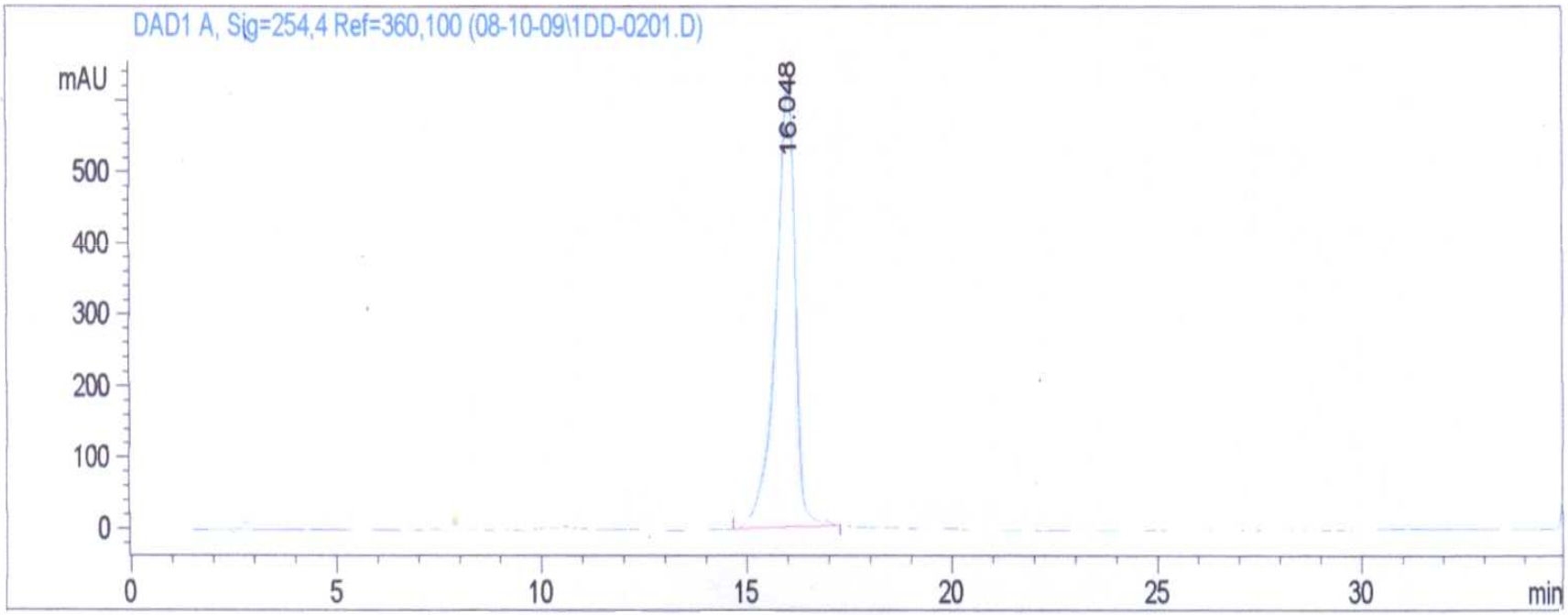
FigureS-119: ^{1}H spectrum (300MHz, $CDCl_3$) of **13d**.



FigureS-120: ^{13}C spectrum (75MHz, $CDCl_3$) of **13d**.

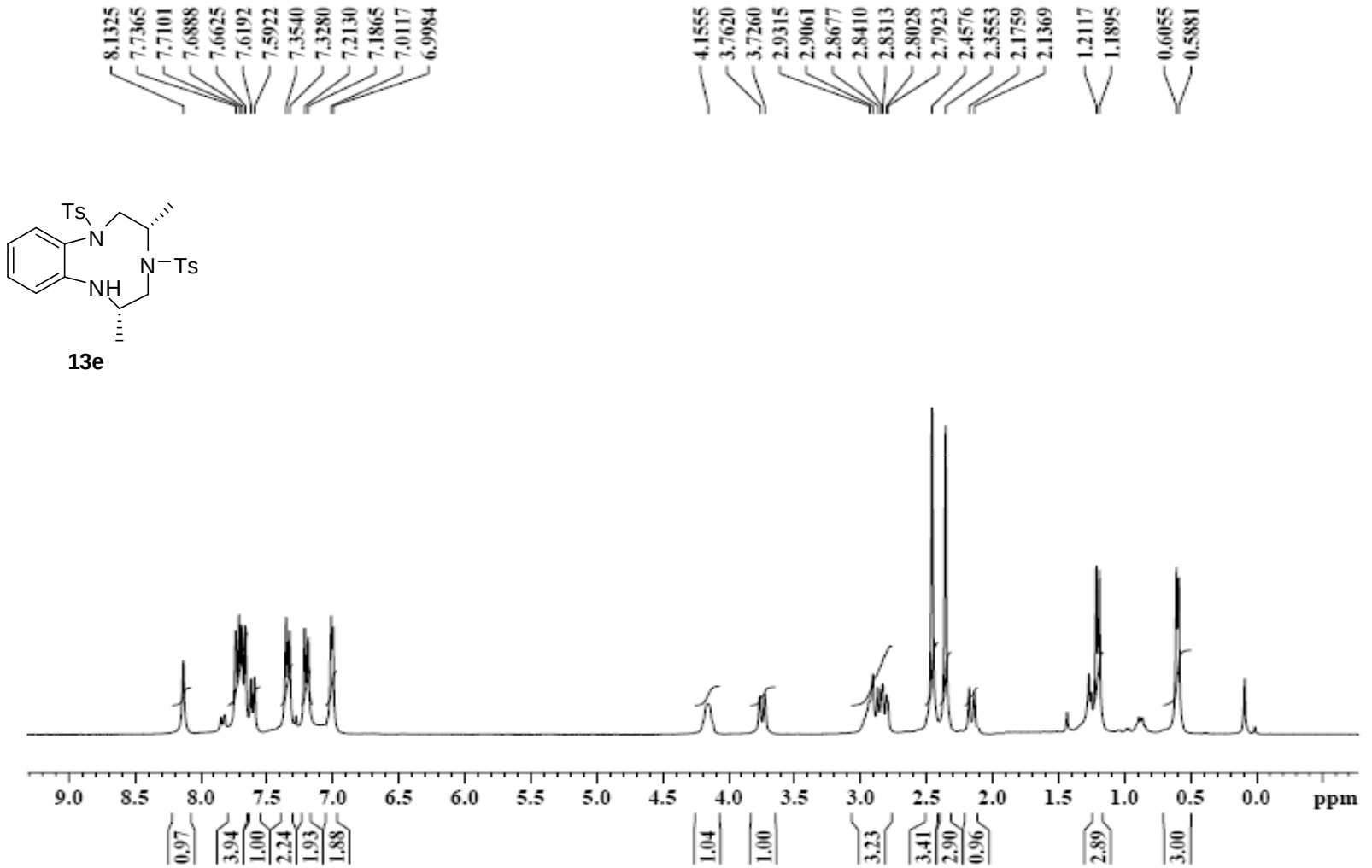


13d

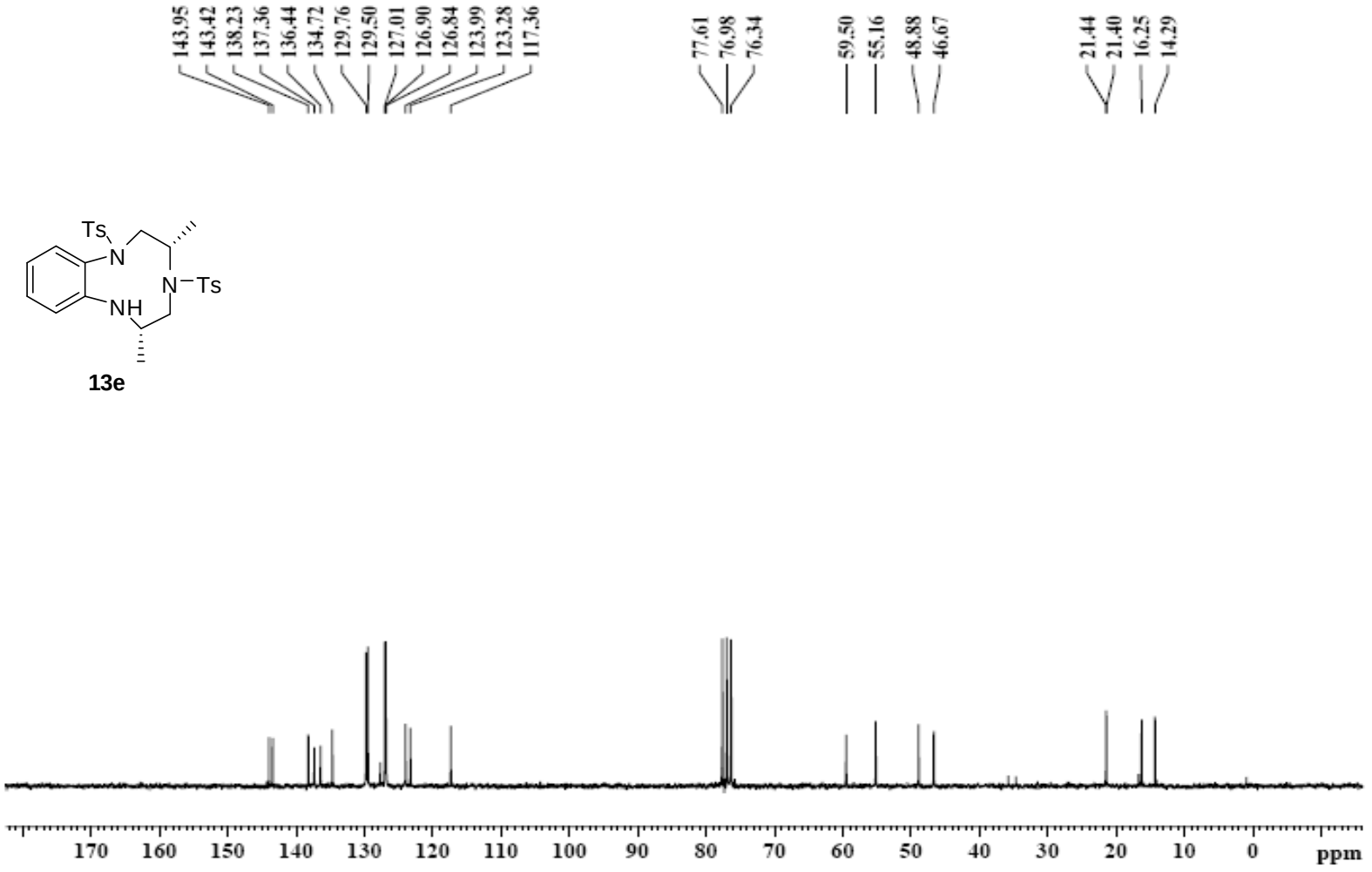


Retention time (min)

FigureS-121: HPLC graph for **13d.**

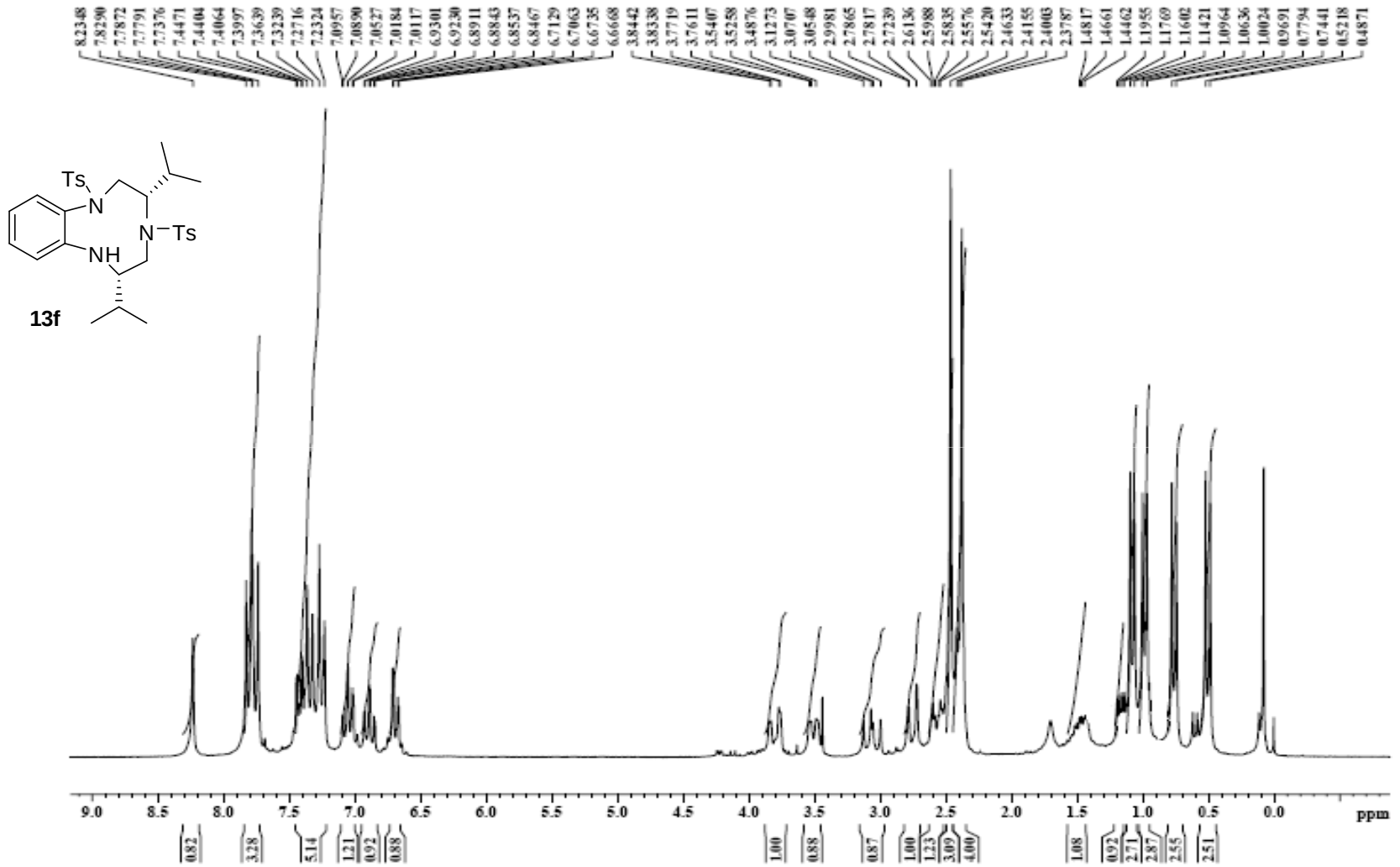


FigureS-122: ^{1}H spectrum (300MHz, $CDCl_3$) of **13e**.

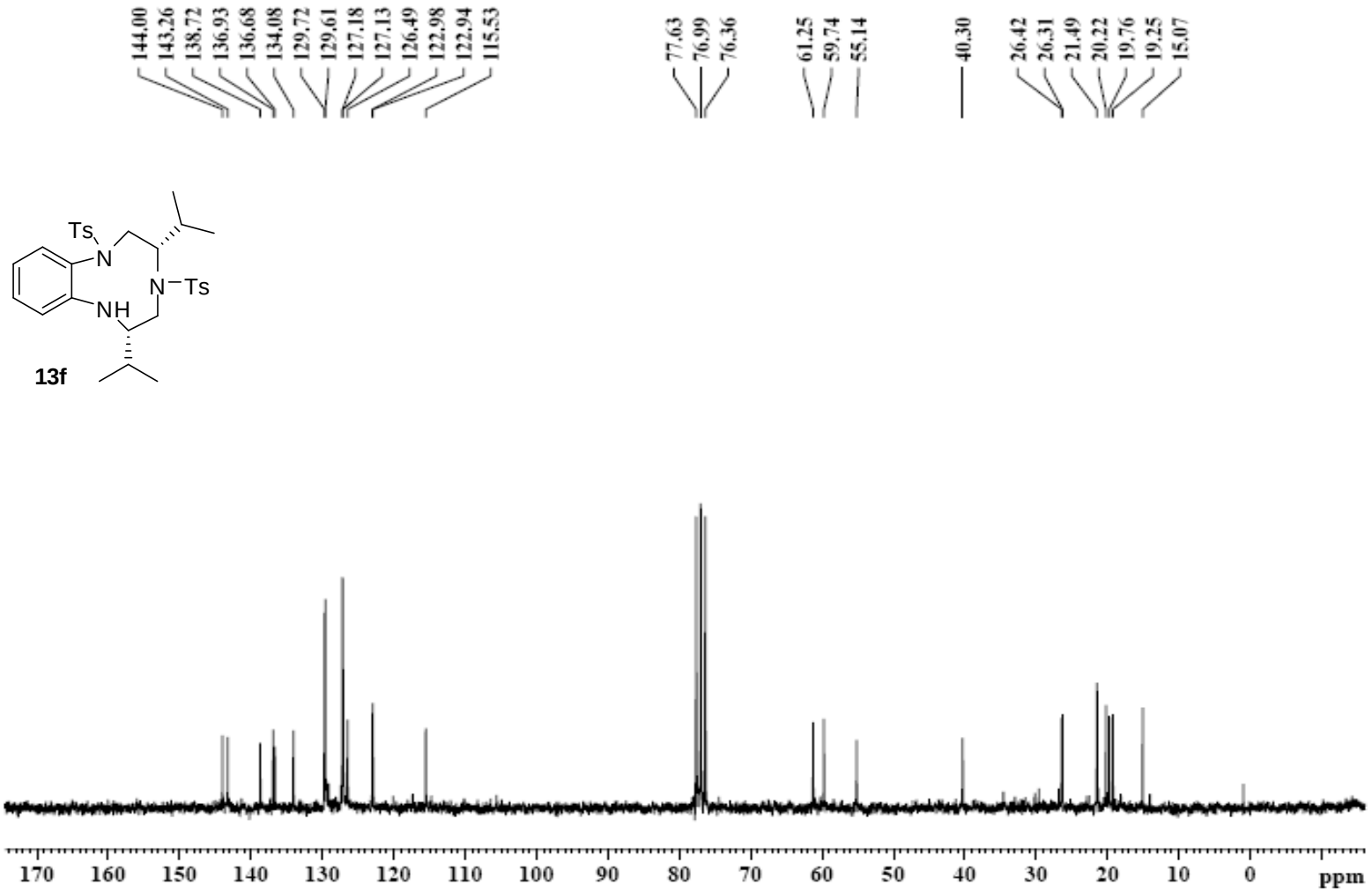


13e

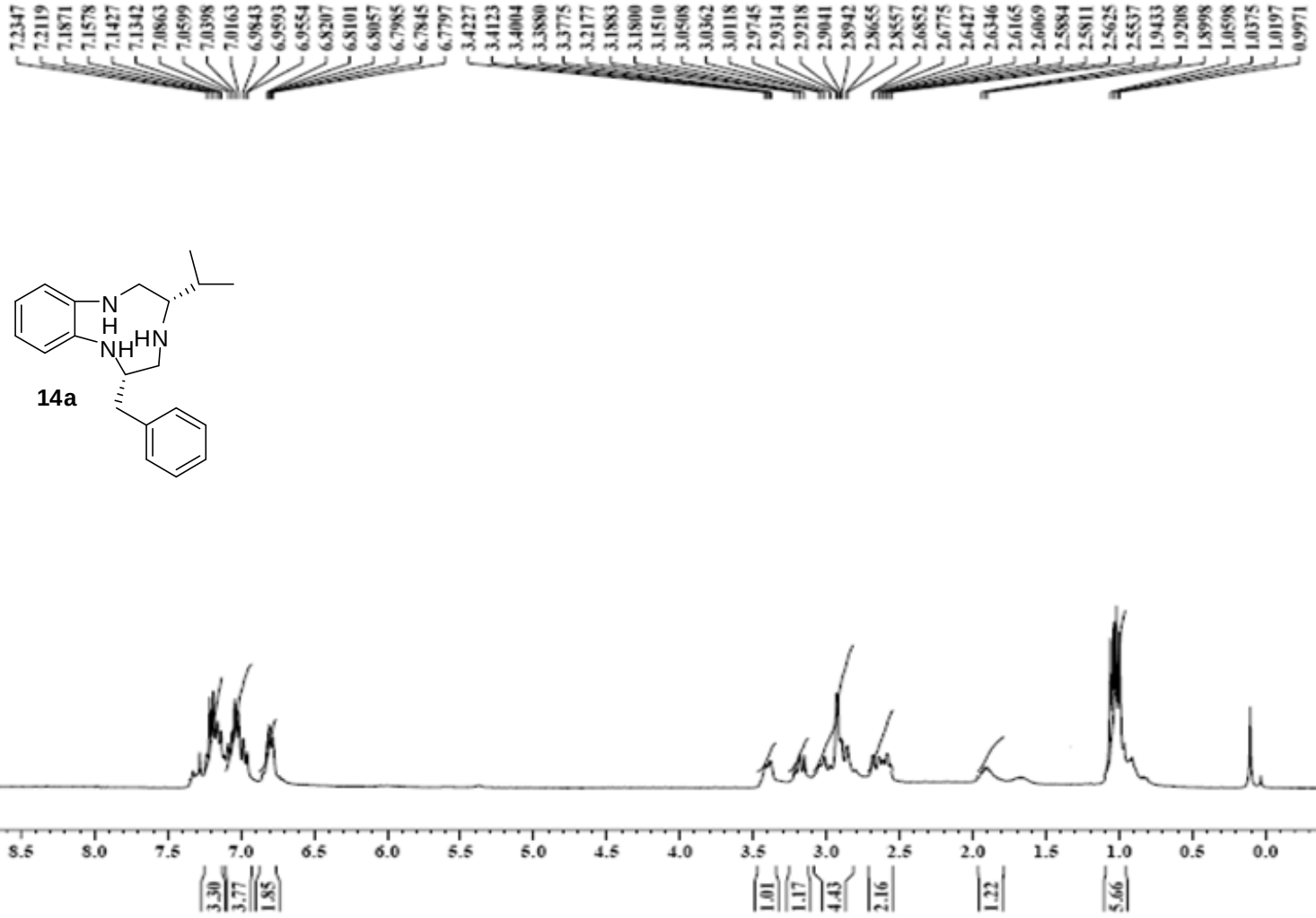
FigureS-123: ^{13}C spectrum (50MHz, $CDCl_3$) of **13e.**



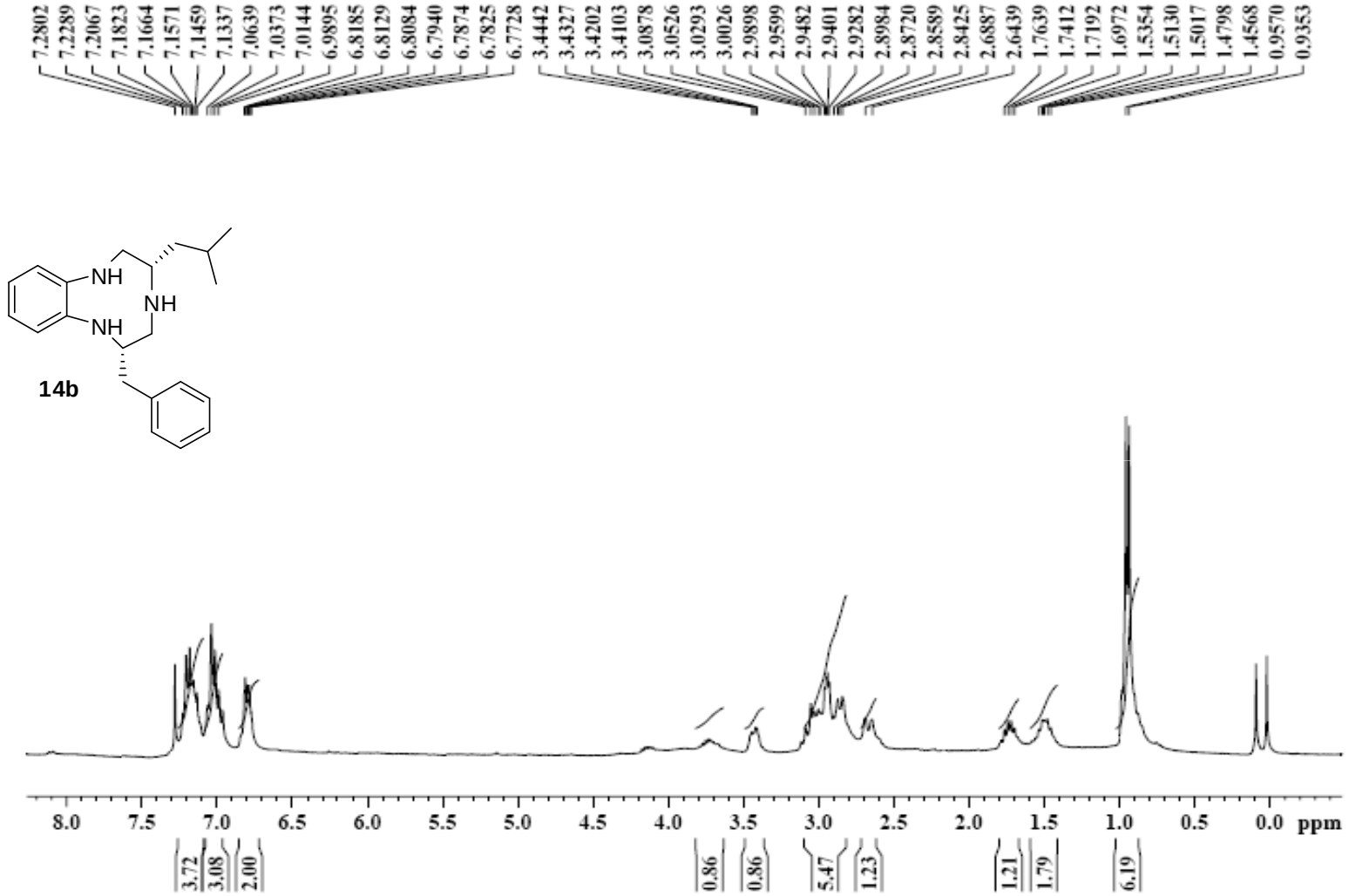
FigureS-124: ^{1}H spectrum (200MHz, $CDCl_3$) of **13f**



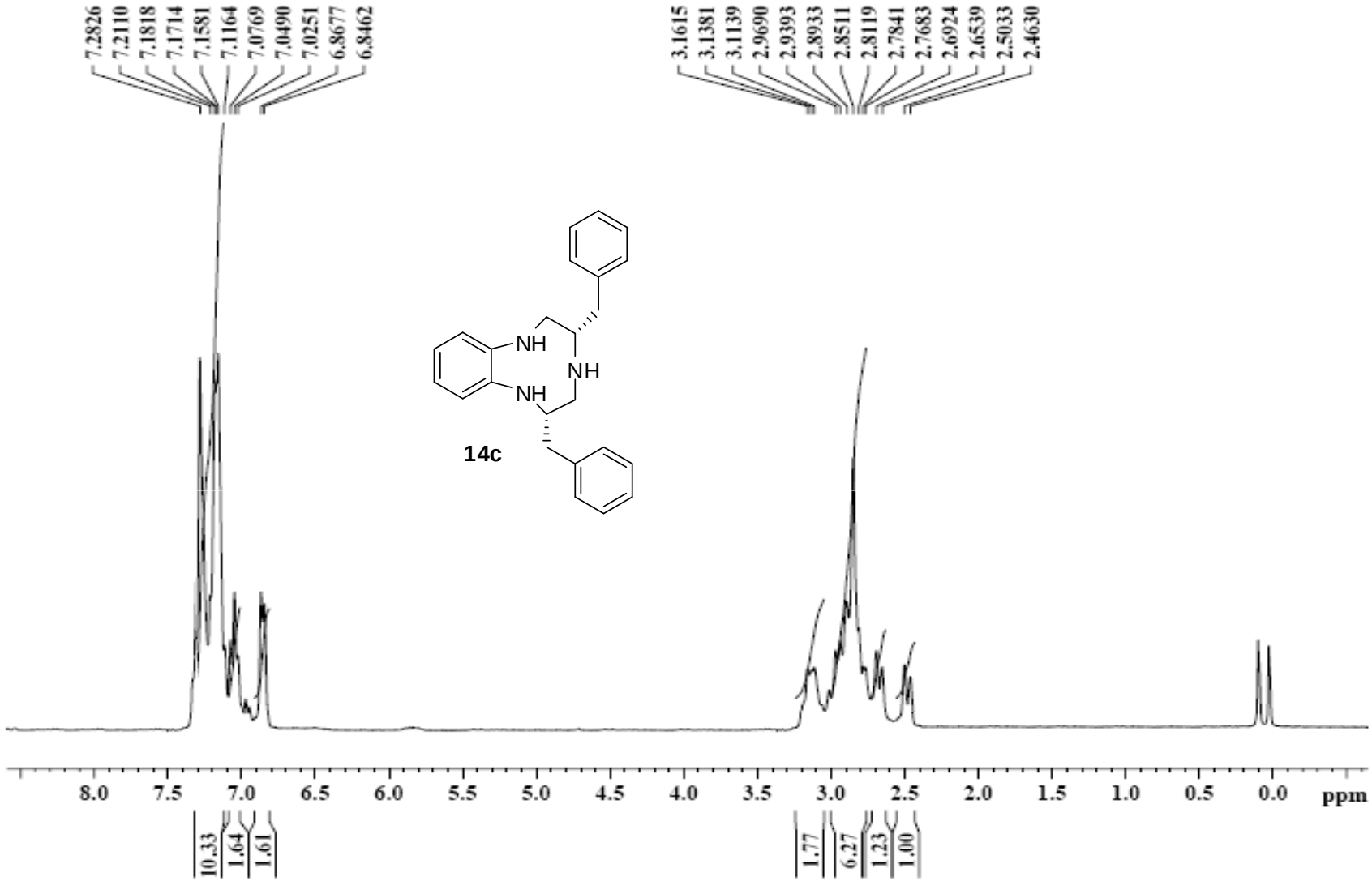
FigureS-125: ^{13}C spectrum (50MHz, $CDCl_3$) of **13e.**



