Supporting Information

One-pot Synthesis of 11-Sulfenyl Dibenzodiazepines via Tandem Sulfenylation/Cyclization of *o*-Isocyanodiaryl Amines and Diaryl Disulfides

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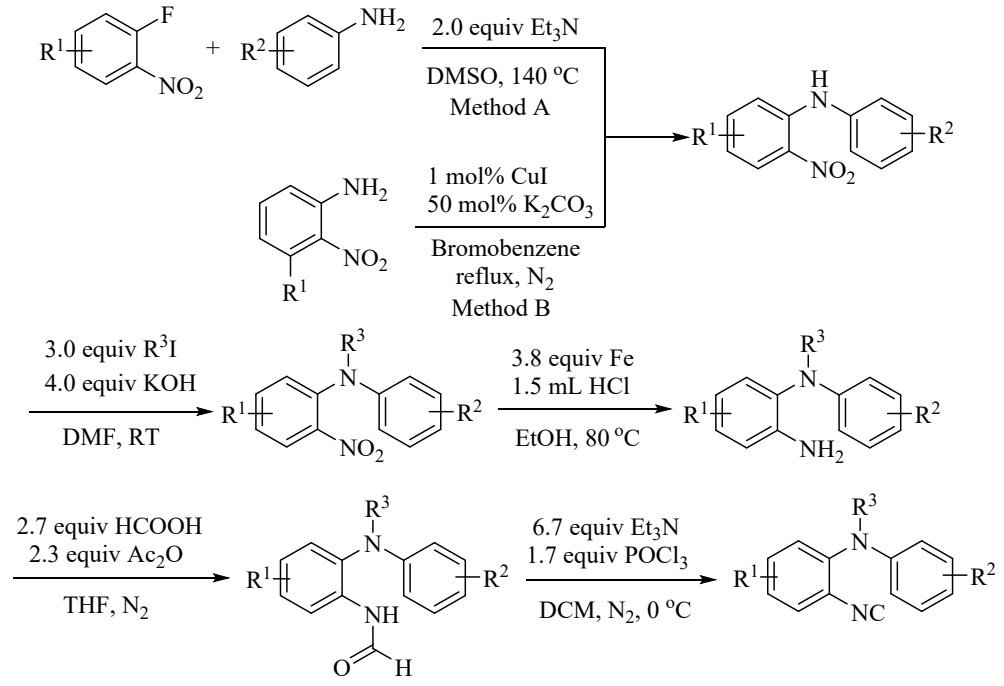
Contents of supporting information

1. General experimental details

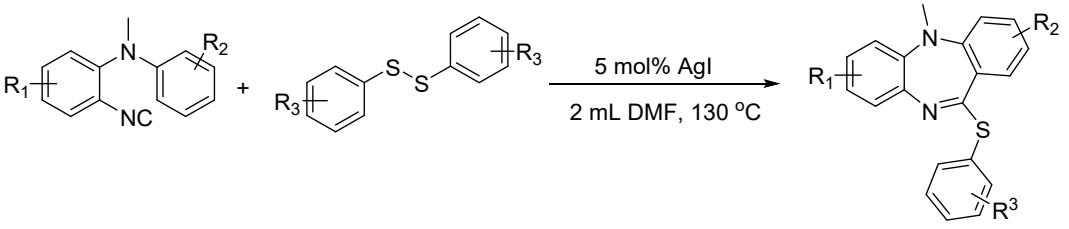
The reaction was monitored by thin layer chromatography (TLC) and observed under UV light. The product was obtained by column chromatography on silica gel (300-400 mesh) from a mixture of petroleum ether and ethyl acetate. ^{1}H and ^{13}C NMR were recorded on a spectrometer at 400 Hz at ambient temperature using $CDCl_3$ as solvent and TMS as internal standard. The chemical shifts are in ppm and the coupling constant J is in Hz. ^{1}H NMR data are reported as chemical shifts, multiplicities, coupling constants and integrals. ^{13}C NMR data are reported as chemical shifts. Unless otherwise stated, chemicals were used directly without purification. Using YCYQ WRX-4 to determine the melting points of the products and The single crystal structure of product **3a** was determined using Agilent SuperNova EG8910B.

2. General synthesis method of substrate 1



Referring to the work of predecessors,[1-5] most substrates are prepared according to the route of Method A. However, if you want to prepare the 3-substituted *o*-arylamino aryl isonitrile, you need to follow the route of Method B.

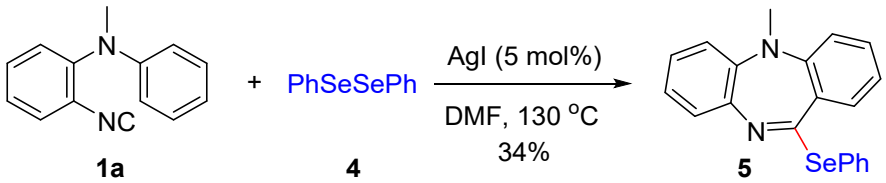
3. General Procedure for the Synthesis of Dibenzodiazepines 3



1 **2** **3**

Functionalized 2-isocyano-*N*-phenylaniline **1** (0.2 mmol, 1 equiv), diaryl disulfide or diphenyl diselenide **2** (0.2 mmol, 1 equiv) and AgI (2.3 mg, 5 mol%) were added to the test tube, respectively, 2 mL of DMF was added to dissolve the mixture. The reaction mixture was stirred at 130 °C for 24 h. The reaction was detected by TLC. After the reaction was completed, it was quenched by adding 5 mL of H_2O, extracted with EA (3 x 5 mL), and the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography eluting with petroleum ether-ethyl acetate (PE/EA) to give the expected product.

4. Selenium etherification of 2-isocyano-*N*-methyl-*N*-phenylaniline

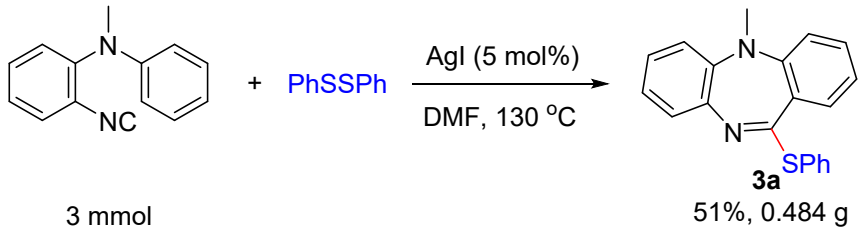


1a **4** **5**

A test tube containing a mixture of 2-isocyano-*N*-methyl-*N*-phenylaniline **1a** (0.2 mmol, 1 equiv), diphenyl diselenide **4** (0.2 mmol, 1 equiv) and AgI (5 mol%) was injected with 2mL DMF, then heated it at 130 ℃ until the consumption of **1a** was

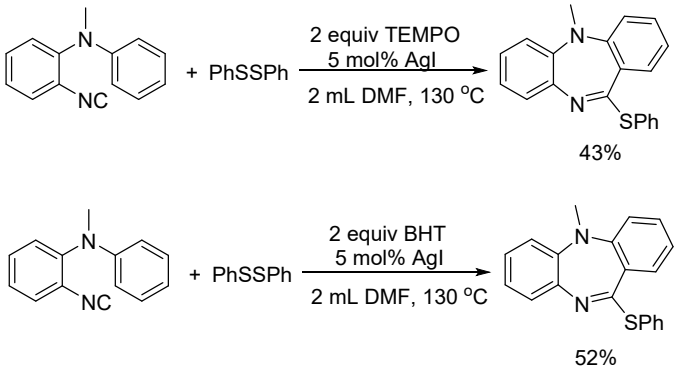
complete. After extracting, drying and vacuum concentration. Using the mixture of petroleum ether and ethyl acetate (PE/EA=200:1) as eluent, 34% product **5** (24.8mg) was obtained by column chromatography.

5. Scale-up Reaction



Add 2-isocyano-*N*-methyl-phenylaniline **1a** (3 mmol, 1equiv), diphenyl disulfide **2a** (3 mmol, 1 equiv) and AgI to a round bottom flask (100 mL) in turn, then inject 30 mL DMF, and react for 96 h at 130℃. After cooling, it was quenched by adding 30 mL of H_2O, extracted with EA (3×30 mL), and the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product is purified by silica gel column chromatography and eluted with petroleum ether ethyl acetate (PE: EA=100:1) to obtain product 3a in 51% yield (0.484 mg).

6. Control experiments



After adding **1a** (0.2 mmol, 1 equiv), **2a** (0.2 mmol, 1 equiv) and AgI (5 mol%), TEMPO (0.4 mmol, 2 equiv) and BHT (0.4 mmol, 2 equiv) were also added, and then 2mL DMF was added to react at 130 ℃ for 24h. Other operations were the same as the

above operations for preparing dibenzodiazepines, and **3a** was finally obtained in 43% and 52% yields, respectively.

7. References

[1] B. D. Palmer, J. B. Smaill, M. Boyd, D. H. Boschelli, A. M. Doherty, J. M. Hamby, S. S. Khatana, J. B. Kramer, A. J. Kraker, R. L. Panek, G. H. Lu, T. K. Dahring, R. T. Winters, H. D. H. Showalter and W. A. Denny, *J. Med. Chem.,* 1998, **41**, 27, 5457–5465.

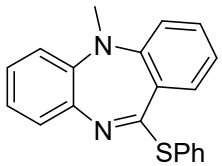
[2] S. Schmid, M. Röttgen, U. Thewaltb and V. Austel, *Org. Biomol. Chem.,* 2005,**3**, 3408-3421

[3] I. Chuckowree, M. A.Syed, G. Getti, A. P. Patel, H. Garner, G. J. Tizzard, S. J. Coles, J. Spencer, *Tetrahedron Lett.,* 2012, **53**, 3607-3611.

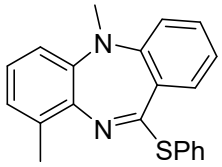
[4] W. Hu, F. Teng, H. Hu, S. Luo and Q. Zhu, *J. Org. Chem.,* 2019, **84**, 6524–6535.

[5] S.-L. Qi, Y. Li, J.-F. Li, T. Zhang, Y.-X. Luan and M. Ye, *Org. Lett.,* 2021, **23** (10), 4034-4039.

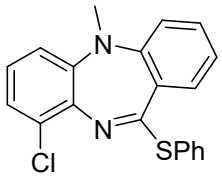
8. Physical data of the compounds



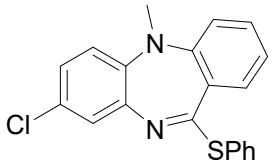
5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3a) : PE/EA = 100:1, yellow solid (23 mg，72%). mp: 120.9 - 121.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.65 (d, *J* = 6.5 Hz, 2H), 7.46 – 7.31 (m, 4H), 7.08 – 6.84 (m, 6H), 3.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 156.5, 145.7, 142.4, 135.0, 132.3, 130.8, 129.1, 128.8, 128.7, 128.6, 126.6, 125.8, 124.0, 123.1, 118.0, 117.3, 37.1. HRMS (ESI) m/z: Calculated for $C_{20}H_{16}N_2S^+$ ($M+H^+$): 317.1107, Found: 317.1112.



5,9-dimethyl-11-(phenylthio)-5*H*-dibenzo[*b*,e][1,4]diazepine (3b) : PE/EA = 100:1, yellow solid (41.1 mg，62%). mp: 101.4 - 103.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.69-7.64 (m, 2H), 7.41 – 7.33 (m, 4H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.91 (t, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.0 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 3.17 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 156.6, 145.8, 140.5, 136.0, 135.6, 135.0, 132.3, 130.6, 128.9, 128.8, 125.6, 125.5, 123.0, 117.4, 115.6, 112.4, 37.3, 18.4. HRMS (ESI) m/z: Calculated for $C_{21}H_{18}N_2S^+$ ($M+H^+$): 331.1263, Found: 331.1271.

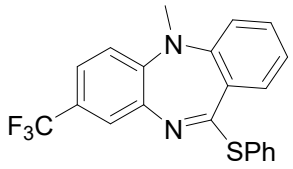


9-chloro-5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3c) : PE/EA = 100:1, yellow solid (32.2 mg，46%). mp: 151.1 - 152.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 3H), 7.37 – 7.27 (m, 4H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.92 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.83 (t, *J* = 8.0 Hz, 1H), 6.68 (dd, *J* = 8.1, 1.1 Hz, 1H), 3.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 156.0, 147.5, 139.2, 135.4, 132.6, 131.1, 129.9, 128.9 (2C), 128.8, 128.7, 125.8, 125.1, 123.5, 117.7, 116.3, 37.3. HRMS (ESI) m/z: Calculated for $C_{20}H_{16}ClN_2S^+$ ($M+H^+$): 351.0717, Found: 351.0714.

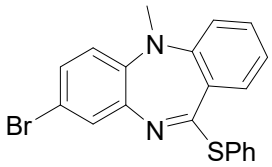


8-chloro-5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3d) : PE/EA = 200:1, yellow solid (32.8 mg，47%). mp: 119.7 - 122.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.55 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.37 – 7.27 (m,

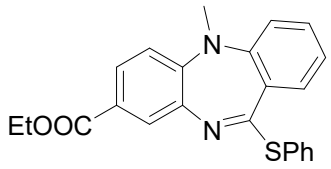
4H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.90 – 6.84 (m, 2H), 6.77 (d, *J* = 2.4 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 1H), 3.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 156.0, 144.4, 143.4, 135.2, 132.6, 130.2, 129.1, 129.0, 128.9 (2C), 128.5, 126.3, 125.3, 123.4, 118.9, 117.4, 37.1. HRMS (ESI) m/z: Calculated for $C_{20}H_{16}ClN_2S^+$ ($M+H^+$): 351.0717, Found: 351.0719.



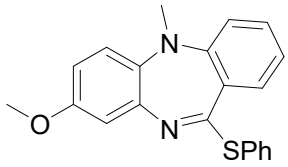
5-methyl-11-(phenylthio)-8-(trifluoromethyl)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3e) : PE/EA = 200:1, yellow solid (36 mg，47%). mp: 115.6 – 116.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.59-7.55 (m, 2H), 7.39 – 7.30 (m, 4H), 7.17 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.02 (d, *J* = 1.8 Hz, 1H), 6.99 (td, *J* = 7.2, 0.8 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 155.5, 148.7, 142.4, 135.2, 132.7, 130.0, 129.09, 129.05, 129.0, 128.5, 126.2 (q, $^2J_{CF}$ = 32.2 Hz), 124.1 (q, $^1J_{CF}$ = 270.0 Hz), 123.9 (q, $^3J_{CF}$ = 3.8 Hz), 123.6, 122.4 (q, $^3J_{CF}$ = 3.7 Hz), 118.2, 117.7, 37.2. HRMS (ESI) m/z: Calculated for $C_{21}H_{16}F_3N_2S^+$ ($M+H^+$): 385.0981, Found: 385.0981.



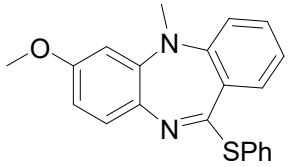
8-bromo-5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3f) : PE/EA = 400:1, yellow solid (39.5 mg，50%). mp: 142.1 – 143.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.63 (dd, *J* = 7.7, 1.4 Hz, 2H), 7.45 – 7.34 (m, 4H), 7.09 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.06 – 6.98 (m, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.71 (d, *J* = 8.6 Hz, 1H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 156.0, 144.9, 143.7, 135.2, 132.6, 130.2, 129.2, 129.1, 129.0, 128.9, 128.5, 128.2, 123.4, 119.3, 117.5, 116.6, 37.1. HRMS (ESI) m/z: Calculated for $C_{20}H_{16}BrN_2S^+$ ($M+H^+$): 395.0212, Found: 395.0201.



ethyl 5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine-8-carboxylate (3g) : PE/EA = 20:1, yellow solid (39.3 mg，51%). mp: 126.6 – 128.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.45 (s, 1H), 7.37 – 7.25 (m, 4H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.14 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 166.2, 155.4, 150.1, 142.0, 135.1, 132.5, 130.2, 129.0, 128.9, 128.6, 128.1, 127.1, 126.2, 123.5, 117.8, 117.7, 60.7, 37.2, 14.4. HRMS (ESI) m/z: Calculated for $C_{23}H_{21}N_2O_2S^+$ ($M+H^+$): 389.1318, Found: 389.1315.

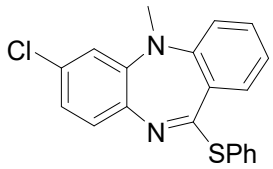


8-methoxy-5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3h) : PE/EA = 20:1, yellow solid (38.7 mg，56%). mp: 92.9 – 93.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.37 (m, 4H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.64 (dd, *J* = 8.8, 3.2 Hz, 1H), 6.53 (d, *J* = 2.8 Hz, 1H), 3.73 (s, 3H), 3.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 156.9, 156.4, 143.2, 139.1, 135.0, 132.4, 130.8, 129.1, 128.9, 128.7, 128.5, 122.9, 118.4, 117.0, 111.6, 111.3, 55.6, 37.1. HRMS (ESI) m/z: Calculated for $C_{21}H_{19}N_2OS^+$ ($M+H^+$): 347.1213, Found: 347.1202.

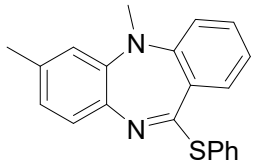


7-methoxy-5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3i) : PE/EA = 50:1, yellow solid (30.9 mg，48%). mp: 188.5 – 191.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.33 – 7.23 (m, 4H), 6.93 (t, *J* =

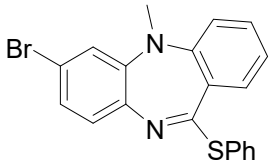
7.4 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.42 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.37 (d, *J* = 2.4 Hz, 1H), 3.65 (s, 3H), 3.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 158.5, 155.7, 146.6, 136.1, 134.8, 132.1, 131.1, 129.1, 128.8, 128.7, 128.5, 127.4, 123.2, 117.4, 108.3, 105.0, 55.5, 37.1. HRMS (ESI) m/z: Calculated for $C_{21}H_{19}N_2OS^+$ ($M+H^+$): 347.1213, Found: 347.1213.



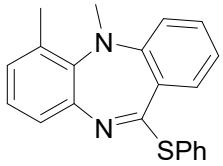
7-chloro-5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3j) : PE/EA = 200:1, yellow solid (41.0 mg，59%). mp: 146.9 – 147.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.35 – 7.26 (m, 4H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.76 (d, *J* = 2.0 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 3.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 155.7, 146.4, 141.0, 135.1, 132.6, 131.4, 130.4, 129.1, 128.9, 128.8, 128.5, 127.5, 124.0, 123.5, 118.5, 117.6, 37.1. HRMS (ESI) m/z: Calculated for $C_{20}H_{16}ClN_2S^+$ ($M+H^+$): 351.0717, Found: 351.0724.



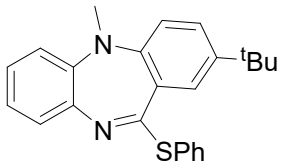
5,7-dimethyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3k) : PE/EA = 150:1, yellow solid (41.1 mg，62%). mp: 173.5 – 174.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.46 – 7.36 (m, 4H), 7.04 (td, *J* = 7.6, 0.8 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.73 (s, 1H), 3.25 (s, 3H), 2.28 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 156.4, 145.4, 140.0, 135.7, 134.9, 132.2, 131.0, 129.1, 128.8, 128.7, 128.6, 126.5, 124.7, 123.0, 118.7, 117.3, 37.1, 21.1. HRMS (ESI) m/z: Calculated for $C_{21}H_{19}N_2S^+$ ($M+H^+$): 331.1263, Found: 331.1263.



7-bromo-5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3l) : PE/EA = 400:1, yellow solid (45.8 mg，58%). mp: 147.7 – 149.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.43 – 7.32 (m, 4H), 7.07 – 7.01 (m, 2H), 6.98 (d, *J* = 1.9 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 155.7, 146.7, 141.4, 135.1, 132.6, 130.4, 129.1 128.9, 128.5, 127.9, 127.0, 123.5, 121.4, 119.2, 117.6, 37.2. HRMS (ESI) m/z: Calculated for $C_{20}H_{16}BrN_2S^+$ ($M+H^+$): 395.0212, Found: 395.0212.

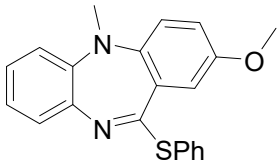


5,6-dimethyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3m) : PE/EA = 200:1, yellow solid (29.3 mg，49%). mp: 87.5 – 88.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.37 – 7.25 (m, 4H), 7.14 (t, *J* = 6.9 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.72 (dd, *J* = 6.2, 3.2 Hz, 1H), 3.09 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 155.2, 146.0, 142.1, 135.7, 135.0, 132.6, 131.1, 130.9, 129.5, 128.8, 128.6, 128.5, 125.7, 125.0, 124.9, 124.5, 40.0, 19.0. HRMS (ESI) m/z: Calculated for $C_{21}H_{19}N_2S^+$ ($M+H^+$): 331.1263, Found: 331.1266.