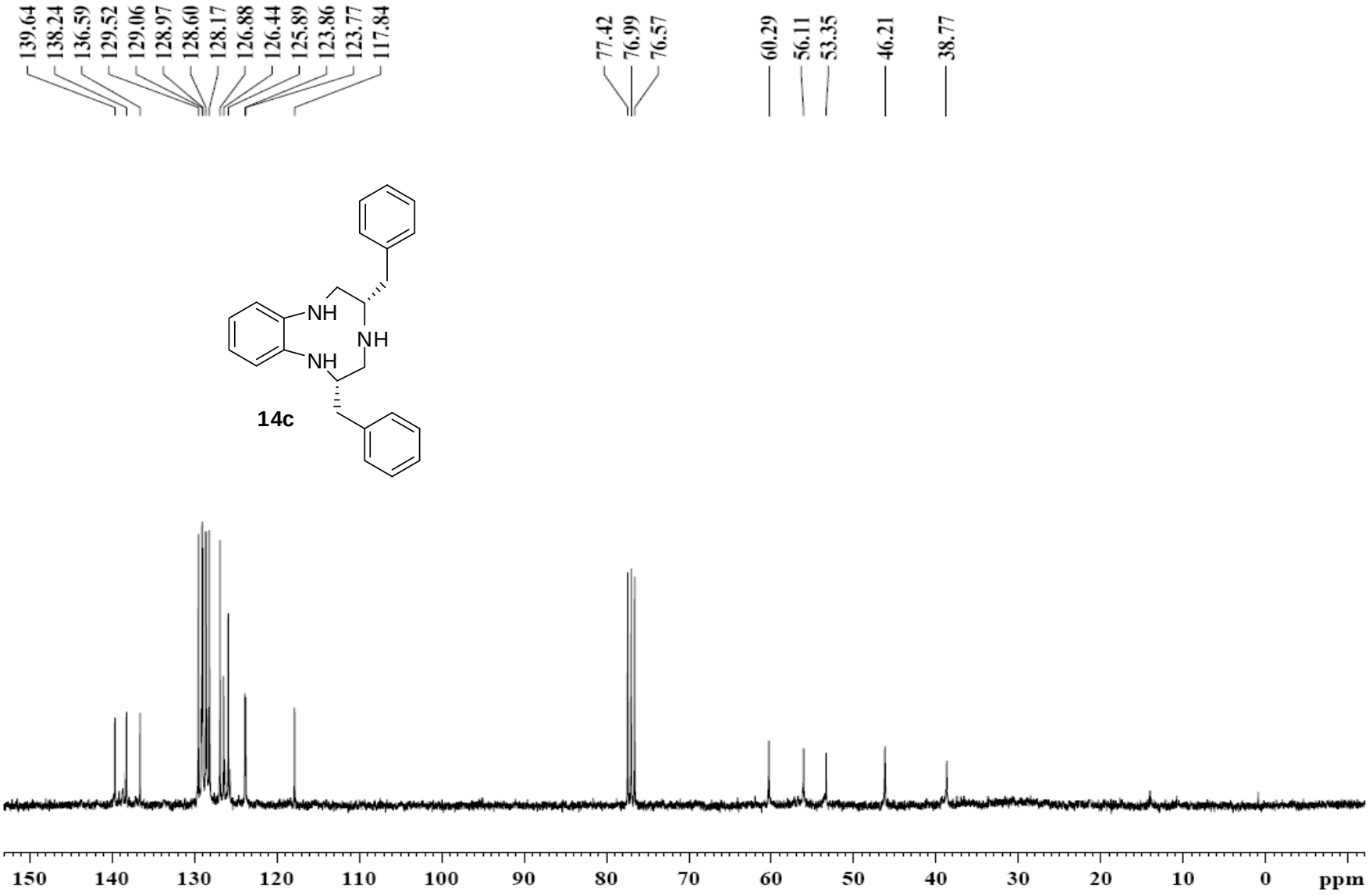
FigureS-126: ^{1}H spectrum (300MHz, $CDCl_3$) of **14a.**



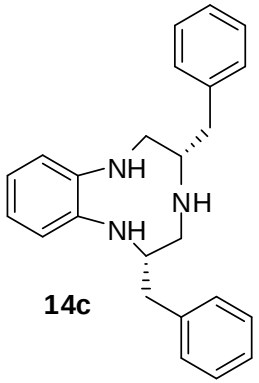
FigureS-127: ^{1}H spectrum (300MHz, $CDCl_3$) of **14b.**



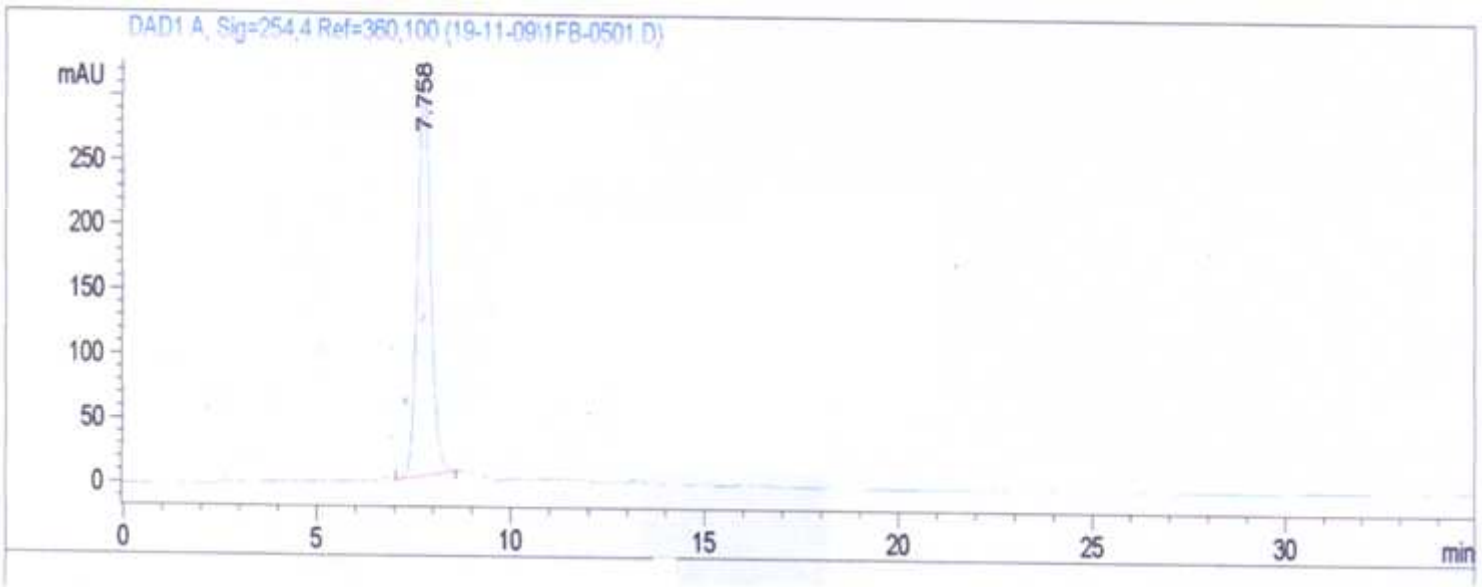
FigureS-128: ^{1}H spectrum (300MHz, $CDCl_3$) of **14c**.



FigureS-129: ^{13}C spectrum (75MHz, $CDCl_3$) of **14c**.

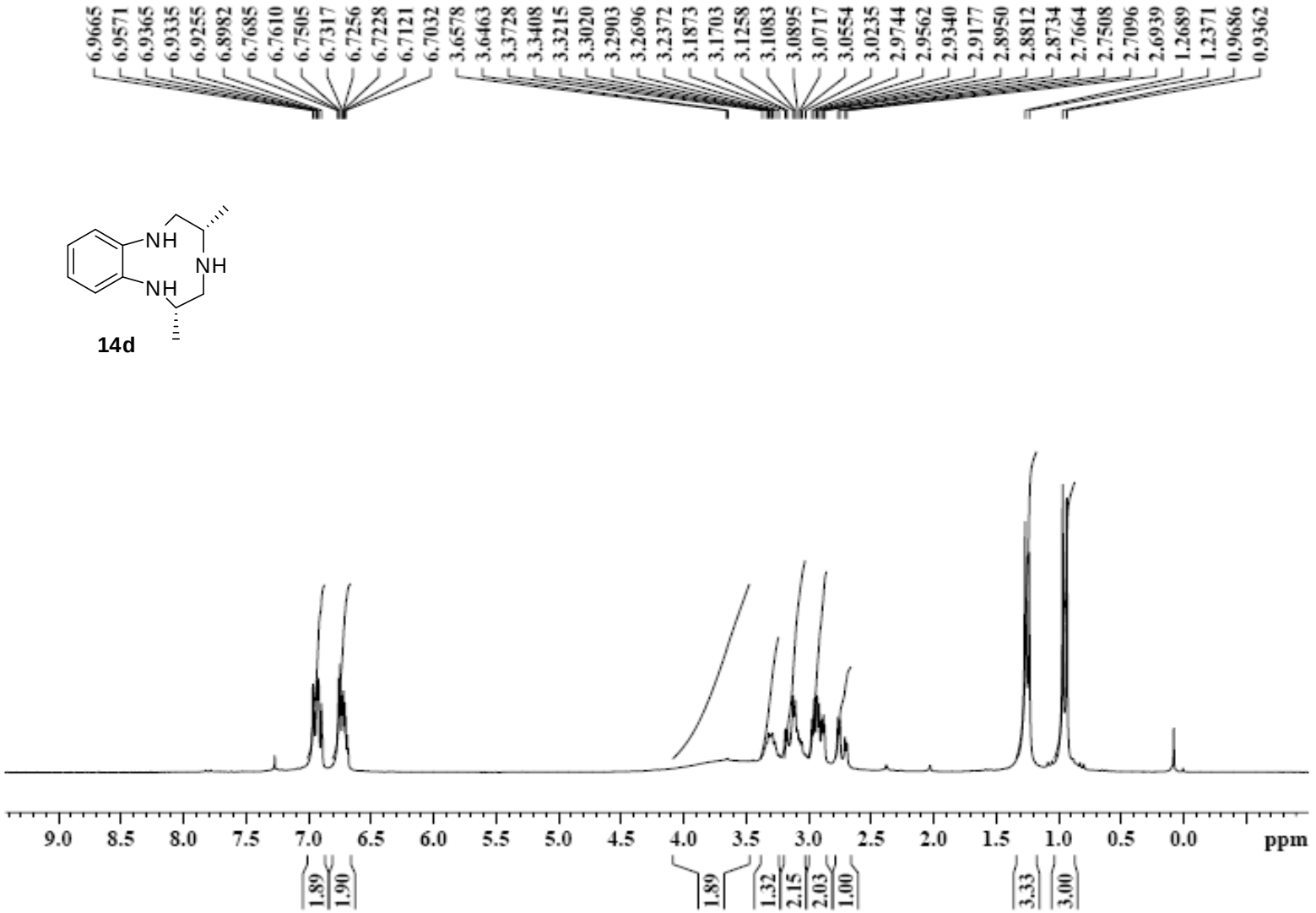


14c

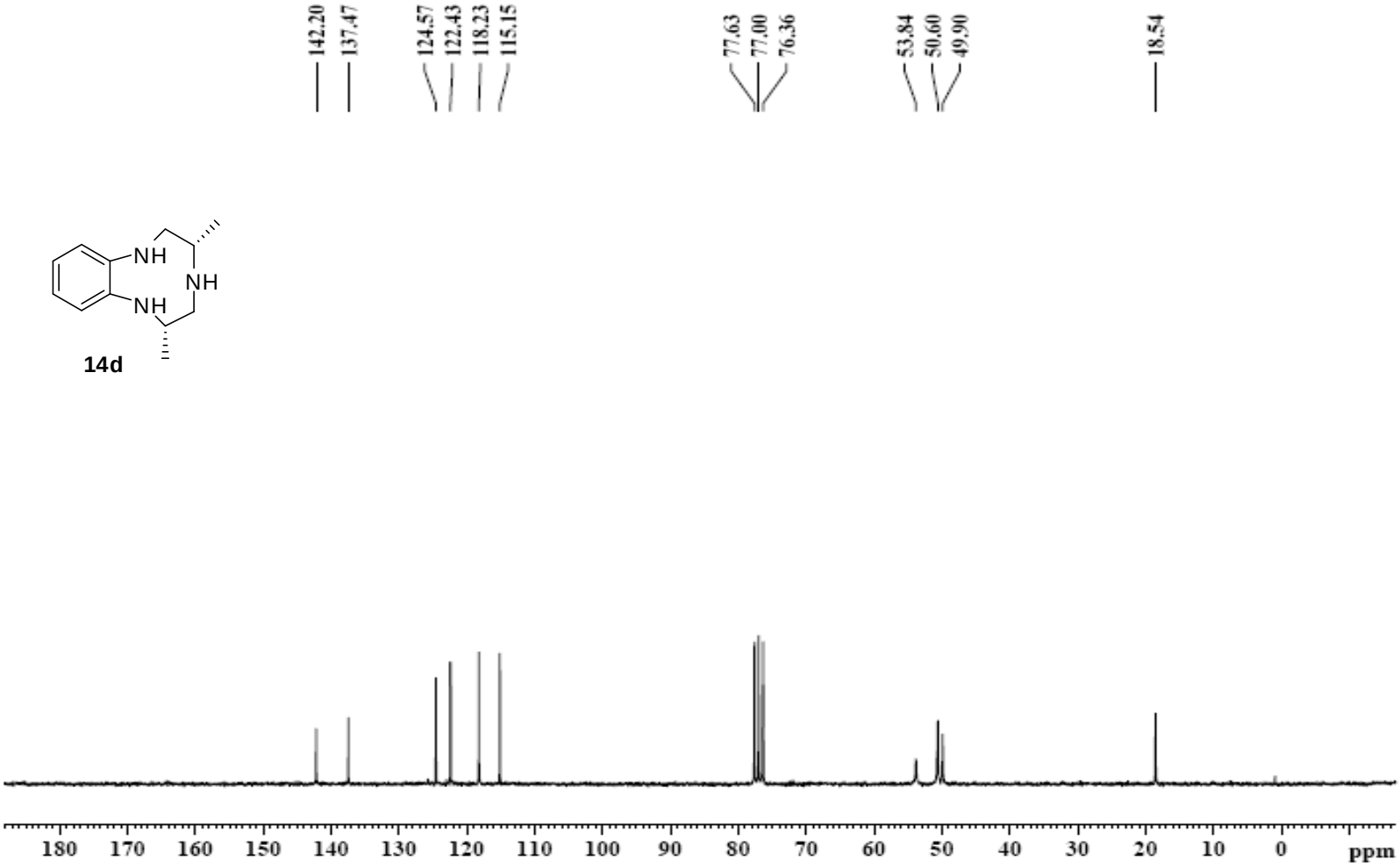


Retention time (min)

FigureS-130: HPLC graph for **14c.**

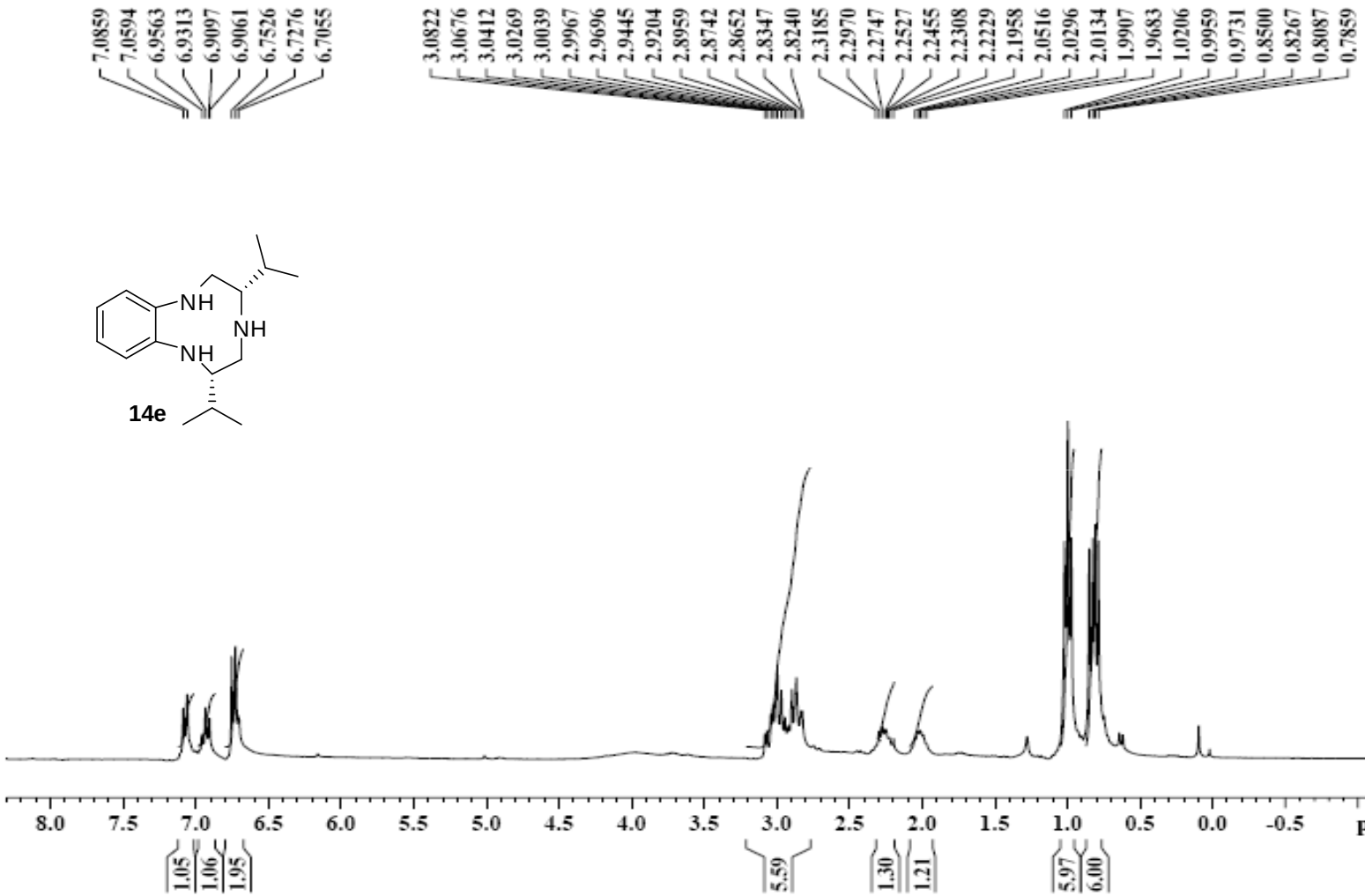


FigureS-131: ^{1}H spectrum (300MHz, $CDCl_3$) of **14d**.

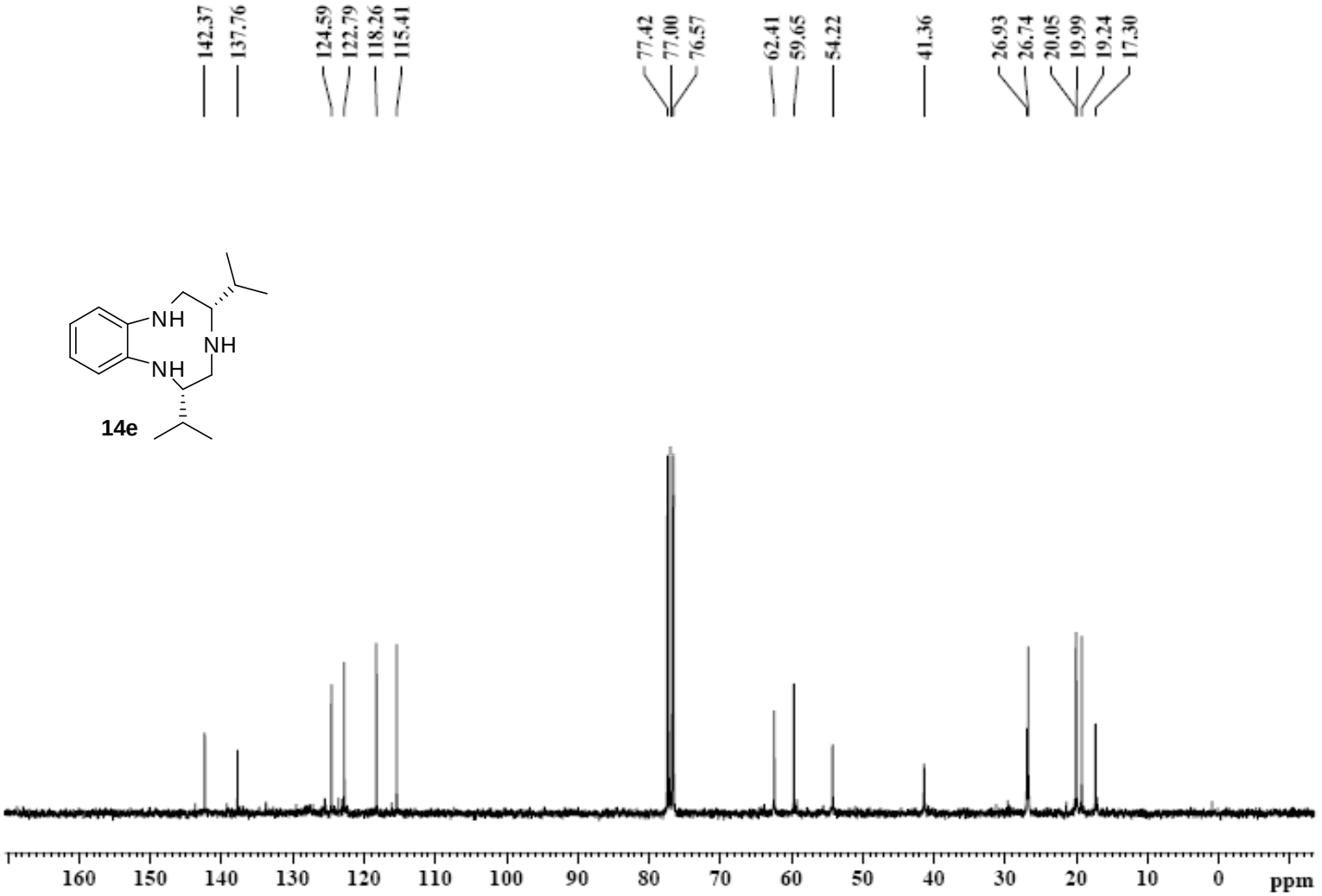


14d

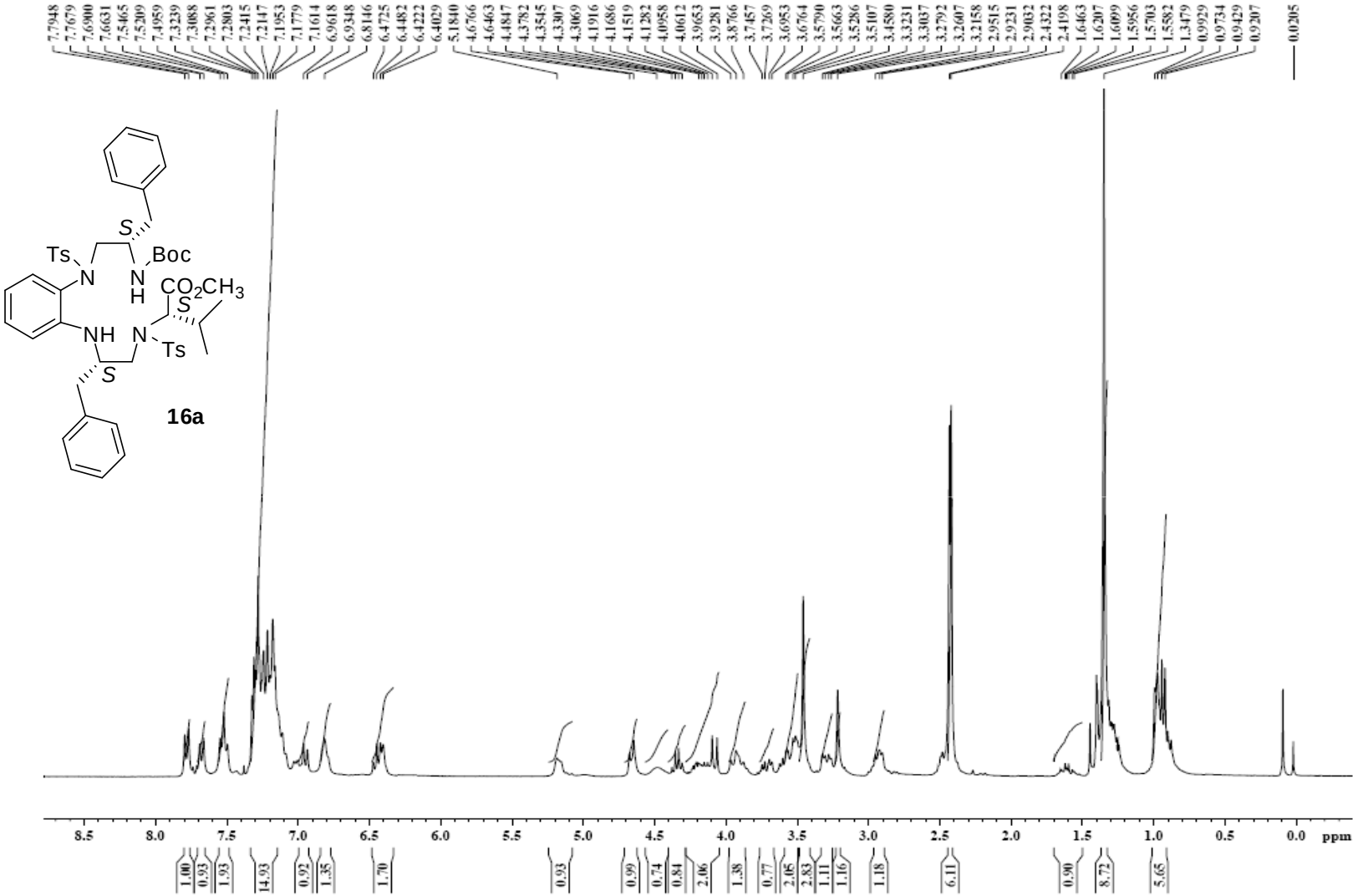
FigureS-132: ^{13}Cspectrum (75MHz, $CDCl_3$) of **14d**.



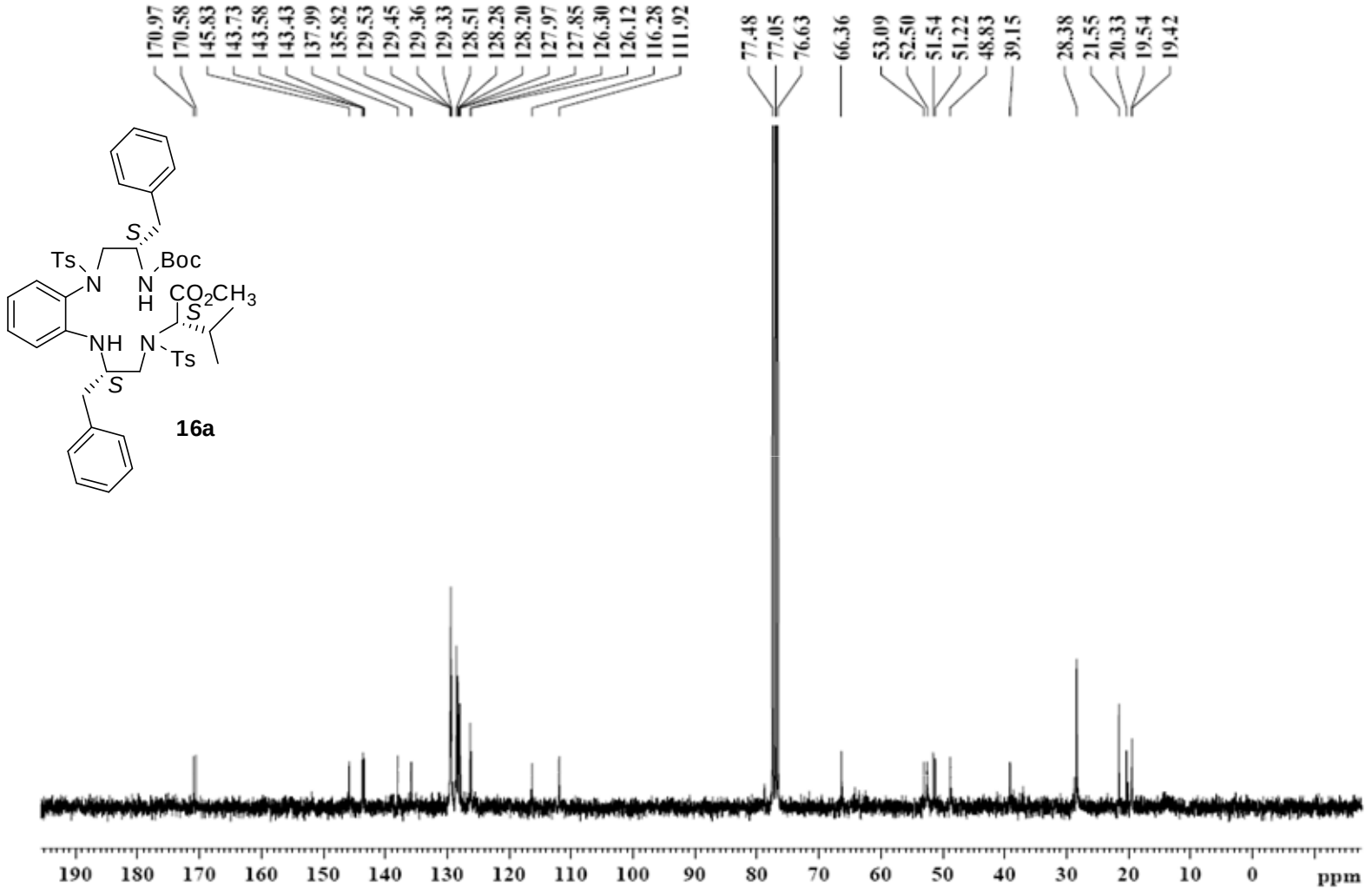
FigureS-133: ^{1}H spectrum (300MHz, $CDCl_3$) of **14e**.