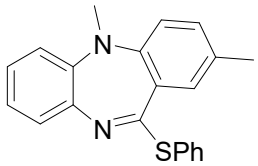


2-(tert-butyl)-5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3n) : PE/EA = 100:1, yellow solid (48 mg，65%). mp: 157.6 – 159.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 3H), 7.31 – 7.20 (m, 4H), 6.97 – 6.89 (m, 1H), 6.85 – 6.82 (m, 2H), 6.80 – 6.76 (m, 2H), 3.10 (s, 3H), 1.15 (s, 9H). ^{13}C NMR (100 MHz,

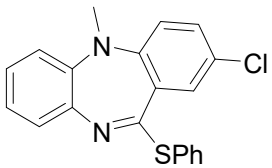
$CDCl_3$) δ 169.1, 154.0, 146.0, 145.9, 142.5, 134.7, 131.2, 129.2, 128.8, 128.5, 127.8, 126.6, 126.2, 125.8, 123.9, 117.8, 116.8, 37.0, 34.3, 31.3. HRMS (ESI) m/z: Calculated for $C_{24}H_{25}N_2S^+$ ($M+H^+$): 373.1733, Found: 373.1739.



2-methoxy-5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3o) : PE/EA = 80:1, yellow solid (30.8 mg，45%). mp: 208.4 – 211.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.37 (m, 3H), 7.29 (d, *J* = 2.0 Hz, 1H), 7.10 – 7.03 (m, 1H), 7.01 – 6.89 (m, 5H), 3.80 (s, 3H), 3.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 155.4, 149.5, 146.1, 142.2, 134.9, 130.7, 129.2, 128.8, 128.7, 126.6, 125.8, 123.8, 118.2, 118.1, 117.6, 113.7, 55.7, 37.1. HRMS (ESI) m/z: Calculated for $C_{21}H_{19}N_2OS^+$ ($M+H^+$): 347.1213, Found: 347.1204.

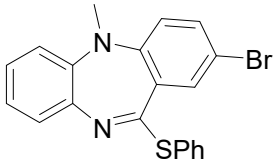


2,5-dimethyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3p) : PE/EA = 100:1, yellow solid (39.1 mg，59%). mp: 147.5 – 148.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.8, 1.0 Hz, 2H), 7.57 (s, 1H), 7.43 (m, 3H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.02 – 6.86 (m, 4H), 3.24 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 154.0, 145.9, 142.4, 135.1, 132.9, 132.6, 130.9, 129.4, 128.8, 128.7, 128.3, 126.6, 125.7, 123.9, 117.8, 117.1, 37.0, 20.6. HRMS (ESI) m/z: Calculated for $C_{21}H_{19}N_2S^+$ ($M+H^+$): 331.1263, Found: 331.1270.

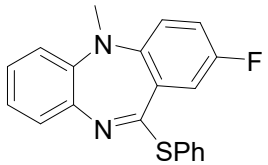


2-chloro-5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3q) : PE/EA = 500:1, yellow solid (36.3 mg，51%). mp: 112.7 – 113.4 ℃. ^{1}H NMR (400 MHz,

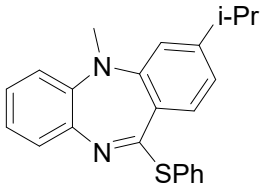
$CDCl_3$) δ 7.59 (d, *J* = 2.4 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.36 – 7.26 (m, 3H), 7.23 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.98 – 6.92 (m, 1H), 6.90 – 6.84 (m, 1H), 6.83 – 6.76 (m, 3H), 3.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 154.9, 145.2, 142.1, 135.1, 132.0, 130.3, 129.8, 128.9, 128.8, 128.4, 126.8, 126.0, 124.3, 118.5, 118.0, 37.1. HRMS (ESI) m/z: Calculated for $C_{20}H_{16}ClN_2S^+$ ($M+H^+$): 351.0717, Found: 351.0720.



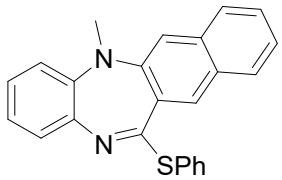
2-bromo-5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3r) : PE/EA = 300:1, yellow solid (38.5 mg，49%). mp: 144.4 – 145.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 2.4 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.40 – 7.25 (m, 4H), 6.94 (td, *J* = 7.6, 1.2 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.82 – 6.75 (m, 2H), 6.73 (d, *J* = 8.8 Hz, 1H), 3.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 155.5, 145.1, 142.1, 135.1, 134.9, 131.7, 130.3, 130.1, 128.9, 126.8, 126.7, 126.0, 124.3, 118.9, 118.0, 115.8, 37.1. HRMS (ESI) m/z: Calculated for $C_{20}H_{16}BrN_2S^+$ ($M+H^+$): 395.0212, Found: 395.0216.



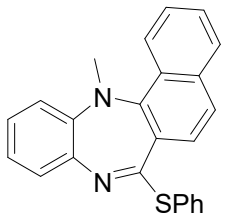
2-fluoro-5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3s) : PE/EA = 50:1, yellow solid (31 mg，46%). mp: 136.5 – 140.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.44 – 7.34 (m, 4H), 7.09 – 7.00 (m, 2H), 6.97 – 6.85 (m, 4H), 3.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 158.4 (d, $^1J_{CF}$ = 241.8 Hz), 152.2 (d, *J* = 2.5 Hz), 145.5, 142.1, 135.0, 130.2, 129.7 (d, $^3J_{CF}$ = 7.0 Hz), 128.9, 128.8, 126.8, 126.0, 124.1, 118.8 (d, $^2J_{CF}$ = 22.3 Hz), 118.4 (d, $^3J_{CF}$ = 8.0 Hz), 117.8, 115.6 (d, $^2J_{CF}$ = 24.2 Hz), 37.3. HRMS (ESI) M/Z: Calculated for $C_{20}H_{15}FN_2SNa^+$ ($M+Na^+$): 357.0832, Found: 357.0825.



3-isopropyl-5-methyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3t) : PE/EA = 50:1, yellow solid (25.4 mg，35%). mp: 131.6 – 132.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.51 (m, 3H), 7.33 – 7.22 (m, 3H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.86 – 6.75 (m, 4H), 6.71 (s, 1H), 3.12 (s, 3H), 2.82 – 2.70 (m, 1H), 1.13 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 156.5, 153.8, 145.8, 142.5, 135.1, 130.9, 129.0, 128.8, 128.6, 126.6, 126.2, 125.6, 123.9, 121.0, 118.0, 115.6, 37.1, 34.4, 23.8, 23.7. HRMS (ESI) m/z: Calculated for $C_{23}H_{23}N_2S^+$ ($M+H^+$): 359.1576, Found: 359.1584.

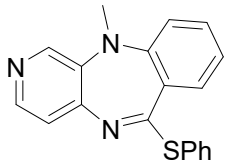


5-methyl-12-(phenylthio)-5*H*-benzo[*b*]naphtho[2,3-*e*][1,4]diazepine (3u) : PE/EA = 200:1, yellow solid (26.6 mg，36%). mp: 189.2 – 190.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.22 (m, 4H), 7.14 – 7.09 (m, 1H), 7.06 – 6.94 (m, 3H), 3.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 156.5, 146.6, 143.9, 134.4, 131.8, 131.1, 131.0, 130.6, 128.5, 128.3, 127.8, 126.4, 126.2, 125.6, 125.1, 124.6, 124.2, 121.4, 118.1, 116.4, 36.8. HRMS (ESI) m/z: Calculated for $C_{24}H_{19}N_2S^+$ ($M+H^+$): 367.1263, Found: 367.1266.

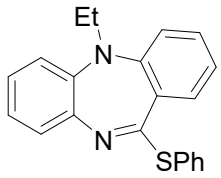


13-methyl-7-(phenylthio)-13*H*-benzo[*b*]naphtho[1,2-*e*][1,4]diazepine (3v) : PE/EA = 300:1, yellow solid (25.6 mg，35%). mp: 126.0 – 127.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.2 Hz, 1H), 7.80 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.72 (d, *J* = 8.0 Hz,

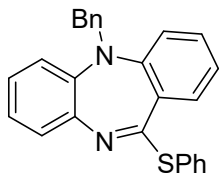
1H), 7.63 – 7.56 (m, 3H), 7.52 (t, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.36 – 7.26 (m, 3H), 7.24 – 7.19 (m, 1H), 7.06 – 6.93 (m, 3H), 3.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 149.7, 146.0, 143.4, 136.4, 135.1, 131.4, 130.6, 128.9, 128.8, 128.5, 128.4, 128.0, 127.8, 127.3, 126.9, 126.8, 126.7, 126.5, 125.3, 124.8, 40.7. HRMS (ESI) m/z: Calculated for $C_{24}H_{19}N_2S^+$ ($M+H^+$): 367.1263, Found: 367.1254.



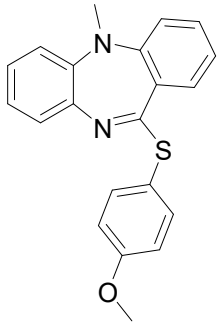
11-methyl-6-(phenylthio)-11*H*-benzo[*e*]pyrido[4,3-*b*][1,4]diazepine (3w) : PE/EA = 50:1, yellow solid (38.2 mg，61%). mp: 122.3 – 125.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.77 (d, *J* = 7.0, 1H), 7.68 (d, *J* = 8.0, 1H), 7.50 – 7.38 (m, 4H), 7.18 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.12 – 7.04 (m, 2H), 6.89 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 154.6, 154.5, 144.0, 136.8, 135.2, 134.3, 132.8, 130.4, 129.0, 128.9 (2C), 128.4, 123.2, 119.7, 118.5, 35.9. HRMS (ESI) M/Z: Calculated for $C_{19}H_{15}N_3SNa^+$ ($M+Na^+$): 340.0879, Found: 340.0886.



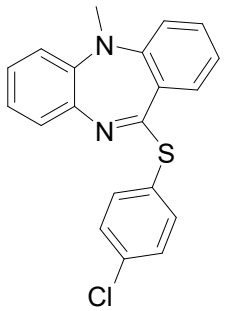
5-ethyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3x) : PE/EA = 200:1, yellow solid (37.3 mg，56%). mp: 133.5 – 136.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.4 Hz, 2H), 7.46 – 7.35 (m, 4H), 7.12-7.04 (m, 1H), 7.05 – 6.98 (m, 4H), 6.93 (d, *J* = 8.0 Hz, 1H), 3.79 – 3.61 (m, 2H), 1.29 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 155.2, 144.7, 143.2, 134.6, 132.1, 131.2, 129.4, 129.2, 128.8, 128.5, 126.5, 125.8, 124.0, 123.2, 119.0, 118.4, 42.8, 13.4. HRMS (ESI) m/z: Calculated for $C_{21}H_{19}N_2S^+$ ($M+H^+$): 331.1263, Found: 331.1257.



5-benzyl-11-(phenylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3y): PE/EA = 100:1, yellow solid [42.8 mg (on 1.0 mmol scale，11%]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 3H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.30 (m, 3H), 7.29 – 7.19 (m, 3H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.01 – 6.88 (m, 6H), 4.92 – 4.75 (m, *J* = 14.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 154.6, 144.7, 143.1, 137.3, 134.7, 132.0, 131.1, 129.4, 129.2, 128.9, 128.6, 128.5, 128.2, 127.2, 126.5, 125.8, 124.3, 123.5, 119.4, 118.9, 52.9. HRMS (ESI) m/z: Calculated for $C_{26}H_{21}N_2S^+$ ($M+H^+$): 393.1420, Found: 393.1417.

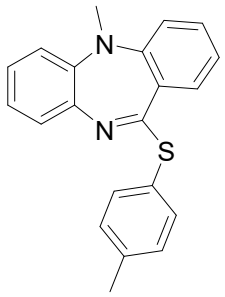


11-((4-methoxyphenyl)thio)-5-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3z) : PE/EA = 50:1, yellow solid (39.6 mg，57%). mp: 140.0 – 140.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 2H), 7.03 – 6.95 (m, 5H), 6.92 (d, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 160.3, 156.4, 145.7, 142.5, 136.9, 132.3, 129.0, 128.6, 126.7, 125.7, 124.0, 123.0, 121.4, 118.0, 117.3, 114.5, 55.4, 37.1. HRMS (ESI) m/z: Calculated for $C_{21}H_{19}N_2OS^+$ ($M+H^+$): 347.1213, Found: 347.1204.

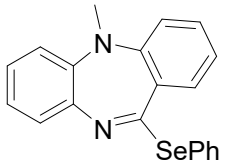


11-((4-chlorophenyl)thio)-5-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3aa) : PE/EA = 300:1, yellow solid (44.4 mg，63%). mp: 153.0 – 154.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.27 (m, 3H), 6.98 – 6.89 (m, 2H), 6.88 – 6.83 (m, 2H), 6.82 – 6.75 (m, 2H), 3.10 (s, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 167.7, 156.5, 145.7, 142.2, 136.4, 135.0, 132.5, 129.2, 129.0, 128.9, 128.5, 126.7, 126.0, 124.1, 123.2, 118.1, 117.5, 37.1. HRMS (ESI) m/z: Calculated for $C_{20}H_{16}ClN_2S^+$ ($M+H^+$): 351.0717, Found: 351.0725.



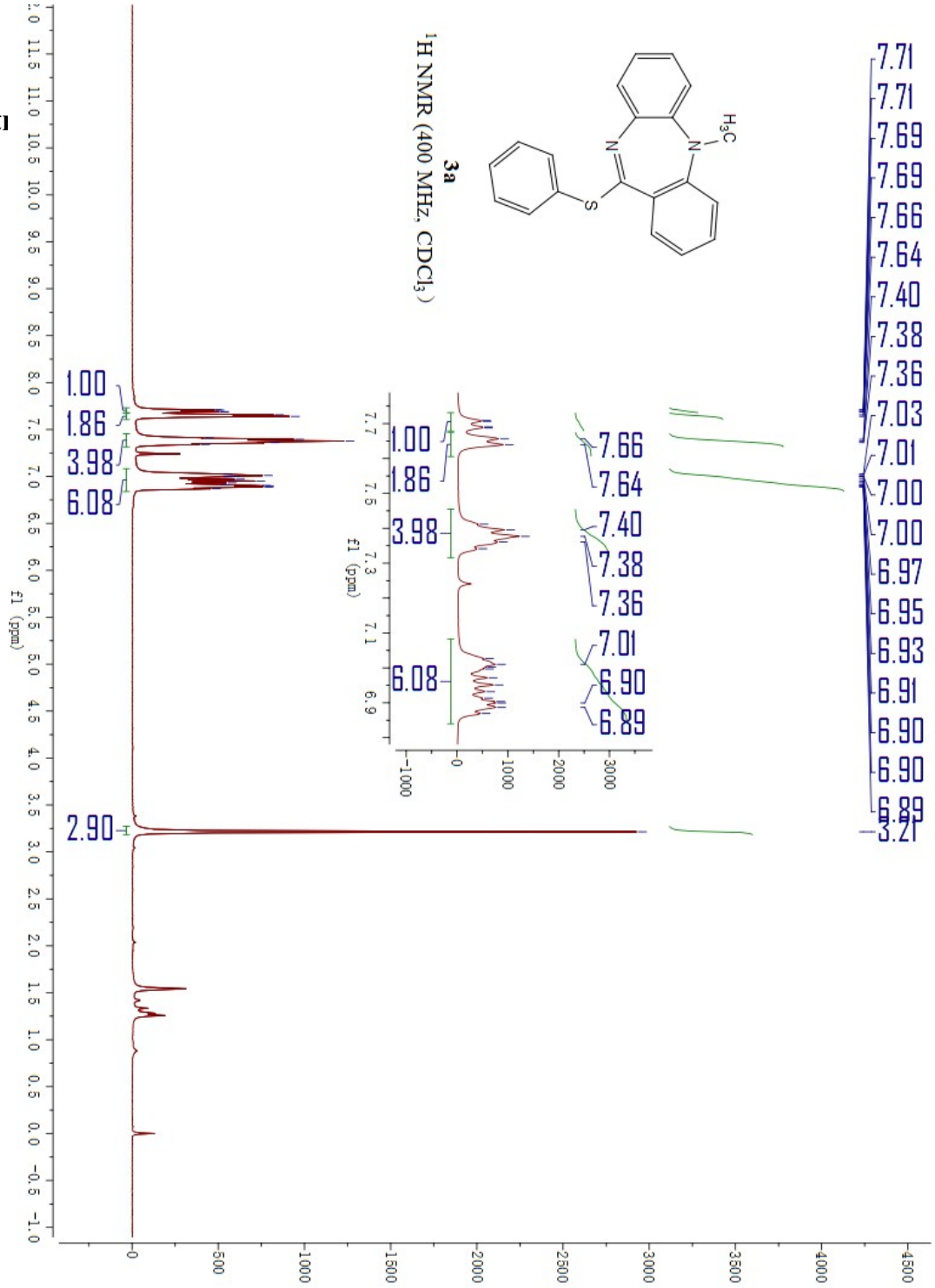
5-methyl-11-(p-tolylthio)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3ab) : PE/EA = 300:1, yellow solid (39.7 mg，60%). mp: 147.0 – 148.7 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 6.8 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.91 (t, *J* = 6.5 Hz, 2H), 6.88 – 6.80 (m, 3H), 6.77 (d, *J* = 8.0 Hz, 1H), 3.10 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 156.4, 145.7, 142.5, 138.8, 135.0, 132.3, 129.7, 129.0, 128.7, 127.2, 126.7, 125.7, 124.0, 123.0, 117.9, 117.3, 37.1, 21.4. HRMS (ESI) m/z: Calculated for $C_{21}H_{19}N_2S^+$ ($M+H^+$): 331.1263, Found: 331.1255.



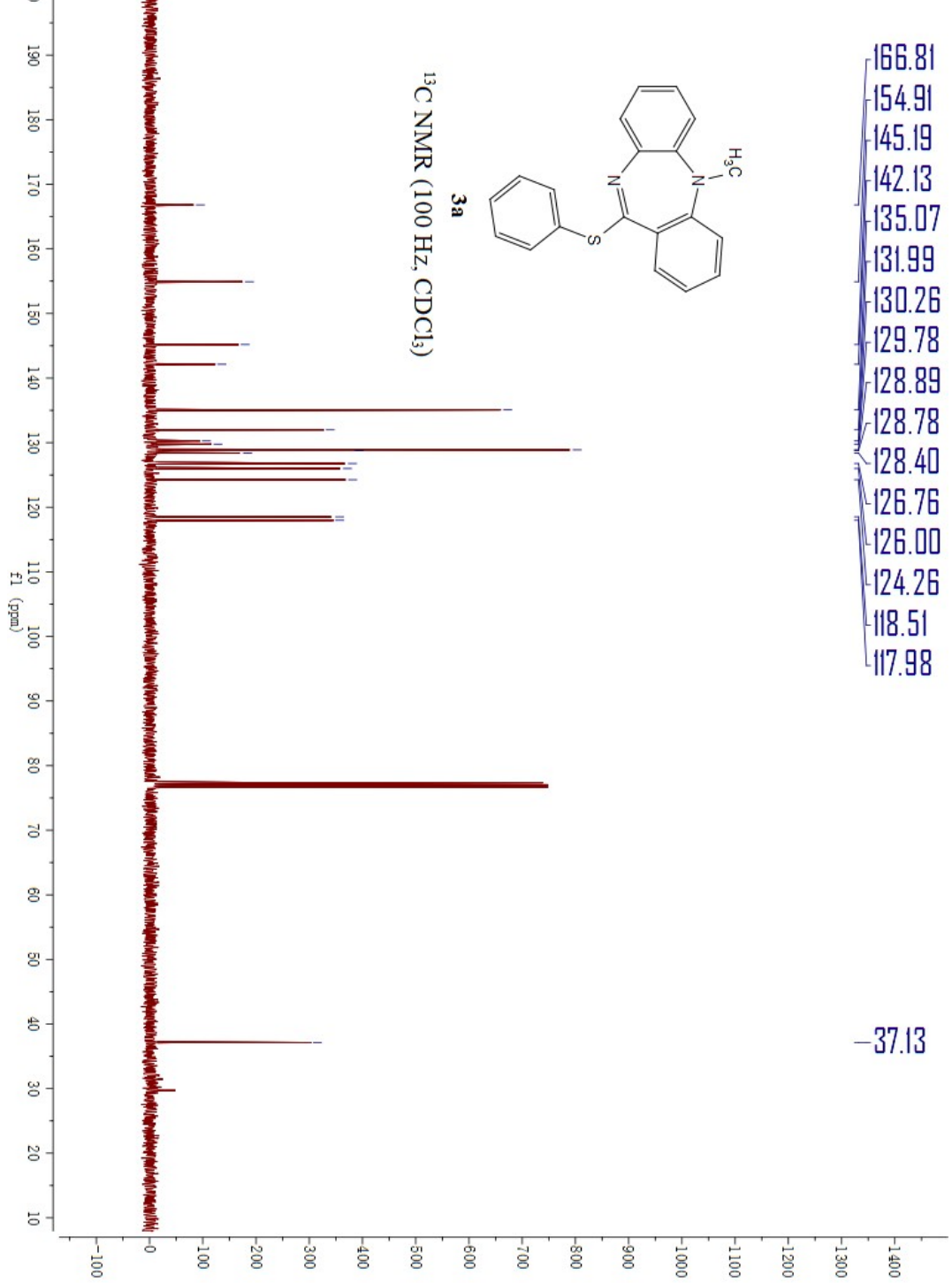
5-methyl-11-(phenylselanyl)-5*H*-dibenzo[*b*,*e*][1,4]diazepine (5) : PE/EA = 200:1, yellow solid (24.8 mg，34%). mp: 127.4 – 129.7 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 2H), 7.62 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.38 – 7.27 (m, 4H), 7.07 – 6.82 (m, 6H), 3.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 156.0, 145.8, 142.8, 135.9, 132.2, 129.7, 129.4, 129.2, 128.9, 128.3, 126.6, 126.0, 124.0, 123.0, 118.1, 117.4, 37.1. HRMS (ESI) m/z: Calculated for $C_{20}H_{17}N_2Se^+$ ($M+H^+$): 365.0552, Found: 365.0564.