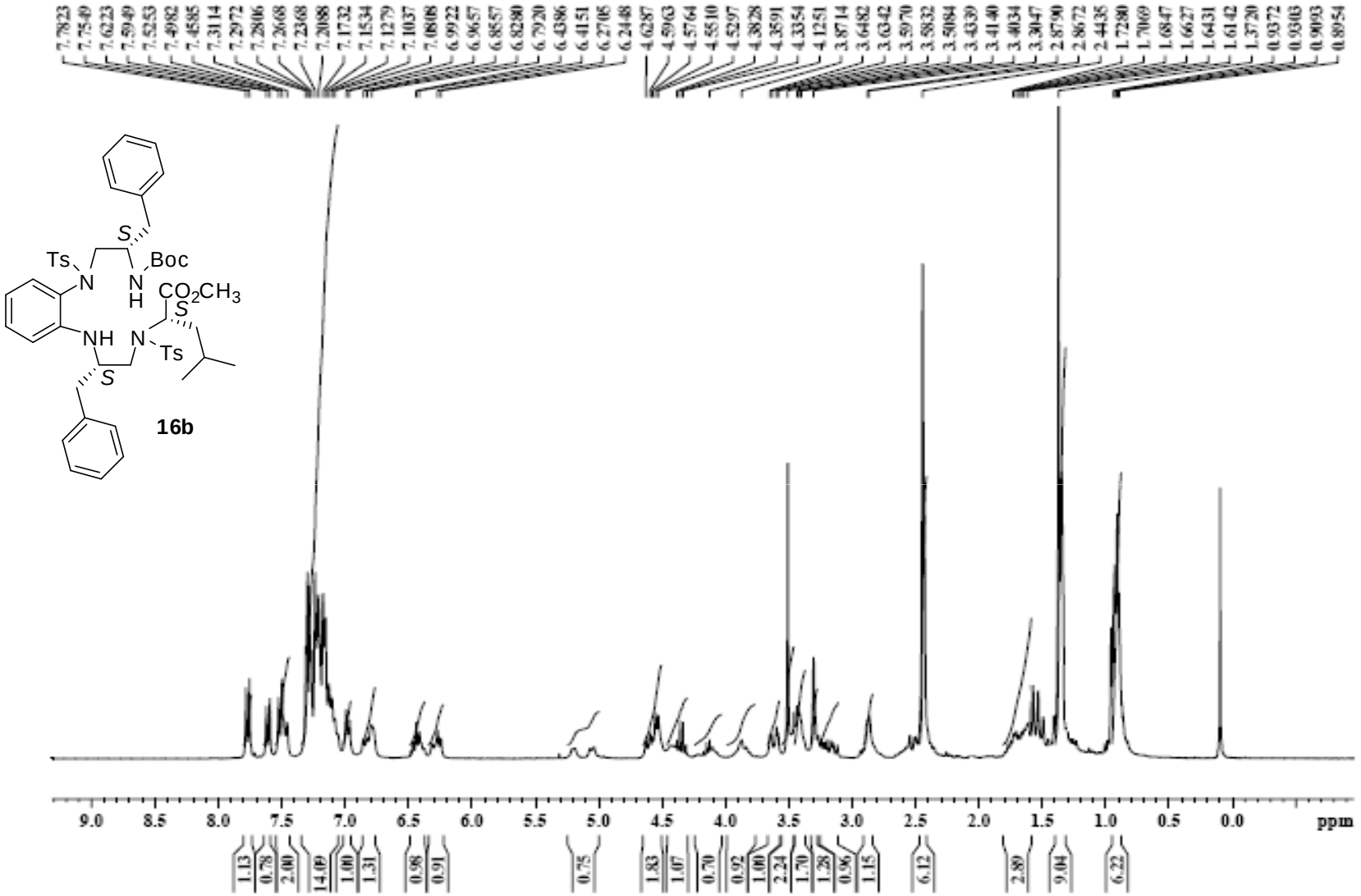
FigureS-134: ^{13}C spectrum (75MHz, $CDCl_3$) of **14e**.



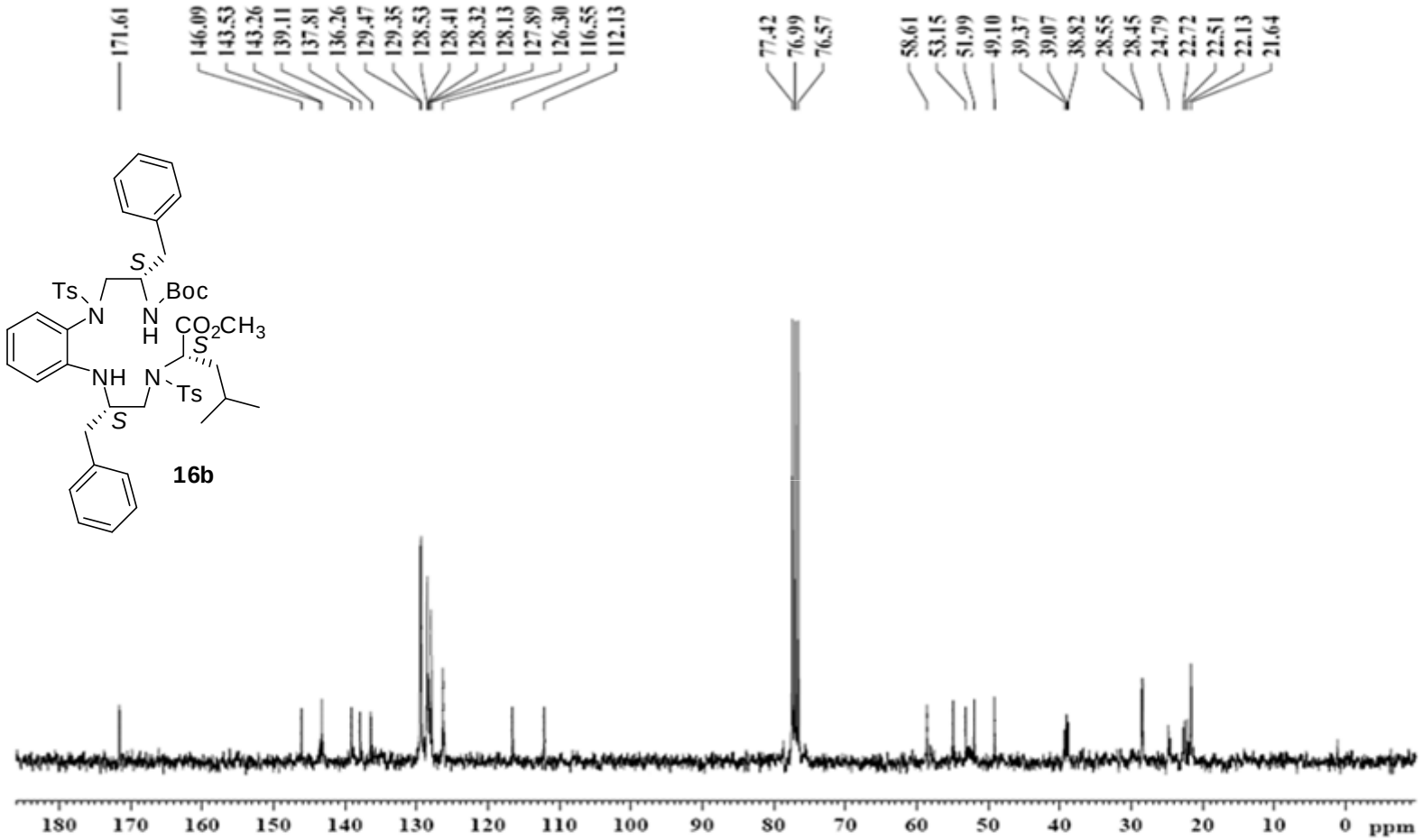
FigureS-135: ^{1}H spectrum (300MHz, $CDCl_3$) of **16a**.



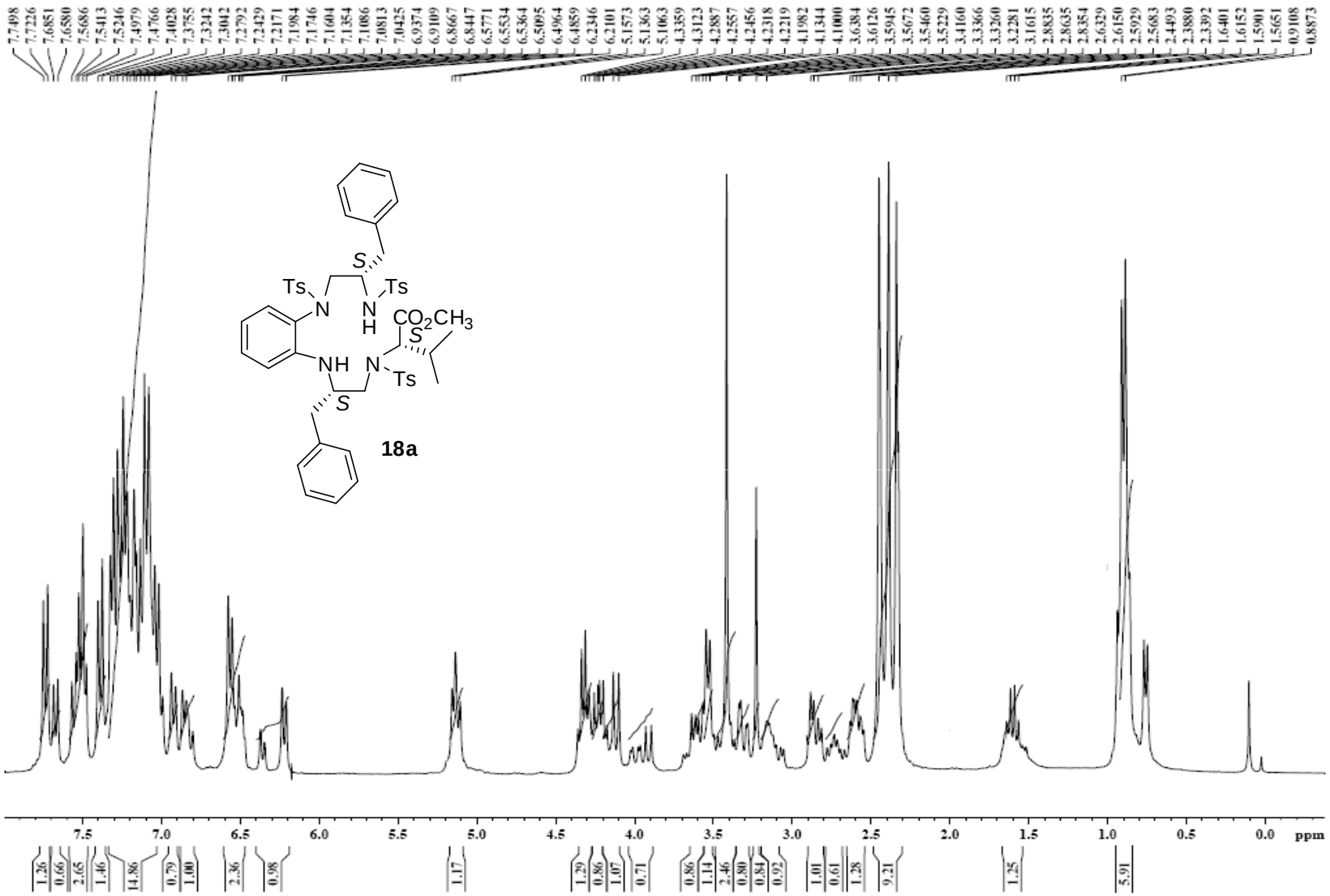
FigureS-136: ^{13}C spectrum (75 MHz, $CDCl_3$) of **16a**.



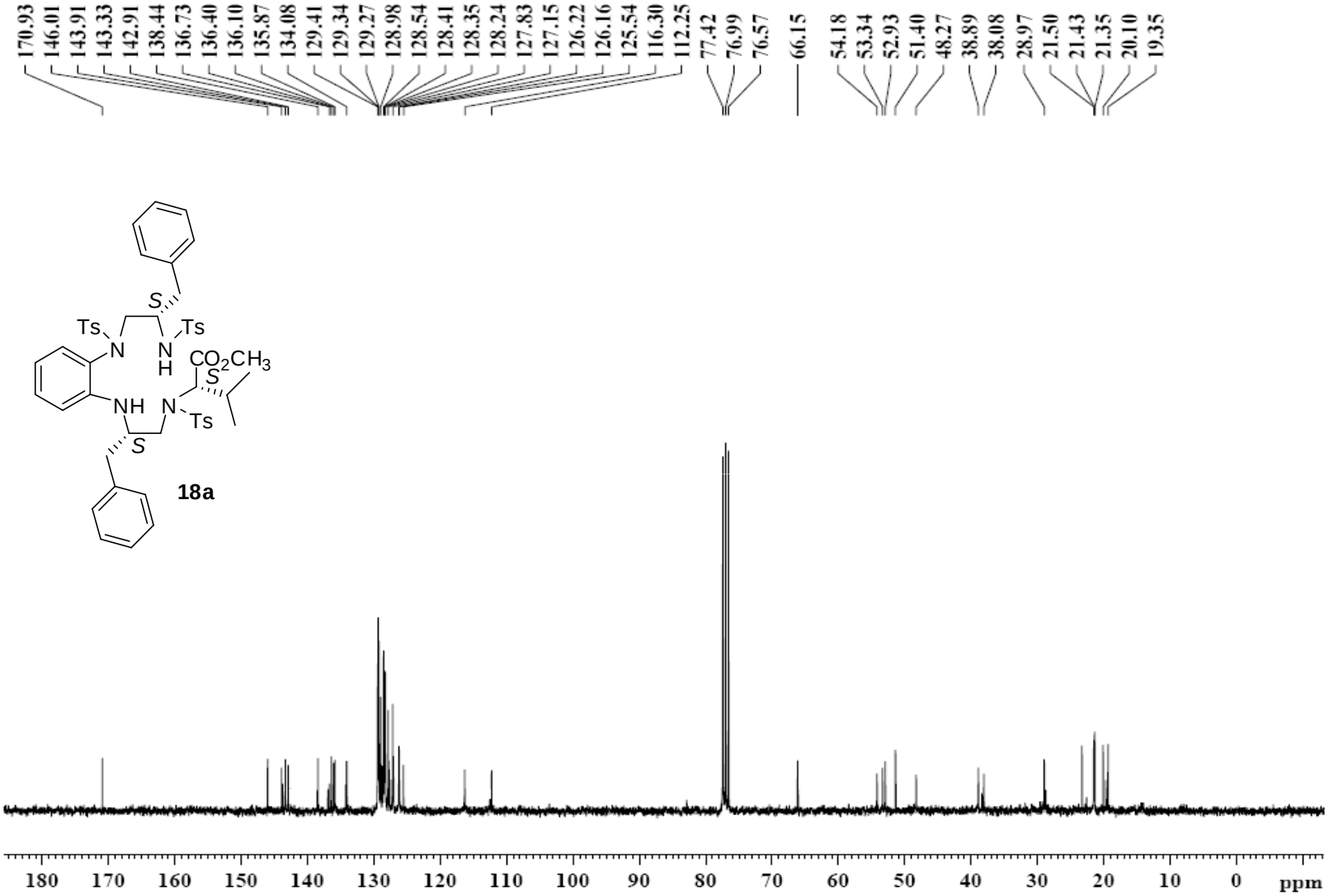
FigureS-137: ^{1}H spectrum (300MHz, $CDCl_3$) of **16b**.



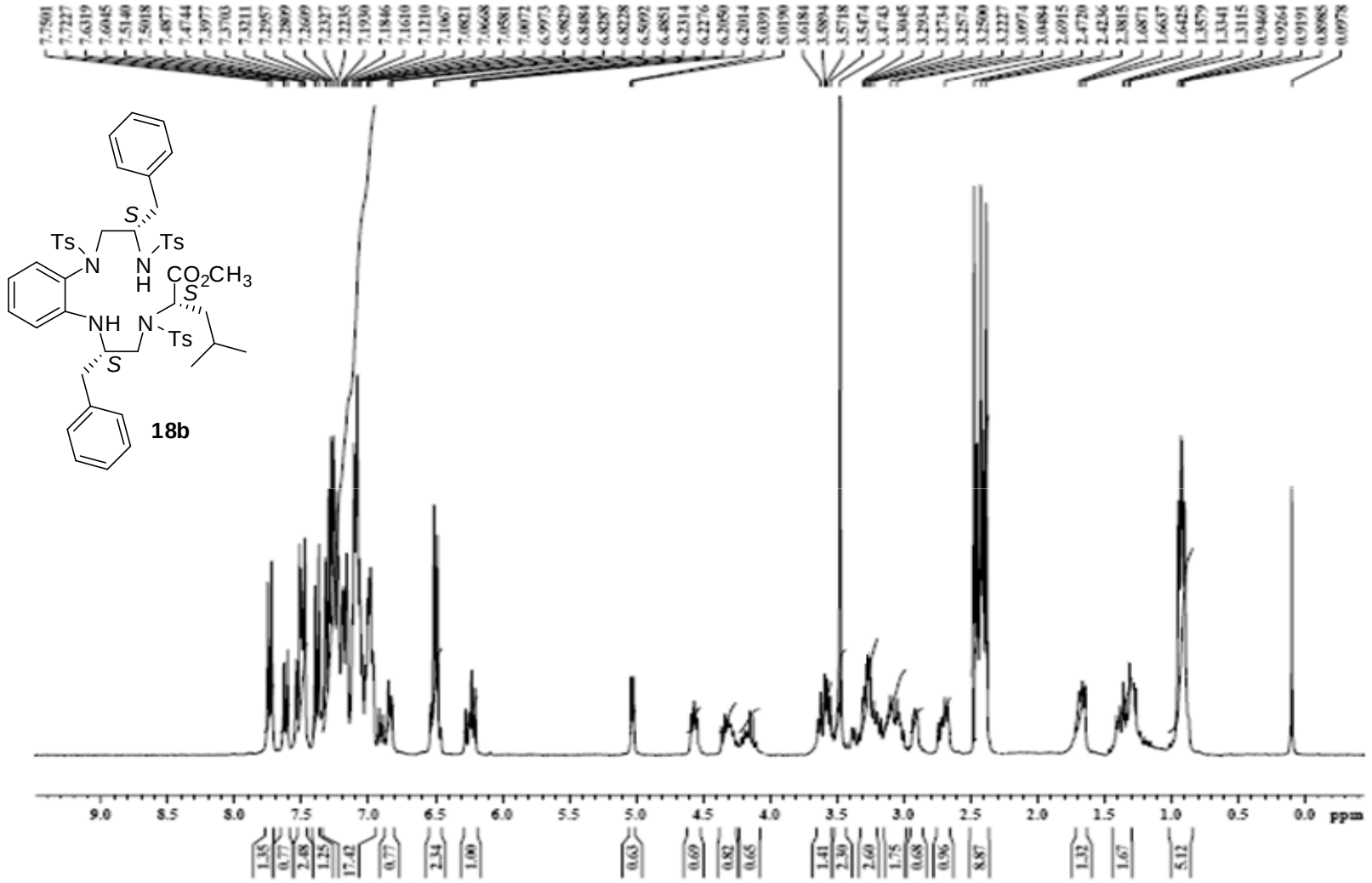
FigureS-138: ^{13}C spectrum (75 MHz, $CDCl_3$) of **16b**.



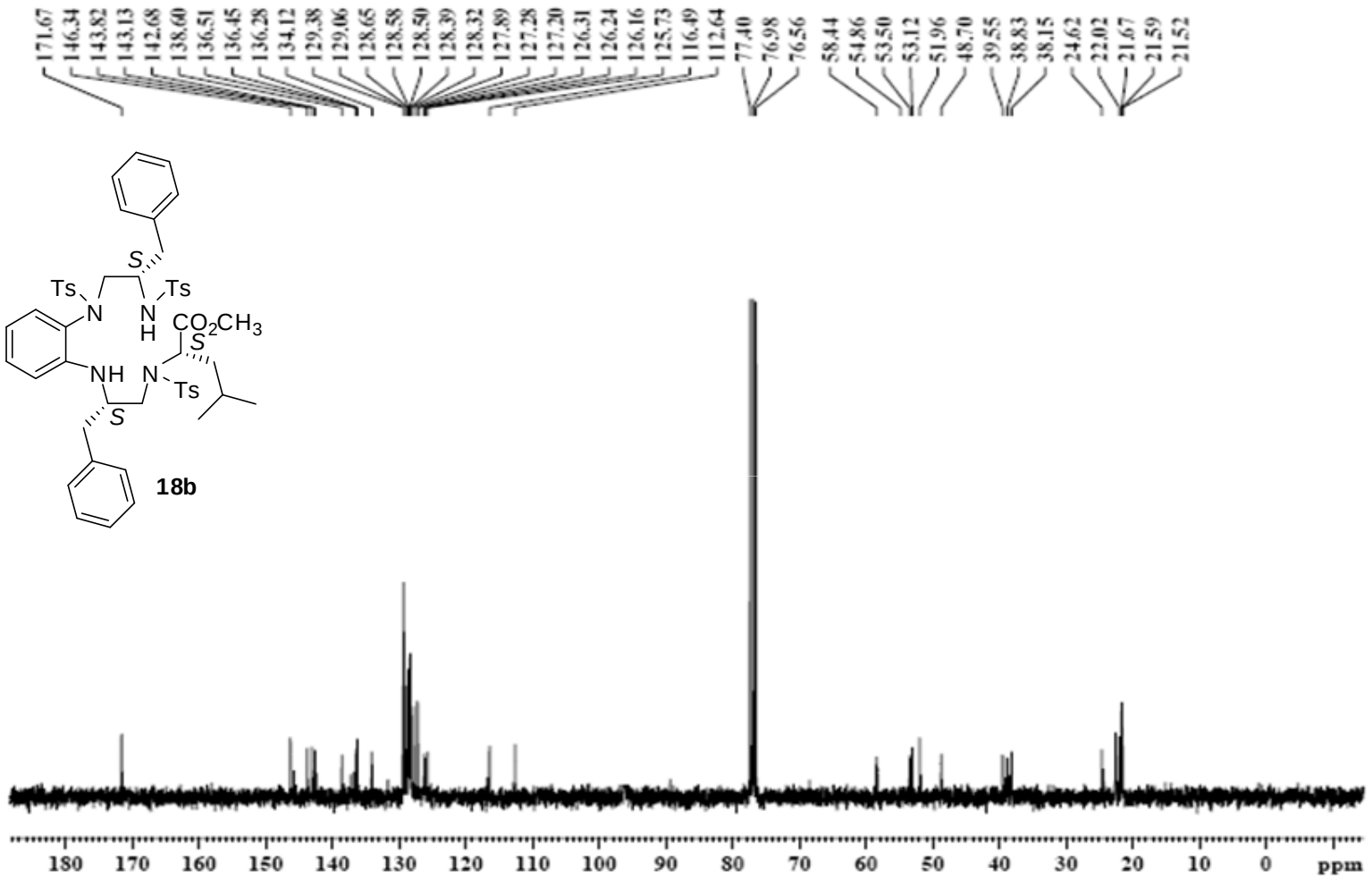
FigureS-139: ^{1}H spectrum (300MHz, $CDCl_3$) of **18a**.



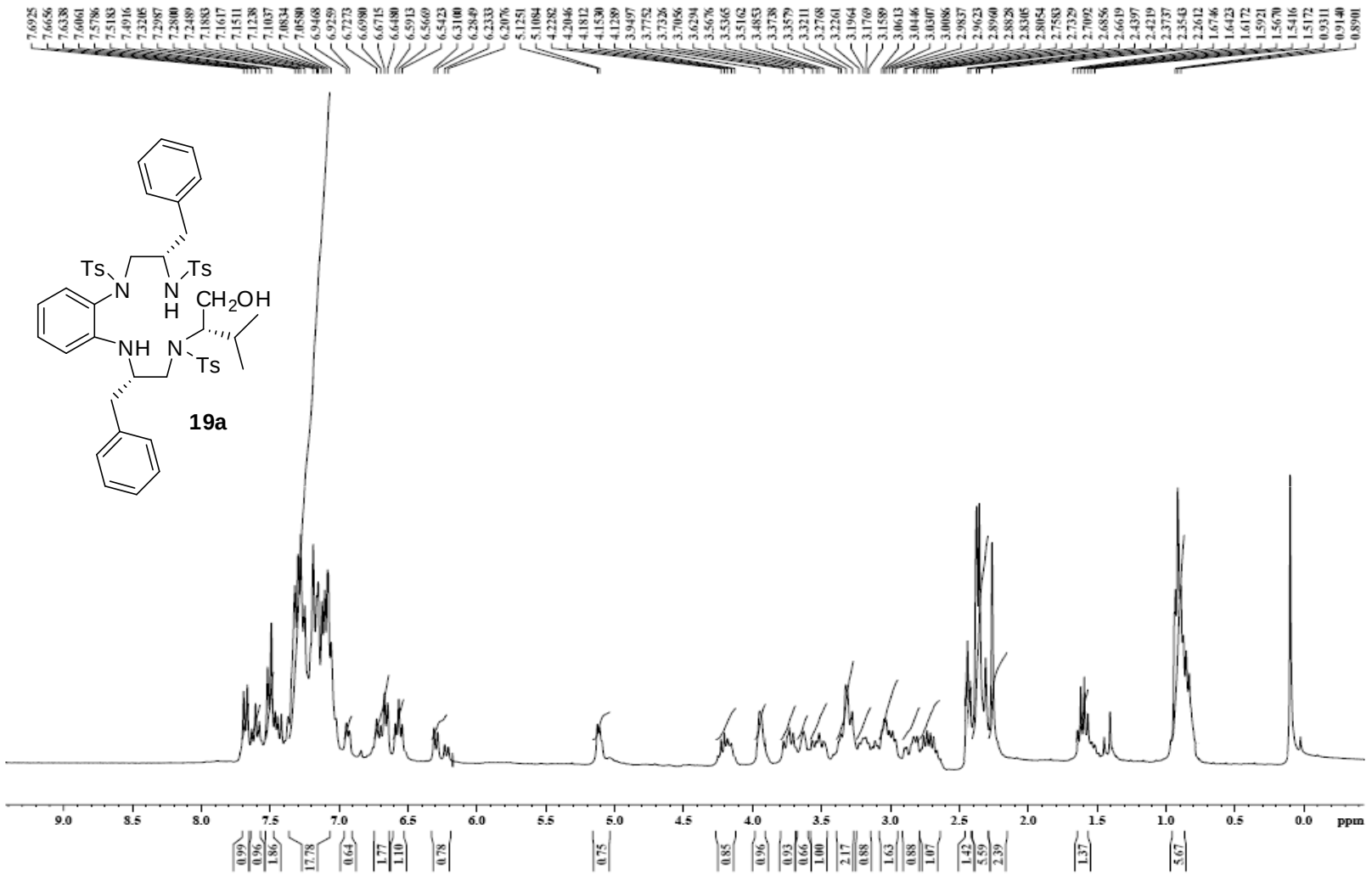
FigureS-140: ^{13}C spectrum (75 MHz, $CDCl_3$) of **18a**.



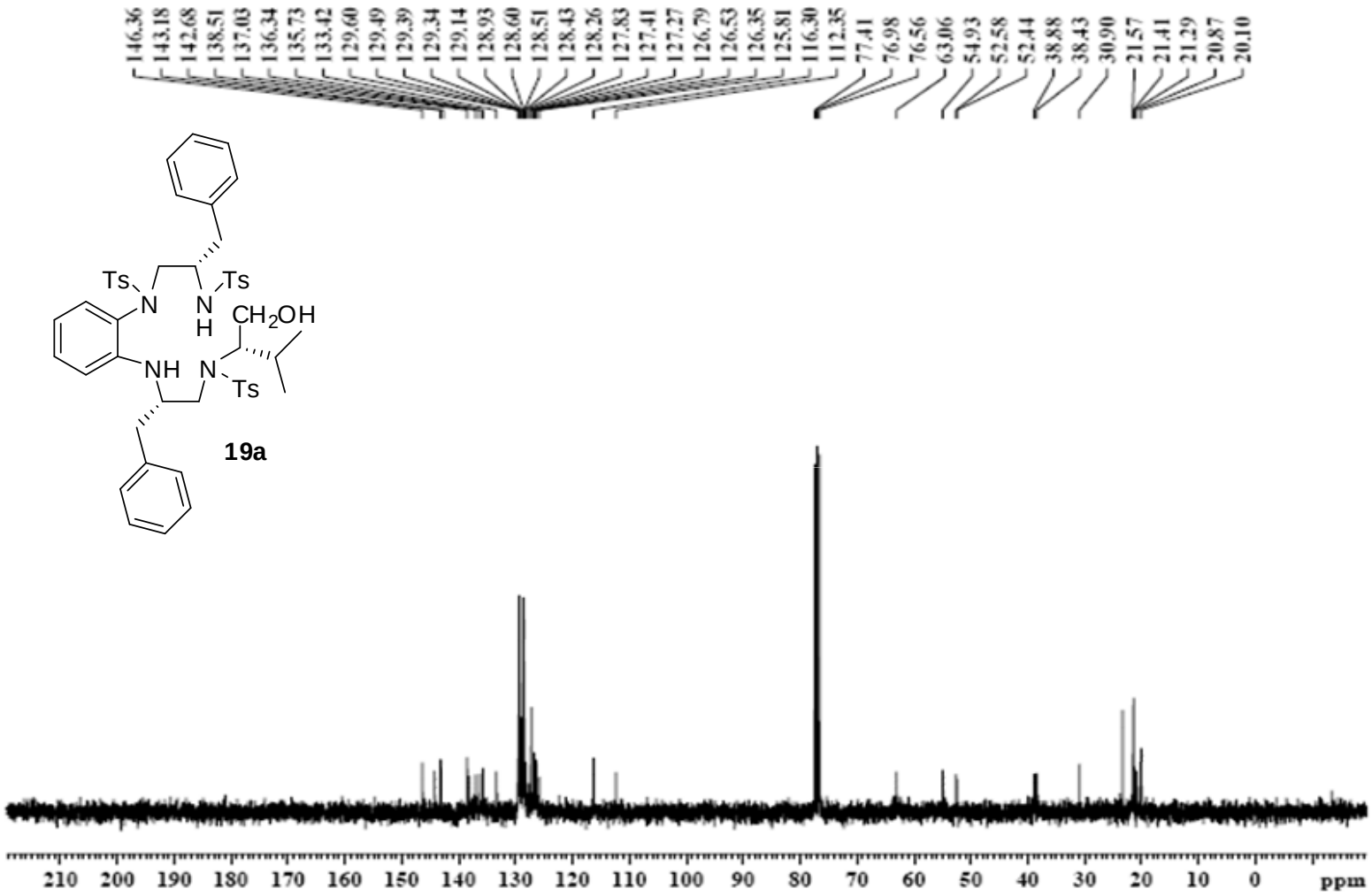
FigureS-141: ^{1}H spectrum (300 MHz, $CDCl_3$) of **18b**.



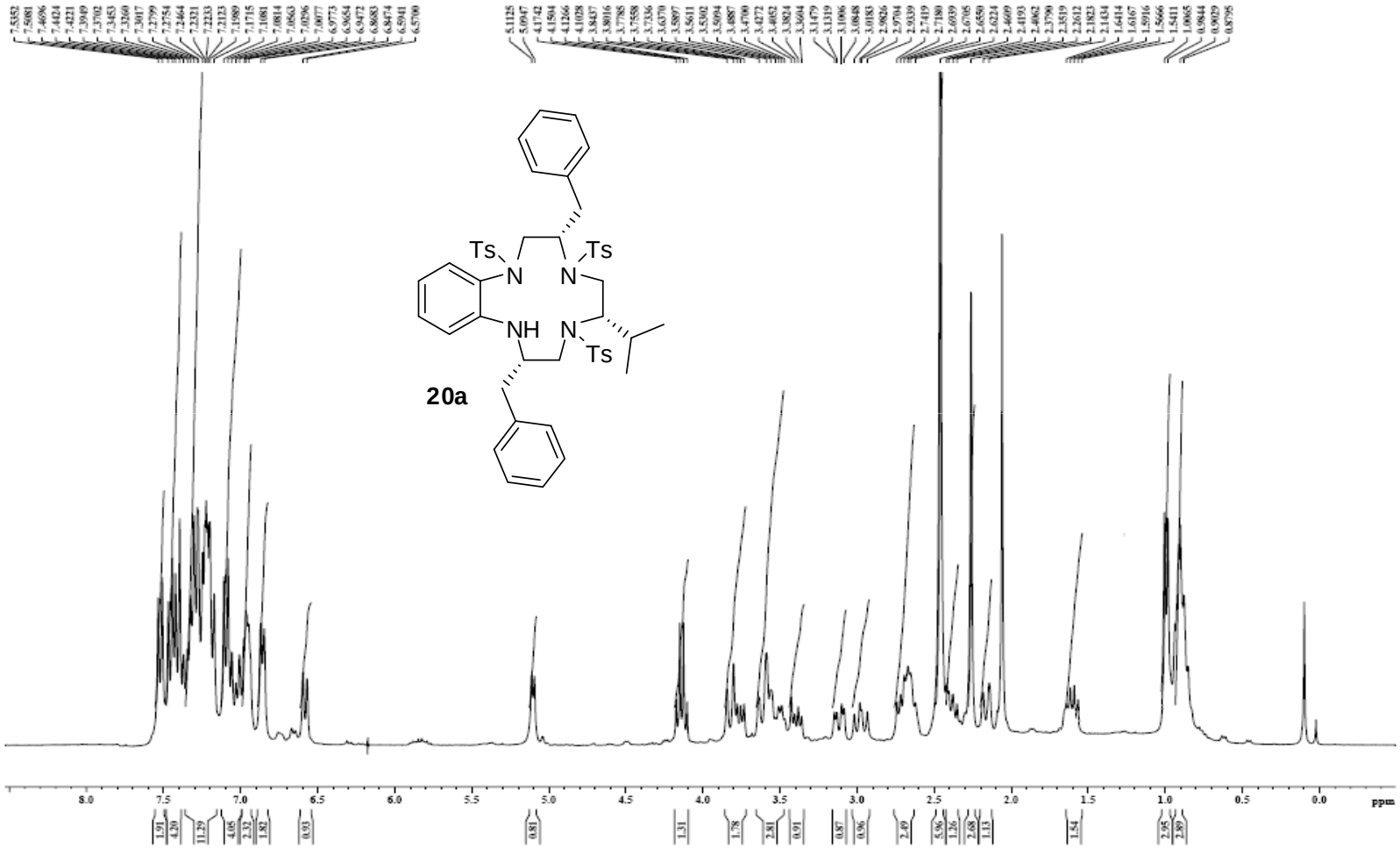
FigureS-142: ^{13}C spectrum (75 MHz, $CDCl_3$) of **18b**.



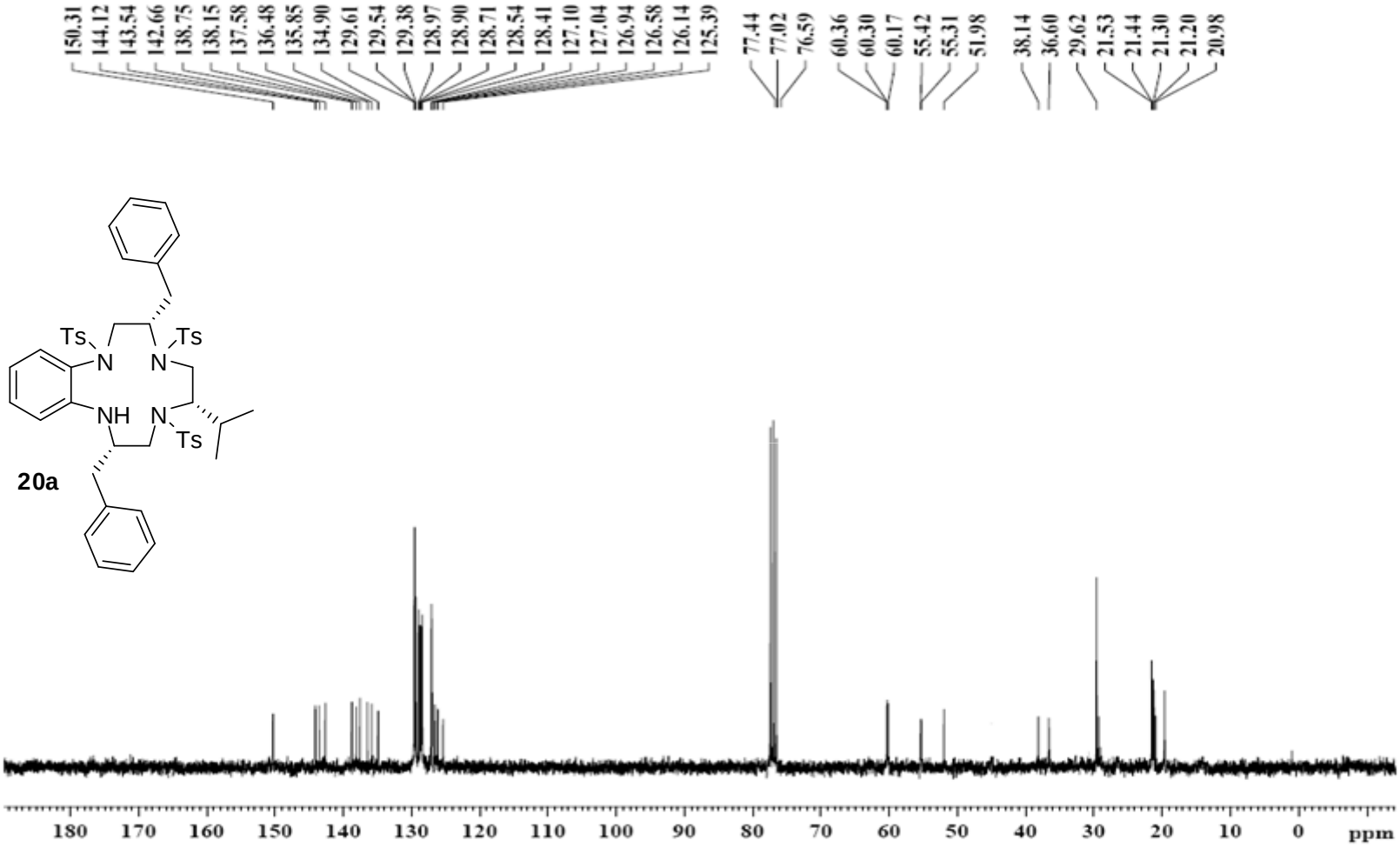
FigureS-143: ^{1}H spectrum (300MHz, $CDCl_3$) of **19a**.



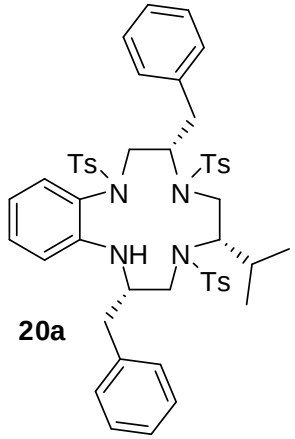
FigureS-144: ^{13}C spectrum (75MHz, $CDCl_3$) of **19a**.



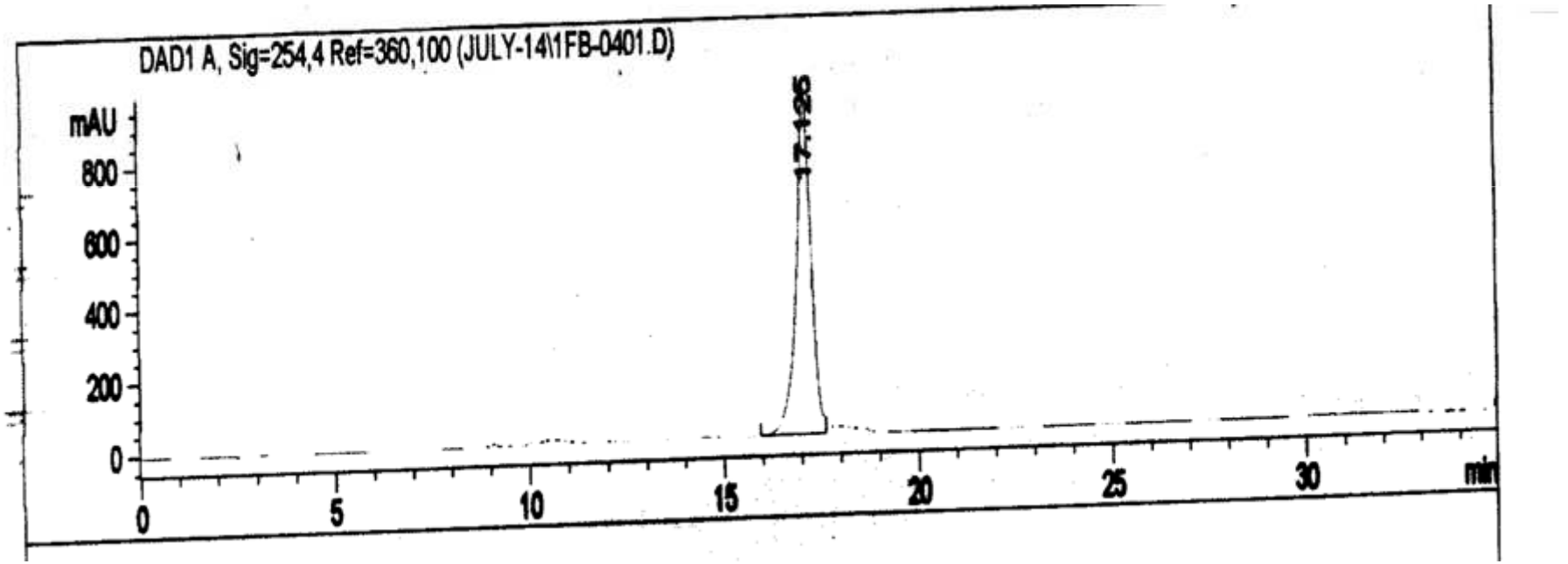
FigureS-145: ^{1}H spectrum (300MHz, $CDCl_3$) of **20a**.



FigureS-146: ^{13}C spectrum (75 MHz, $CDCl_3$) of **20a**.

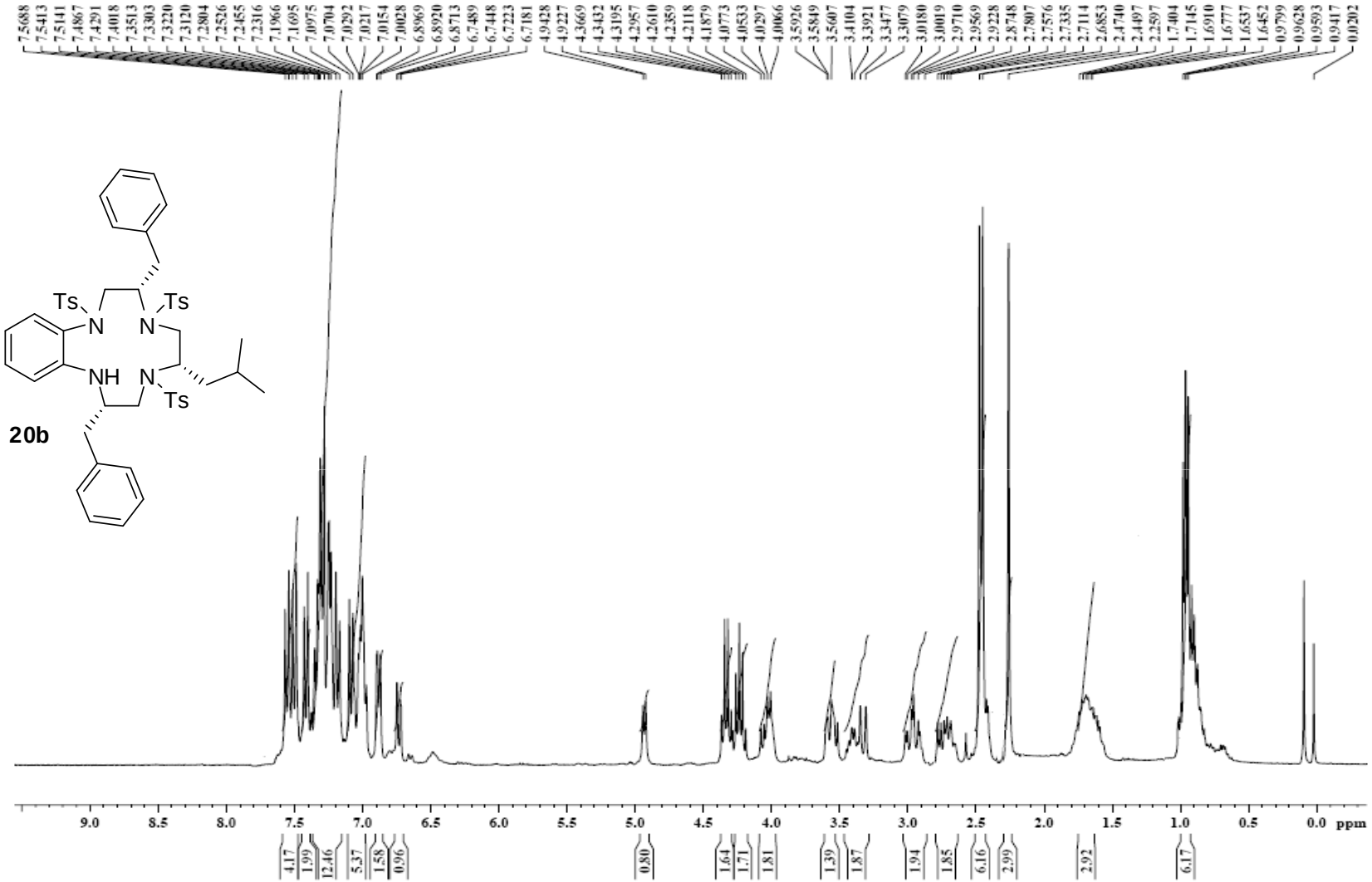


20a

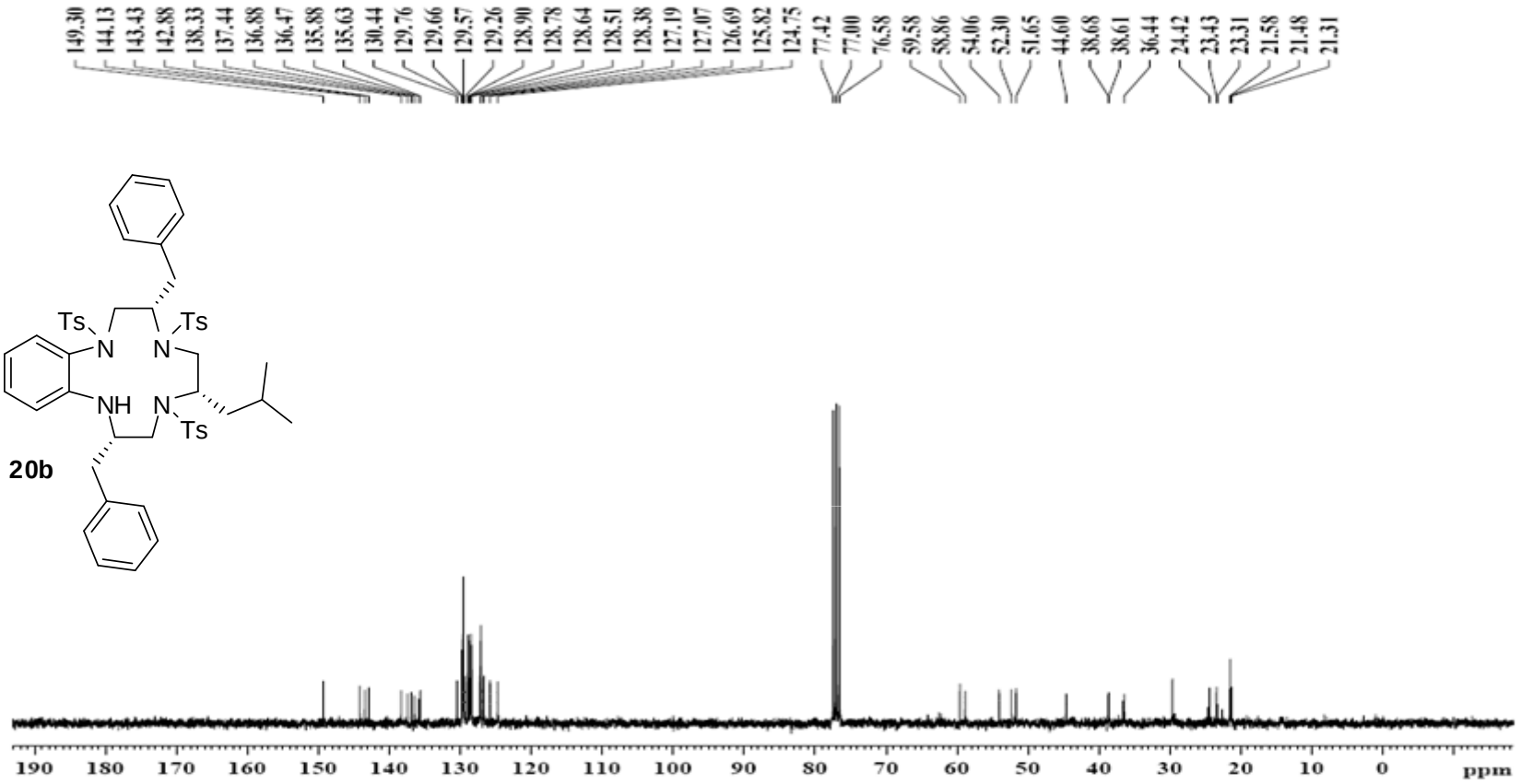


Retention time (min)

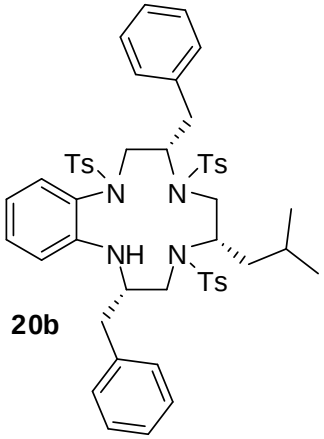
FigureS-147: HPLC graph for **20a**



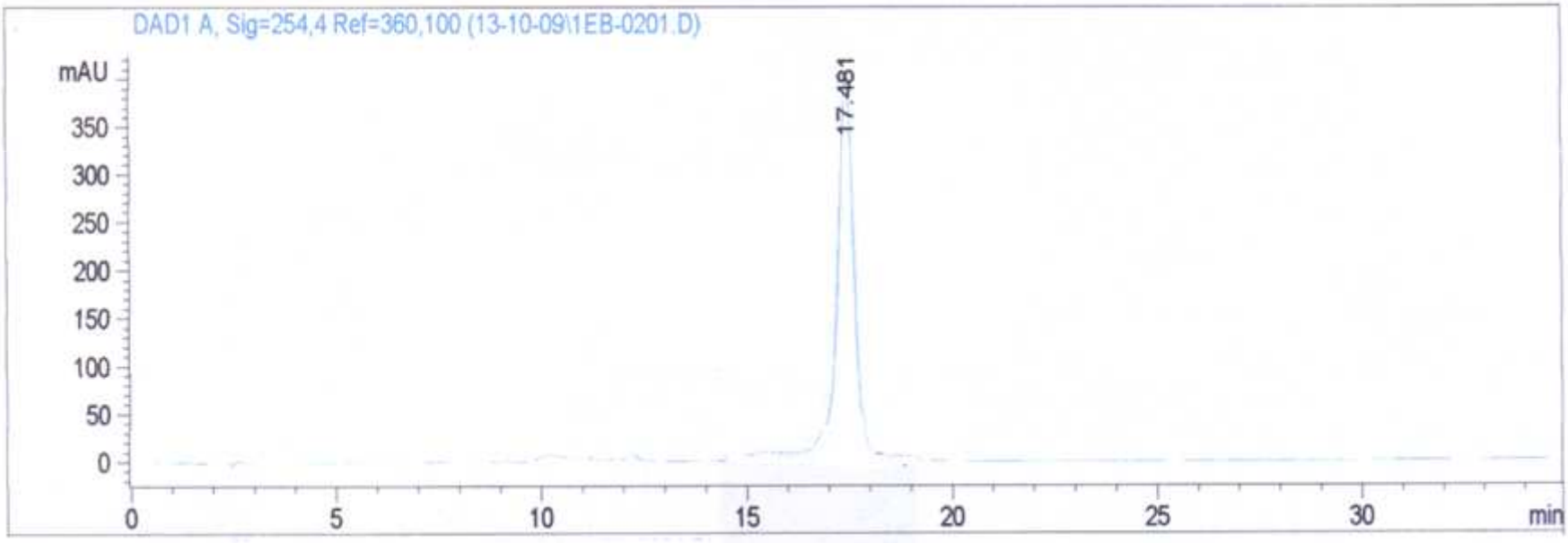
FigureS-148: ^{1}H spectrum (300MHz, $CDCl_3$) of **20b**.



FigureS-149: ^{13}C spectrum (75MHz, $CDCl_3$) of **20b**.

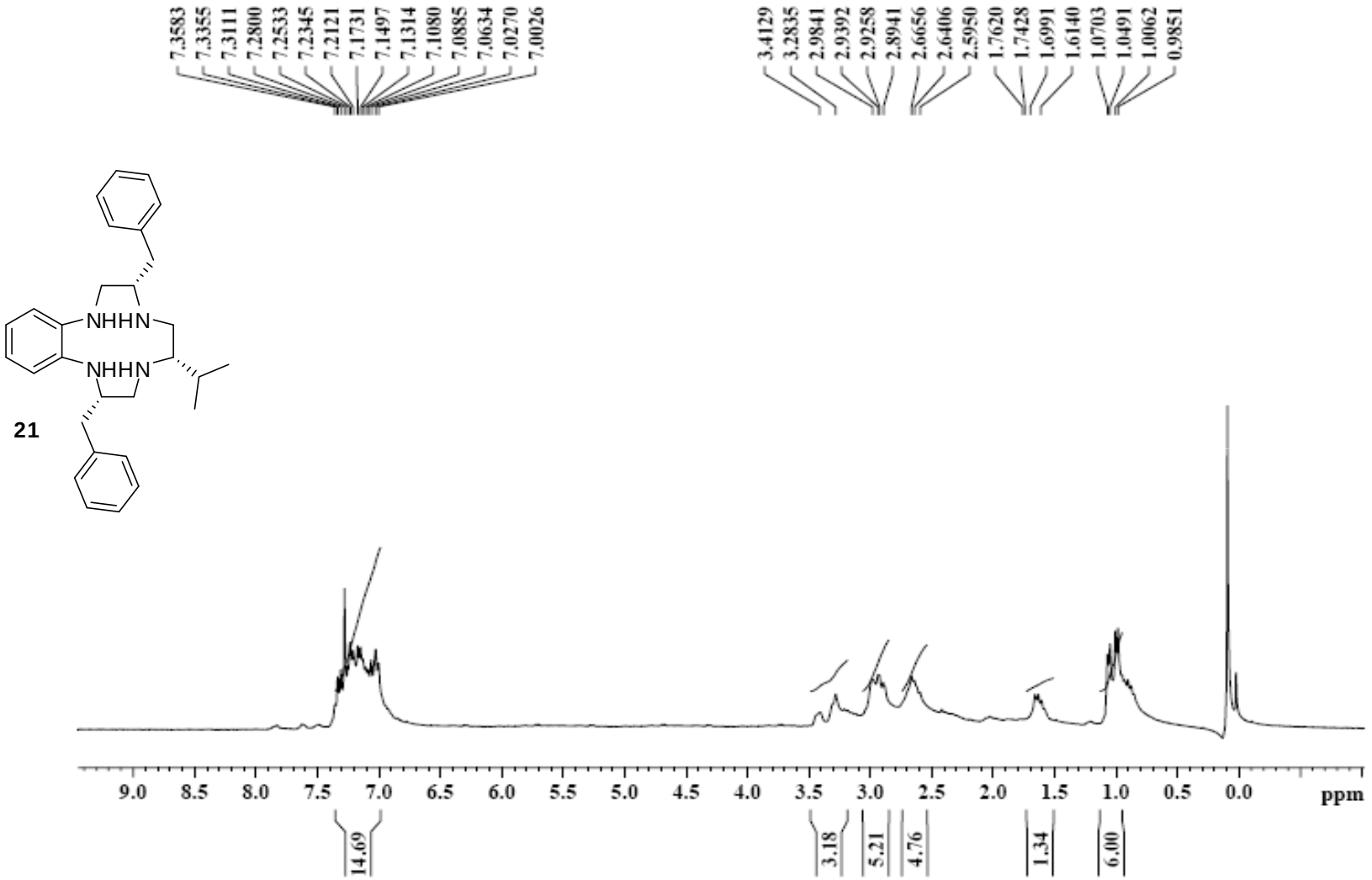


20b

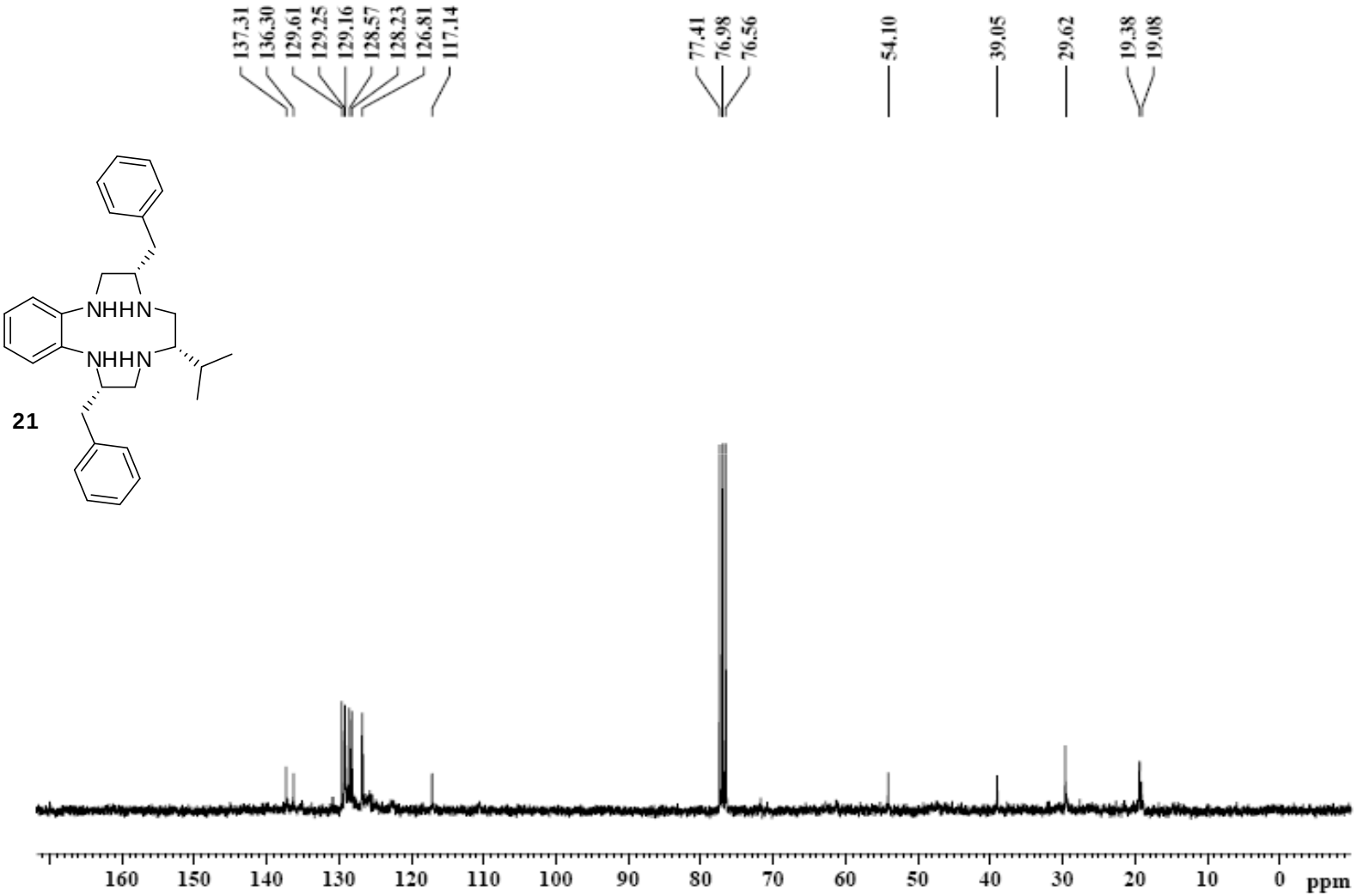


Retention time (min)

FigureS-150: HPLC graph for **20b**



FigureS-151: ^{1}H spectrum (300MHz, $CDCl_3$) of **21**.



FigureS-152: ^{13}C spectrum (75MHz, $CDCl_3$) of **21**.