9. NMR Spectı

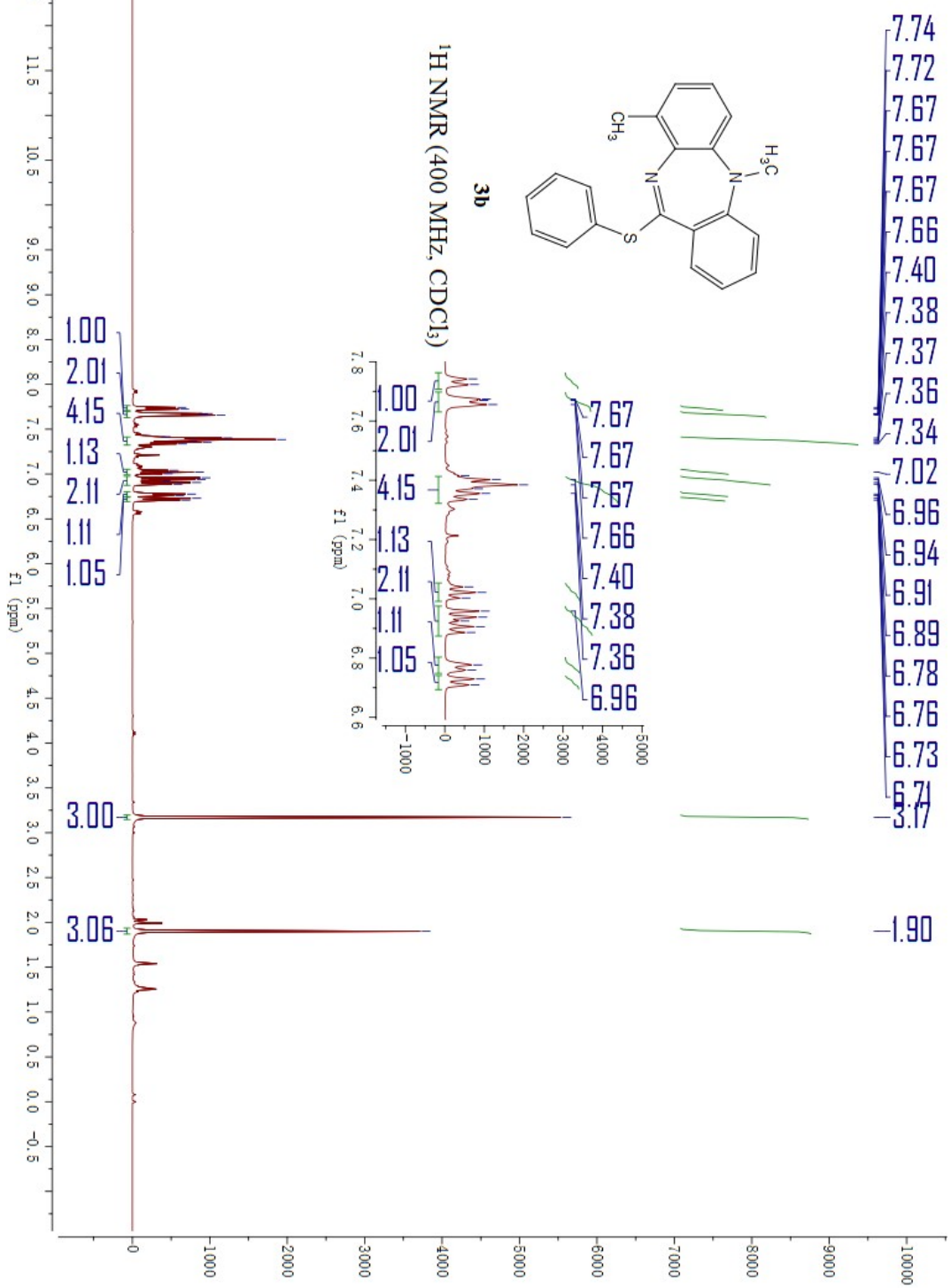
3a.[1]H NMR



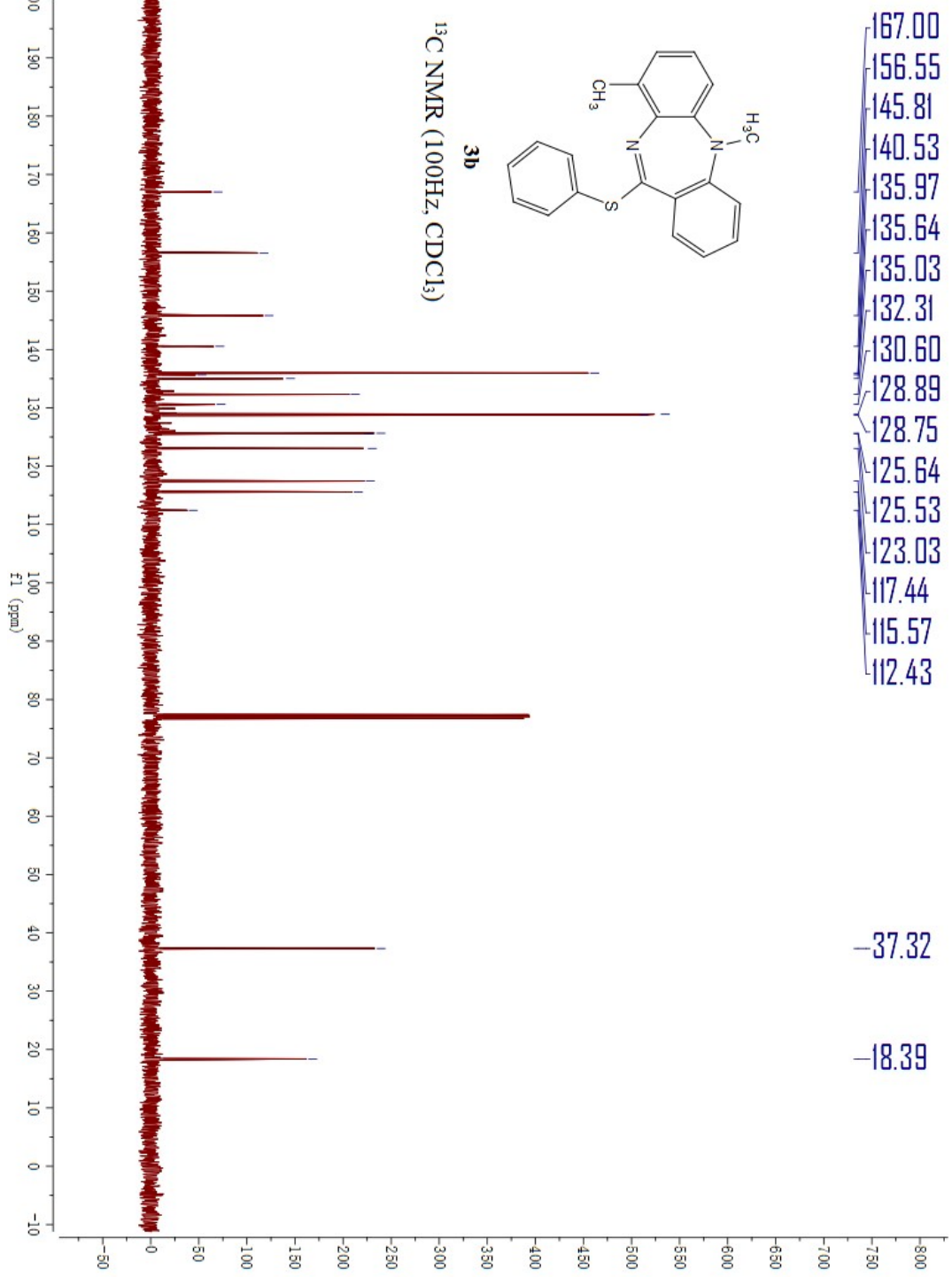
3a. [13]C NMR


166.81
154.91
145.19
142.13
135.07
131.99
130.26
129.78
128.89
128.78
128.40
126.76
126.00
124.26
118.51
117.98
37.13
3a
13C NMR (100 Hz, CDCl3)
f1 (ppm)

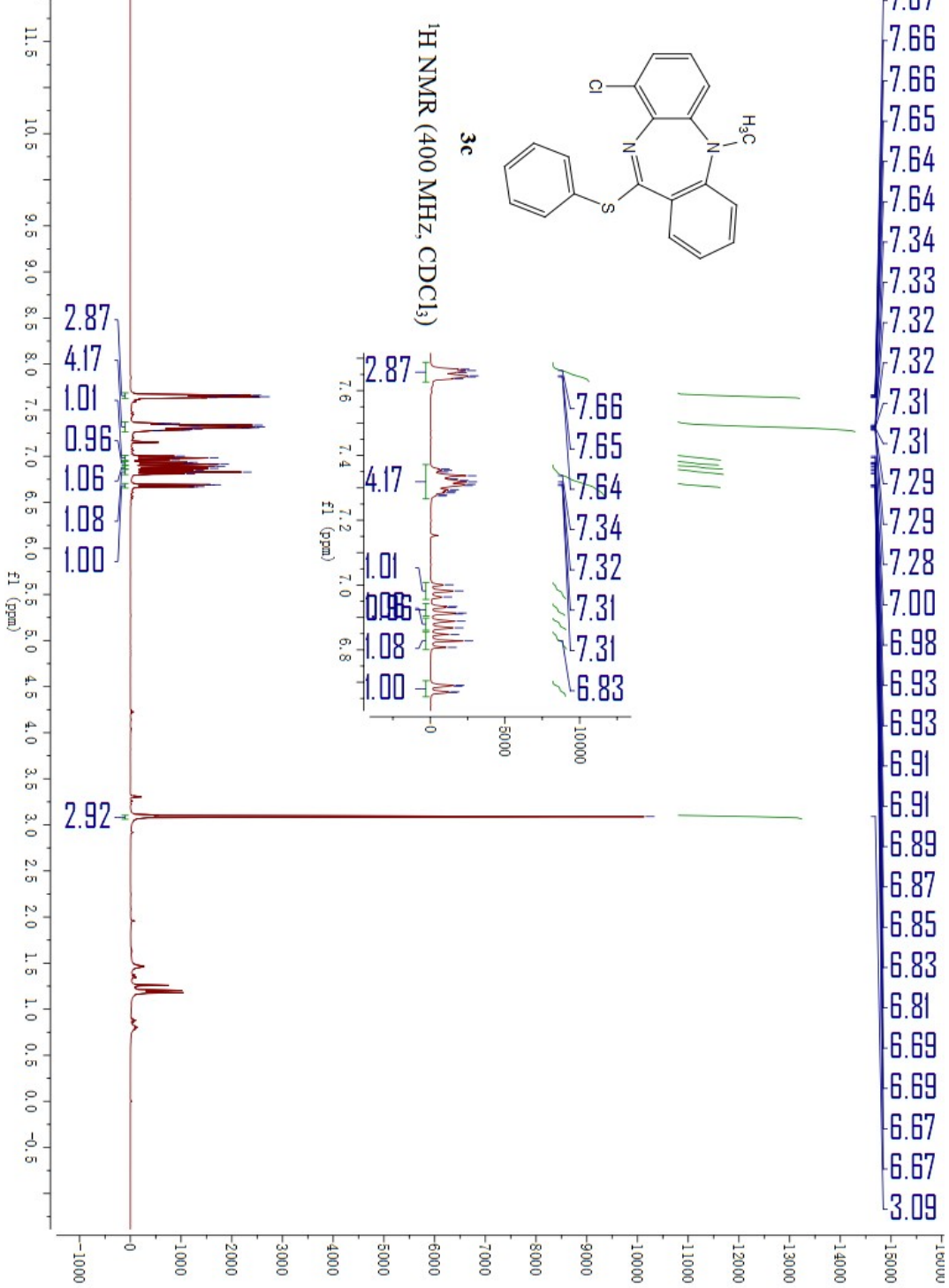
3b. ^{1}H NMR


3b
^{1}H NMR (400 MHz, CDCl$_3$)
CH$_3$
H$_3$C
N
N
S
1.00
2.01
4.15
1.13
2.11
1.11
1.05
3.00
3.06
7.74
7.72
7.67
7.67
7.67
7.66
7.40
7.38
7.37
7.36
7.34
7.02
6.96
6.94
6.91
6.89
6.78
6.76
6.73
6.71
3.17
1.90
f1 (ppm)

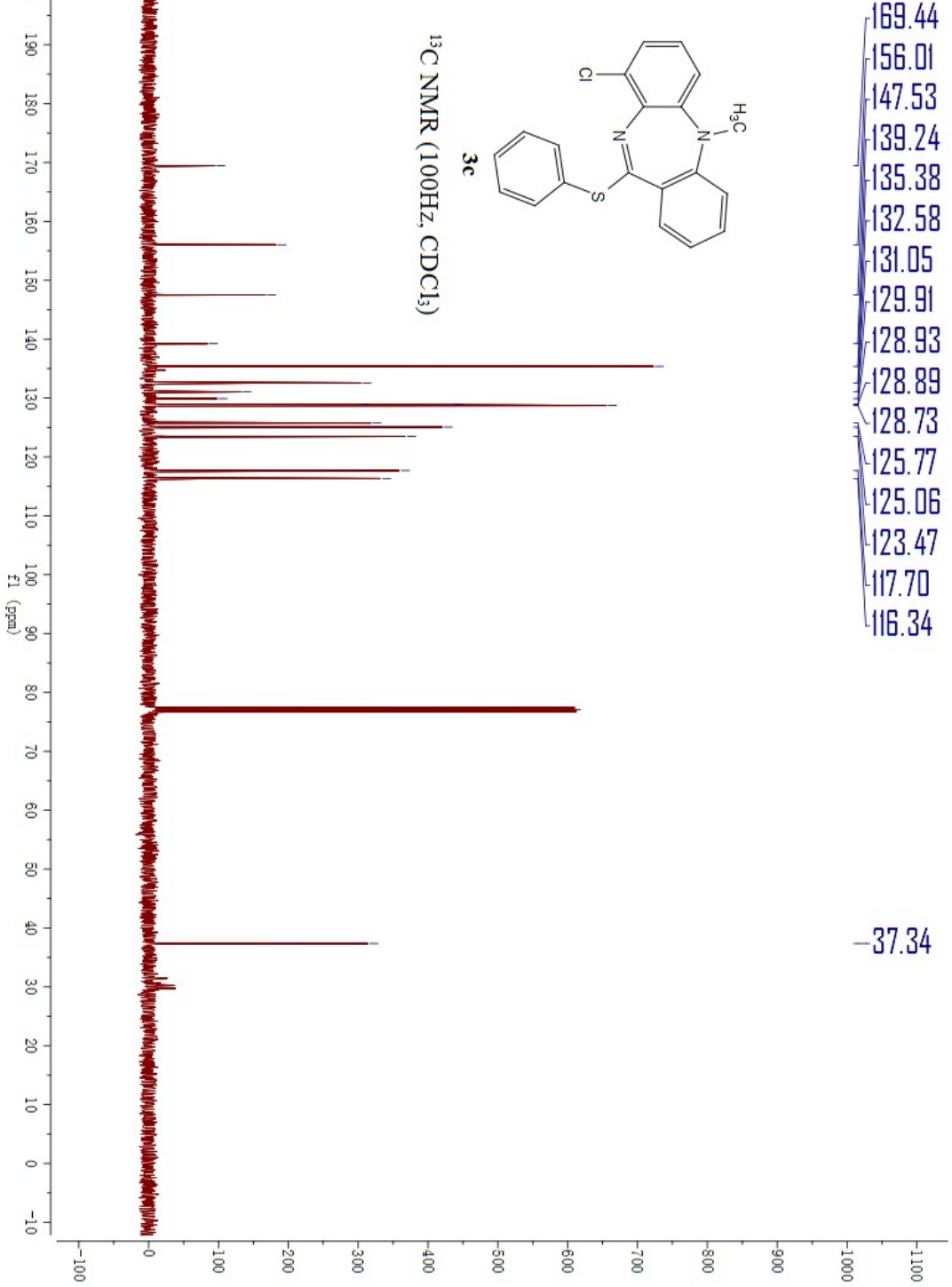
3b. ^{13}C NMR


^{13}C NMR (100Hz, CDCl$_3$)
3b
CH$_3$
H$_3$C
N
N
S
167.00
156.55
145.81
140.53
135.97
135.64
135.03
132.31
130.60
128.89
128.75
125.64
125.53
123.03
117.44
115.57
112.43
37.32
18.39
f1 (ppm)

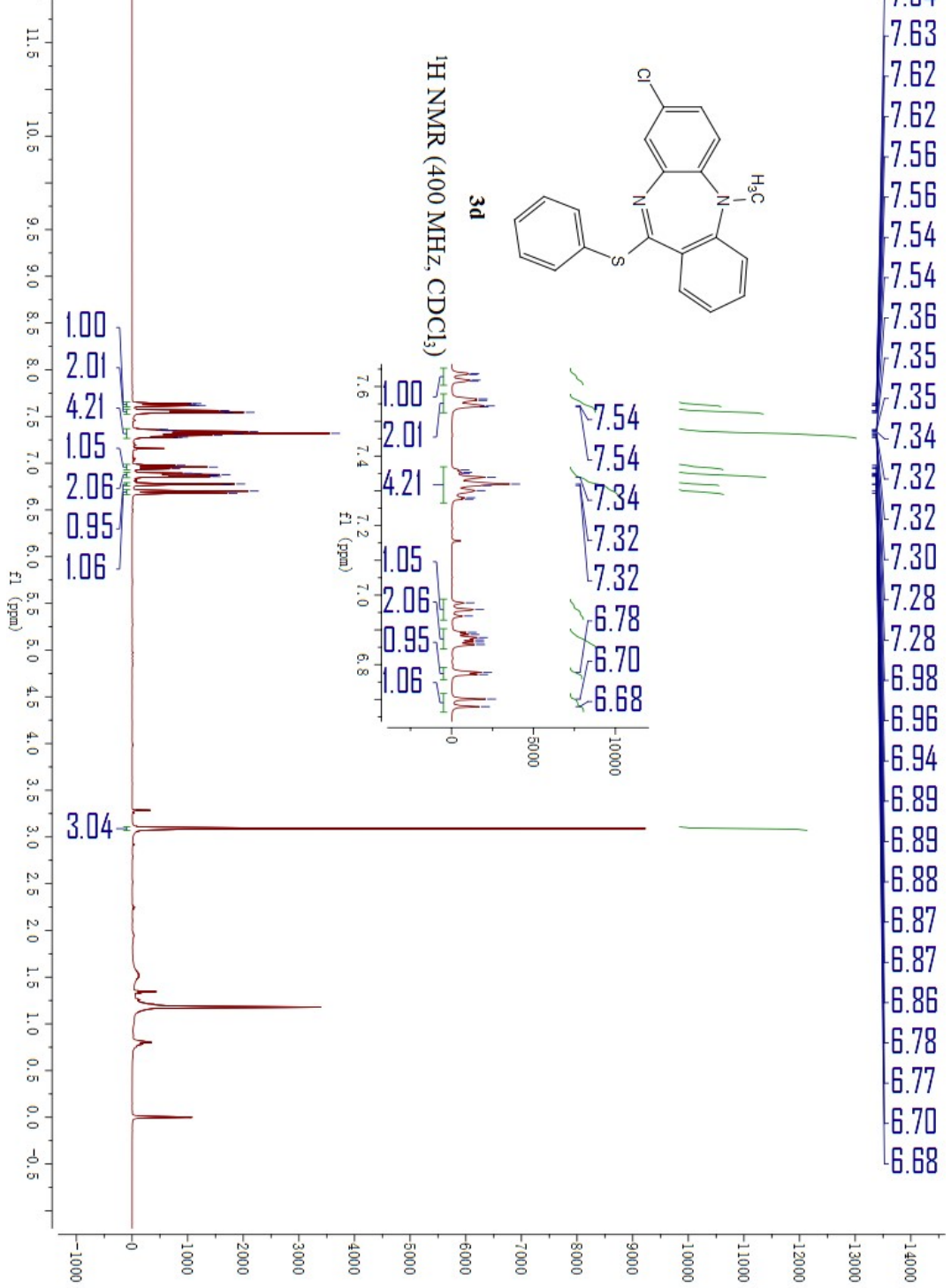
3c. ^{1}H NMR


3c
^{1}H NMR (400 MHz, CDCl$_3$)
Cl
N
N
H$_3$C
S
2.87
4.17
1.01
0.96
1.06
1.08
1.00
2.92
7.66
7.65
7.64
7.34
7.32
7.31
7.31
6.83
f1 (ppm)

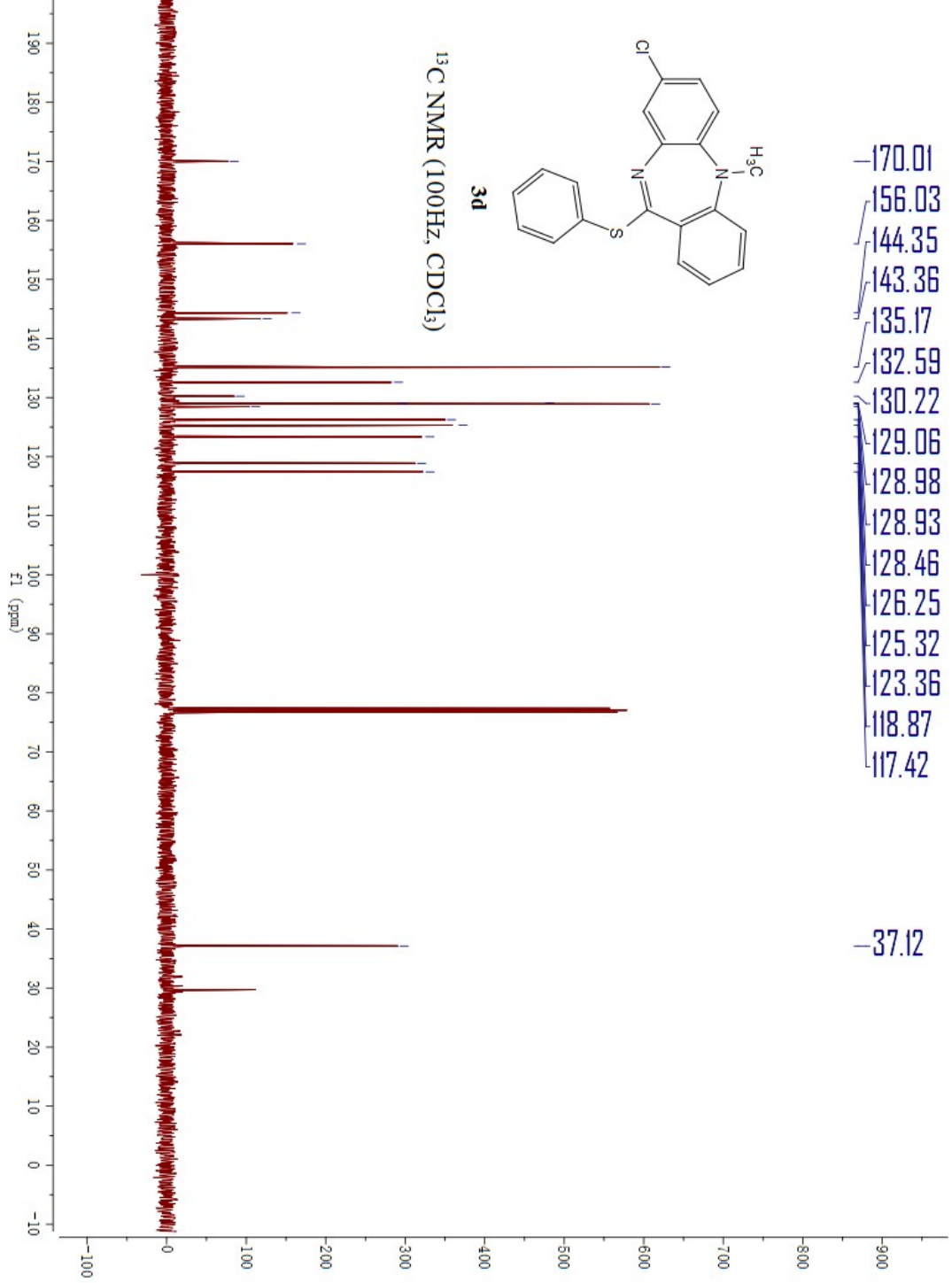
3c. ^{13}C NMR


169.44
156.01
147.53
139.24
135.38
132.58
131.05
129.91
128.93
128.89
128.73
125.77
125.06
123.47
117.70
116.34
37.34
^{13}C NMR (100Hz, CDCl$_3$)
3c
Cl
N
N
S
H$_3$C
f1 (ppm)

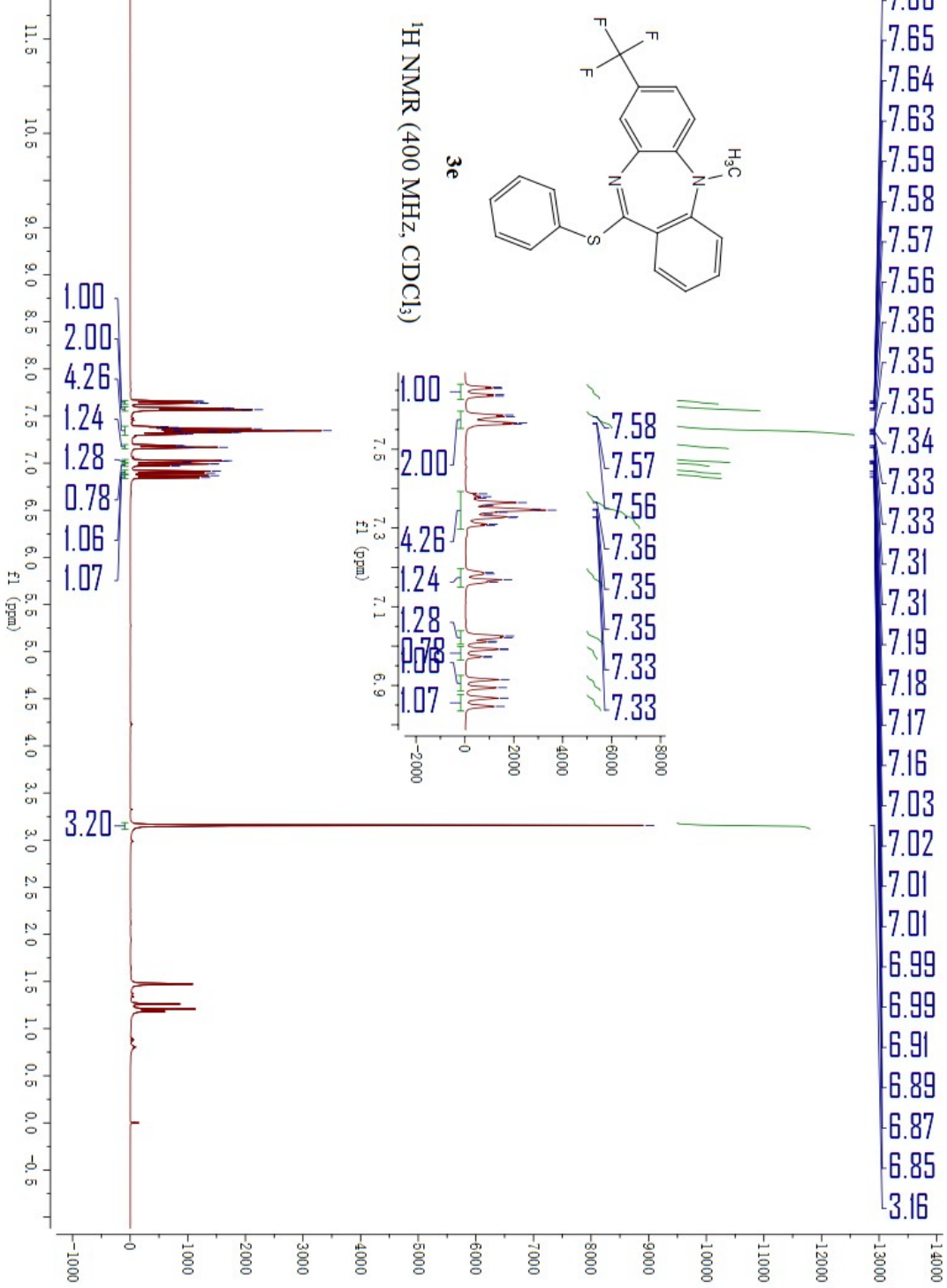
3d. ^{1}H NMR


3d
^{1}H NMR (400 MHz, $CDCl_3$)
Cl
H_3C
N
N
S
1.00
2.01
4.21
1.05
2.06
0.95
1.06
3.04
7.54
7.54
7.34
7.32
7.32
6.78
6.70
6.68
f1 (ppm)

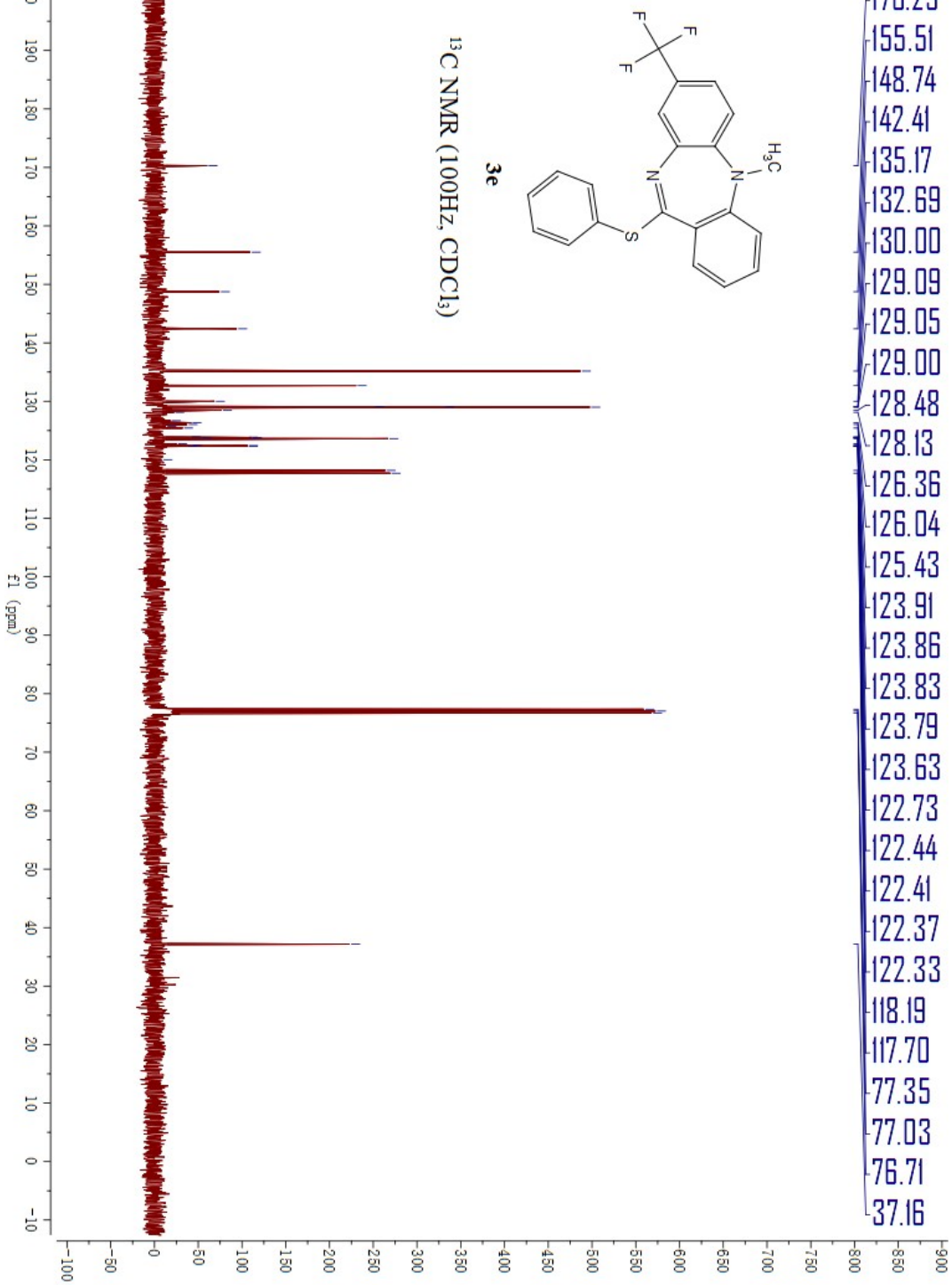
3d. ^{13}C NMR


13C NMR (100Hz, CDCl3)
3d
Cl
N
N
H3C
S
170.01
156.03
144.35
143.36
135.17
132.59
130.22
129.06
128.98
128.93
128.46
126.25
125.32
123.36
118.87
117.42
37.12
f1 (ppm)

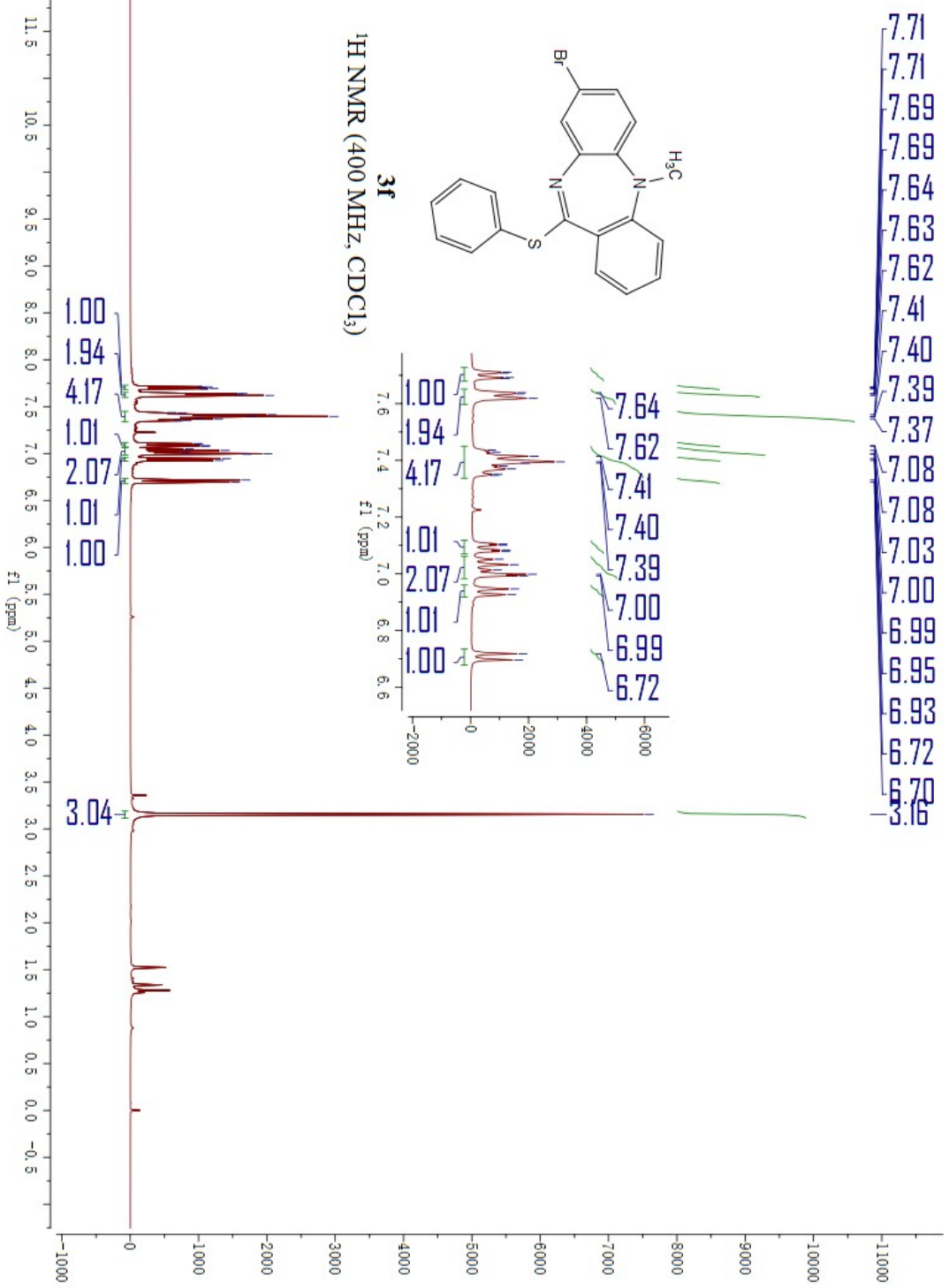
3e. ^{1}H NMR


3e
^{1}H NMR (400 MHz, CDCl$_3$)
F
F
F
H$_3$C
N
N
S
1.00
2.00
4.26
1.24
1.28
0.78
1.06
1.07
3.20
7.58
7.57
7.56
7.36
7.35
7.35
7.33
7.33
f1 (ppm)

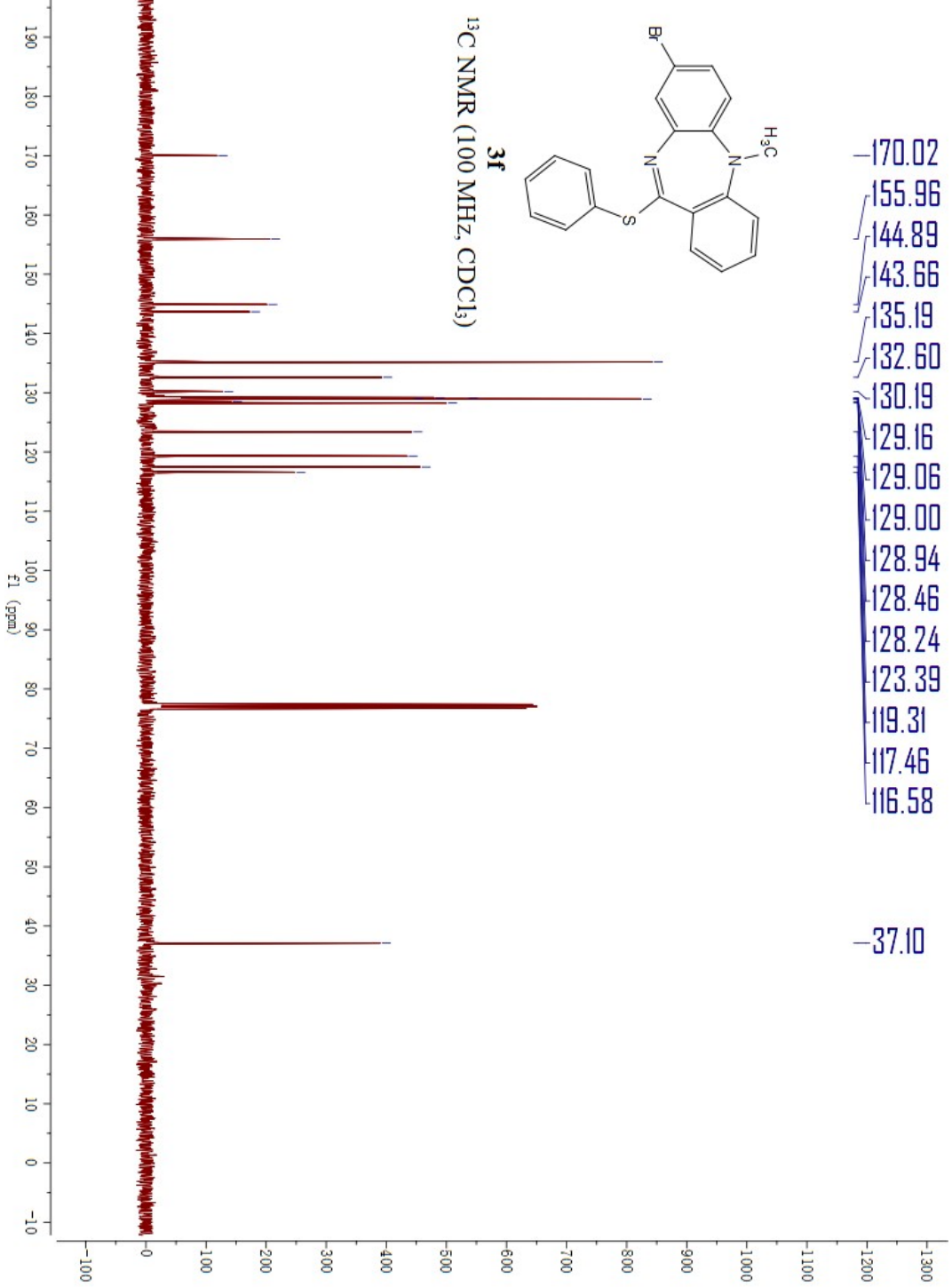
3e. ^{13}C NMR


^{13}C NMR (100Hz, CDCl$_3$)
3e
f1 (ppm)
155.51
148.74
142.41
135.17
132.69
130.00
129.09
129.05
129.00
128.48
128.13
126.36
126.04
125.43
123.91
123.86
123.83
123.79
123.63
122.73
122.44
122.41
122.37
122.33
118.19
117.70
77.35
77.03
76.71
37.16