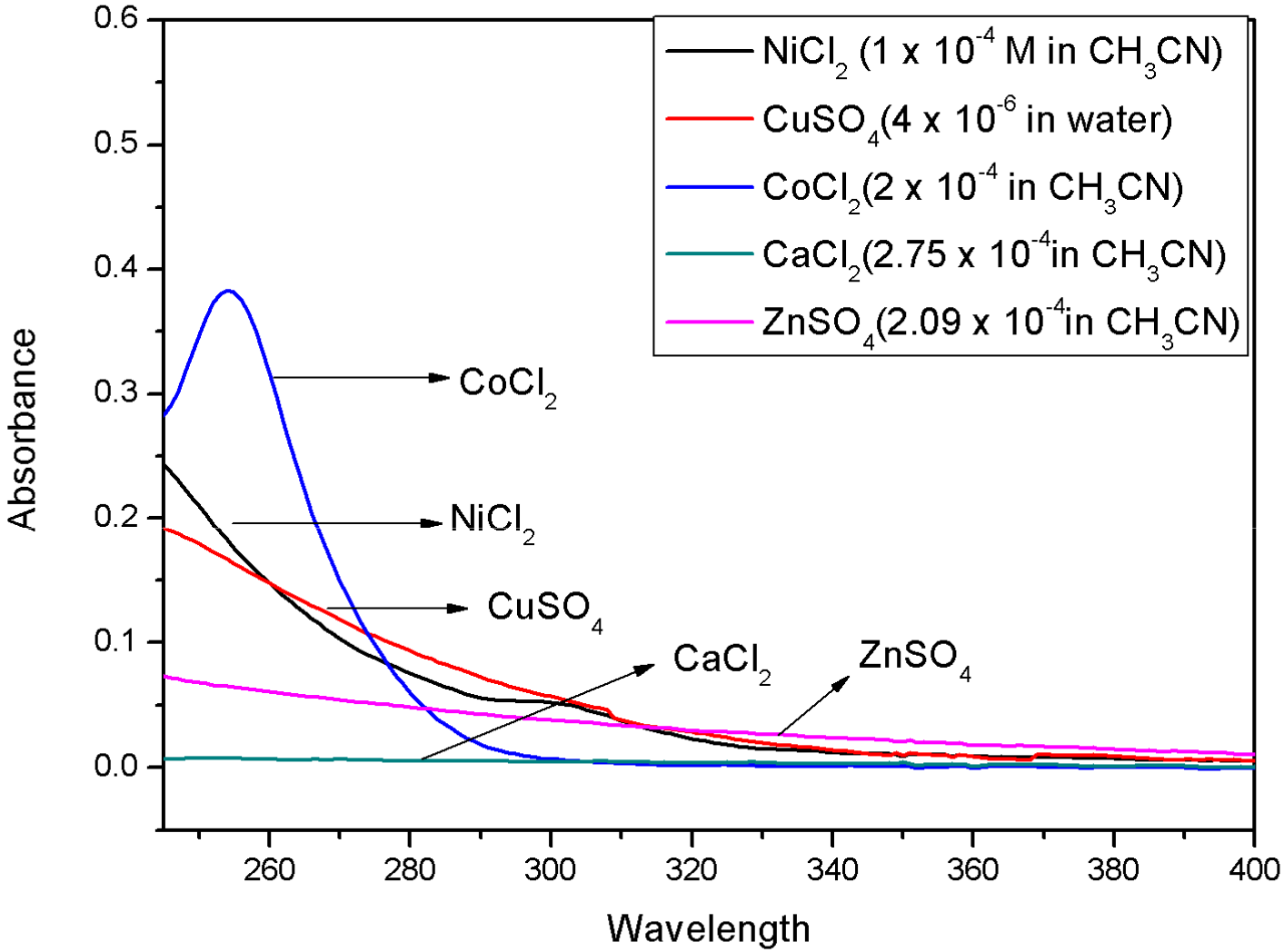


Fig. S-153: UV-Visible spectra of various cations in solution which have been used.

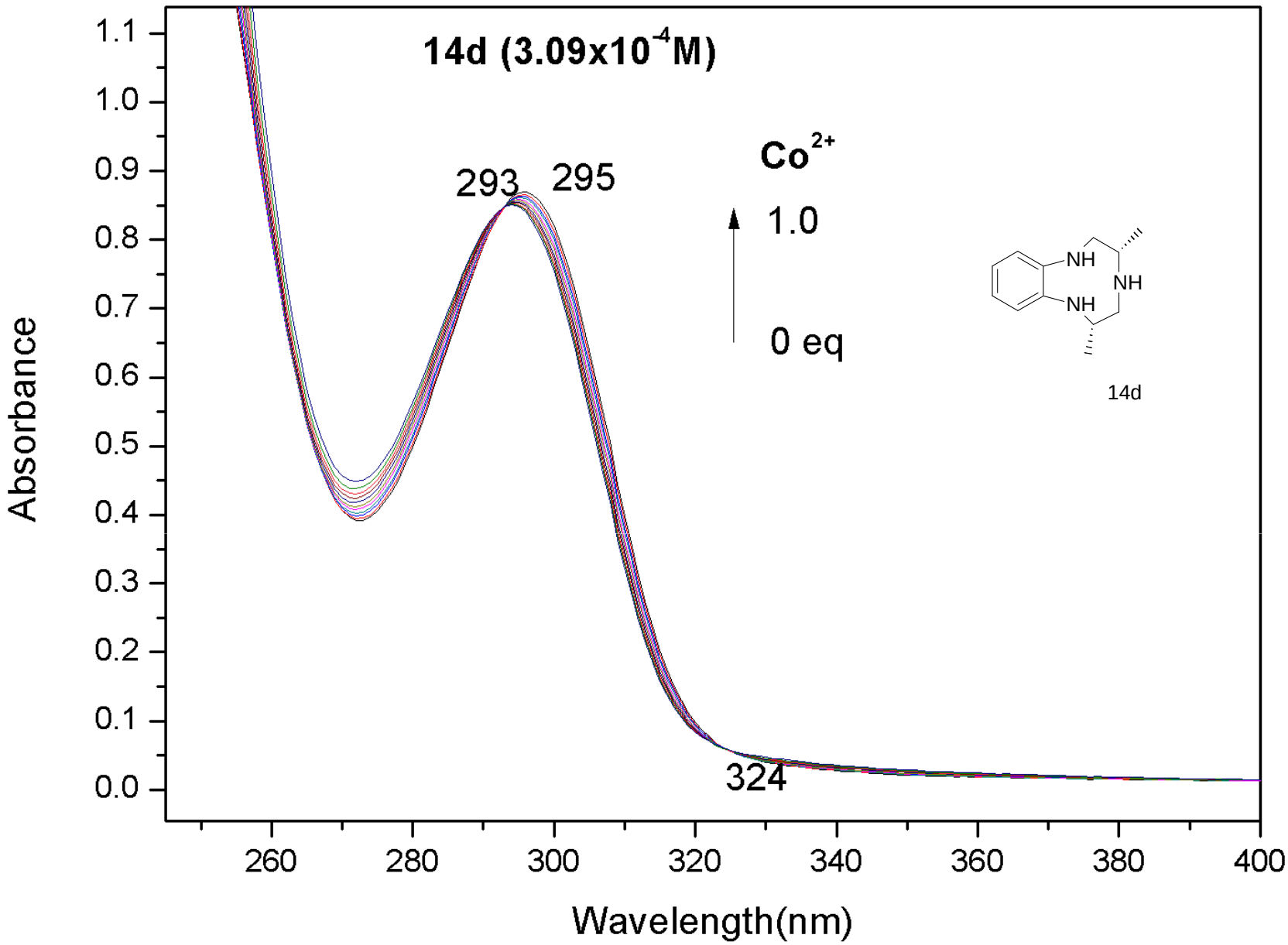


Fig. S-154: UV-visible spectra of **14d** with gradual addition of Co^{2+} solution. Figure depicts the different kinds of response on addition the same cation.

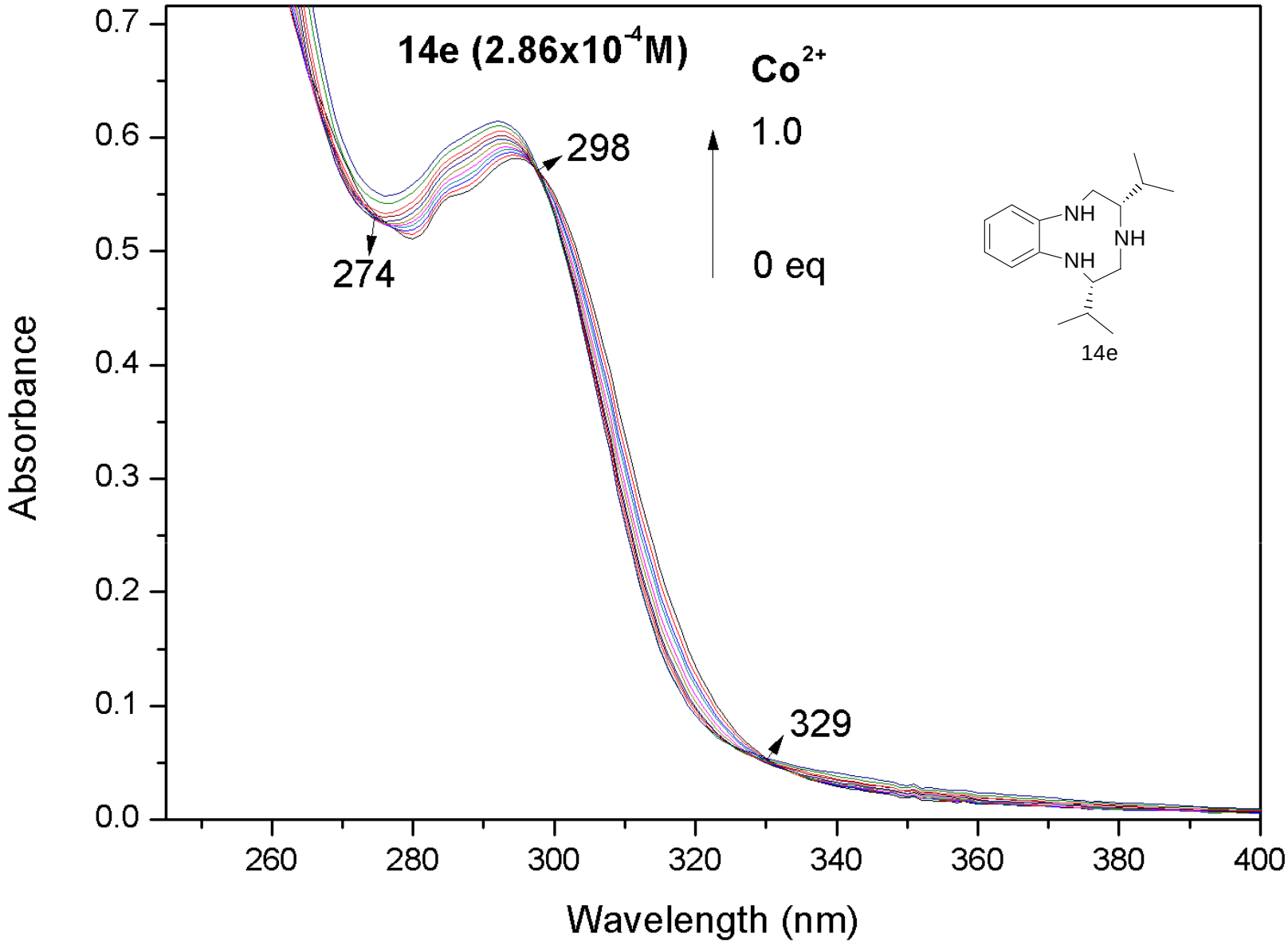


Fig. S-155: UV-visible spectra of **14e**with gradual addition of Co^{2+} solution. Figure depicts the different kinds of response on addition the same cation.

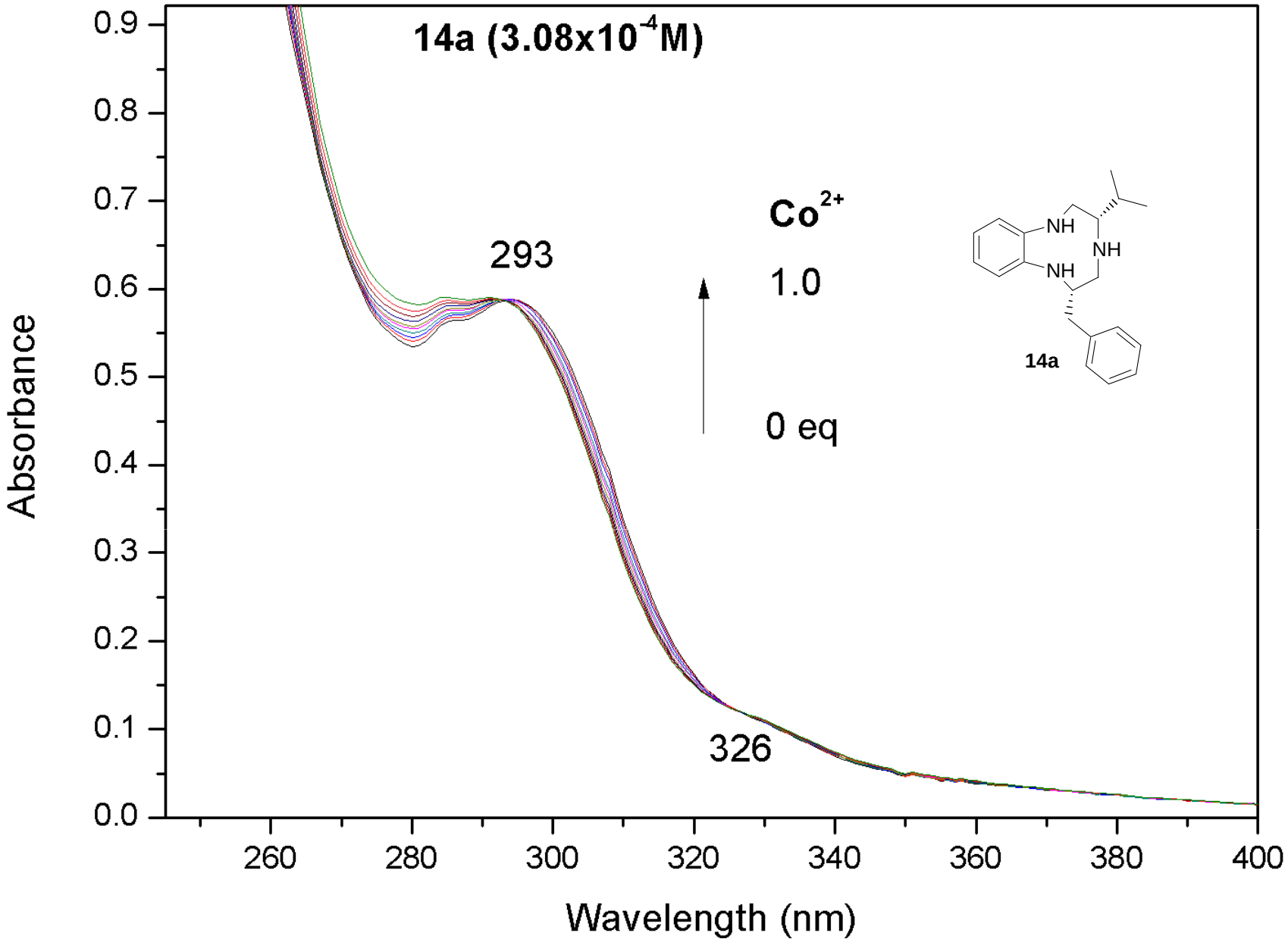


Fig. S-156: UV-visible spectra of **14a** with gradual addition of Co^{2+} solution. Figure depicts the different kinds of response on addition the same cation.

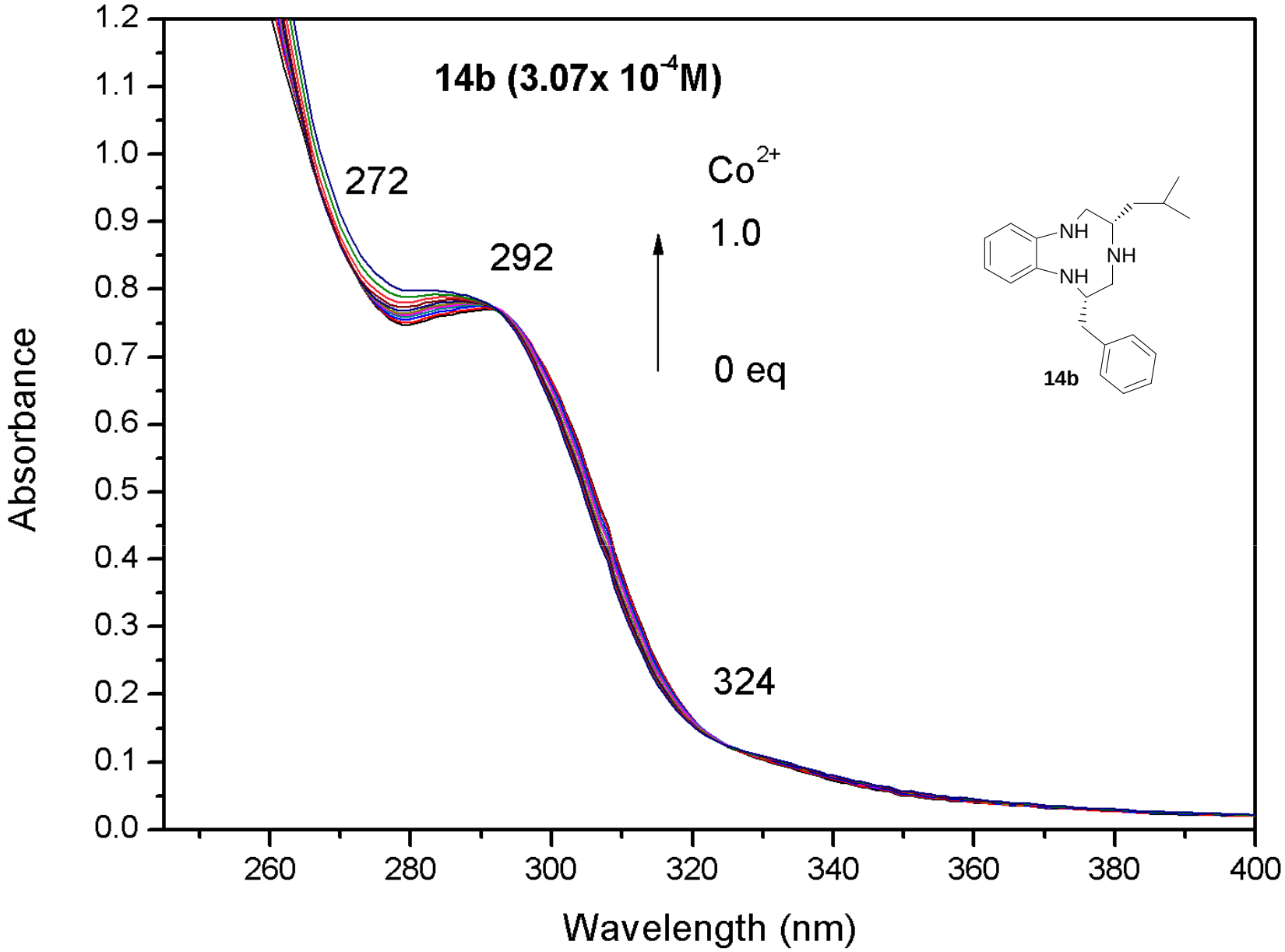


Fig. S-157: UV-visible spectra of **14b** with gradual addition of Co^{2+} solution. Figure depicts the different kinds of response on addition the same cation.

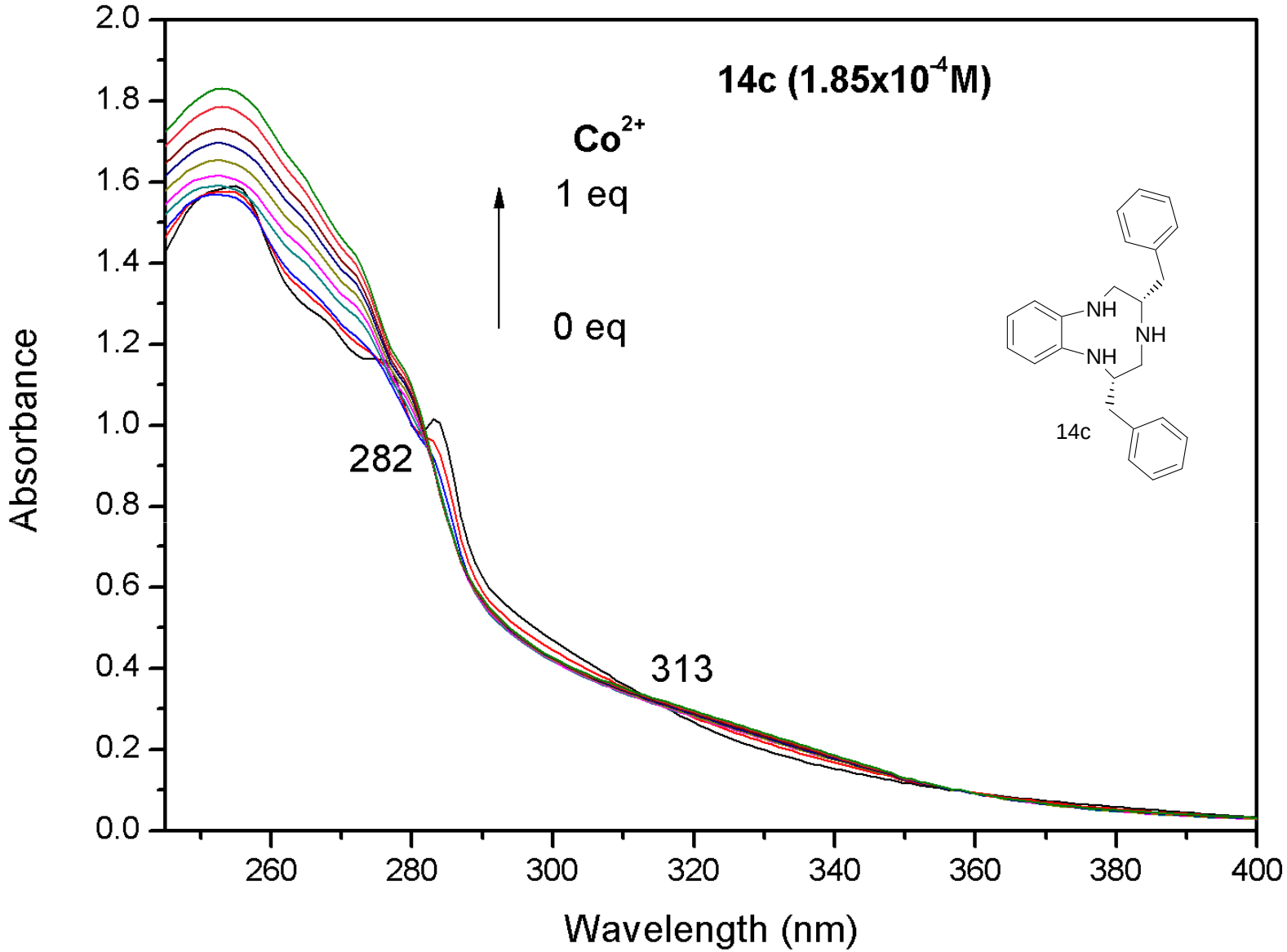


Fig. S-158: UV-visible spectra of **14c** with gradual addition of Co^{2+} solution. Figure depicts the different kinds of response on addition the same cation.

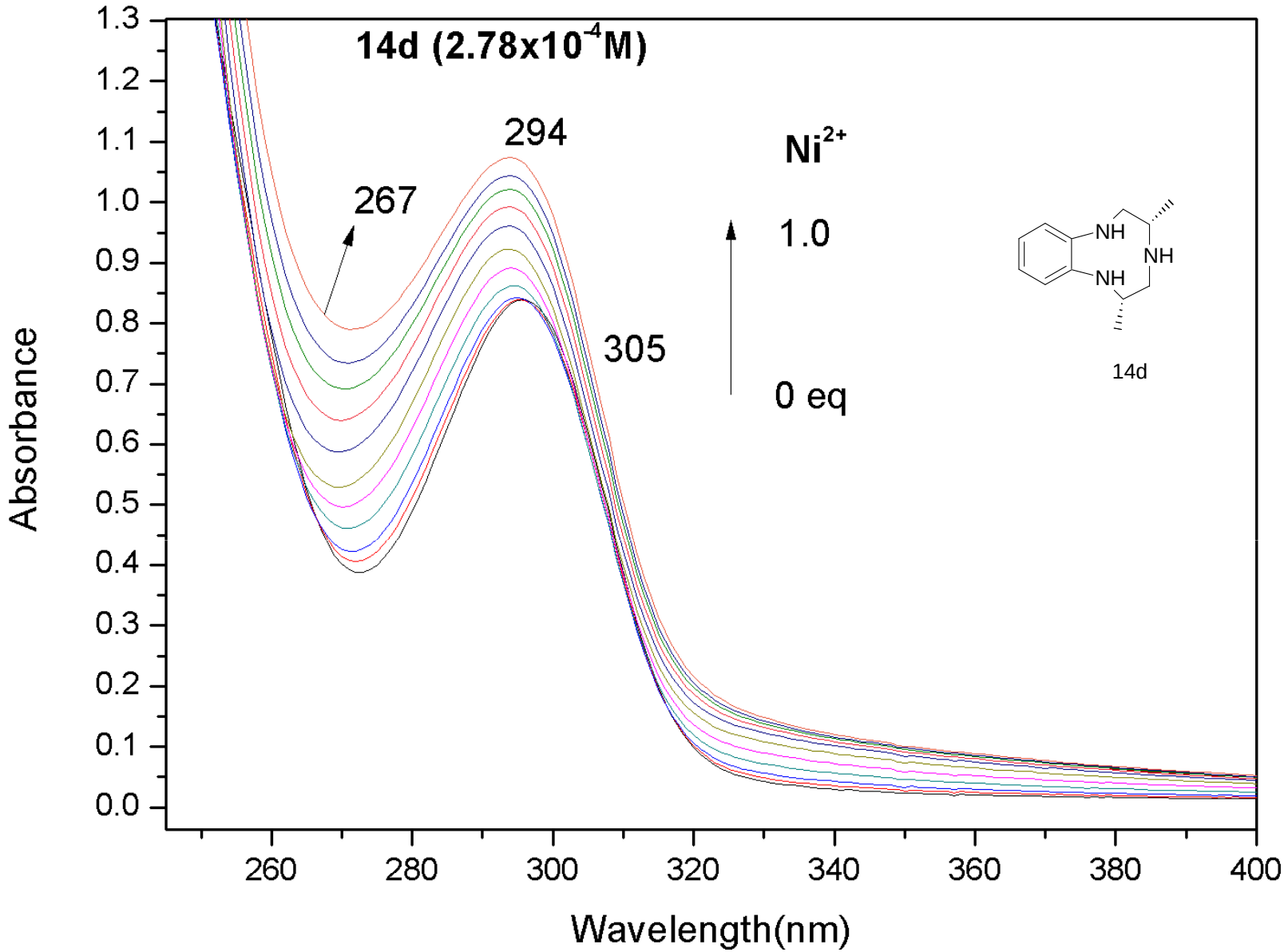


Fig. S-159: UV-visible spectra of **14d** with gradual addition of Ni^{2+} solution.

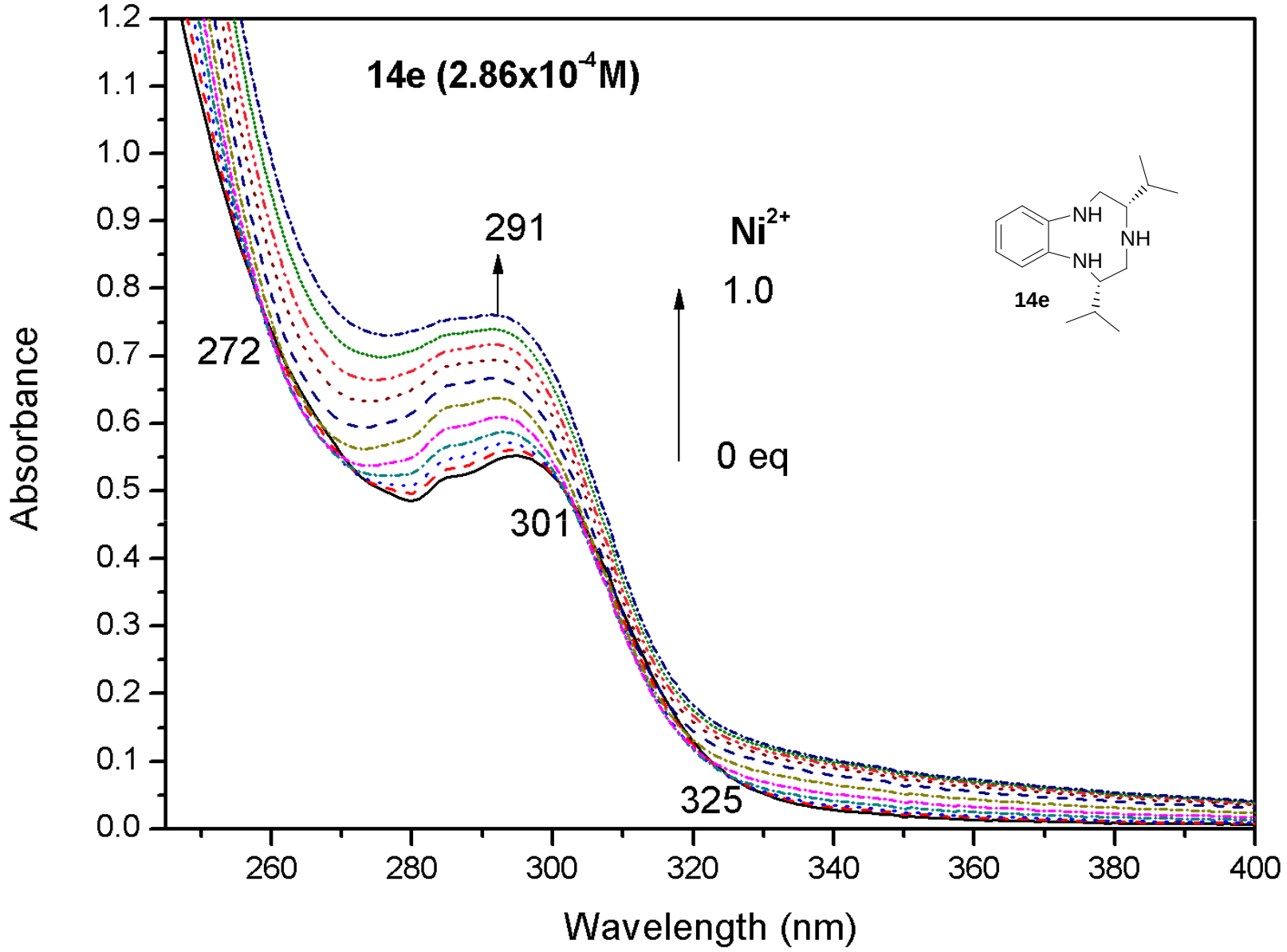


Fig. S-160: UV-visible spectra of **14e** with gradual addition of Ni^{2+} solution.

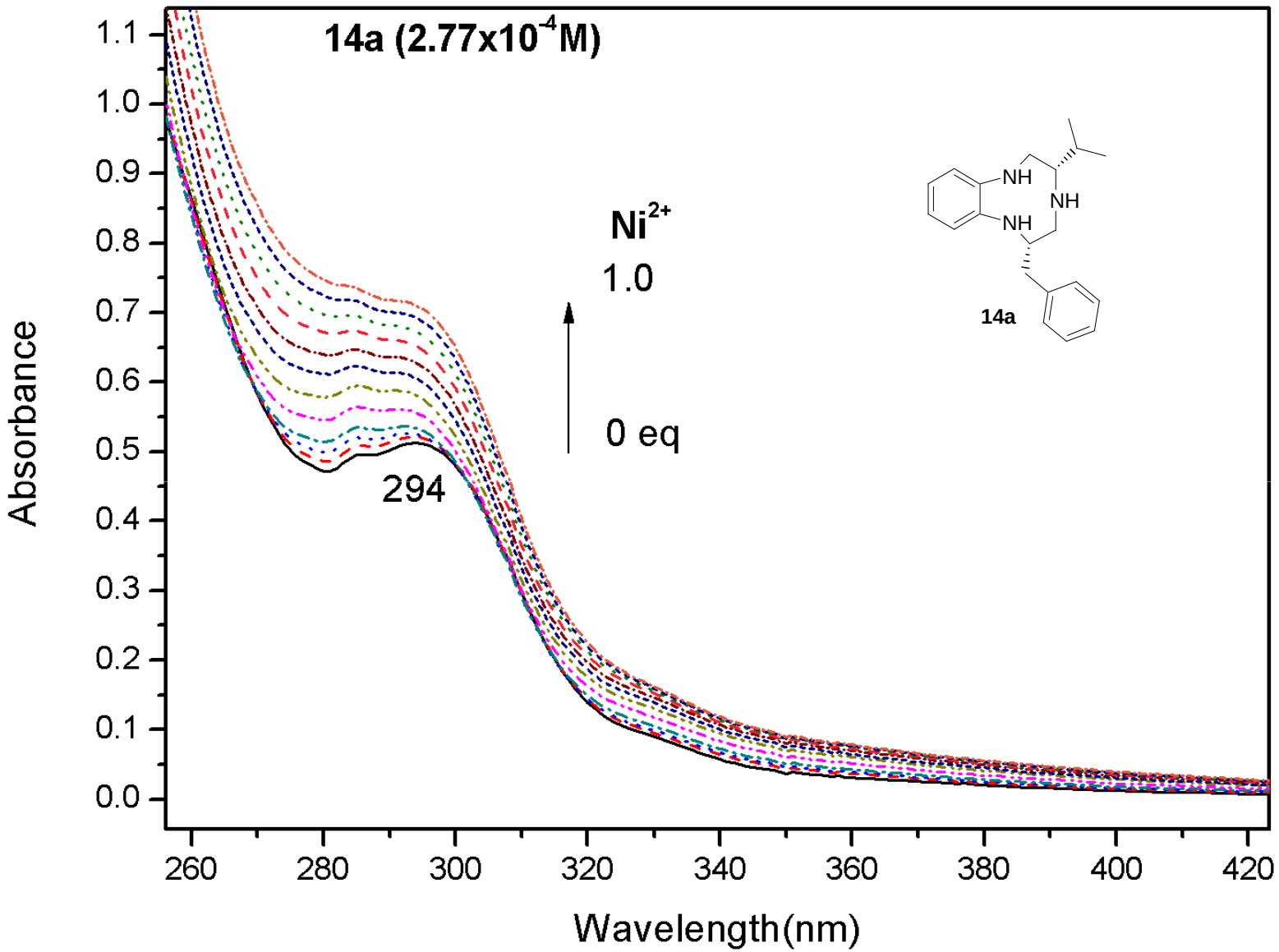


Fig. S-161: UV-visible spectra of **14a** with gradual addition of Ni^{2+} solution.

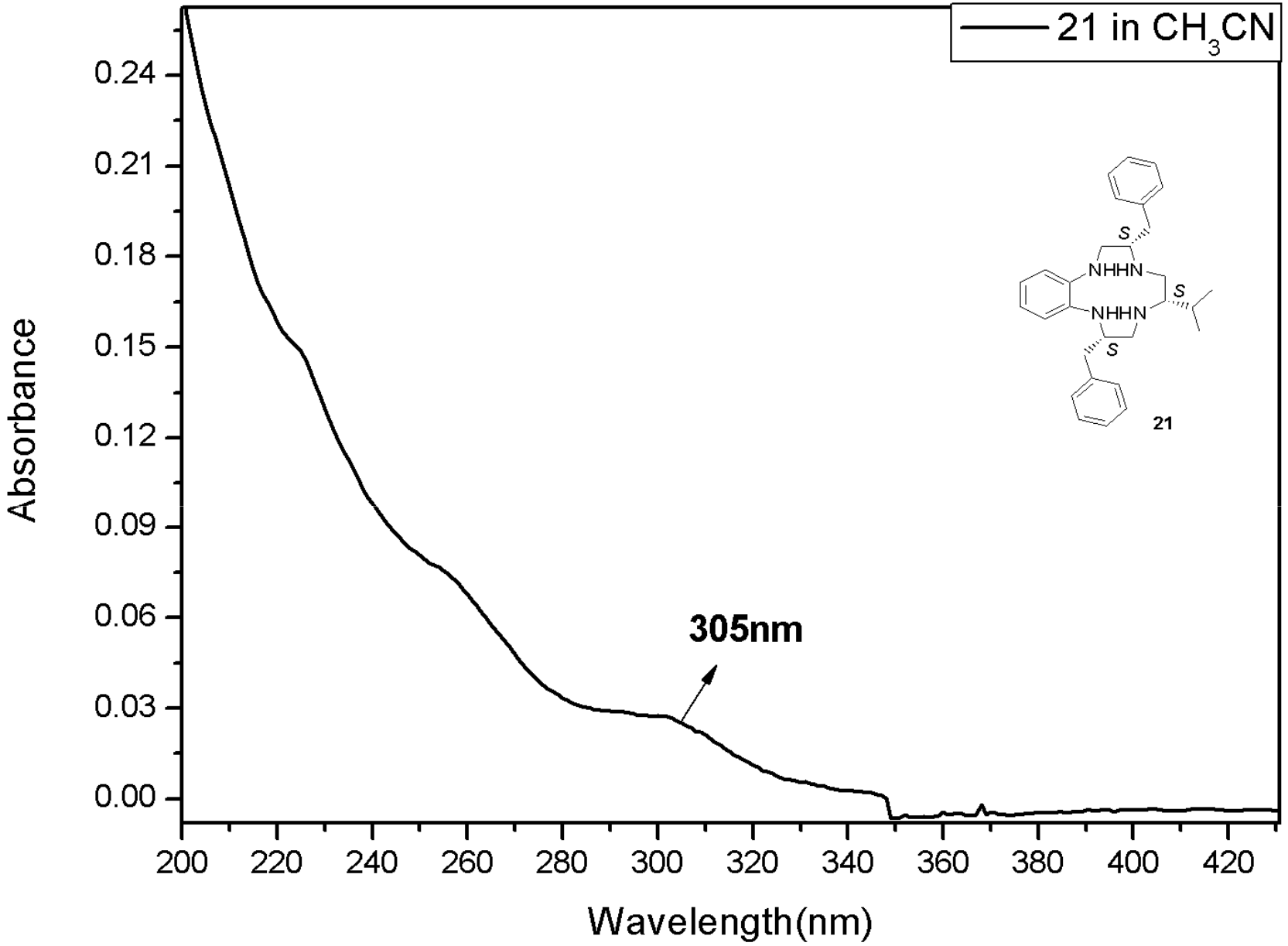


Fig. S-162: UV-visible spectra of **21** in acetonitrile.

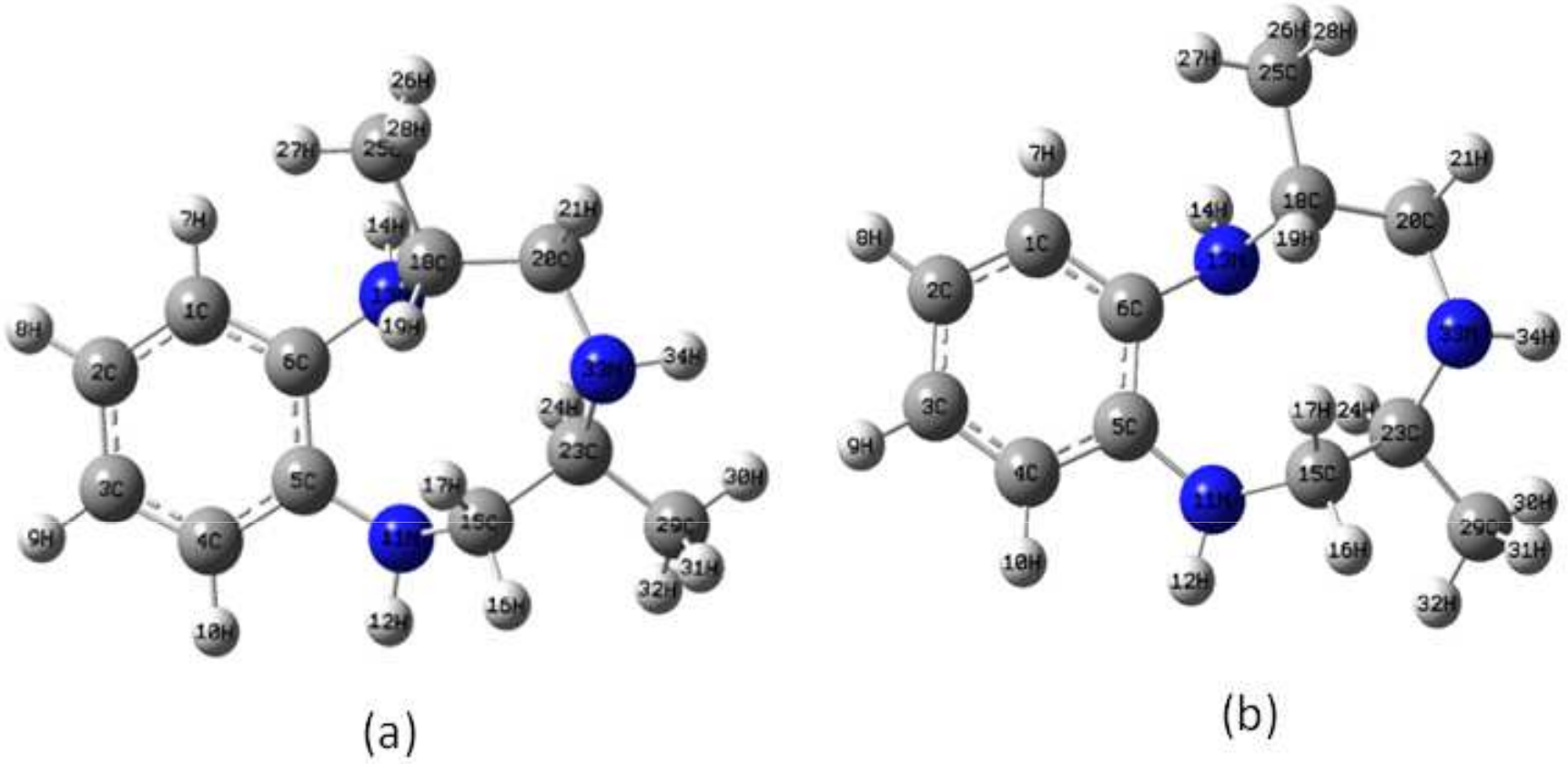


Fig. S-163: (a)**14d** optimised in PCM mode (Acetonitrile) (b) gaseous phase.

	Polarizable Continuum Model(PCM) **opt b3lyp/6-31++g(d,p) scrf=(solvent=acetonitrile)**	**gas phase** **opt b3lyp/6-31++g(d,p)**
Energy	**-397223.99 kcal/mol**	**-397212.88 kcal/mol**
Di hedral angle **C3-C4-C5-N11**	**-174.34^0**	**-175.03^0**
C2-C1-C6-N13	**172.86^0**	**173.21^0**
C6-N13-C18-C25	**-90.67^0**	**-89.80^0**
N13-C18-C20-N33	**-79.07^0**	**-76.93^0**
N11-C15-C23-N33	**135.28^0**	**135.34^0**
C18-C20-N33-C23	**60.38^0**	**60.4^0**
C15-C23-N33-C20	**-90.56^0**	**-89.80^0**
C25-C18-C20-N33	**156.78^0**	**158.53^0**
N11-C15-C23-C29	**-103.2^0**	**-103.28^0**
C3-C4-C5-N11	**-174.34^0**	**-175.03^0**
C2-C1-C6-N13	**172.86^0**	**173.21^0**
C5-N11-C15-C23	**-104.63^0**	**-103.28^0**
Bond Angle **C6-N13-C18**	**120.11^0**	**120.91^0**
C5-N11-C15	**121.92^0**	**122.44^0**
N13-C18-C25	**112.21^0**	**112.59^0**
C25-C18-C20	**110.65^0**	**110.85^0**
C20-N33-C23	**116.06^0**	**116.95^0**
N33-C23-C15	**109.66^0**	**109.36^0**
C29-C23-C15	**111.09^0**	**111.24^0**
C23-C15-N11	**115.80^0**	**115.58^0**

Fig. S-164: Comparisons of Energies, selected bond angles and dihedral angles of **14d** calculated by DFT in PCM mode and gaseous phase.

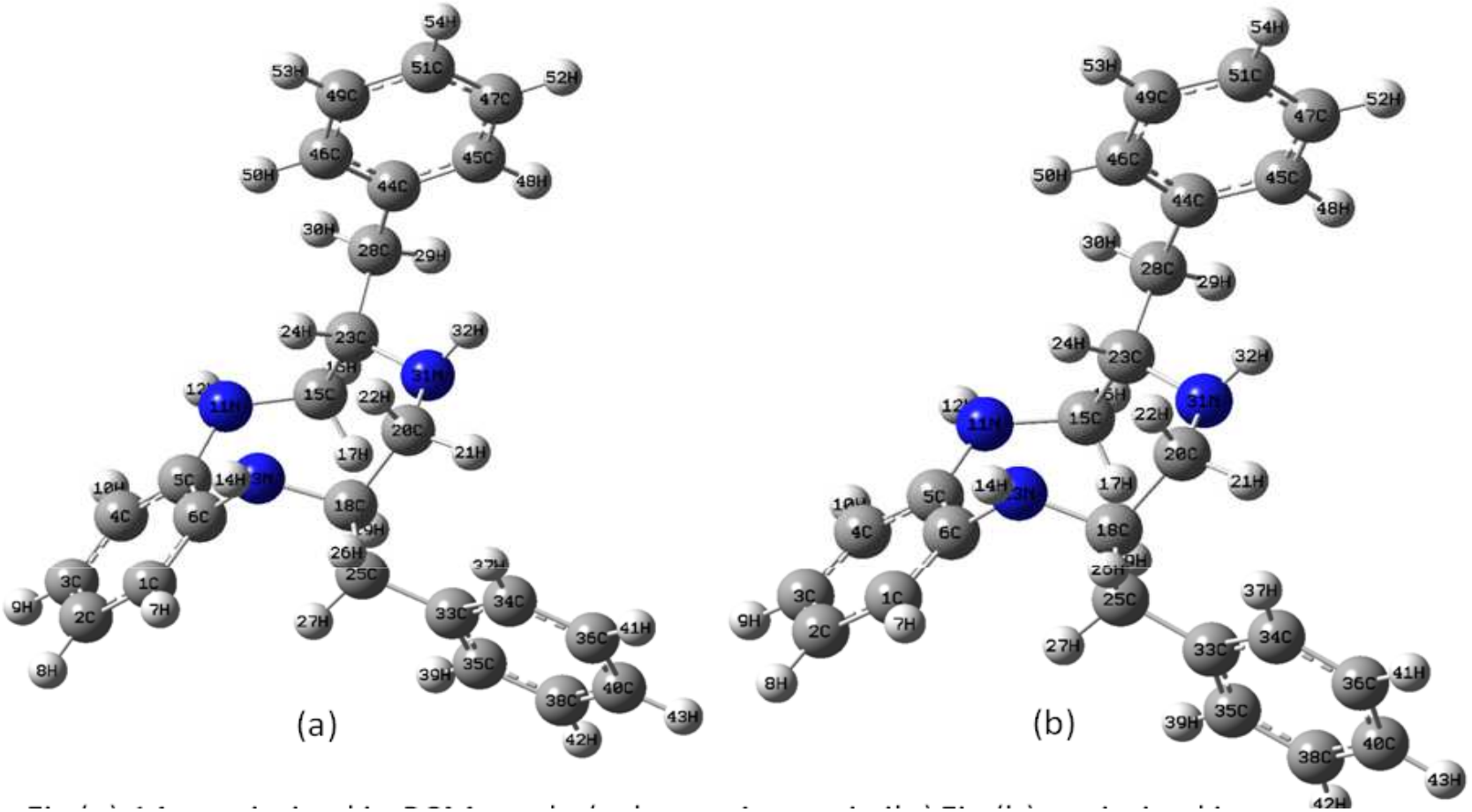


Fig. S-165: (a)**14c** optimised in PCM mode (Acetonitrile) (b) gaseous phase.

	Polarizable Continuum Model(PCM)opt b3lyp/6-31++g(d,p) scrf=(solvent=acetonitrile)	gas phase opt b3lyp/6-31++g(d,p)
Energy	-687219.46 kcal/mol	-687203.58 kcal/mol
Di hedral angle C3-C4-C5-N11	-173.96^0	-174.66^0
C2-C1-C6-N13	173.27^0	173.20^0
C4-5C-N11-15C	-134.90^0	-135.81^0
C1-C6-N13-C18	91.28^0	88.86^0
N11-C15-C23-N31	135.91^0	135.78^0
N11-C15-C23-C28	-102.3^0	-102.8^0
C6-N13-C18-C20	146.23^0	147.34^0
C5-N11-C15-C23	-103.38^0	-102.70^0
C15-C23-C28-C44	171.68^0	174.1^0
C20-C18-C25-C33	-65.84^0	-66.72^0
N13-C18-C20-N31	-79.09^0	-76.79^0
C44-C28-C20-N31	-66.92^0	-64.89^0
C15-C23-N31-C20	-91.02^0	-91.12^0
C1-C6-N13-C18	91.28^0	88.86^0
C4-C5-N11-C15	-134.98^0	-135.81^0
C18-C25-C33-C34	109.50^0	108^0
C18-C25-C33-C35	-70.73^0	-71.95^0
Bond Angle C6-N13-C18	120.35^0	120.16^0
C5-N11-C15	122.14^0	122.62^0
C18-C25-C33	115.03	115.03
N13-C18-C20	109.3^0	108.92^0
C20-N31-C23	115.89^0	116.96^0
N11-C15-C23	115.64^0	115.6^0
C15-C23-N31	109.56^0	109.5^0
C23-C28-C44	114.65^0	114.52^0
C28-C23-N31	110.66^0	110.18^0
C28-C23-C15	110.27	110.27

Fig. S-166: Comparisons of Energies, selected bond angles and dihedral angles of **14c** calculated by DFT in PCM mode and gaseous phase.

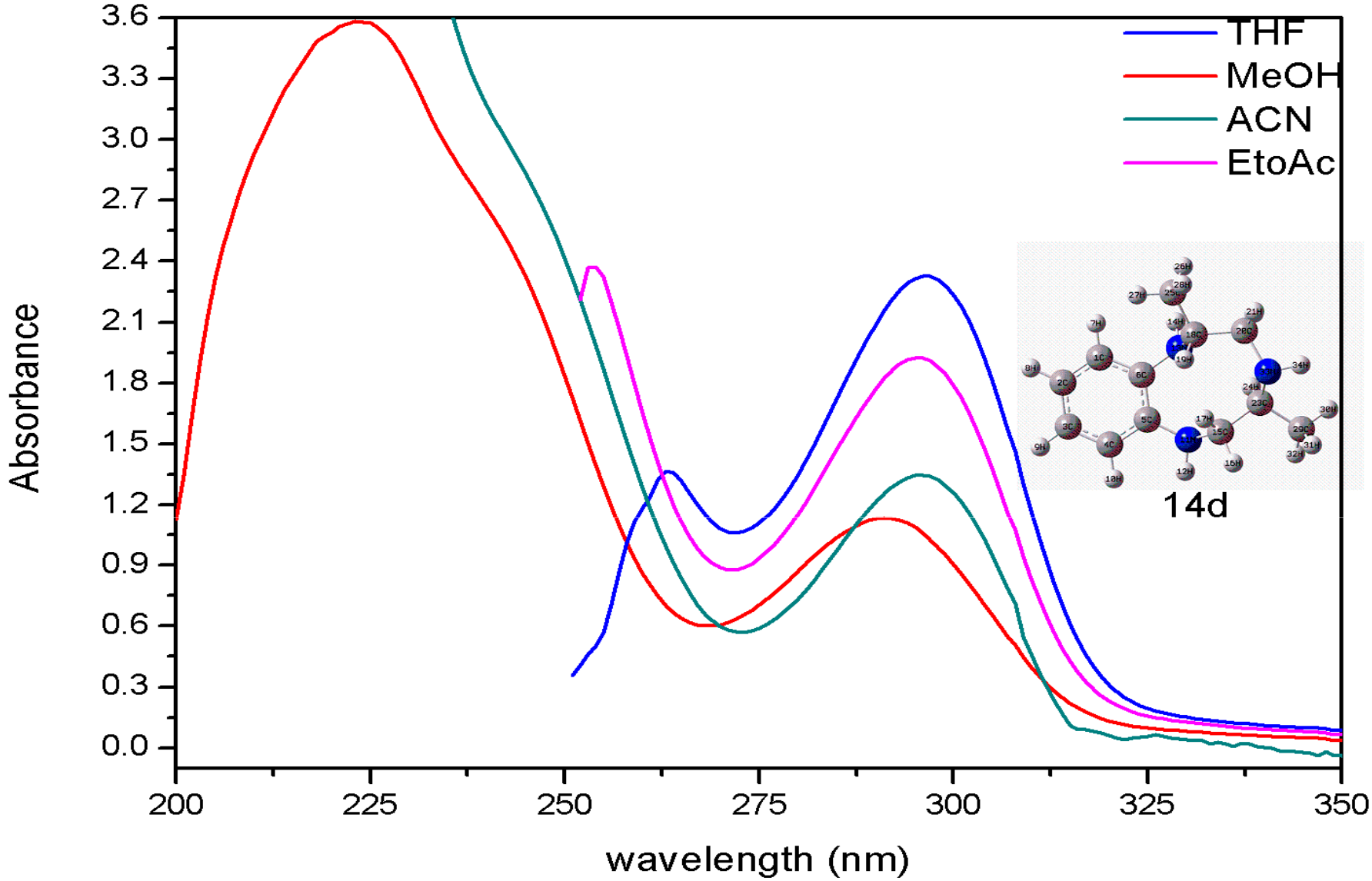


Fig. S-167: UV Visible spectra of **14d** in different solvents (THF= Tetra hydro furan, MeOH= Methanol, ACN=Acetonitrile, EtOAc= Ethyl acetate)

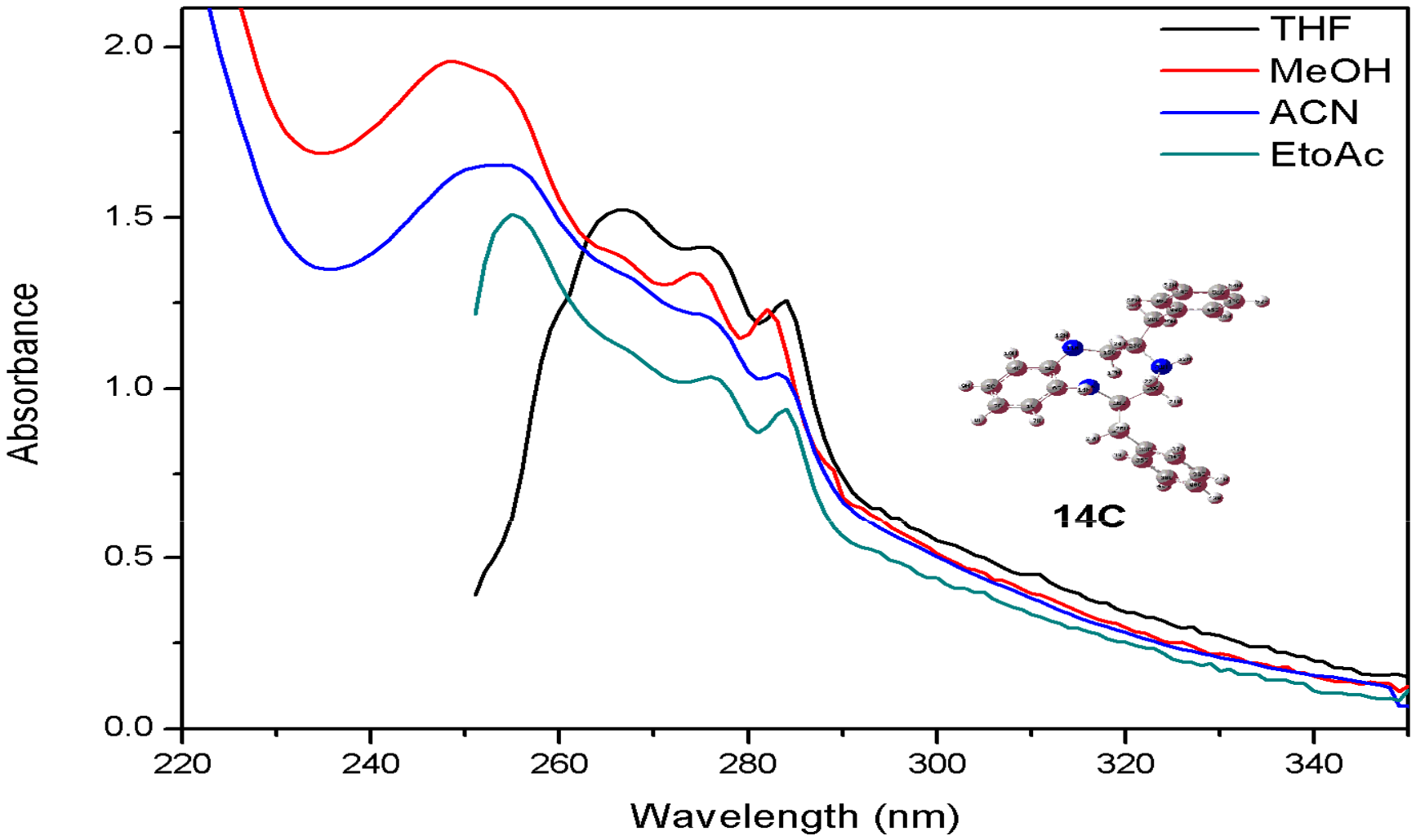


Fig. S-168: UV Visible spectra of **14c** in different solvents (THF= Tetra hydro furan, MeOH= Methanol, ACN=Acetonitrile, EtOAc= Ethyl acetate)

(2*S*)-2-(2-Nitrophenylamino)-3-phenylpropionic Acid Methyl Ester (3b). Yellow oil; yield, 65% (based on two steps); R_f = 0.53 (8.5/1.5, hexane/EtOAc); HPLC analysis: ee > 99 (t_R = 19.7 min, hexane/propanol); IR ν_{max} (neat, cm^{-1}) 3451, 2927, 2857, 2372, 1744, 1619, 1511, 1269, 750; ^1H NMR (200 MHz, $CDCl_3$) δ 8.17 (d, 1H, J = 1.6), 8.13 (d, 1H), 7.38-7.20 (m, 6H), 6.71-6.64 (m, 2H), 4.48-4.45 (m, 1H), 3.72 (s, 3H), 3.28-3.20 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 143.7, 136.1, 135.4, 132.6, 129.0, 128.7, 127.3, 126.8, 116.3, 113.6, 57.2, 52.4, 38.5; MS (ESI): *m/z* 301 $[M + H]^+$; Anal. calcd. (%) for $C_{16}H_{16}N_2O_4$: C 63.99; H, 5.37; N, 9.33; Found: C, 63.91; H, 5.41; N, 9.39.

(2*S*)-4-Methyl-2-(2-nitrophenylamino)pentanoic Acid Methyl Ester (3c). Yellow oil; yield, 64% (based on two steps); R_f = 0.53 (8.5/1.5, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3448, 2935, 2856, 2356, 1743, 1620, 1511, 1268, 748; ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, 1H, J = 1.6), 8.18 (d, 1H, J = 1.6), 7.47-7.42 (m, 1H), 6.76-6.69 (m, 2H), 4.29-4.22 (m, 1H), 3.76 (s, 3H), 1.85-1.82 (m, 3H), 1.03 (d, 3H, J = 6.3), 0.96 (d, 3H, J = 6.3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 144.2, 136.3, 132.6, 127.0, 116.2, 113.6, 54.5, 52.4, 41.6, 24.9, 22.7, 21.9; MS (ESI): *m/z* 267 $[M + H]^+$; Anal. calcd. (%) for $C_{13}H_{18}N_2O_4$: C, 58.63; H, 6.81; N, 10.52; Found: C, 58.67; H, 6.84; N, 10.55.

(2*S*,3*S*)-Methyl-3-methyl-2-(2-nitrophenylamino)pentanoic Acid Methyl Ester (3d). Yellow oil; yield, 66% (based on two steps); R_f = 0.56 (8.5/1.5, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3451, 2625, 2856, 1744, 1619, 1265, 744; ^1H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, 1H), 8.21 (dd, 1H, J_1 = 1.5, J_2 = 8.5), 7.47-7.41 (m, 1H), 6.77-6.68 (m, 2H), 4.17-4.13 (m, 1H), 3.77 (s, 3H), 2.12-2.03 (m, 1H), 1.71-1.62 (m, 1H), 1.45-1.35 (m, 1H), 1.05 (d, 3H, J = 6.9), 1.00 (t, 3H, J = 7.3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 144.4, 136.3, 132.6, 127.0, 116.1, 113.6, 60.5, 52.2, 37.8, 25.5, 15.6, 11.4; MS (ESI): *m/z* 267 $[M + H]^+$; Anal. calcd. (%) for $C_{13}H_{18}N_2O4$: C, 58.63; H, 6.81; N, 10.52; Found: C, 58.61, H, 6.88; N, 10.56.