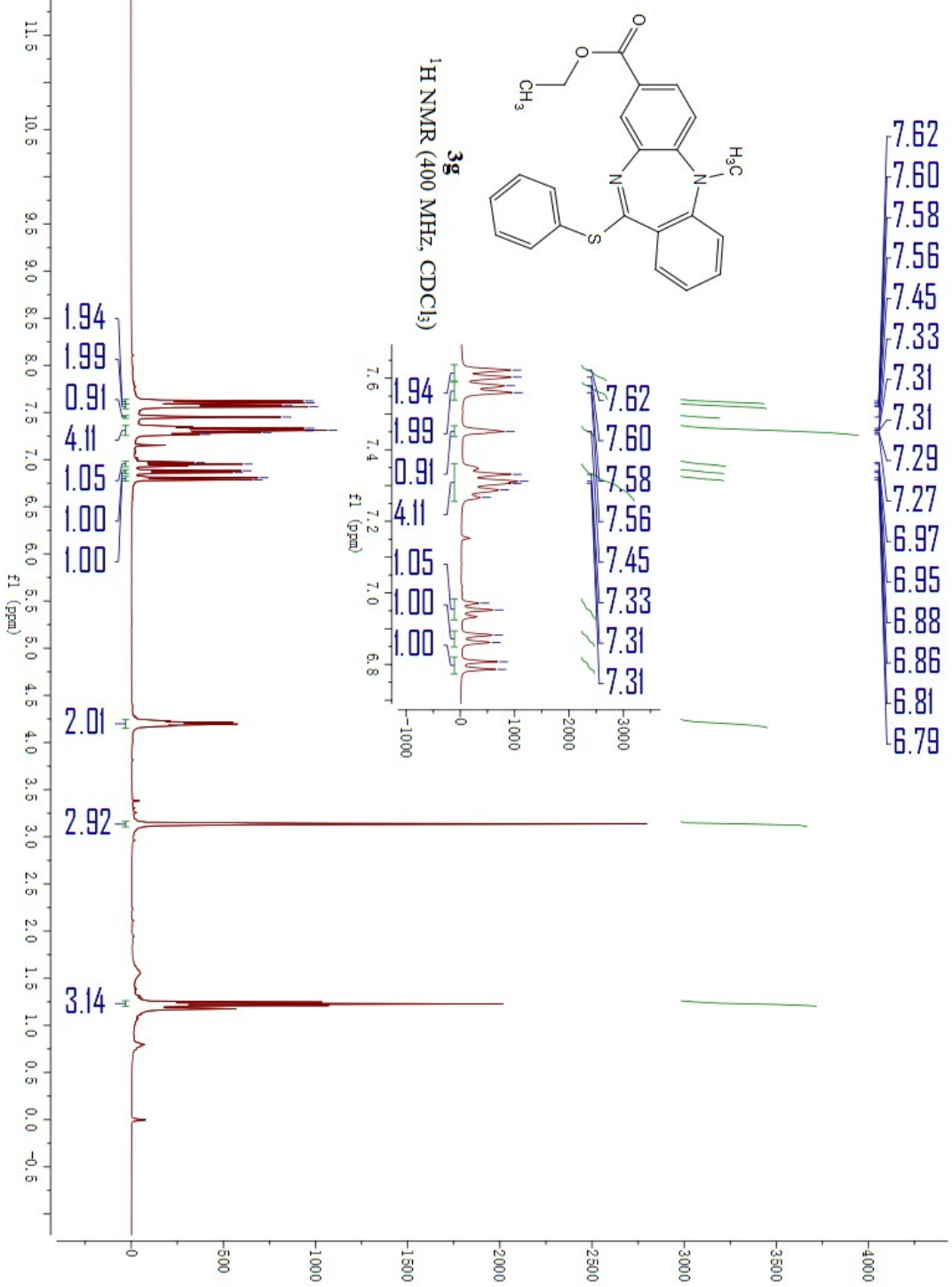
3f. ^{1}H NMR


3f
^{1}H NMR (400 MHz, CDCl$_3$)
Br
N
N
H$_3$C
S
1.00
1.94
4.17
1.01
2.07
1.01
1.00
3.04
7.71
7.71
7.69
7.69
7.64
7.63
7.62
7.41
7.40
7.39
7.37
7.08
7.08
7.03
7.00
6.99
6.95
6.93
6.72
6.70
3.16
f1 (ppm)

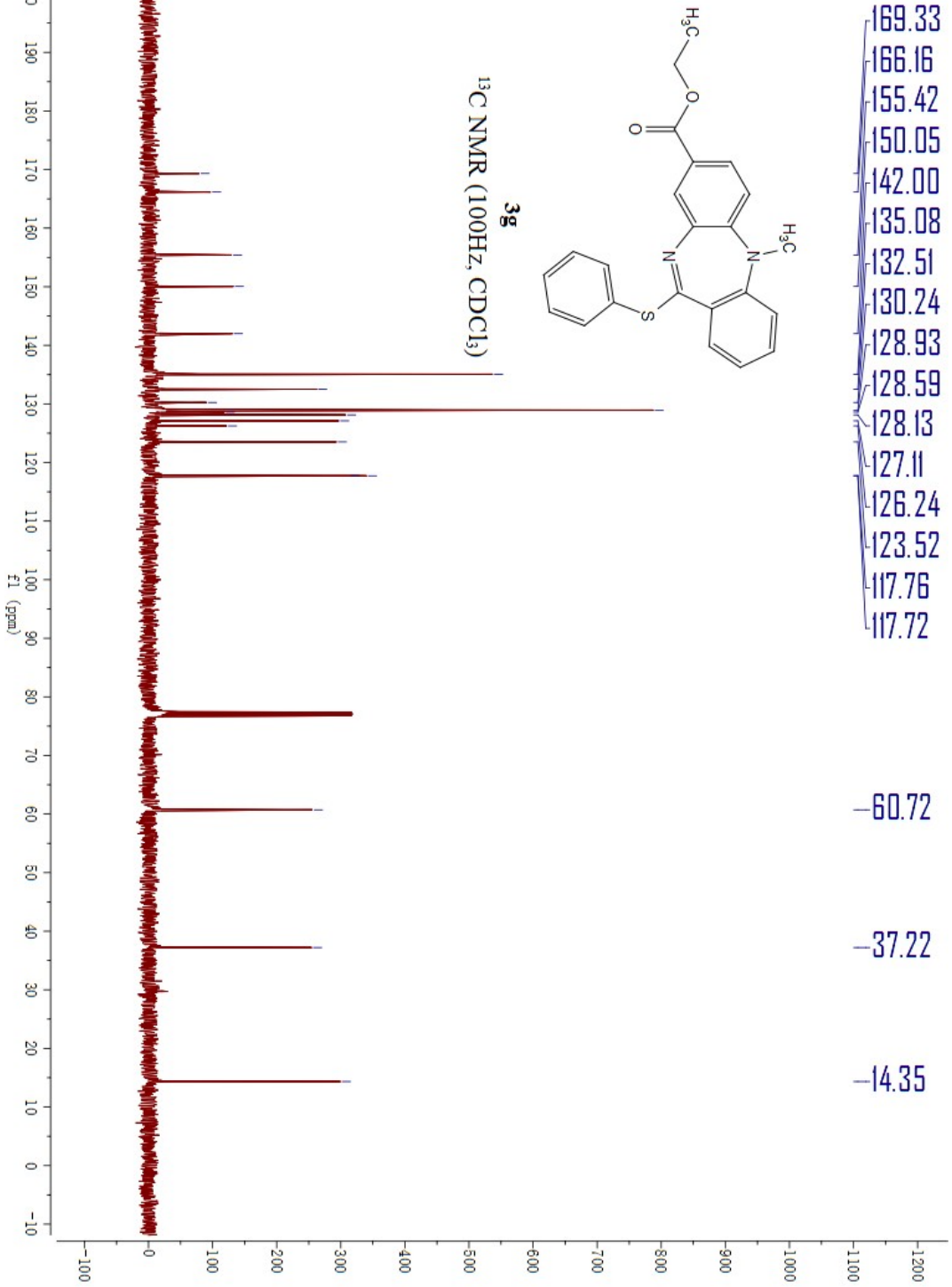
3f. ^{13}C NMR


3f
13C NMR (100 MHz, CDCl3)
Br
H3C
N
N
S
170.02
155.96
144.89
143.66
135.19
132.60
130.19
129.16
129.06
129.00
128.94
128.46
128.24
123.39
119.31
117.46
116.58
37.10
f1 (ppm)

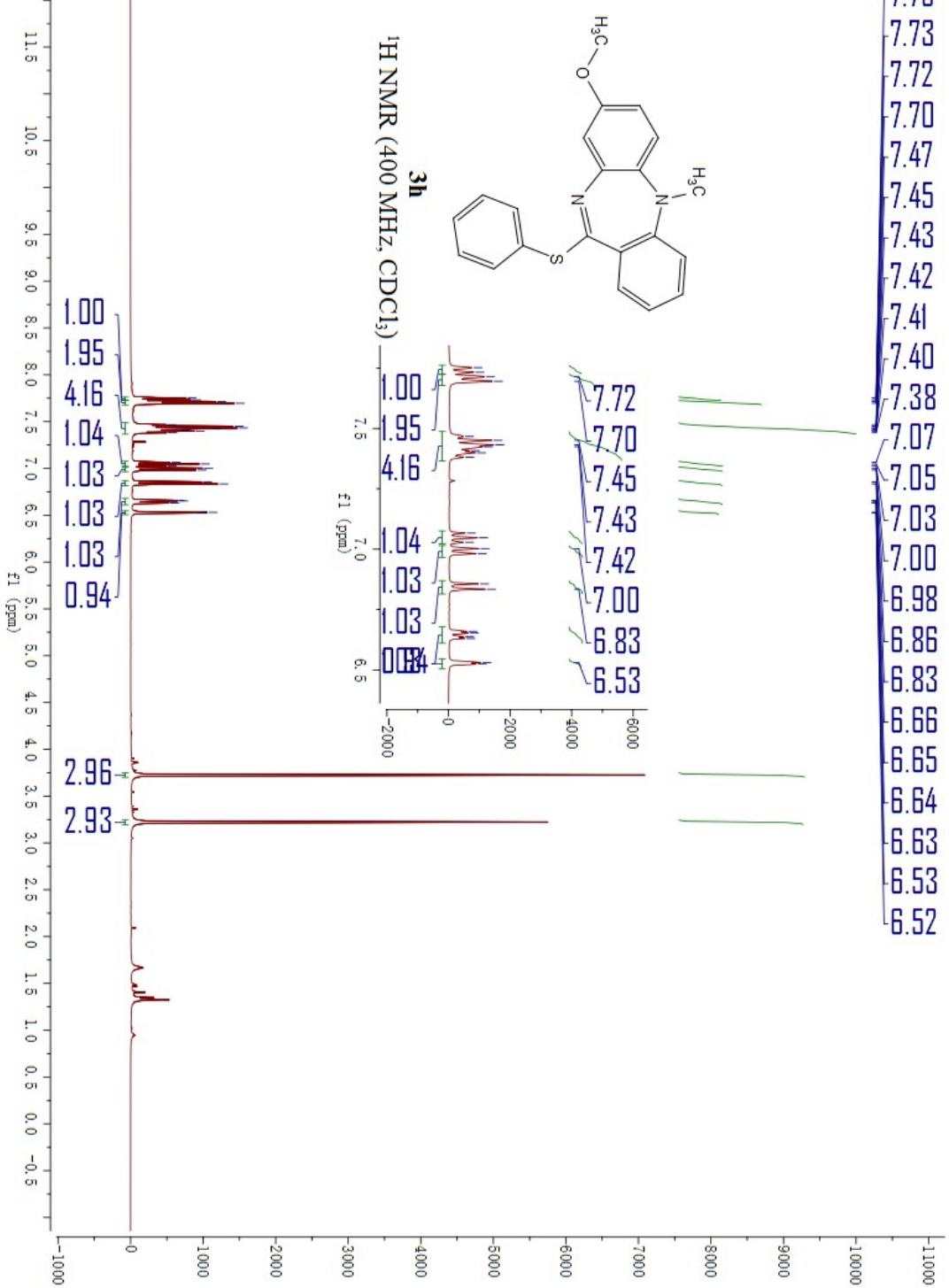
3g. ^{1}H NMR


3g
^{1}H NMR (400 MHz, CDCl$_3$)
1.94
1.99
0.91
4.11
1.05
1.00
1.00
2.01
2.92
3.14
7.62
7.60
7.58
7.56
7.45
7.33
7.31
7.31
7.29
7.27
6.97
6.95
6.88
6.86
6.81
6.79
f1 (ppm)

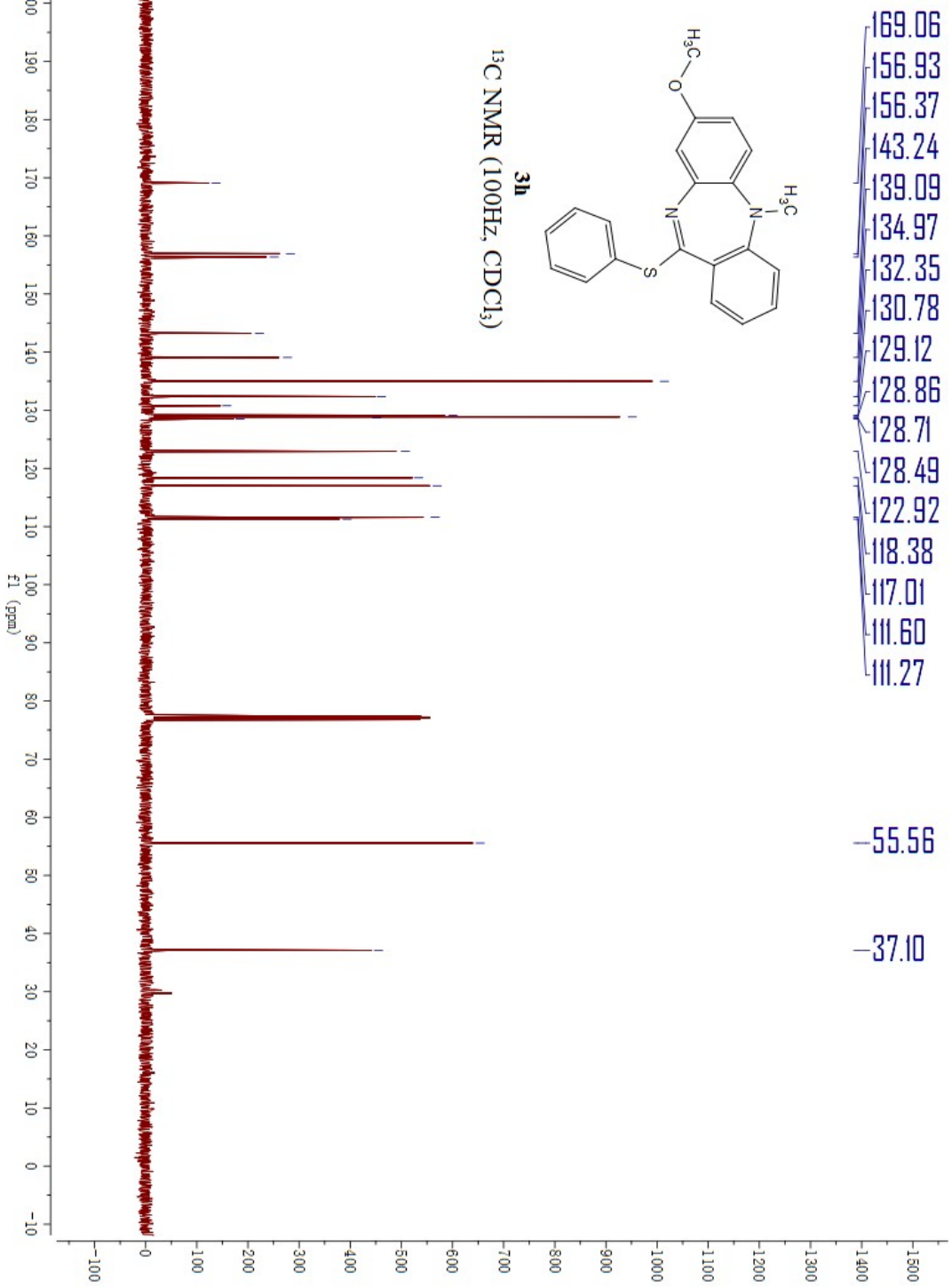
3g. ^{13}C NMR


3g
^{13}C NMR (100Hz, $CDCl_3$)
169.33
166.16
155.42
150.05
142.00
135.08
132.51
130.24
128.93
128.59
128.13
127.11
126.24
123.52
117.76
117.72
60.72
37.22
14.35
f1 (ppm)

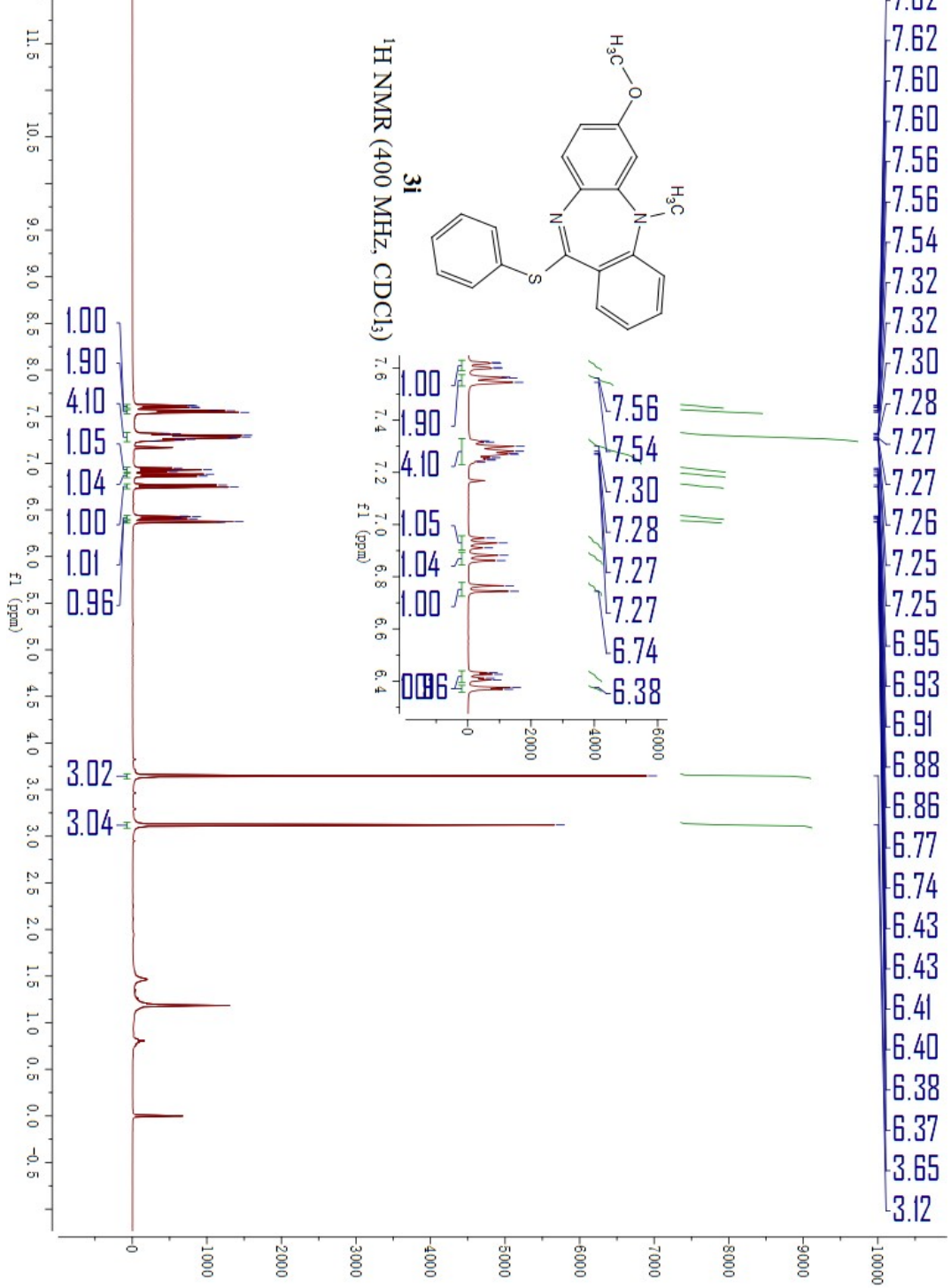
3h. ^{1}H NMR


3h
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
1.95
4.16
1.04
1.03
1.03
1.03
0.94
2.96
2.93
7.72
7.70
7.45
7.43
7.42
7.00
6.83
6.53
7.73
7.72
7.70
7.47
7.45
7.43
7.42
7.41
7.40
7.38
7.07
7.05
7.03
7.00
6.98
6.86
6.83
6.66
6.65
6.64
6.63
6.53
6.52
f1 (ppm)

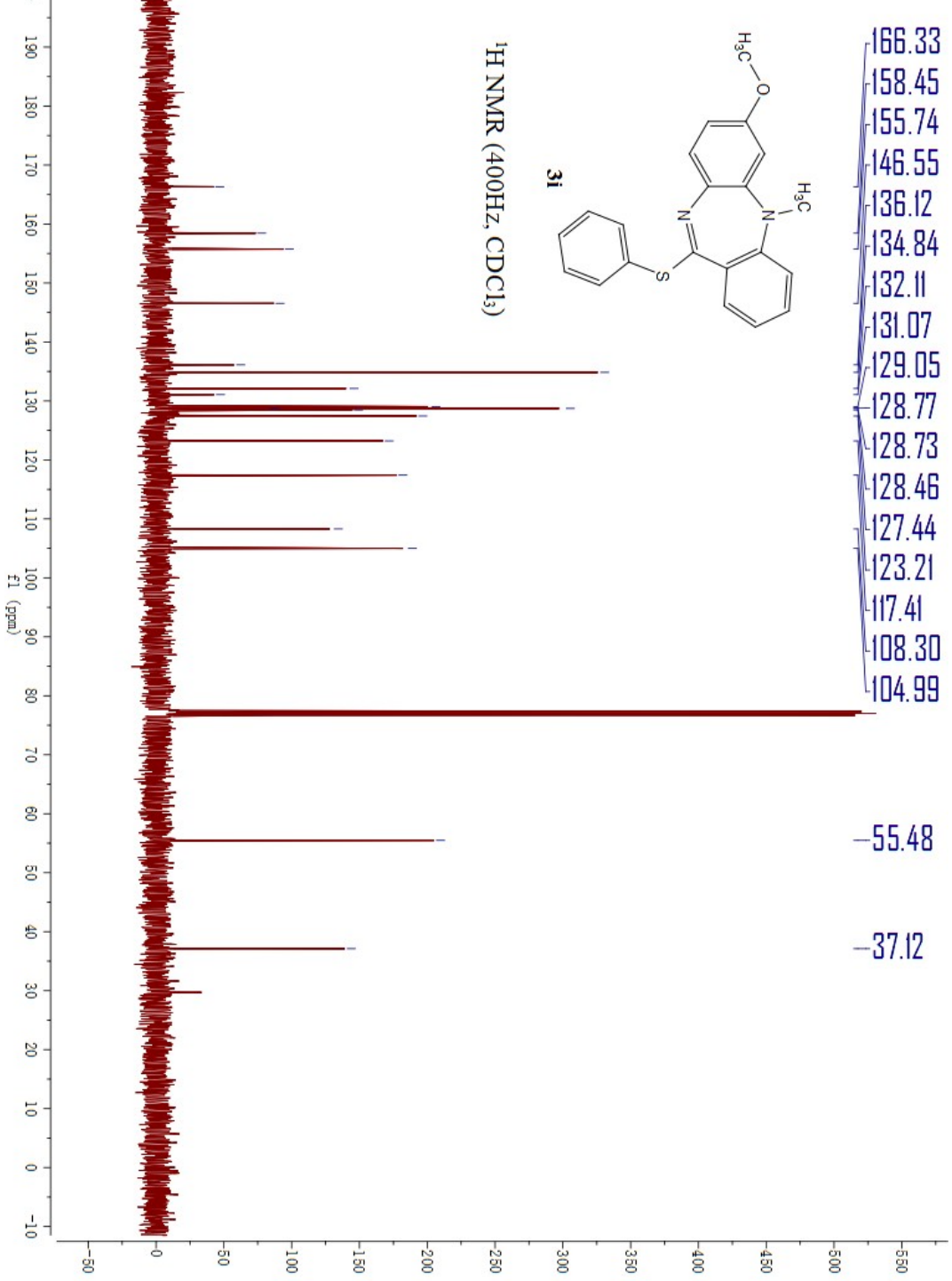
3h. ^{13}C NMR


3h
^{13}C NMR (100Hz, CDCl$_3$)
169.06
156.93
156.37
143.24
139.09
134.97
132.35
130.78
129.12
128.86
128.71
128.49
122.92
118.38
117.01
111.60
111.27
55.56
37.10
f1 (ppm)

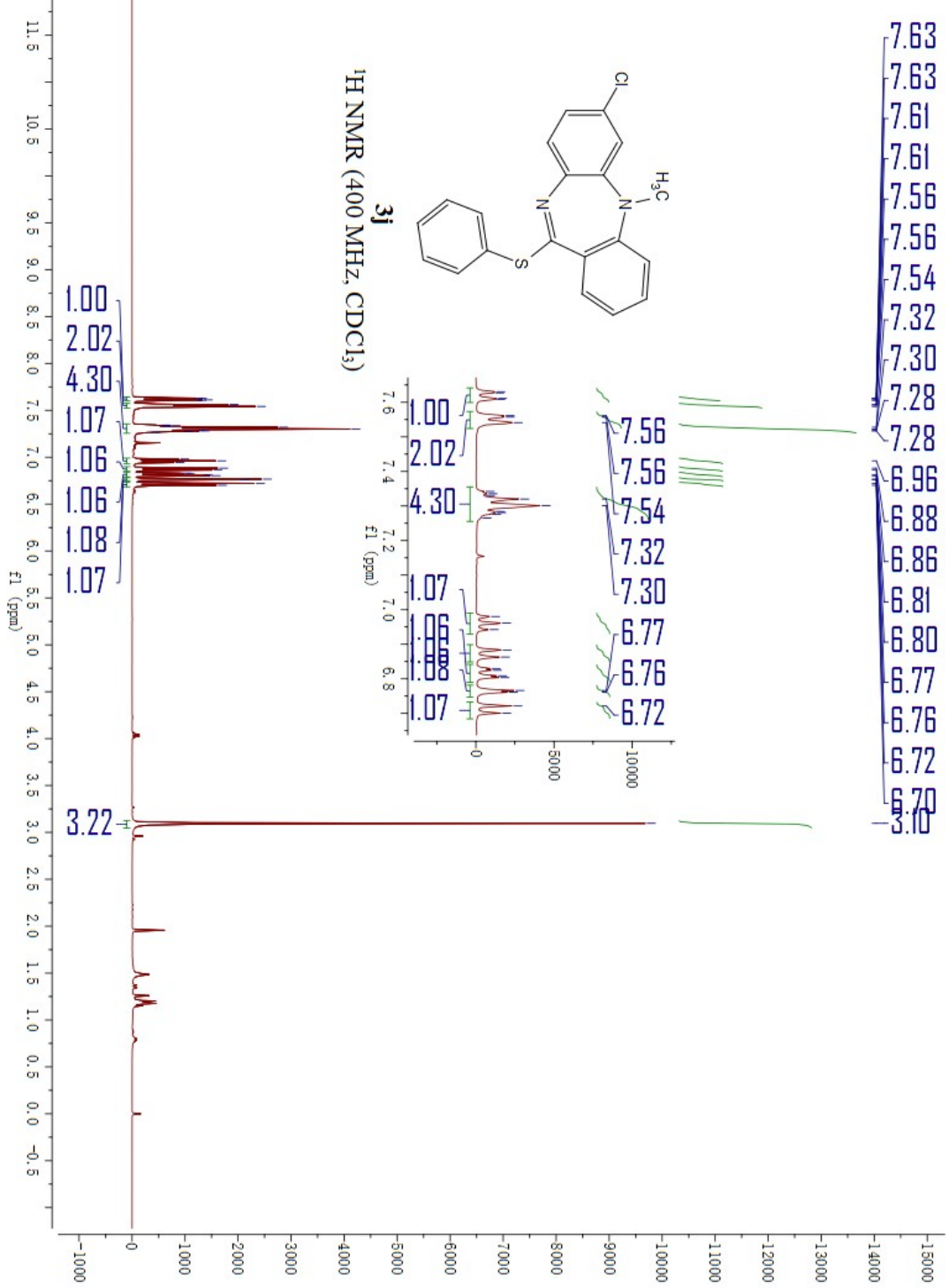
3i. ^{1}H NMR


3i
^{1}H NMR (400 MHz, CDCl$_3$)
H$_3$C
O
N
N
H$_3$C
S
1.00
1.90
4.10
1.05
1.04
1.00
1.01
0.96
3.02
3.04
7.56
7.54
7.30
7.28
7.27
7.27
6.74
6.38
f1 (ppm)

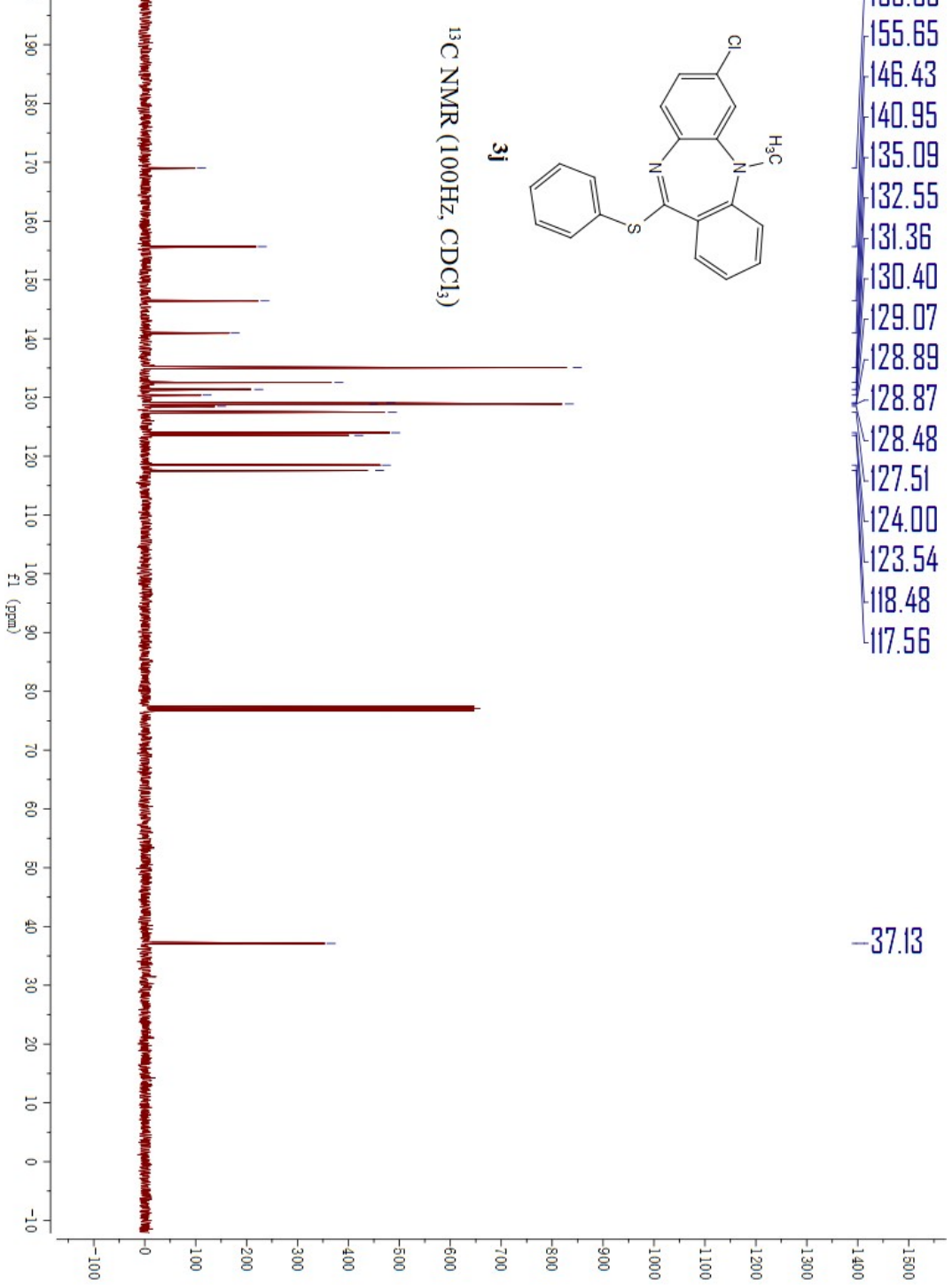
3i. ^{13}C NMR


166.33
158.45
155.74
146.55
136.12
134.84
132.11
131.07
129.05
128.77
128.73
128.46
127.44
123.21
117.41
108.30
104.99
55.48
37.12
3i
^{1}H NMR (400Hz, CDCl$_3$)
f1 (ppm)

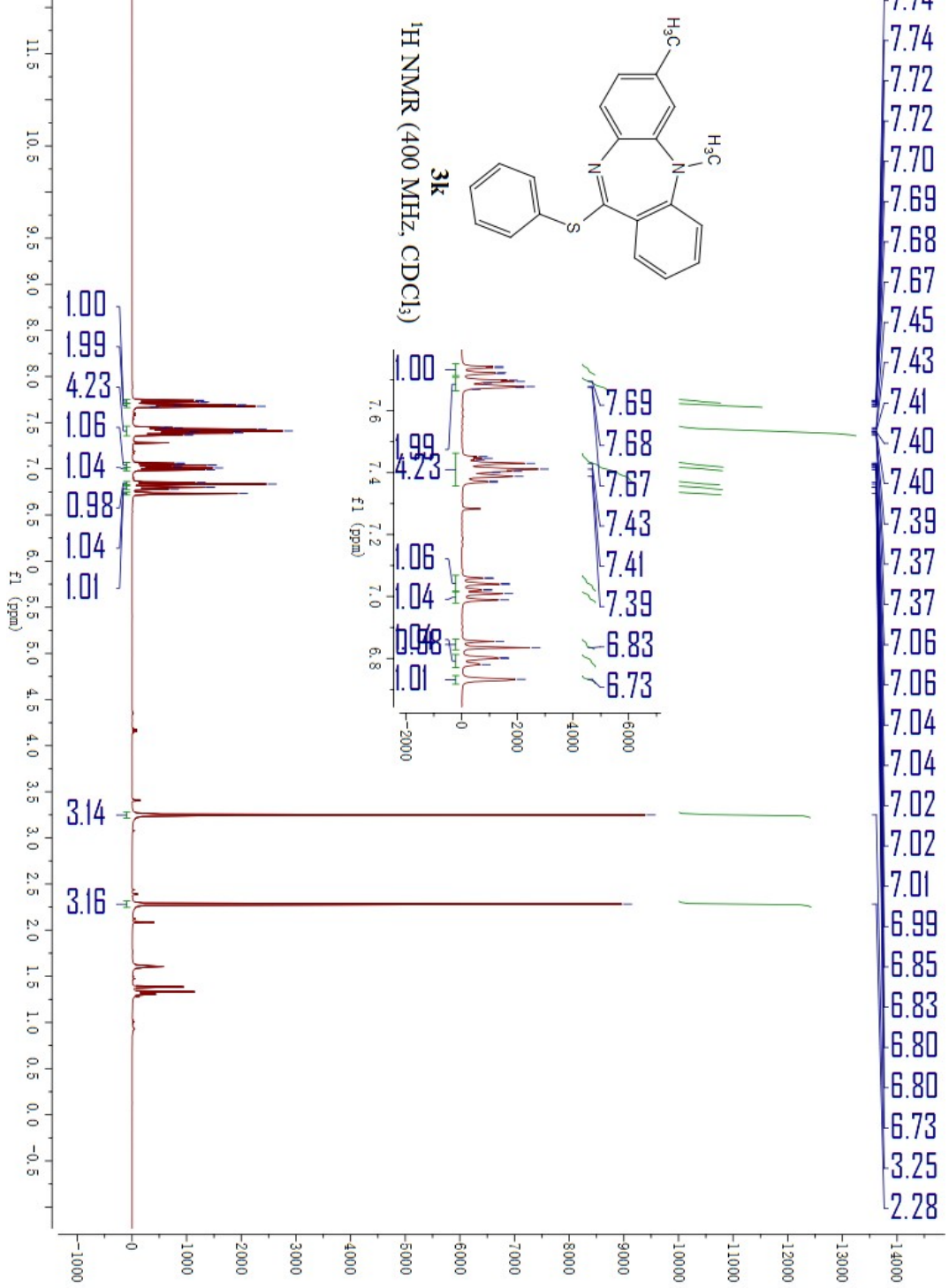
3j. ^{1}H NMR


3j
¹H NMR (400 MHz, CDCl₃)
Cl
H₃C
N
N
S
1.00
2.02
4.30
1.07
1.06
1.06
1.08
1.07
3.22
7.63
7.63
7.61
7.61
7.56
7.56
7.54
7.32
7.30
7.28
7.28
6.96
6.88
6.86
6.81
6.80
6.77
6.76
6.72
6.70
3.10
f1 (ppm)

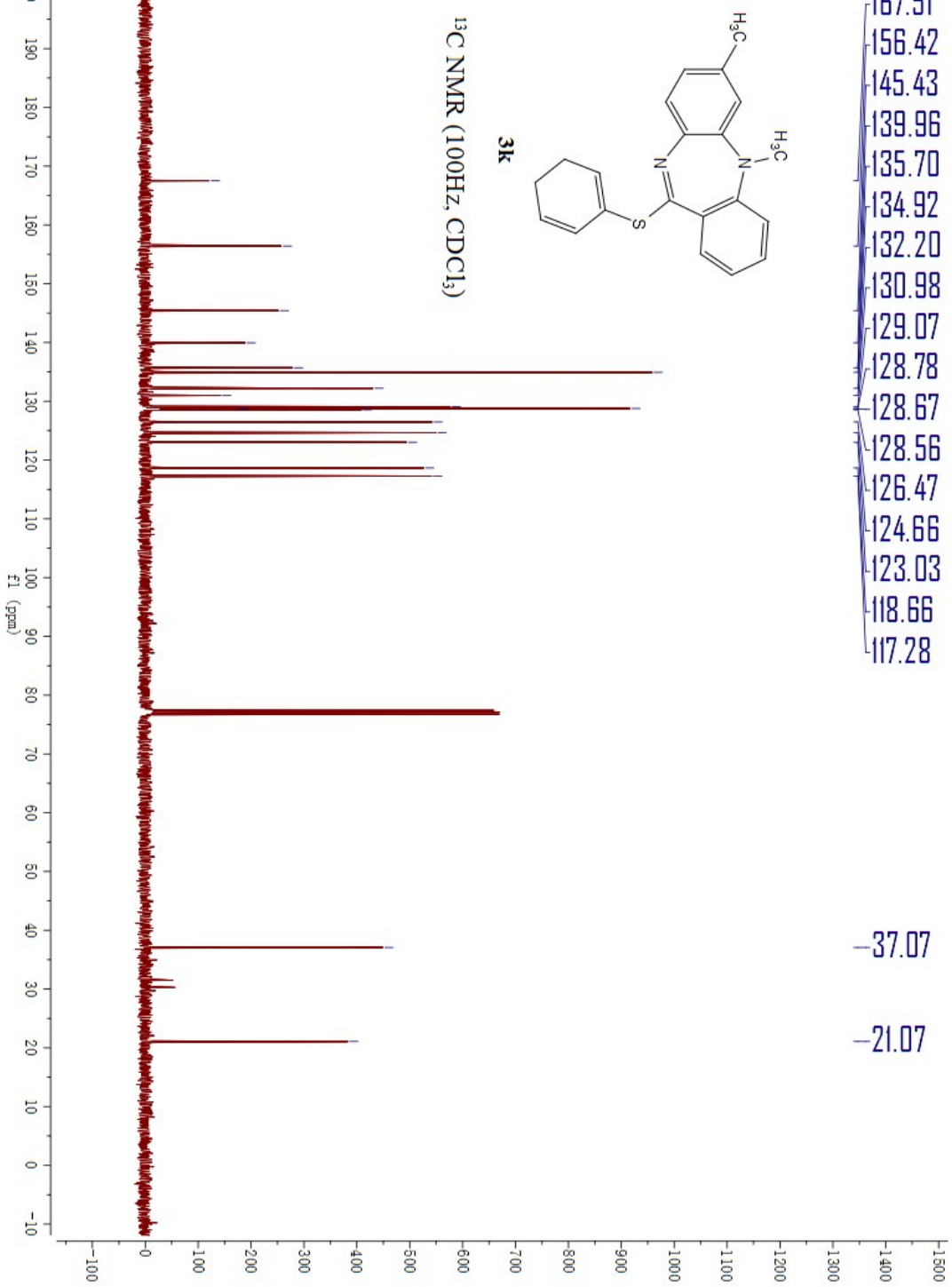
3j. ^{13}C NMR


155.65
146.43
140.95
135.09
132.55
131.36
130.40
129.07
128.89
128.87
128.48
127.51
124.00
123.54
118.48
117.56
37.13
3j
^{13}C NMR (100Hz, $CDCl_3$)
Cl
H_3C
N
N
S
f1 (ppm)

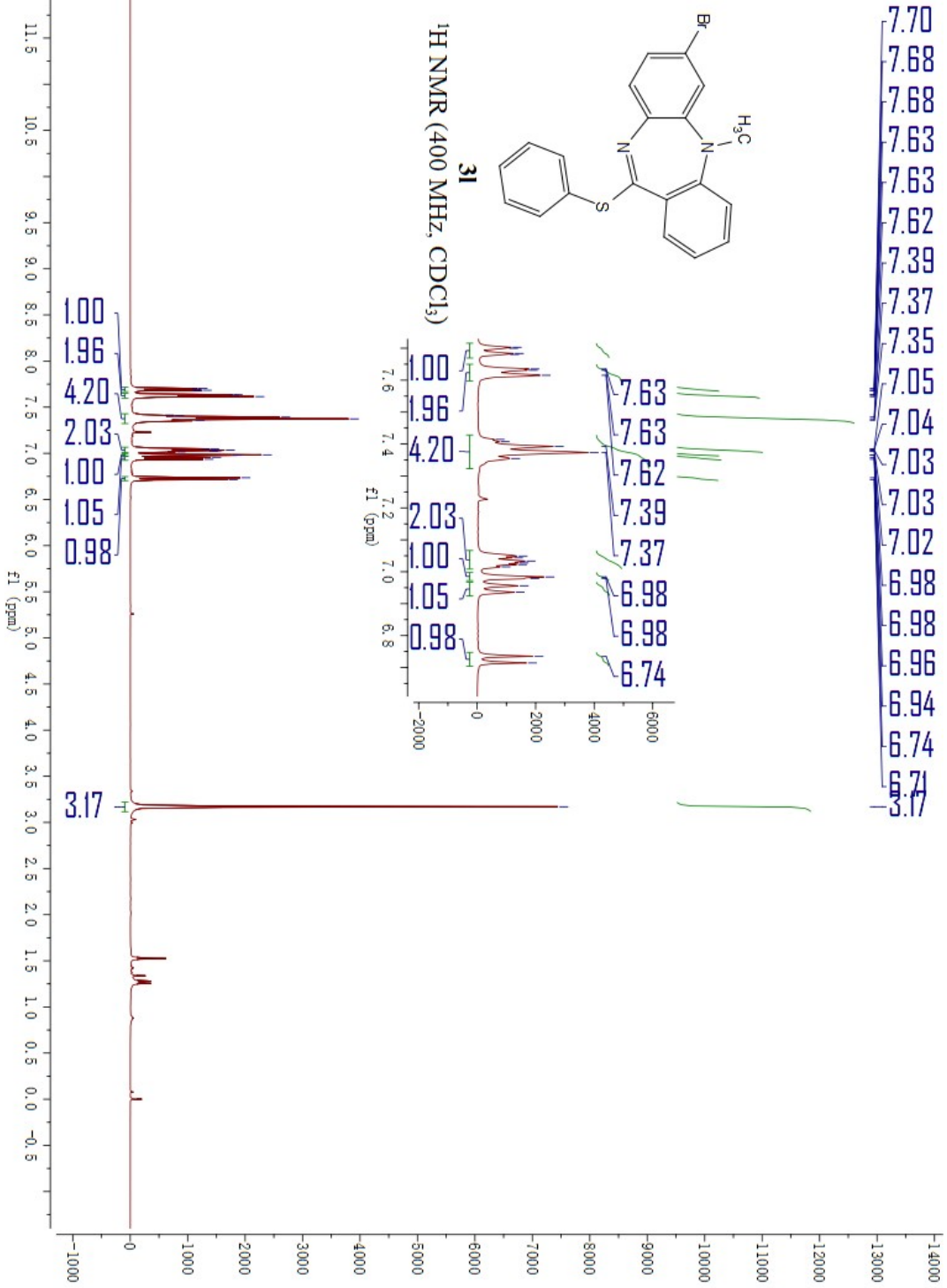
3k. ^{1}H NMR


3k
^{1}H NMR (400 MHz, CDCl$_3$)
H$_3$C
H$_3$C
N
N
S
1.00
1.99
4.23
1.06
1.04
0.98
1.04
1.01
3.14
3.16
7.69
7.68
7.67
7.43
7.41
7.39
6.83
6.73
f1 (ppm)