(2*S*)-3-(1*H*-Indol-3-yl)-2-(2-nitrophenylamino)propionic Acid Methyl Ester (3e). Yellow oil; yield, 63% (based on two steps); R_f = 0.45 (8.5/1.5, hexane/EtOAc); HPLC analysis: ee > 99 (t_R = 12.9 min, hexane/propanol); IR ν_{max} (neat, cm^{-1}) 3448, 2984, 2368, 1744, 1642, 1460, 1296, 751; ^1H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, 1H, J = 6.9), 8.24 (bs, 1H), 8.16 (dd, 1H, J_1 = 1.6, J_2 = 8.9), 7.60 (d, 1H, J = 7.7), 7.40-7.34 (m, 2H), 7.24-7.12 (m, 3H), 6.70-6.65 (m, 2H), 4.61-4.55 (m, 1H), 3.72 (s, 3H), 3.55-3.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 144.0, 136.25, 136.17, 132.6, 127.0, 126.9, 123.5, 122.3, 119.6, 118.2, 116.2, 113.8, 111.4, 109.3, 56.2, 52.5, 28.6; MS (ESI): *m/z* 340 $[M + H]^+$; Anal. calcd. (%) for $C_{18}H_{17}N_3O_4$: C, 63.71; H, 5.05; N, 12.38; Found: C, 63.68; H, 5.13; N, 12.43.

(2*S*)-4-Methylsulfanyl-2-(2-nitrophenylamino)butyric Acid Methyl Ester (3g). Yellow oil; yield, 69% (based on two steps); R_f = 0.54 (8.5/1.5, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3397, 2967, 2366, 1743, 1620, 1512, 1160, 747; ^1H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, 1H, J = 7.8), 8.19 (dd, 1H, J_1 = 1.6, J_2 = 8.6), 7.47-7.42 (m, 1H), 6.82 (d, 1H, J = 8.4), 6.75-6.70 (m, 1H), 4.54-4.47 (m, 1H), 3.78 (s, 3H), 2.68-2.60 (m, 2H), 2.30-2.16 (m, 2H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 144.0, 136.2, 132.8, 126.9, 116.4, 113.7, 54.3, 52.6, 31.7, 30.0, 15.4; MS (ESI): *m/z* 285 $[M + H]^+$; Anal. calcd. (%) for $C_{12}H_{16}N_2O_4S$: C, 50.69; H, 5.67; N, 9.85; Found: C, 50.74; H, 5.64; N, 9.89.

(2*S*)-2-(2-Aminophenylamino)-4-methylpentan-1-ol (4c). Brown oil; yield, 38%; R_f = 0.52 (6.5/3.5, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3651, 3451, 2926, 2369, 1653, 1628, 1380, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 6.86-6.80 (m, 1H), 6.75-6.67 (m, 3H), 3.80-3.76 (m, 1H), 3.57-3.47 (m, 2H), 1.80-1.71 (m, 1H), 1.56-1.37 (m, 2H), 0.98 (d, 3H, J = 6.5), 0.92 (d, 3H, J = 6.5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.9, 134.3, 120.9, 118.9, 117.4, 113.1, 64.2, 52.9, 41.4, 24.9, 22.8, 22.8; MS (ESI): *m/z* 209 $[M + H]^+$; Anal. calcd. (%) for $C_{12}H_{20}N_2O$: C, 69.19; H, 9.68; N, 13.45; Found: C, 69.24; H, 9.65; N, 13.52.

(2*S*,3*S*)-2-(2-Aminophenylamino)-3-methylpentan-1-ol (4d). Brown oil; yield, 35%; R_f = 0.50 (6.5/3.5, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3654, 3450, 2925, 2369, 1628, 1380, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 6.87-6.81 (m, 1H), 6.78-6.67 (m, 3H), 3.80 (dd, 1H, J_1 = 3.9, J_2 = 11.2), 3.59 (dd, 1H, J_1 = 6.9, J_2 = 11.2), 3.44-3.38 (m, 1H), 1.77-1.70 (m, 1H), 1.64-1.56 (m, 1H), 1.33-1.19 (m, 1H), 0.95 (d, 3H, J = 6.8), 0.94 (t, 3H, J = 7.3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 134.2, 121.0, 118.7, 117.6, 113.2, 61.5, 58.9, 36.0, 26.2, 14.9, 11.8; MS (ESI): *m/z* 209 $[M + H]^+$; Anal. calcd. (%) for $C_{12}H_{20}N_2O$: C, 69.19; H, 9.68; N, 13.45; Found: C, 69.28; H, 9.63; N, 13.40.

(2*S*)-2-(2-Aminophenylamino)-3-(1*H*-Indol-3-yl)-propan-1-ol (4e). Brown oil; yield, 24%; R_f = 0.45 (6.5/3.5, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3652, 3438, 2926, 1600, 1458, 1163,750; ^1H NMR (300 MHz, $CDCl_3$) δ 8.12 (bs, 1H), 7.62 (d, 1H, J = 7.7), 7.34 (d, 1H, J = 8.0), 7.23-7.11 (m, 2H), 6.97 (d, 1H, J = 1.8), 6.87-6.71 (m, 4H), 3.85-3.74 (m, 2H), 3.60-3.55 (m, 1H), 3.15-3.06 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2, 135.2, 127.7, 122.7, 122.1, 120.7, 119.5, 118.7, 117.1, 113.9, 111.9, 111.2, 63.5, 55.1, 26.9; MS (ESI): *m/z* 282 $[M + H]^+$; Anal. calcd. (%) for $C_{17}H_{19}N_3O$: C, 72.57; H, 6.81; N, 14.94; Found: C, 72.52; H, 6.85; N, 14.98.

(2*S*)-2-(2-Aminophenylamino)-3-methylbutan-1-ol (4f). Brown oil; yield, 42%; R_f = 0.53 (6.5/3.5, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3654, 3425, 2927, 2341, 1652, 1460, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 6.86-6.80 (m, 1H), 6.72-6.66 (m, 3H), 3.78 (dd, 1H, J_1 = 4.0, J_2 =11.1), 3.58 (dd, 1H, J_1 = 6.5, J_2 =11.1), 3.33-3.27 (m, 1H), 3.06 (bs, 4H), 2.02-1.90 (m, 1H), 1.03 (d, 3H, J = 7.0), 0.98 (d, 3H, J = 7.0); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 134.2, 121.0, 118.7, 117.6, 113.3, 62.0, 60.4, 29.6, 19.3, 18. 8; MS (ESI): *m/z* 195 $[M + H]^+$; Anal. calcd. (%) for $C_{11}H_{18}N_2O$: C, 68.01; H, 9.34; N, 14.42; Found: C, 68.10; H, 9.38; N, 14.45.

(2*S*)-2-(2-Aminophenylamino)-4-methylsulfanylbutan-1-ol (4g). Brown oil; yield, 23%; R_f = 0.52 (6.5/3.5, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3651, 3422, 2926, 2341, 1658, 1461, 758; ^1H NMR (300 MHz, $CDCl_3$) δ 6.85-6.80 (m, 1H), 6.75-6.67 (m, 3H), 3.76 (dd, 1H, J_1 = 3.6, J_2 = 10.8), 3.66-3.52 (m, 2H), 3.14 (bs, 4H), 2.64-2.52 (m, 2H), 2.11 (s, 3H), 1.92-1.85 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.0, 134.9, 121.4, 119.6, 117.9, 114.0, 64.0, 54.2, 31.6, 31.4, 16.0; MS (ESI): *m/z* 227 $[M + H]^+$; Anal. calcd. (%) for $C_{11}H_{18}N_2OS$: C, 58.37; H, 8.02; N, 12.38; Found: C, 58.40; H, 8.11; N, 12.43.

(*S*)-N-[2-(1-Hydroxymethyl-2-phenylethylamino)phenyl]-4-methylbenzenesulfonamide (5b). Brown oil; yield, 76%; R_f = 0.53 (6.0/4.0, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3653, 3422, 2926, 2859, 1600, 1485, 1158, 748; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2H), 7.30-7.23 (m, 7H), 7.12-7.07 (m, 1H), 6.70 (d, 1H, *J* = 8.2), 6.52 (m, 1H), 6.44-6.43 (m, 2H), 4.72 (m, 1H), 3.77-3.74 (m, 2H), 3.51-3.46 (m, 1H), 2.92-2.77 (m, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 144.0, 138.4, 135.5, 129.6, 129.3, 129.2, 128.8, 128.4, 127.6, 126.3, 120.7, 116.7, 112.7, 62.6, 56.1, 37.6, 21.5; MS (ESI): *m/z* 397 $[M + H]^+$; Anal. calcd. (%) for $C_{22}H_{24}N_2O_3S$: C, 66.64; H, 6.10; N, 7.07; Found: C, 66.68; H, 6.17; N, 7.12.

(*S*)-N-[2-(1-Hydroxymethyl-3-methyl-butylamino)phenyl]-4-methylbenzene- sulfonamide (5c). Brown oil; yield, 75 %; R_f = 0.52 (6.0/4.0, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3658, 3431, 2924, 1634, 1159, 746; ^1H NMR (300 MHz, $CDCl_3$) δ 7.63-7.60 (m, 2H), 7.27-7.25 (m, 2H), 7.12-7.07 (m, 1H), 6.73 (d, 1H, *J* = 8.26), 6.50 (bs, 1H), 6.40-6.39 (m, 2H), 4.50 (bs, 1H), 3.81 (dd, 1H, J_1 = 3.8, J_2 = 11.4), 3.60 (bs, 1H), 3.47 (dd, 1H, J_1 = 5.0, J_2 = 11.4), 2.82 (bs, 1H), 2.43 (s, 3H), 1.79-1.65 (m, 1H), 1.47-1.32 (m, 2H), 0.95 (d, 3H, *J* = 6.5), 0.91 (d, 3H, *J* = 6.5); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.2, 144.4, 136.0, 130.0, 129.9, 129.4, 128.1, 120.7, 116.6, 112.8, 64.6, 52.9, 41.3, 25.1, 23.3, 23.0, 22.0; MS (ESI): *m/z* 363 $[M + H]^+$; Anal. calcd. (%) for $C_{19}H_{26}N_2O_3S$: C, 62.95; H, 7.23; N, 7.73; Found: C, 62.90; H, 7.28; N, 7.75.

N-(2-((2*S*,3*S*)-1-Hydroxy-3-methylpentan-2-ylamino)phenyl)-4-methylbenzene- sulfonamide (5d). Brown oil; yield, 76%; R_f = 0.53 (6.0/4.0, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3654, 3433, 2926, 1437, 1159, 746; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2H), 7.28-7.25 (m, 2H), 7.12-7.06 (m, 1H), 6.70 (d, 1H, *J* = 8.2), 6.50 (bs, 1H), 6.38-6.35 (m, 2H), 4.68 (bs, 1H), 3.81 (dd, 1H, J_1 = 3.1, J_2 = 11.6), 3.61 (dd, 1H, J_1 = 6.5, J_2 = 11.6), 3.39 (bs, 1H), 2.86 (bs, 1H), 2.43 (s, 3H), 1.71-1.55 (m, 2H), 1.27-1.17 (m, 1H), 0.96 (d, 3H, *J* = 6.6), 0.92 (t, 3H, *J* = 7.34); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.3, 144.0, 135.4, 129.5, 129.4, 128.9, 127.7, 120.0, 115.9, 112.2, 62.2, 59.0, 36.4, 25.9, 21.5, 15.3, 11.5; MS (ESI): *m/z* 363 $[M + H]^+$; Anal. calcd. (%) for $C_{19}H_{26}N_2O_3S$: C, 62.95; H, 7.23; N, 7.73; Found: C, 62.92; H, 7.27; N, 7.78.

(*S*)-N-{2-[1-Hydroxymethyl-2-(1*H*-indol-3-yl)-ethylamino] phenyl}-4-methylbenzenesulfonamide (5e): Brown oil; yield, 72%; R_f = 0.50 (6.0/4.0, hexane/ethylacetate); IR ν_{max} (neat, cm^{-1}) 3654, 3445, 2928, 1631, 1158, 746; ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (bs, 1H), 7.65-7.56 (m, 3H), 7.38 (d, 1H, *J* = 8.0), 7.25-7.08 (m, 6H), 6.75 (d, 1H, *J* = 8.2), 6.46-6.45 (m, 2H), 6.08 (bs, 1H), 4.67 (bs, 1H), 3.86 (bs, 1H), 3.76-3.72 (bs, 1H), 3.52-3.49 (bs, 1H), 3.06-3.04 (m, 2H), 2.41 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.22, 136.17, 135.0, 127.8, 122.7, 122.1, 120.8, 119.5, 119.5, 118.7, 117.2, 114.1, 111.9, 111.2, 63.4, 55.2, 26.9; MS (ESI): *m/z* 436 $[M + H]^+$; Anal. calcd. (%) for $C_{24}H_{25}N_3O_3S$: C, 66.18; H, 5.79; N, 9.65; Found: C, 66.25; H, 5.82; N, 9.70.

(*S*)-N-[2-(1-Hydroxymethyl-2-methylpropylamino)phenyl]-4-methylbenzenesulfonamide (5f). Brown oil; yield, 73%; R_f = 0.55 (6.0/4.0, hexane/ethylacetate); IR ν_{max} (neat, cm^{-1}) 3653, 3418, 2926, 1600, 1159, 751; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 7.29-7.26 (m, 2H,), 7.12-7.06 (m, 1H), 6.72 (d, 1H, *J* = 8.1), 6.39-6.29 (m, 2H), 6.24 (bs, 1H), 4.66 (bs, 1H), 3.82-3.78 (m, 1H), 3.63-3.57 (m, 1H), 3.31 (bs, 1H), 2.76 (bs, 1H), 2.44 (s, 3H), 1.95-1.84 (m, 1H), 1.01 (d, 3H, *J* = 6.9), 0.99 (d, 3H, *J* = 6.7); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 144.1, 135.3, 129.5, 128.9, 127.7, 119.8, 115.8, 112.3, 62.5, 60.5, 30.0, 21.5, 19.4, 19.3; MS (ESI): *m/z* 349 $[M + H]^+$; Anal. calcd. (%) for $C_{18}H_{24}N_2O_3S$: C, 62.04; H, 6.94; N, 8.04; Found: C, 62.10; H, 6.98; N, 8.10;

(*S*)-N-[2-(1-Hydroxymethyl-3-methylsulfanylpropylaminophenyl]-4-methylbenzenesulfonamide (5g). Brown oil; yield, 75%; R_f = 0.54 (6.0/4.0, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3654, 3420, 2926, 1602, 1325, 1162, 751; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 7.29-7.26 (m, 2H), 7.14-7.09 (m, 1H), 6.74 (d, 1H, J = 6.7), 6.50 (bs, 1H), 6.47-6.34 (m, 2H), 3.84-3.75 (m, 2H), 3.56-3.51 (m, 1H), 2.64-2.58 (m, 2H), 2.44 (s, 3H), 2.11 (s, 3H), 1.89-1.83 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.2, 144.5, 135.8, 130.03, 129.97, 129.4, 128.1, 120.7, 116.9, 113.1, 64.3, 53.8, 31.5, 31.3, 22.0, 15.9; MS (ESI): *m/z* 381 [M + H]+; Anal. calcd. (%) for $C_{18}H_{24}N_2O_3S_2$: C, 56.81; H, 6.36; N, 7.36; Found: C, 56.85; H, 6.43; N, 7.41.

(3*S*)-3-Isobutyl-1-tosyl-1,2,3,4-tetrahydroquinoxaline (6c). Light yellow oil; yield, 75%; overall yield, 13.7%; R_f = 0.56 (8.0/2.0, hexane/EtOAc); $[\alpha]_D^{30}$ -58.2 (c 0.11, MeOH), HPLC analysis: ee > 99 (t_R = 8.5 min, CH_3CN/H_2O); IR ν_{max} (neat, cm^{-1}) 3395, 2962, 1601,1495, 1342, 748; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (dd, 1H, J_1 = 1.2, J_2 = 8.2), 7.48-7.45 (m, 2H), 7.21-7.19(m, 2H), 7.01-6.96 (m, 1H), 6.73-6.67 (m, 1H), 6.48 (dd, 1H, J_1 = 1.1, J_2 = 8.0), 4.23 (dd, 1H, J_1 = 3.1, J_2 = 13. 9), 3.66 (bs, 1H), 2.88 (dd, 1H, J_1 = 10.3, J_2 = 13.8), 2.70-2.67 (m, 1H), 2.38 (s, 3H), 1.63-1.57 (m, 1H), 1.19-1.14 (m, 2H), 0.87 (d, 3H, J = 6.5), 0.80 (d, 3H, J = 6.5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 137.7, 136.5, 129.5, 127.3, 126.3, 125.8, 121.9, 117.1, 114.6, 49.3, 45.5, 42.9, 24.2, 22.9, 22.2, 21.4; MS (ESI): *m/z* 345 $[M + H]^+$; Anal. calcd. (%) for $C_{19}H_{24}N_2O_2S$: C, 66.25; H, 7.02; N, 8.13; Found: C, 66.29; H, 7.10; N, 8.11.

***(3S,4S)*-3-Secbutyl-1-tosyl-1,2,3,4-Tetrahydroquinoxaline (6d).** Yellow semi-solid; yield, 74%; overall yield, 13.0%; R_f = 0.54 (8.0/2.0, hexane/EtOAc); $[\alpha]_D^{30}$ +35.7 (c 0.11, MeOH), HPLC analysis: ee > 99 (t_R = 12.3 min, CH_3CN/H_2O); IR ν_{max} (KBr, cm^{-1}) 3399, 2964, 1603, 1497, 1346, 750; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (dd, 1H, J_1 = 1.3, J_2 = 8.2), 7.49-7.47 (m, 2H), 7.23-7.20 (m, 2H), 7.02-6.96 (m, 1H), 6.73-6.67 (m, 1H), 6.50 (dd, 1H, J_1 = 1.3, J_2 = 8.0), 4.26 (dd, 1H, J_1 = 3.0, J_2 = 13.9), 3.67 (bs, 1H), 3.00 (dd, 1H, J_1 = 10.4, J_2 = 14.0), 2.59-2.57 (m, 1H), 2.40 (s, 3H), 1.41-1.19 (m, 3H), 0.88 (d, 3H, J = 6.7), 0.86 (t, 3H, J = 7.4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 138.2, 136.6, 129.5, 127.3, 126.3, 125.7, 122.0, 117.0, 114.6, 51.1, 46.1, 37.6, 25.2, 21.5, 13.9, 11.1; MS (ESI): *m/z* 345 $[M + H]^+$; Anal. calcd. (%) for $C_{19}H_{24}N_2O_2S$: C, 66.25; H, 7.02; N, 8.13; Found: C, 66.29; H, 7.06; N, 8.19.

(3*S*)-3-(1*H*-Indol-3-ylmethyl)-1-tosyl-1,2,3,4-tetrahydroquinoxaline (6e). Yellow, solid; mp 172-174 ^oC; yield, 72%; overall yield, 7.8%; R_f = 0.50 (8.0/2.0, hexane/EtOAc); $[\alpha]_D^{30}$ -53.1 (c 0.11, MeOH), HPLC analysis: ee > 99 (t_R = 11.9 min, CH_3CN/H_2O); IR ν_{max} (KBr, cm^{-1}) 3373, 2923, 1704, 1343, 1235, 1163, 750; ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (bs, 1H), 7.72 (dd, 1H, J_1 = 1.3, J_2 = 8.3), 7.42-7.37 (m, 3H), 7.33-7.22 (m, 2H), 7.15-7.09 (m, 3H), 7.02 (d, 1H, J = 2.1), 6.98-6.92 (m, 1H), 6.73-6.66 (m, 1H), 6.37 (dd, 1H, J_1 = 1.3, J_2 = 8.0), 4.34-4.33 (m, 1H), 3.78 (bs, 1H), 3.09 (dd, 1H, J_1 = 10.4, J_2 = 13.8), 3.01-2.84 (m, 2H), 2.60 (dd, 1H, J_1 = 8.5, J_2 = 13.8), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 137.8, 136.6, 135.9, 129.6, 127.1, 126.9, 126.3, 125.7, 123.1, 122.0, 121.6, 119.1, 118.5, 117.0, 114.6, 111.4, 50.3, 46.6, 29.8, 21.4; MS (ESI): *m/z* 418 $[M + H]^+$; Anal. calcd. (%) for $C_{24}H_{23}N_3O_2S$: C, 69.04; H, 5.55; N, 10.06; Found: C, 69.10; H, 5.63; 10.13.

(3*S*)-3-Isopropyl-1-tosyl-1,2,3,4-tetrahydroquinoxaline (6f). Yellow, semi-solid; yield, 75%; overall yield, 15.6%; R_f = 0.54 (8.0/2.0, hexane/EtOAc); $[\alpha]_D^{30}$ -45.9 (c 0.12, MeOH), HPLC analysis: ee > 99 (t_R = 32.5 min, hexane/propanol); IR ν_{max} (KBr, cm^{-1}) 3404, 2962, 1602, 1499, 1346, 1162, 751; ^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (dd, 1H, J_1 = 1.0, J_2 = 8.2), 7.49-7.46 (m, 2H), 7.22-7.19 (m, 2H), 7.01-6.95 (m, 1H), 6.71-6.66 (m, 1H), 6.51 (dd, 1H, J_1 = 0.9, J_2 = 8.1), 4.27 (dd, 1H, J_1 = 3.2, J_2 = 13.9), 3.7 (bs, 1H), 3.00 (dd, 1H, J_1 = 10.4, J_2 = 13.9), 2.46-2.42 (m, 1H), 2.39 (s, 3H), 1.61-1.45 (m, 1H), 0.90 (d, 3H, J = 6.6), 0.89 (d, 3H, J = 6.9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 138.1, 136.4, 129.5, 127.3, 126.2, 125.5, 121.9, 117.0, 114.6, 52.7, 46.6, 30.8, 21.5, 18.1, 17.7; MS (ESI): *m/z* 331 $[M + H]^+$; Anal. calcd. (%) for $C_{18}H_{22}N_2O_2S$: C, 65.42; H, 6.71; N, 8.48; Found: C, 65.52; H, 6.75; N, 8.59.

(3*S*)-3-(2-Methylsulfanylethyl)-1-tosyl-1,2,3,4-tetrahydro quinoxaline (6g). Yellow, semi-solid; yield, 74%; overall yield, 8.8%; R_f = 0.52 (8.0/2.0, hexane/ethylacetate); $[\alpha]_D^{30}$ +12.03 (c 0.13, MeOH), HPLC analysis: ee > 99 (t_R = 11.0 min, CH_3CN/H_2O); IR ν_{max} (KBr, cm^{-1}) 3411, 2928, 2375, 1601,1493, 1163, 748; ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, 1H, J_1 = 0.9, J_2 = 8.1), 7.51-7.48 (m, 2H), 7.23-7.20 (m, 2H), 7.00-6.95 (m, 1H), 6.73-6.67 (m, 1H), 6.49 (dd, 1H, J_1 = 1.0, J_2 = 8.0), 4.24 (dd, 1H, J_1 = 3.0, J_2 = 13.7), 3.96 (bs, 1H), 3.05 (dd, 1H, J_1 = 10.0, J_2 = 13.7), 2.93-2.85 (m, 1H), 2.57-2.46 (m, 2H), 2.39 (s, 3H), 2.10 (s, 3H), 1.74-1.54 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 137.4, 136.4, 129.6, 127.2, 126.2, 125.2, 122.0, 117.4, 114.8, 48.7, 47.1, 32.7, 30.1, 21.5, 15.6; MS (ESI): *m/z* 363 $[M + H]^+$; Anal. calcd. (%) for $C_{18}H_{22}N_2O_2S_2$: C, 59.64; H, 6.12; N, 7.73; Found: C, 59.68; H, 6.19; N, 7.75.

(*S*)-2-(2-Nitro-phenylamino)-3-phenyl-propan-1-ol (7b). This product was isolated as yellow oil. Yield, 68%, R_f = 0.50 (7/3, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3361, 2949, 1618, 1508, 1260, 1027, 744; ^1H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, 1H, J = 8.2), 8.06 (dd, 1H, J_1 = 1.4, J_2 = 8.8), 7.35-7.16 (m, 6H), 6.86 (d, 1H, J = 8.6), 6.58-6.53 (m, 1H), 3.99-3.91 (m, 1H), 3.77-3.67 (m, 2H), 3.05-2.88 (m, 2H), 2.62 (bs, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.9, 137.3, 136.1, 129.2, 128.7, 127.0, 126.8, 115.5, 114.1, 63.4, 55.5, 37.6; MS (ESI): *m/z* 273 $[M + H]^+$; Anal. calcd. (%) for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92; N, 10.29; Found: C, 66.21; H, 5.85; N, 10.32.

(*S*)-3-Methyl-2-(2-nitro-phenylamino)-butan-1-ol (7c): This product was isolated as yellow oil. yield, 66%, R_f = 0.48 (7/3, hexane/EtOAc), IR ν_{max} (neat, cm^{-1}) 3375, 3022, 2364, 1586, 1217, 770; ^1H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, 1H, J = 8.7), 7.98 (dd, 1H, J_1 = 1.1, J_2 = 8.6), 7.29-7.24 (m, 1H), 6.85 (d, 1H, J = 8.7), 6.50-6.45 (m, 1H), 3.70-3.59 (m, 2H), 3.51- 3.43 (m, 1H), 2.44 (bs, 1H), 2.05-1.92 (m, 1H), 0.95 (d, 3H, J = 6.6), 0.93 (d, 3H, J = 6.5); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.1, 136.0, 132.0, 127.1, 115.1, 114.4, 62.8, 59.9, 29.7, 19.6, 18.4; MS (ESI): *m/z* 225 $[M + H]^+$; Anal. calcd. (%) for $C_{11}H_{16}N_2O_3$: C, 58.91; H, 7.19; N, 12.49; Found: C, 58.98; H, 7.11; N, 12.56.

(*S*)-2-Benzyl-1,2,3,4-tetrahydroquinoxaline (8b). Brown oil; yield, 68%; overall yield, 10.8%; R_f = 0.53 (8.0/2.0, hexane/EtOAc); $[\alpha]_D^{30}$ -293.6 (c 0.10, MeOH), HPLC analysis: ee > 99 (t_R = 8.8 min, CH_3CN/H_2O); IR ν_{max} (neat, cm^{-1}) 3426, 3023, 2362, 1638, 1216, 762; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41-7.26 (m, 5H), 6.64-6.45 (m, 4H), 3.68-3.61 (m, 1H), 3.45-3.40 (m, 3H), 3.20 (dd, 1H, J_1 = 7.1, J_2 = 10.7), 2.89 (dd, 1H, J_1 = 5.5, J_2 = 13.3), 2.76 (dd, 1H, J_1 = 8.5, J_2 = 13.3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 133.2, 133.0, 129.2, 128.6, 126.6, 118.75, 118.68, 114.5, 114.4, 51.2, 46.2, 40.5; MS (ESI): *m/z* 225 $[M + H]^+$; Anal. calcd. (%) for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49; Found: C, 80.41; H, 7.24; N, 12.41.

(S)-Methyl-4-methyl-2-(4-methyl-N-((S)-2-(2-nitrophenylamino)-3-phenylpropyl)phenylsulfonamido)pentanoate (10c). Yellow oil; yield, 73%; R_f = 0.51 (8.0/2.0, hexane/EtOAc); IR ν_{max} (neat, cm^1) 3024, 2959, 1740, 1507, 1216, 1156, 761; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14-8.11 (m, 2H), 7.65-7.62 (m, 2H), 7.43-7.37 (m, 1H), 7.29-7.21 (m, 7H), 7.05 (dd, 1H, *J* = 8.5), 6.65-6.60 (m, 1H), 4.55-4.39 (m, 2H), 3.54 (dd, 1H, J_1 = 6.6, J_2 = 15.4), 3.41 (s, 3H), 3.34 (dd, 1H, J_1 = 7.3, J_2 = 15.4), 3.19 (dd, 1H, J_1 = 5.3, J_2 = 13.8), 2.73 (dd, 1H, J_1 = 8.4, J_2 = 13.8), 2.40 (s, 3H), 1.70-1.59 (m, 1H), 1.48-1.39 (m, 2H), 0.91 (d, 3H, *J* = 6.1), 0.90 (d, 3H, *J* = 6.3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 144.8, 143.8, 137.4, 136.1, 135.7, 132.3, 129.5, 129.1, 128.6, 127.5, 126.9, 126.7, 115.5 114.2, 58.5, 54.3, 52.0, 49.0, 39.4, 39.2, 24.7, 22.4, 21.9, 21.5; MS (ESI): m/z 576 $[M + Na]^+$; Anal. calcd. (%) for $C_{29}H_{35}N_3O_6S$: C, 62.91; H, 6.37; N, 7.59; Found: C, 62.95; H, 6.42; N, 7.61.

(S)-Methyl-2-(4-methyl-N-((S)-2-(2-nitrophenylamino)-3-phenylpropyl)phenylsulfonamido)-3-phenylpropanoate (10d). Yellow oil; yield, 76%; R_f = 0.50 (8.0/2.0, hexane/EtOAc); IR ν_{max} (neat, cm^1) 3021, 2361, 1739, 1509, 1216, 760; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.13-8.06 (m, 2H), 7.55-7.51 (m, 2H), 7.25-7.18 (m, 11H), 7.11-7.07 (m, 2H), 6.94 (d, 1H, *J* = 8.6), 6.64-6.65 (m, 1H), 4.79-4.71 (m, 1H), 4.45-4.31 (m, 1H), 3.55-3.50 (m, 1H), 3.31 (s, 3H), 3.25-3.14 (m, 1H), 3.09-2.99 (m, 2H), 2.86-2.73 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.5, 144.6, 143.8, 137.2, 136.0, 135.9, 135.8, 132.3, 129.5, 129.3, 129.1, 128.9, 128.6, 128.5, 127.4, 127.1, 127.0, 126.8, 126.7, 115.5, 114.2, 61.5, 54.0, 52.0, 48.9, 39.6, 36.4, 21.4; MS (ESI): m/z 587 $[M + H]^+$; Anal. calcd. (%) for $C_{32}H_{33}N_3O_6S$: C, 65.40; H, 5.66; N, 7.15; Found: C, 65.48; H, 5.64; N, 7.21.