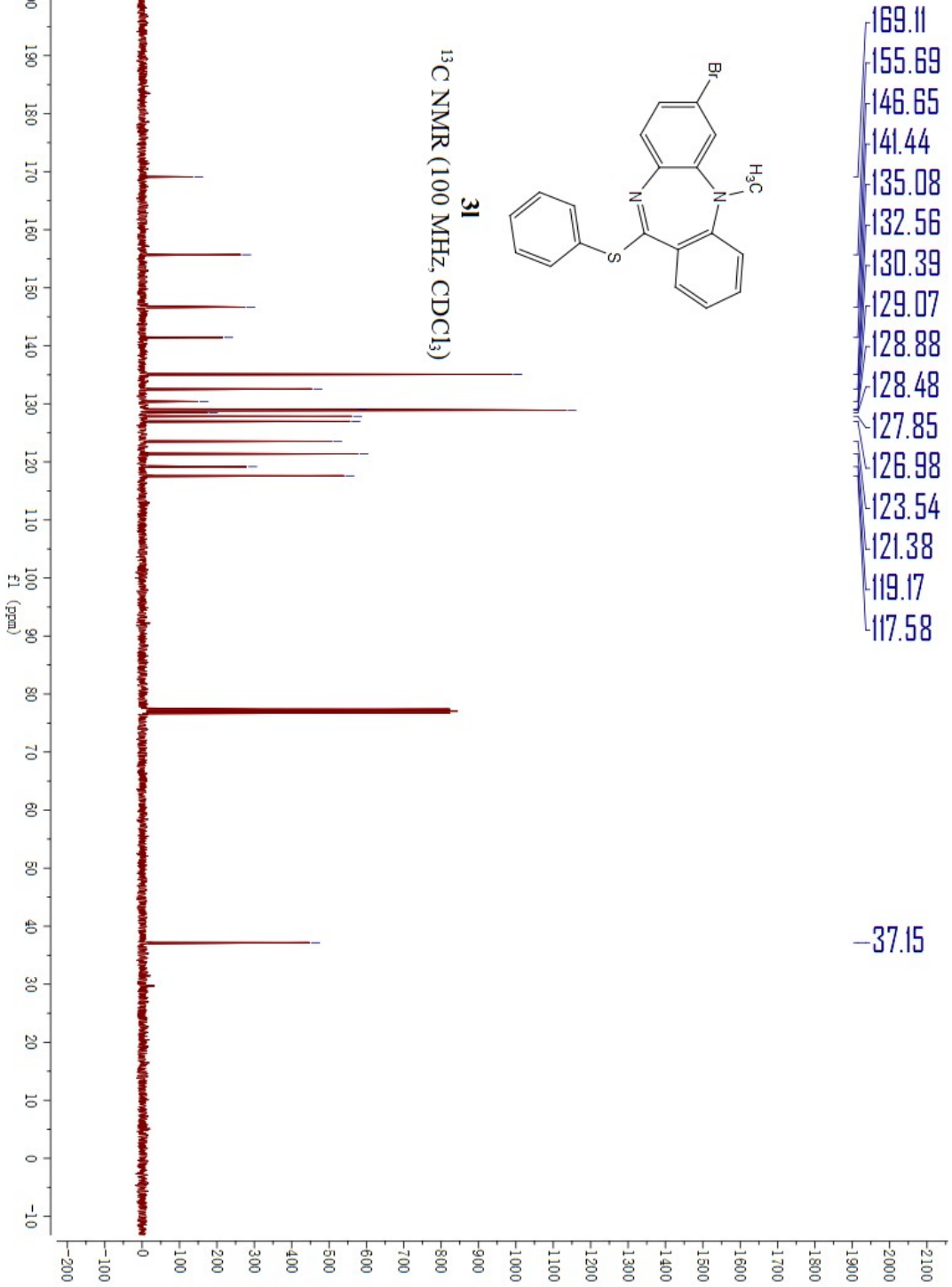
3k. ^{13}C NMR


^{13}C NMR (100Hz, CDCl$_3$)
3k
H$_3$C
H$_3$C
N
N
S
167.51
156.42
145.43
139.96
135.70
134.92
132.20
130.98
129.07
128.78
128.67
128.56
126.47
124.66
123.03
118.66
117.28
37.07
21.07
f1 (ppm)

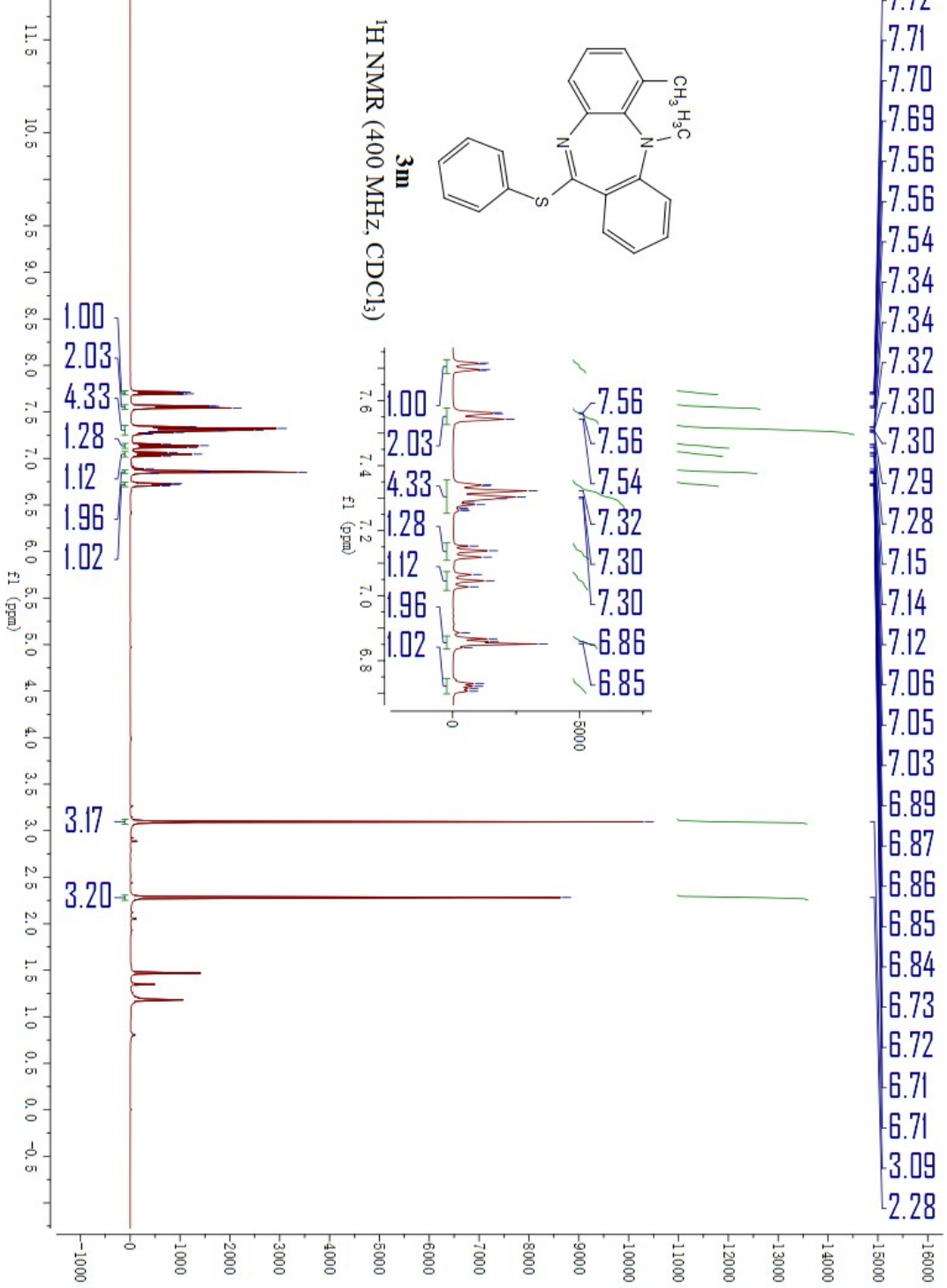
3l. ^{1}H NMR


3l
^{1}H NMR (400 MHz, CDCl$_3$)
Br
H$_3$C
N
N
S
1.00
1.96
4.20
2.03
1.00
1.05
0.98
3.17
7.70
7.68
7.68
7.63
7.63
7.62
7.39
7.37
7.35
7.05
7.04
7.03
7.03
7.02
6.98
6.98
6.96
6.94
6.74
6.71
f1 (ppm)

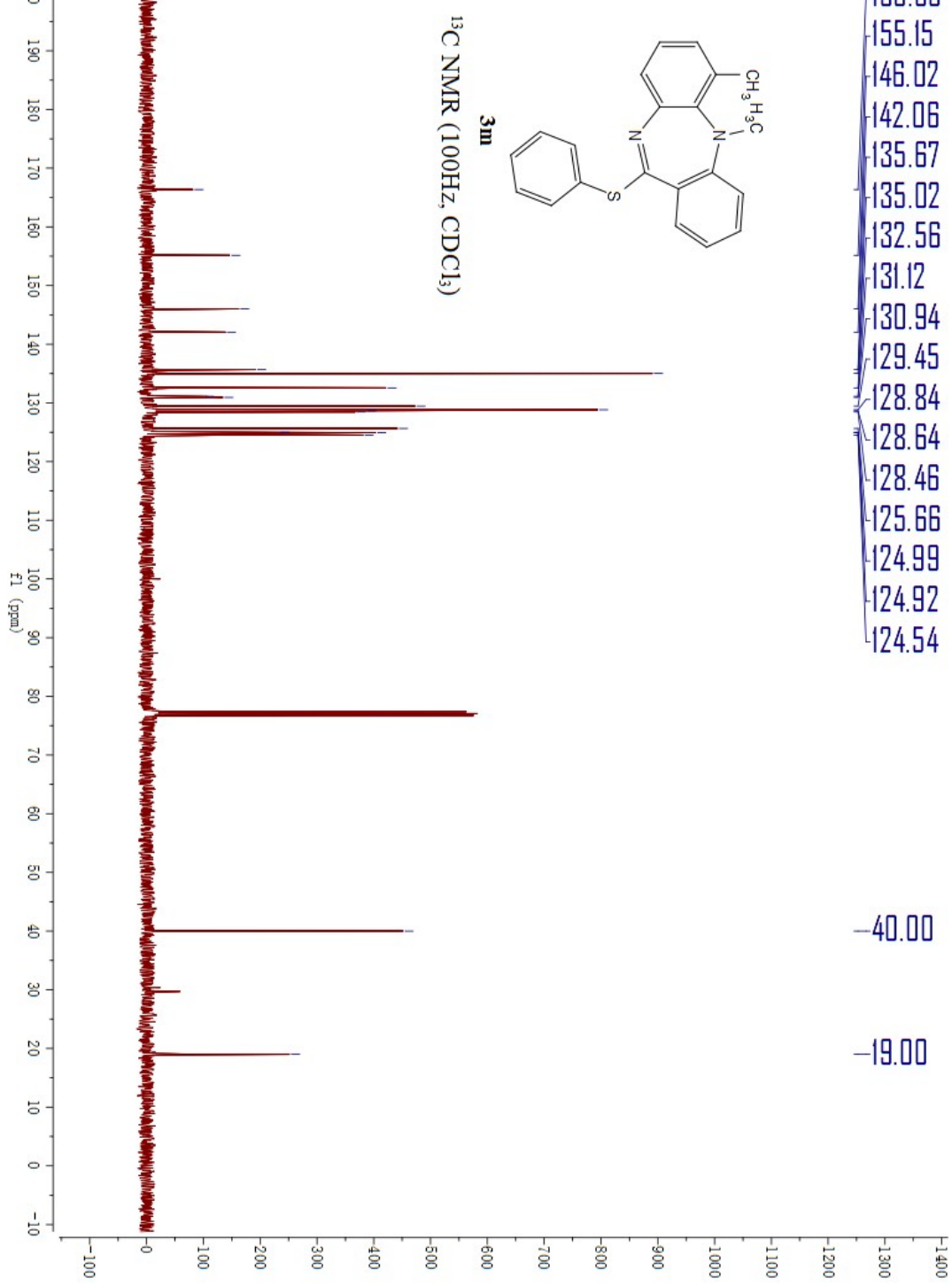
3l. ^{13}C NMR


3l
^{13}C NMR (100 MHz, CDCl$_3$)
Br
H$_3$C
N
N
S
169.11
155.69
146.65
141.44
135.08
132.56
130.39
129.07
128.88
128.48
127.85
126.98
123.54
121.38
119.17
117.58
37.15
f1 (ppm)

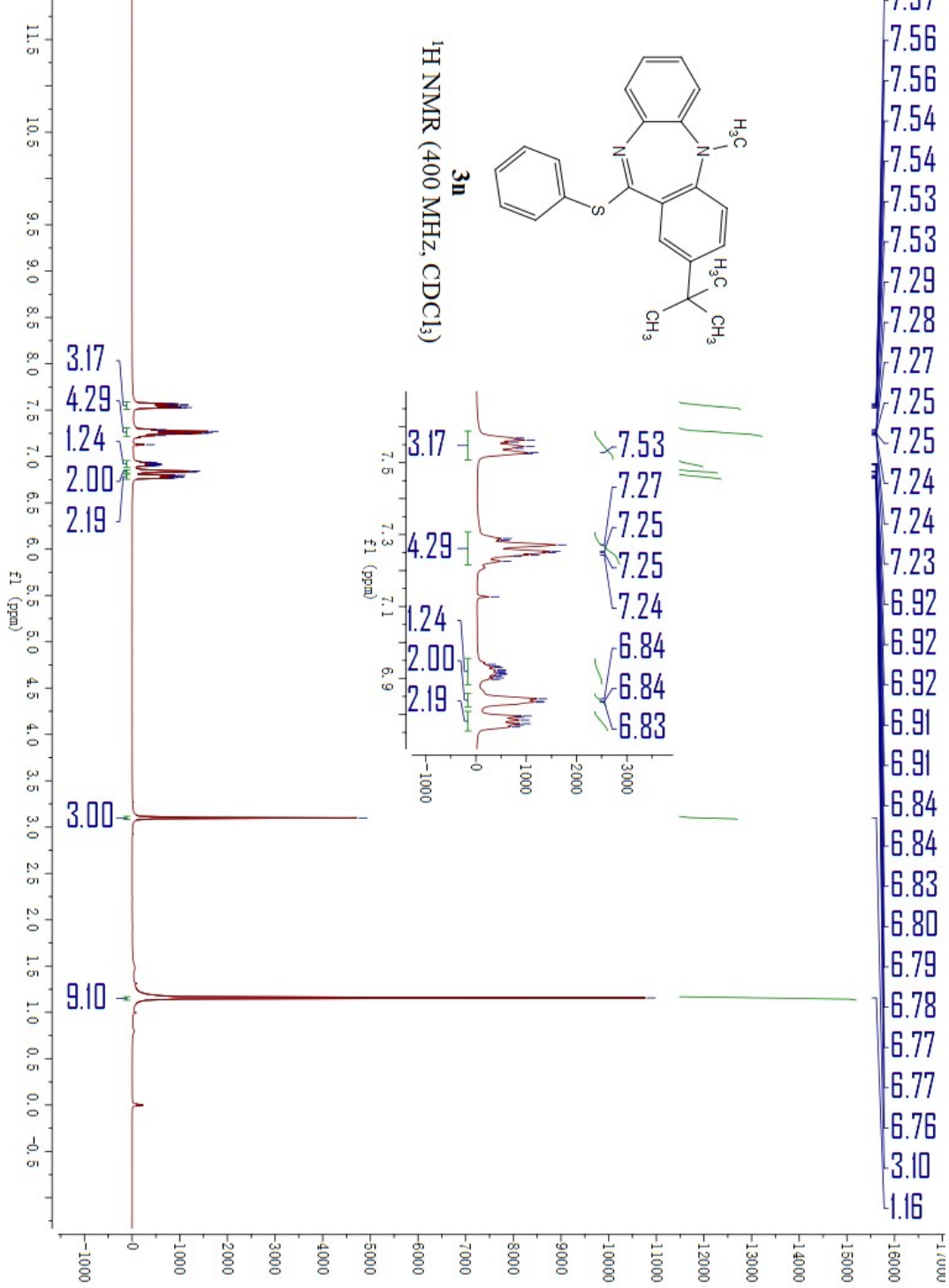
3m. ^{1}H NMR


3m
^{1}H NMR (400 MHz, CDCl$_3$)
CH$_3$ H$_3$C
N
N
S
1.00
2.03
4.33
1.28
1.12
1.96
1.02
3.17
3.20
7.56
7.56
7.54
7.32
7.30
7.30
6.86
6.85
f1 (ppm)

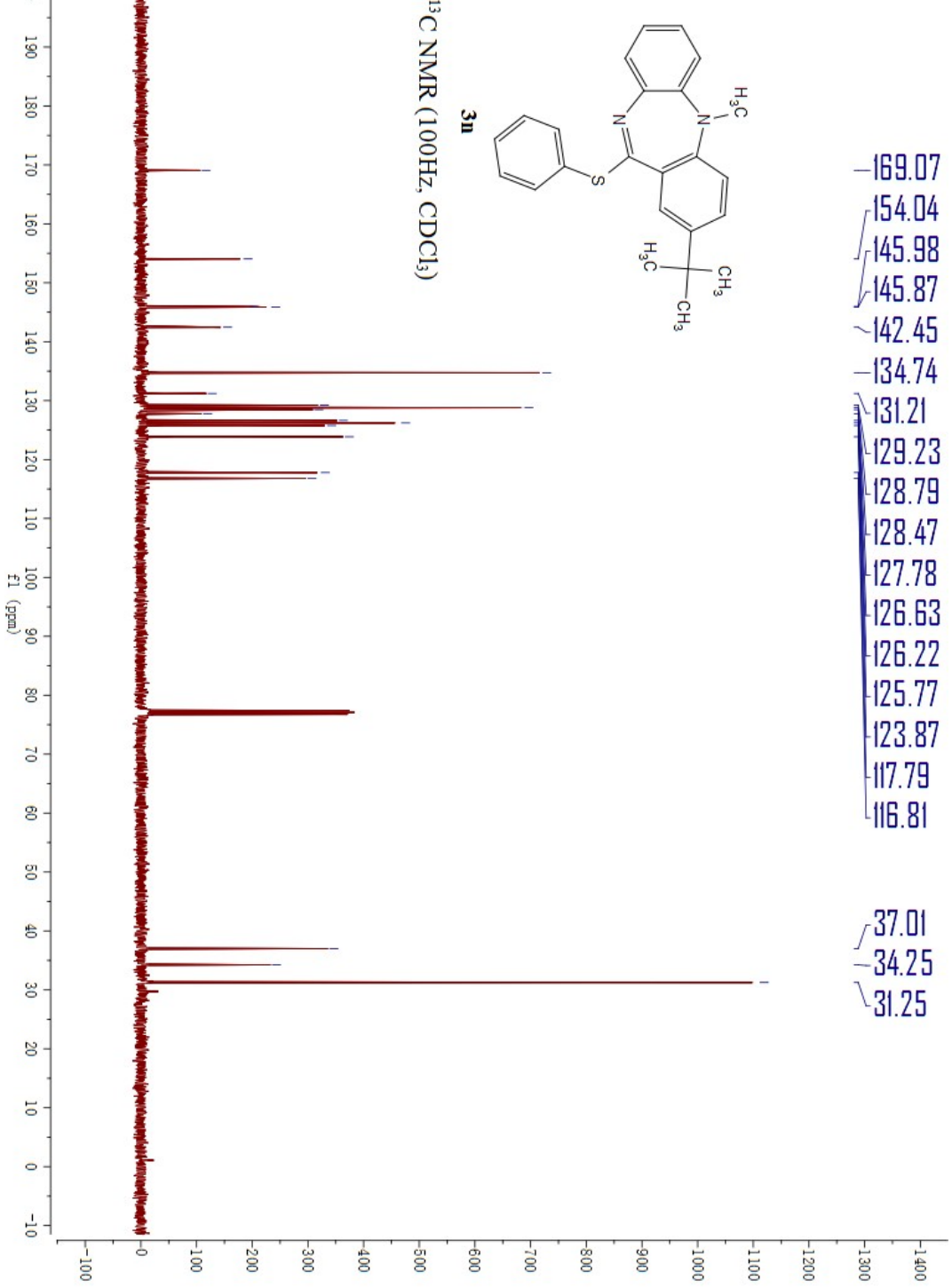
3m. ^{13}C NMR


3m
^{13}C NMR (100Hz, $CDCl_3$)
155.15
146.02
142.06
135.67
135.02
132.56
131.12
130.94
129.45
128.84
128.64
128.46
125.66
124.99
124.92
124.54
40.00
19.00
f1 (ppm)