(S)-Methyl-3-methyl-2-(4-methyl-N-((S)-2-(2-nitrophenylamino)-3-phenylpropyl)phenylsulfonamido)butanoate (10b). Yellow oil; yield, 72%; R_f = 0.53 (8.0/2.0, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3021, 2360, 1736, 1601, 1216, 761; ^1H NMR (300 MHz, $CDCl_3$) δ 8.12-8.07 (m, 2H), 7.63-7.61 (m, 2H), 7.33-7.21 (m, 6H), 7.15-7.13 (m, 2H), 6.85 (d, 1H, *J* = 8.9), 6.62-6.57 (m, 1H), 4.46-4.37 (m, 1H), 4.15-4.10 (m, 1H), 3.63-3.58 (m, 2H), 3.48 (s, 3H), 3.11 (dd, 1H, J_1 = 5.5, J_2 = 14.0), 2.78 (dd, 1H, J_1 = 7.3, J_2 = 14.0), 2.34 (s, 3H), 2.03-1.98 (m, 1H), 0.98 (d, 3H, *J* = 6.5), 0.89 (d, 3H, *J* = 6.5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 144.5, 143.6, 137.2, 136.4, 135.9, 132.2, 129.6, 129.3, 129.1, 128.6, 127.3, 127.2, 127.0, 126.8, 115.3, 113.9, 66.2, 53.2, 51.7, 48.5, 39.3, 29.0, 21.5, 19.9, 19.2; MS (ESI): m/z 562 $[M + Na]^+$; Anal. calcd. (%) for $C_{28}H_{33}N_3O_6S$: C, 62.32; H, 6.16; N, 7.79; Found: C, 62.43; H, 6.19; N, 7.75.

(S)-Methyl-2-(4-methyl-N-((S)-2-(2-nitrophenylamino)propyl)phenylsulfonamido)propanoate (10e). Yellow semi-solid; yield, 74%; R_f = 0.51 (8.0/2.0, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3360, 3023, 2923, 1742, 1507, 1346, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 8.17 (dd, 1H, J_1 = 1.5, J_2 = 8.6), 7.99 (d, 1H, *J* = 7.7), 7.67-7.65 (m, 2H), 7.52-7.46 (m, 1H), 7.25-7.22 (m, 2H), 7.15 (d, 1H, *J* = 8.6), 6.70-6.64 (m, 1H), 4.67 (q, 1H, *J* = 7.3), 4.30-4.23 (m, 1H), 3.55 (dd, 1H, J_1 = 5.7, J_2 = 15.0), 3.45 (s, 3H), 3.07 (dd, 1H, J_1 = 8.8, J_2 = 15.0), 2.38 (s, 3H), 1.46 (d, 3H, *J* = 7.3), 1.37 (d, 3H, *J* = 6.3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.5, 144.5, 143.8, 136.3, 135.9, 129.5, 127.3, 126.9, 115.5, 114.3, 55.9, 52.1, 50.2, 47.8, 21.5, 18.9, 17.1; MS (ESI): m/z 436 $[M + H]^+$; Anal. calcd. (%) for $C_{20}H_{25}N_3O_6S$: C, 55.16; H, 5.79; N, 9.65; Found: C, 55.11; H, 5.75; N, 9.69.

(*S*)-Methyl-4-methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)phenylamino)-3-phenylpropyl)phenyl sulfonamido)pentanoate (11c). Brown oil; yield, 66%, (based on two steps); R_f = 0.53 (7.5/2.5, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3419, 3022, 1738, 1216, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2H), 7.53-7.50 (m, 2H), 7.33-7.12 (m, 9H), 7.09-7.05 (m, 2H), 6.63-6.54 (m, 3H), 4.61-4.58 (m, 1H), 4.48-4.44 (m, 1H), 3.70-3.67 (m, 1H), 3.39 (dd, 1H, J_1 = 3.8, J_2 = 15.6), 3.31 (s, 3H), 3.11 (dd, 1H, J_1 = 9.6, J_2 = 15.6), 2.74 (dd, 1H, J_1 = 4.6, J_2 = 14.0), 2.43 (s, 3H), 2.39 (s, 3H), 2.11 (dd, 1H, J_1 = 8.6, J_2 = 14.0), 1.62-1.38 (m, 3H), 0.82 (d, 3H, J = 6.1), 0.81 (d, 3H, J = 5.8); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 143.6, 143.4, 142.8, 137.9, 137.4, 136.1, 129.4, 129.0, 128.6, 128.4, 128.3, 127.5, 127.4, 126.5, 121.6, 117.0, 111.2, 57.9, 54.3, 52.0, 48.0, 39.1, 38.7, 24.2, 22.6, 21.54, 21.48; MS (ESI): *m/z* 700 $[M + Na]^+$; Anal. calcd. (%) for $C_{36}H_{43}N_3O_6S_2$: C, 63.79; H, 6.39; N, 6.20; Found: C, 63.81; H, 6.42; N, 6.28.

***(S)*-Methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido)phenylamino)-3-phenylpropyl) phenylsulfonamido)-3-phenylpropanoate (11d).** Brown oil; yield, 62%, (based on two steps); R_f = 0.51 (7.5/2.5, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3022, 2926, 2360, 1738, 1600, 1216, 759; ^1H NMR (200 MHz, $CDCl_3$) δ 7.75-7.71 (m, 2H), 7.37-7.07 (m, 16H), 7.02-6.92 (m, 3H), 6.61-6.53 (m, 3H), 4.76-4.69 (m, 1H), 4.50-4.46 (m, 1H), 3.82-3.78 (m, 1H), 3.22 (s, 3H), 3.18-3.05 (m, 2H), 2.83-2.72 (m, 2H), 2.41 (s, 3H), 2.36 (s, 3H), 2.28-2.09 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.3, 143.5, 142.9, 137.9, 137.3, 136.1, 129.5, 129.4, 129.1, 128.9, 128.61, 128.56, 128.4, 128.2, 127.6, 127.4, 126.9, 126.5, 121.9, 117.3, 111.8, 61.2, 54.2, 52.1, 48.3, 39.1, 36.1, 21.55, 21.48; MS (ESI): m/z 712 $[M + H]^+$, 734 $[M + Na]^+$; Anal. calcd. (%) for $C_{39}H_{41}N_3O_6S_2$: C, 65.80; H, 5.81; N, 5.90; Found: C, 65.86; H, 5.86; N, 5.95.

N-((*S*)-1-Hydroxy-4-methylpentan-2-yl)-4-methyl-N-((*S*)-2-(2-(4-methylphenylsulfonamido) phenylamino)-3-phenyl propyl)benzenesulfonamide (12c). Brown oil; yield, 65%; R_f = 0.54 (4.0/3.0, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3692, 3021, 2361, 1216, 763; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2H), 7.39-7.24 (m, 9H), 7.15-7.05 (m, 4H), 6.84 (d, 1H, *J* = 8.1), 6.55-6.48 (m, 2H), 4.32-4.29 (m, 1H), 3.99-3.94 (m, 1H), 3.70 (dd, 1H, J_1 = 3.7, J_2 = 12.2), 3.57-3.53 (m, 1H), 3.23 (dd, 1H, J_1 = 2.4, J_2 = 15.2), 3.01 (dd, 1H, J_1 = 4.0, J_2 = 14.0), 2.86 (dd, 1H, J_1 = 10.4, J_2 = 15.1), 2.42-2.33 (m, 7H), 1.41-1.35 (m, 1H), 1.19-1.13 (m, 2H), 0.79 (d, 3H, *J* = 6.6), 0.75 (d, 3H, *J* = 6.6); MS (ESI): *m/z* 650 $[M + H]^+$, 672 $[M + Na]^+$; Anal. calcd. (%) for $C_{35}H_{43}N_3O_5S_2$: C, 64.69; H, 6.67; N, 6.47; Found: C, 64.65; H, 6.72; N, 6.56.

N-((S)-1-Hydroxy-3-phenylpropan-2-yl)-4-methyl-N-((S)-2-(2-(4-methylphenylsulfonamido) phenylamino)-3-phenyl propyl)benzenesulfonamide (12d). Brown oil; yield, 64%; R_f = 0.52 (7.0/3.0, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3661, 3022, 2927, 1600, 1216, 759; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.65 (m, 2H), 7.42-7.37 (m, 4H), 7.32-7.19 (m, 9H), 7.11-7.09 (m, 3H), 7.05-7.02 (m, 2H), 6.94-6.91 (m, 2H), 6.52-6.51 (m, 1H), 4.41 (bs, 1H), 4.18-4.11 (m, 1H), 3.58-3.53 (m, 2H), 3.41-3.35 (m, 1H), 3.09-3.00 (m, 2H), 2.60-2.46 (m, 2H), 2.42 (s, 3H), 2.40-2.38 (m, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.5, 143.9, 143.4, 138.0, 137.4, 136.5, 136.2, 129.6, 129.3, 129.1, 129.0, 128.6, 128.1, 127.7, 127.3, 126.6, 126.5, 122.2, 118.1, 113.5, 61.9, 61.7, 55.3, 47.3, 39.6, 35.0, 21.6, 21.5; MS (ESI): m/z 684 $[M + H]^+$; Anal. calcd. (%) for $C_{38}H_{41}N_3O_5S_2$: C, 66.74; H, 6.04; N, 6.14; Found: C, 66.71; H, 6.11; N, 6.10.

N-((S)-1-Hydroxypropan-2-yl)-4-methyl-N-((S)-2-(2-(4-methylphenylsulfonamido)phenylamino) propyl)benzenesulfonamide (12e). Brown oil; yield, 57%, (based on three steps); R_f = 0.46 (7.0/3.0, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3663, 3023, 2928, 1597, 1216, 761; ^1H NMR (300 MHz, $CDCl_3$) δ 7.71-7.69 (m, 2H), 7.64-7.61 (m, 2H), 7.27-7.17 (m, 5H), 7.09-7.04 (m, 1H), 6.70 (d, 1H, *J* = 7.9), 6.61 (dd, 1H, J_1 = 1.4, J_2 = 7.8), 6.53-6.47 (m, 1H), 4.08-3.99 (m, 2H), 3.63-3.54 (m, 2H), 3.32 (dd, 1H, J_1 = 3.6, J_2 = 15.2), 2.82 (dd, 1H, J_1 = 10.1, J_2 = 15.2), 2.39 (s, 3H), 2.35 (s, 3H), 1.93 (bs, 1H), 1.04 (d, 3H, *J* = 6.3), 0.84 (d, 3H, *J* = 6.8); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.9, 143.6, 143.4, 137.23, 136.19, 129.6, 129.4, 128.6, 127.8, 127.4, 127.1, 122.5, 117.9, 113.1, 63.9, 55.8, 49.1, 48.7, 21.5, 21.4, 18.2, 13.4; MS (ESI): m/z 532 $[M + H]^+$; Anal. calcd. (%) for $C_{26}H_{33}N_3O_5S_2$: C, 58.73; H, 6.26; N, 7.90; Found: C, 58.78; H, 6.18; N, 7.94.

N-((S)-1-Hydroxy-3-methylbutan-2-yl)-4-methyl-N-((S)-3-methyl-2-(2-(4-methylphenylsulfona mido)phenylamino) butyl)benzenesulfonamide (12f). Brown oil; yield, 54%, (based on three steps); R_f = 0.50 (7.0/3.0, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3667, 3029, 2929, 1603, 1217, 759; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70-7.63 (m, 4H), 7.28-7.23 (m, 2H), 7.07-7.05 (m, 2H), 6.95-6.90 (m, 1H), 6.77 (bs, 1H), 6.55-6.40 (m, 2H), 6.19 (d, 1H, *J* = 8.0), 4.84 (bs, 1H), 3.71-3.60 (m, 4H), 3.38 (bs, 1H), 3.07-2.99 (m, 1H), 2.40 (s, 3H), 2.29 (s, 3H), 1.89-1.87 (m, 2H), 0.99-0.97 (m, 6H), 0.85 (d, 3H, *J* = 6.7), 0.82 (d, 3H, *J* = 6.9); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.1, 143.7, 142.9, 139.2, 136.5, 129.5, 129.3, 128.4, 128.0, 127.5, 127.0, 121.7, 117.1, 112.8, 67.0, 62.3, 55.8, 45.2, 29.8, 27.7, 21.5, 21.4, 20.7, 20.2, 18.6, 16.6; MS (ESI): m/z 588 $[M + H]^+$; Anal. calcd. (%) for $C_{30}H_{41}N_3O_5S_2$: C, 61.30; H, 7.03; N, 7.15; Found: C, 61.36; H, 7.11; N, 7.10.

(3*S*,6*S*)-6-Benzyl-3-isopropyl-1,4-ditosyl-2,3,4,5,6,7-hexahydro-1H-benzo[b] [1,4,7]triazonine (13b). Light brown semi-solid; yield, 73%; R_f = 0.50 (8.0/2.0, hexane/EtOAc);); $[\alpha]_D^{30}$ -147.0 (c 0.11, MeOH), HPLC analysis: ee > 99 (t_R = 21.0 min, hexane/propanol); IR ν_{max} (KBr, cm^{-1}) 3024, 2926, 2869, 1493, 1217, 765; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (bs, 1H), 7.79-7.76 (m, 2H), 7.61 (dd, 1H, J_1 = 1.0, J_2 = 8.1), 7.49-7.46 (m, 2H), 7.28-7.20 (m, 7H), 7.17-7.11 (m, 1H), 7.01-6.96 (m, 1H), 6.79-6.76 (m, 3H), 3.62-3.56 (m, 2H), 2.92-2.83 (m, 1H), 2.73-2.69 (m, 1H), 2.64-2.59 (m, 1H), 2.58-2.52 (m, 1H), 2.47-2.42 (m, 4H), 2.27 (s, 3H), 2.17-2.11 (m, 1H), 1.55-1.54 (m, 1H), 1.04-1.02 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 143.1, 138.3, 137.8, 136.7, 134.9, 129.7, 128.6, 128.4, 127.1, 127.0, 126.6, 123.8, 122.9, 116.8, 59.8, 59.6, 54.3, 45.5, 36.5, 26.1, 21.5, 21.4, 20.1, 19.8; MS (ESI): *m/z* 618 $[M + H]^+$, 640 $[M + Na]^+$; Anal. calcd. (%) for $C_{34}H_{39}N_3O_4S_2$: C, 66.10; H, 6.36; N, 6.80; Found: C, 66.17; H, 6.42; N, 6.88.

(3S,6S)-6-Benzyl-3-isobutyl-1,4-ditosyl-2,3,4,5,6,7-hexahydro-1H-benzo[b][1,4,7]triazonine (13c). Colorless semi-solid; yield, 74%; R_f = 0.52 (8.0/2.0, hexane/EtOAc); $[\alpha]_D^{30}$ -40.0 (c 0.10, MeOH), HPLC analysis: ee > 99 (t_R = 16.1 min, CH_3CN/H_2O); IR ν_{max} (KBr, cm^{-1}) 3029, 2926, 1493, 1340, 1163, 753; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (bs, 1H), 7.75-7.73 (m, 2H), 7.67 (d, 1H, J = 8.1), 7.52-7.49 (m, 2H), 7.27- 7.14 (m, 8H), 7.04-7.00 (m, 1H), 6.89 (d, 1H, J = 7.8), 6.82-6.80 (m, 2H), 4.10-4.07 (m, 1H), 3.59-3.55 (m, 1H), 2.90 (dd, 1H, J_1 = 10.8, J_2 = 14.0), 2.80-2.77 (m, 1H), 2.73-2.67 (m, 1H), 2.46 (s, 3H), 2.33-2.29 (m, 4H), 2.23 (dd, 1H, J_1 = 2.9, J_2 = 13.9), 1.80-1.69 (m, 2H), 1.53-1.44 (m, 2H), 1.01 (d, 3H, J = 6.4), 0.98 (d, 3H, J = 6.5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 143.3, 138.1, 137.8, 136.7, 134.9, 129.65, 129.62, 128.6, 128.4, 127.1, 126.9, 126.6, 124.1, 123.0, 117.6, 59.8, 57.2, 51.4, 45.0, 38.3, 36.6, 24.8, 22.6, 22.3, 21.5, 21.4; MS (ESI): m/z 632 $[M + H]^+$, 654 $[M + Na]^+$; Anal. calcd. (%) for $C_{35}H_{41}N_3O_4S_2$: C, 66.53; H, 6.54; N, 6.65; Found: C, 66.61; H, 6.58; N, 6.61.

(3S,6S)-3,6-Dibenzyl-1,4-ditosyl-2,3,4,5,6,7-hexahydro-1H-benzo[b][1,4,7] triazonine (13d). Brown semi-solid; yield, 73%; R_f = 0.51 (8.0/2.0, hexane/EtOAc); $[\alpha]_D^{30}$ +64.6 (c 0.11, MeOH), HPLC analysis: ee > 99 (t_R = 16.0 min, CH_3CN/H_2O); IR ν_{max} (KBr, cm^{-1}) 3022, 2361, 1493, 1216, 1161, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 8.34 (bs, 1H), 7.80-7.77 (m, 2H), 7.64 (d, 1H, *J* = 7.8), 7.41-7.38 (m, 2H), 7.31-7.14 (m, 13H), 7.07-7.02 (m, 2H), 6.84-6.82 (m, 2H), 4.34 (bs, 1H), 3.66-3.56 (m, 1H), 3.15-3.07 (m, 1H), 3.03-2.96 (m, 3H), 2.81-2.76 (m, 1H), 2.50-2.38 (m, 4H), 2.34-2.20 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 143.3, 137.9, 137.4, 137.3, 136.7, 136.6, 135.0, 129.72, 129.66, 129.1, 128.8, 128.6, 128.5, 127.3, 127.04, 127.00, 126.6, 124.1, 123.4, 117.2, 60.9, 55.9, 54.6, 45.3, 36.6, 35.4, 21.5, 21.4; MS (ESI): m/z 666 $[M + H]^+$; Anal. calcd. (%) for $C_{38}H_{39}N_3O_4S_2$: C, 68.54; H, 5.90; N, 6.31; Found: C, 68.59; H, 5.97; N, 6.36.

(3S,6S)-3,6-Dimethyl-1,4-ditosyl-2,3,4,5,6,7-hexahydro-1H-benzo[b][1,4,7] triazonine (13e). Brown oil; yield, 75%; R_f = 0.51 (8.0/2.0, hexane/EtOAc); $[\alpha]_D^{30}$ +44.5 (c 0.10, MeOH), IR ν_{max} (neat, cm^{-1}) 3244, 3026, 2925, 1493, 1335, 1161, 766; ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.73-7.66 (m, 4H), 7.60 (d, 1H, *J* = 8.1), 7.35-7.32 (m, 2H), 7.21-7.18 (m, 2H), 7.01-6.99 (m, 2H), 4.15 (bs, 1H), 3.76-3.72 (m, 1H), 2.93-2.79 (m, 3H), 2.45 (s, 3H), 2.35 (s, 3H), 2.17-2.13 (m, 1H), 1.20 (d, 3H, *J* = 6.6), 0.59 (d, 3H, *J* = 5.2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 143.4, 138.2, 137.4, 136.4, 134.7, 129.8, 129.5, 127.0, 126.9, 126.8, 124.0, 123.3, 117.4, 59.5, 55.2, 48.9, 46.7, 21.44, 21.40, 16.2, 14.3; MS (ESI): m/z 514 $[M + H]^+$; Anal. calcd. (%) for $C_{26}H_{31}N_3O_4S_2$: C, 60.79; H, 6.08; N, 8.18; Found: C, 60.73; H, 6.14; N, 8.12.

(3S,6S)-3,6-Di-isopropyl-1,4-ditosyl-2,3,4,5,6,7-hexahy-dro-1H-benzo[b][1,4,7] triazonine (13f). Light brown oil; yield, 76%; R_f = 0.51 (7.5/2.5, hexane/EtOAc); $[\alpha]_D^{30}$ +74.6 (c 0.11, MeOH), IR ν_{max} (neat, cm^{-1}) 3234, 3029, 2362, 1493, 1217, 763; ^1H NMR (300 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.82-7.73 (m, 3H), 7.44-7.23 (m, 5H), 7.09-7.01 (m, 1H), 6.93-6.84 (m, 1H), 6.71-6.66 (m, 1H), 3.84-3.76 (m, 1H), 3.54-3.48 (m, 1H), 3.12-2.99 (m, 1H), 2.78-2.72 (m, 1H), 2.61-2.54 (m, 1H), 2.46 (s, 3H), 2.41-2.40 (m, 1H), 2.37 (s, 3H), 1.48-1.44 (m, 1H), 1.19-1.14 (m, 1H), 1.08 (d, 3H, *J* = 6.5), 0.98 (d, 3H, *J* = 6.5), 0.76 (d, 3H, *J* = 7.1), 0.50 (d, 3H, *J* = 6.9); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.0, 143.3, 138.7, 136.9, 136.7, 134.1, 129.7, 129.6, 127.2, 127.1, 126.5, 123.0, 122.9, 115.5, 61.2, 59.7, 55.1, 40.3, 26.4, 26.3, 21.5, 20.2, 19.8, 19.2, 15.1; MS (ESI): m/z 570 $[M + H]^+$; Anal. calcd. (%) for $C_{30}H_{39}N_3O_4S_2$: C, 63.24; H, 6.90; N, 7.37; Found: C, 63.29; H, 6.94; N, 7.45.

(2S,5S)-2,5-Dibenzyl-2,3,4,5,6,7-hexahydro-1H-benzo[b] [1,4,7]triazonine (14c). Brown oil; yield 68%; overall yield, 6.6%; R_f = 0.51 (0.5/9.5, MeOH-$CHCl_3$); $[\alpha]_D^{30}$ +34.7 (c 0.10, MeOH), HPLC analysis: ee > 99 (t_R = 7.7 min, CH_3CN/H_2O); IR ν_{max} (neat, cm^{-1}) 3451, 3022, 1637, 1216, 766, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28-7.11 (m, 10H), 7.07-7.02 (m, 2H), 6.86-6.84 (m, 2H), 3.16-3.11 (m, 2H), 2.96-2.76 (m, 6H), 2.69-2.65 (m, 1H), 2.50-2.46 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 138.2, 136.6, 129.5, 129.1, 129.0, 128.6, 128.2, 126.9, 126.4, 125.9, 123.9, 123.8, 117.8, 60.3, 56.1, 53.3, 46.2, 38.8; MS (ESI): m/z 358 $[M + H]^+$; Anal. calcd. (%) for $C_{24}H_{27}N_3$: C, 80.63; H, 7.61; N, 11.75; Found: C, 80.68; H, 7.71; N, 11.70.

(2S,5S)-2,5-Dimethyl-2,3,4,5,6,7-hexahydro-1H-benzo[b] [1,4,7]triazonine (14d). Brown oil; yield 66%; overall yield, 8.9%; R_f = 0.51 (2.0/8.0, MeOH/$CHCl_3$); IR ν_{max} (neat, cm^{-1}) 3233, 2928, 1596, 1453, 763; ^1H NMR (200 MHz, $CDCl_3$) δ 6.96-6.89 (m, 2H), 6.76-6.70 (m, 2H), 3.65-3.64 (bs, 2H), 3.37-3.23 (m, 1H), 3.18-3.02 (m, 2H), 2.97-2.87 (m, 2H), 2.76-2.69 (m, 2H), 1.25 (d, 3H, *J* = 6.5), 0.95 (d, 3H, *J* = 6.5); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.2, 137.5, 124.6, 122.4, 118.2, 115.1, 53.8, 50.6, 49.9, 18.5; MS (ESI): m/z 206 $[M + H]^+$; Anal. calcd. (%) for $C_{12}H_{19}N_3$: C, 70.20; H, 9.33; N, 20.47; Found: C, 70.24; H, 9.41; N, 20.53.

(2*S*,5*S*)-2,5-Di-isopropyl-2,3,4,5,6,7-hexahydro-1H-benzo[b] [1,4,7]triazonine (14e). Brown oil; yield 64%; overall yield, 8.8%; R_f = 0.51 (1.2/8.8, MeOH/$CHCl_3$); IR ν_{max} (neat, cm^{-1}) 3236, 3022, 2923, 1597, 1216, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, 1H, *J* = 7.9), 6.95-6.90 (m, 1H), 6.75-6.70 (m, 2H), 3.08-2.82 (m, 6H), 2.31-2.19 (m, 1H), 2.05-1.96 (m, 1H), 1.02-0.97 (m, 6H), 0.83 (d, 3H, *J* = 7.0), 0.79 (d, 3H, *J* = 6.8); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.4, 137.8, 124.6, 122.8, 118.3, 115.4, 62.4, 59.6, 54.2, 41.4, 26.9, 26.7, 20.05, 19.99, 19.2, 17.3; MS (ESI): *m/z* 262 $[M + H]^+$; Anal. calcd. (%) for $C_{16}H_{27}N_3$; C, 73.51; H, 10.41; N, 16.07; Found: C, 73.58; H, 10.44; N, 16.13.

(S)-Methyl-2-(N-((S)-2-(2-(N-((S)-2-(tert-butoxycarbonylamino)-3-phenyl-propyl)-4-methylphenylsulfonamido)phenylamino)-3-phenylpropyl)-4-methylphenylsulfona mido)-4-methylpentanoate (16b). Colorless oil; yield, 64%; R_f = 0.51 (7.5/2.5, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3407, 3021, 2957, 2359, 1714, 1738, 1342, 1217, 767; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, 1H, *J* = 8.2), 7.60 (d, 1H, *J* = 8.2), 7.52-7.45 (m, 2H), 7.31-7.08 (m, 14H), 6.97 (d, 1H, *J* = 7.9), 6.85-6.79 (m, 1H), 6.48-6.37 (m, 1H), 6.31-6.24 (m, 1H), 5.20-5.03 (m, 1H), 4.62-4.52 (m, 2H), 4.40-4.31 (m, 1H), 4.20-4.10 (m, 1H), 3.87-3.83 (m, 1H), 3.61 (dd, 1H, J_1 = 4.1, J_2 = 15.3), 3.50 (s, 3H), 3.43-3.40 (m, 2H), 3.30 (bs, 1H), 3.15 (dd, 1H, J_1 = 9.8, J_2 = 15.3), 2.87-2.86 (m, 1H), 2.44 (s, 6H), 1.79-1.61 (m, 3H), 1.37 (s, 9H), 0.93-0.89 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 146.1, 143.5, 143.3, 139.1, 137.8, 136.3, 129.5, 129.3, 128.5, 128.4, 128.3, 128.1, 127.9, 126.3, 116.5, 112.1, 58.6, 53.1, 52.0, 49.1, 39.4, 39.1, 38.8, 28.5, 28.4, 24.8, 22.7, 22.5, 22.1, 21.6; MS (ESI): m/z 911 $[M + H]^+$; Anal. calcd. (%) for $C_{50}H_{62}N_4O_8S_2$: C, 65.91; H, 6.86; N, 6.15; Found: C, 65.96; H, 6.91; N, 6.21.

(*S*)-Methyl-4-methyl-2-(4-methyl-N-((*S*)-2-(2-(4-methyl-N-((*S*)-2-(4-methylphenylsulfonamido)-3-phenyl propyl)phenylsulfonamido)phenylamino)-3-phenylpropyl)phenylsulfonamido)pentanoate (18b). Brown oil; yield, 58%, (based on two steps); R_f = 0.51 (7.0/3.0, hexane/EtOAc); IR ν_{max} (neat, cm^{-1}) 3383, 3022, 2359, 1736, 1342, 1215, 760; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, 1H, *J* = 8.1), 7.61 (d, 1H, *J* = 8.2), 7.51-7.47 (m, 2H), 7.38 (d, 1H, *J* = 8.2), 7.32-6.98 (m, 17H), 6.84-6.82 (m, 1H), 6.53-6.45 (m, 3H), 6.27-6.20 (m, 1H), 5.03-5.01 (m, 1H), 4.58-4.54 (m, 1H), 4.35-4.29 (m, 1H), 4.20-4.12 (m, 1H), 3.63-3.54 (m, 1H), 3.47 (s, 3H), 3.30-3.22 (m, 3H), 3.13-2.99 (m, 2H), 2.92-2.89 (m, 1H), 2.69-2.67 (m, 1H), 2.47 (s, 3H), 2.42 (s, 3H), 2.38 (s, 3H), 1.68-1.61 (m, 1H), 1.41-1.31 (m, 2H), 0.93 (d, 3H, *J* = 6.0), 0.90 (d, 3H, *J* = 6.2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 146.3, 143.8, 143.1, 142.7, 138.6, 136.5, 136.4, 136.3, 134.1, 129.4, 129.1, 128.65, 128.58, 128.5, 128.4, 128.3, 127.9, 127.3, 127.2, 126.3, 126.24, 126.16, 125.7, 116.5, 112.6, 58.4, 54.9, 53.5, 53.1, 52.0, 48.7, 39.5, 38.8, 38.1, 24.6, 22.0, 21.7, 21.6, 21.5; MS (ESI): *m/z* 965 $[M + H]^+$; Anal. calcd. (%) for $C_{52}H_{60}N_4O_8S_3$: C, 64.70; H, 6.27; N, 5.80; Found: C, 64.78; H, 6.23; N, 5.89.

(3S,6S,9S)-3,9-Dibenzyl-6-isobutyl-1,4,7-tritosyl-1,2,3,4,5,6,7,8,9,10-decahydrobenzo[b][1,4,7,10]tetraaza-cyclododecine (20b). Light brown, semi-solid; yield, 49%, (based on two steps); overall yield, 3.9%; R_f = 0.52 (7.5/2.5, hexane/EtOAc); $[\alpha]_D^{30}$ -168.7 (c 0.10, MeOH), HPLC analysis: ee > 99 (t_R = 17.5 min, CH_3CN/H_2O); IR ν_{max} (KBr, cm^{-1}) 3021, 2928, 2361, 1216, 761; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.48 (m, 4H), 7.42-7.40 (m, 2H), 7.35-7.16 (m, 12H), 7.09-7.00 (m, 5H), 6.89-6.87 (m, 2H), 6.73 (dd, 1H, J_1 = 1.2, J_2 = 8.0), 4.94-4.92 (m, 1H), 4.36-4.29 (m, 2H), 4.26-4.18 (m, 2H), 4.07-4.00 (m, 2H), 3.59-3.56 (m, 1H), 3.41-3.30 (m, 2H), 3.01-2.87 (m, 2H), 2.78-2.68 (m, 2H), 2.47 (s, 3H), 2.44 (s, 3H), 2.25 (s, 3H), 1.74-1.64 (m, 3H), 0.97 (d, 3H, *J* = 6.2), 0.95 (d, 3H, *J* = 6.3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 144.1, 143.4, 142.9, 138.3, 137.4, 136.9, 136.5, 135.9, 135.6, 130.4, 129.8, 129.7, 129.6, 129.2, 128.9, 128.8, 128.6, 128.5, 128.4, 127.2, 127.1, 126.7, 125.8, 124.7, 59.6, 58.9, 54.1, 52.3, 51.6, 44.6, 38.7, 38.6, 36.4, 24.4, 23.4, 23.3, 21.6, 21.5, 21.3; MS (ESI): m/z 919 $[M + H]^+$; Anal. calcd. (%) for $C_{51}H_{58}N_4O_6S_3$: C, 66.64; H, 6.36; N, 6.10; Found: C, 66.60; H, 6.41; N, 6.19.