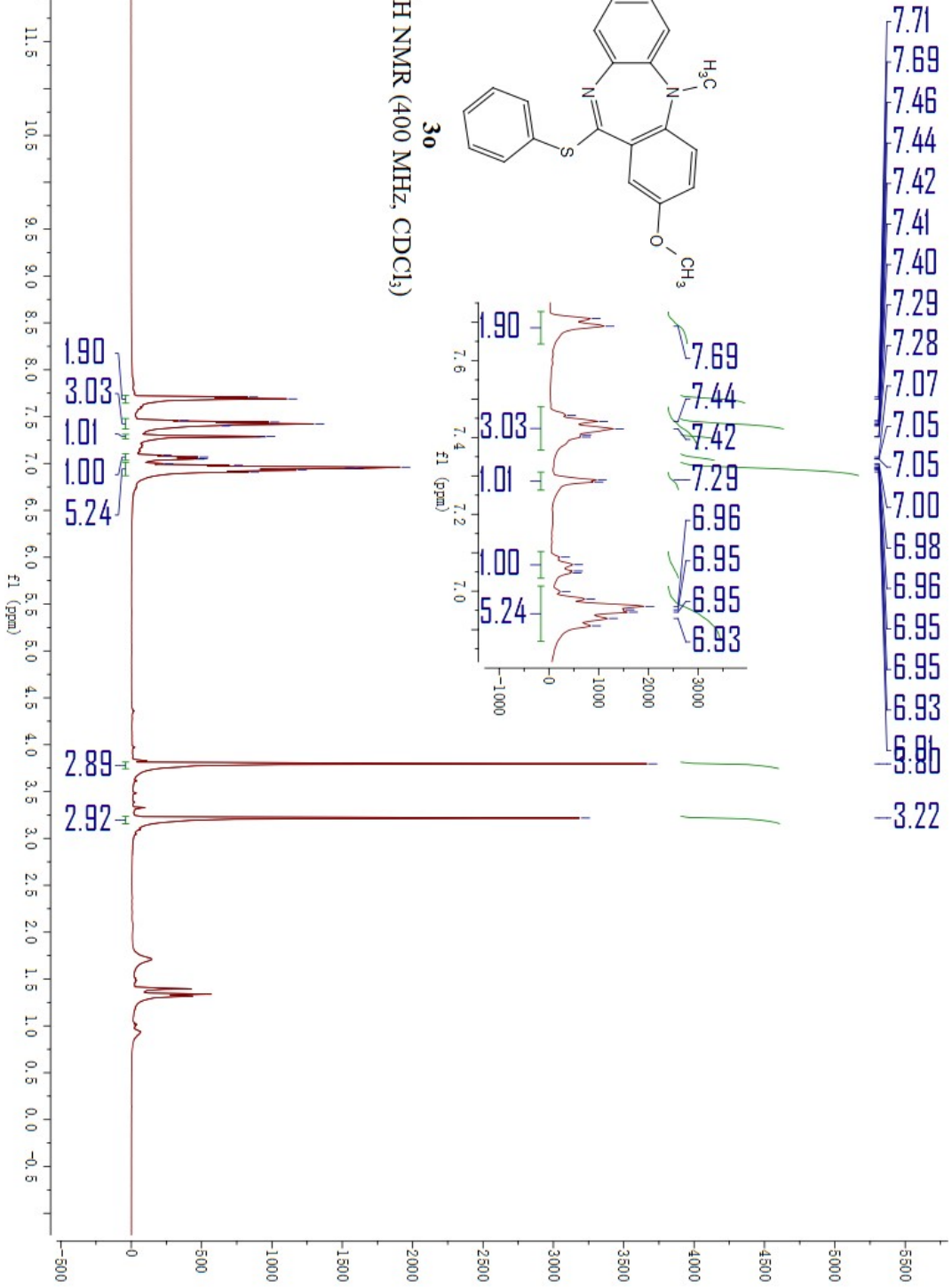
3n. ^{1}H NMR


3n
^{1}H NMR (400 MHz, CDCl$_3$)
3.17
4.29
1.24
2.00
2.19
3.00
9.10
7.53
7.27
7.25
7.25
7.24
6.84
6.84
6.83
f1 (ppm)

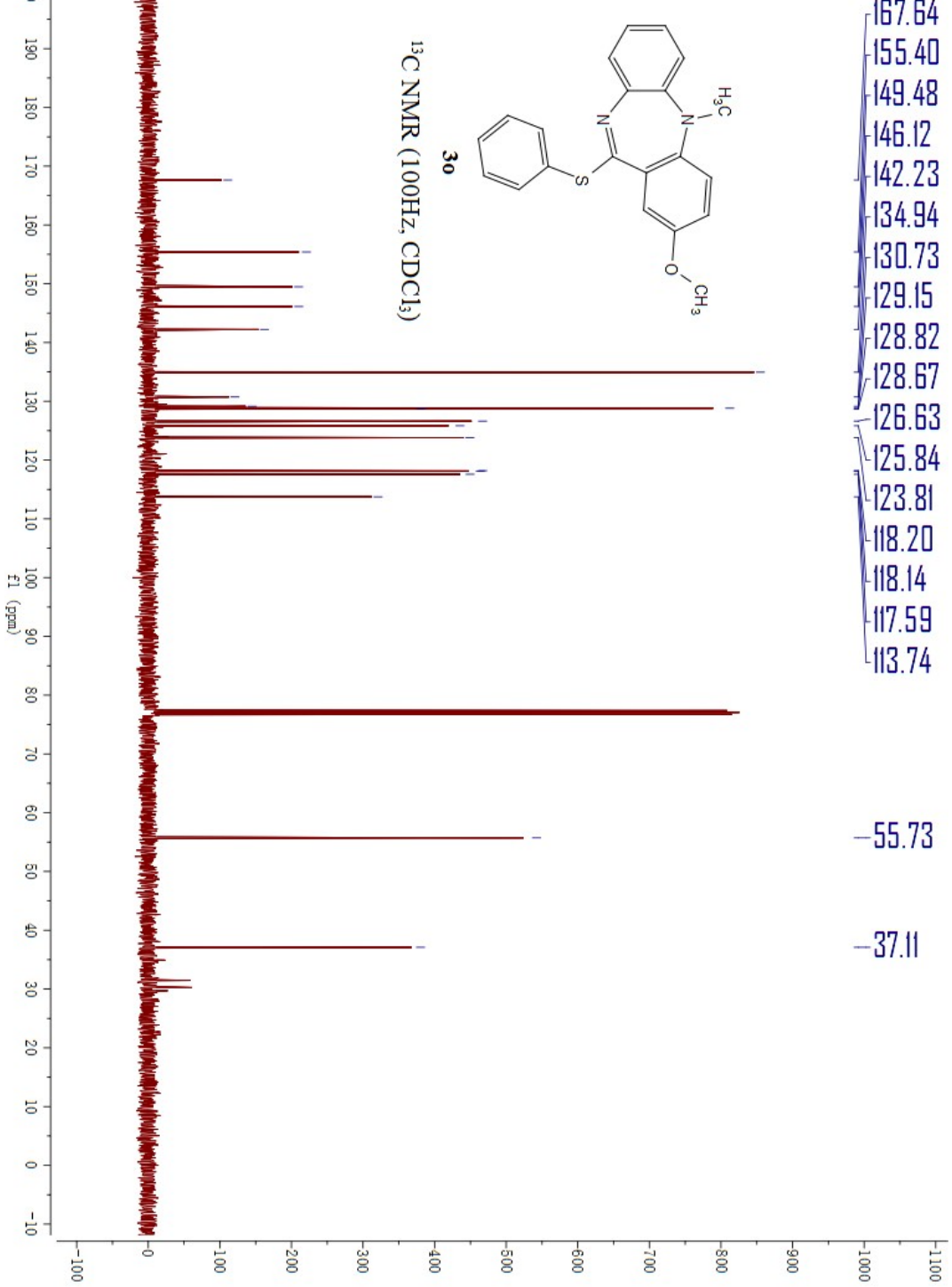
3n. ^{13}C NMR


^{13}C NMR (100Hz, CDCl$_3$)
3n
169.07
154.04
145.98
145.87
142.45
134.74
131.21
129.23
128.79
128.47
127.78
126.63
126.22
125.77
123.87
117.79
116.81
37.01
34.25
31.25
f1 (ppm)

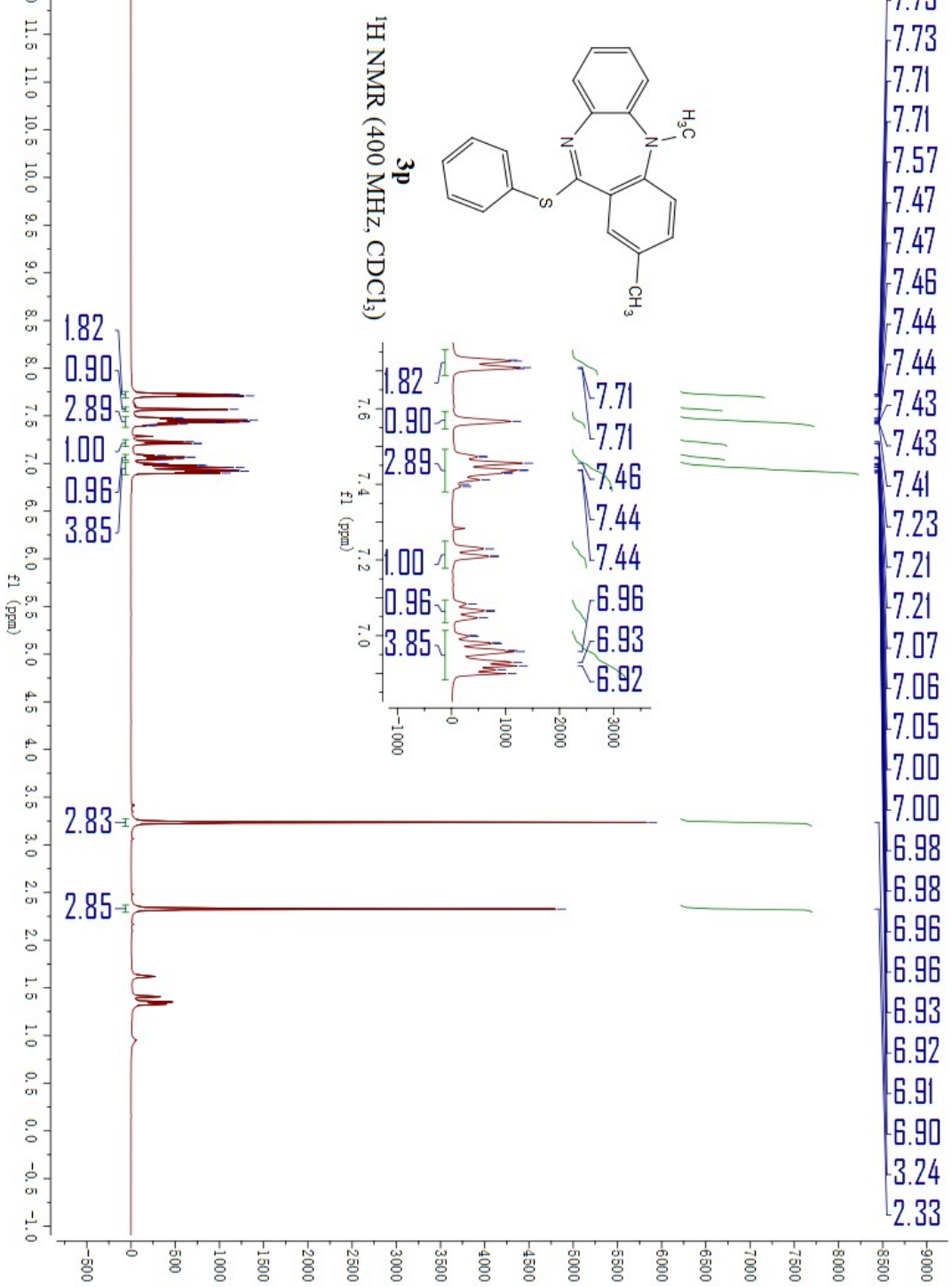
3o. ^{1}H NMR


3o
H NMR (400 MHz, CDCl3)
1.90
3.03
1.01
1.00
5.24
2.89
2.92
7.71
7.69
7.46
7.44
7.42
7.41
7.40
7.29
7.28
7.07
7.05
7.05
7.00
6.98
6.96
6.95
6.95
6.93
3.80
3.22
f1 (ppm)

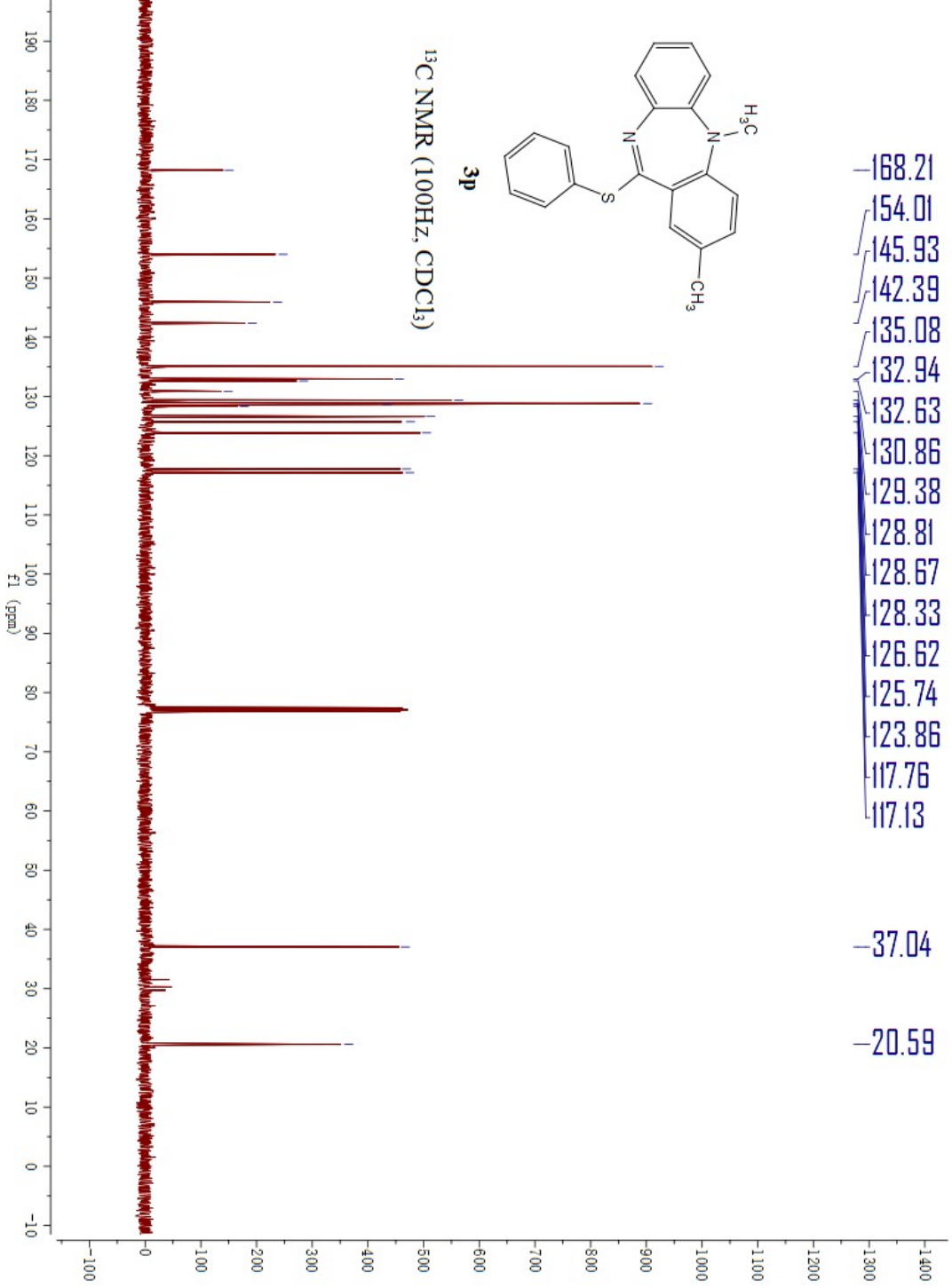
3o. ^{13}C NMR


3o
^{13}C NMR (100Hz, CDCl$_3$)
H$_3$C
N
N
S
O
CH$_3$
167.64
155.40
149.48
146.12
142.23
134.94
130.73
129.15
128.82
128.67
126.63
125.84
123.81
118.20
118.14
117.59
113.74
55.73
37.11
f1 (ppm)

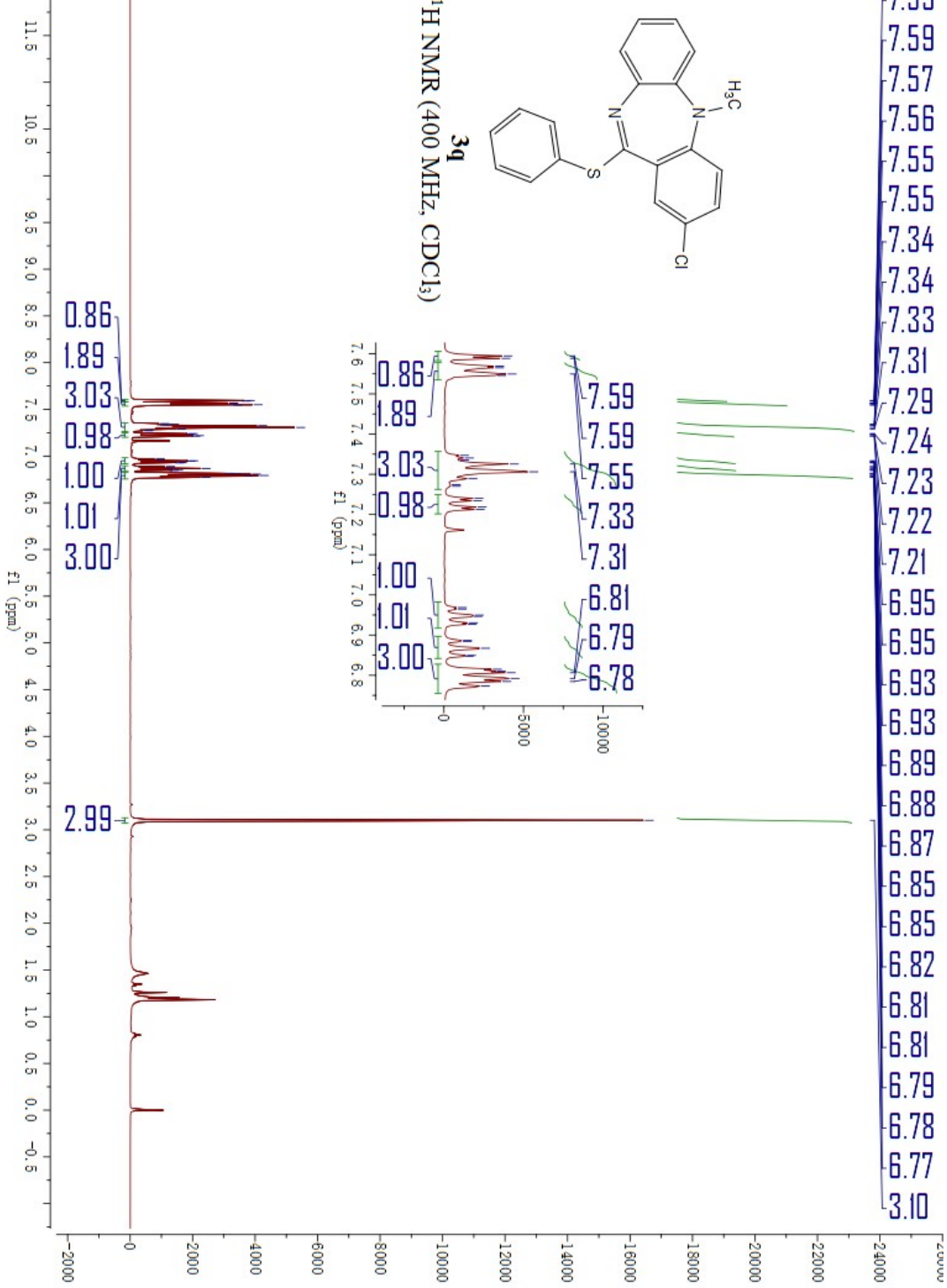
3p. ^{1}H NMR


3p
^{1}H NMR (400 MHz, $CDCl_3$)
1.82
0.90
2.89
1.00
0.96
3.85
2.83
2.85
7.71
7.71
7.46
7.44
7.44
6.96
6.93
6.92
7.73
7.71
7.71
7.57
7.47
7.47
7.46
7.44
7.44
7.43
7.43
7.41
7.23
7.21
7.21
7.07
7.06
7.05
7.00
7.00
6.98
6.98
6.96
6.96
6.93
6.92
6.91
6.90
3.24
2.33
f1 (ppm)

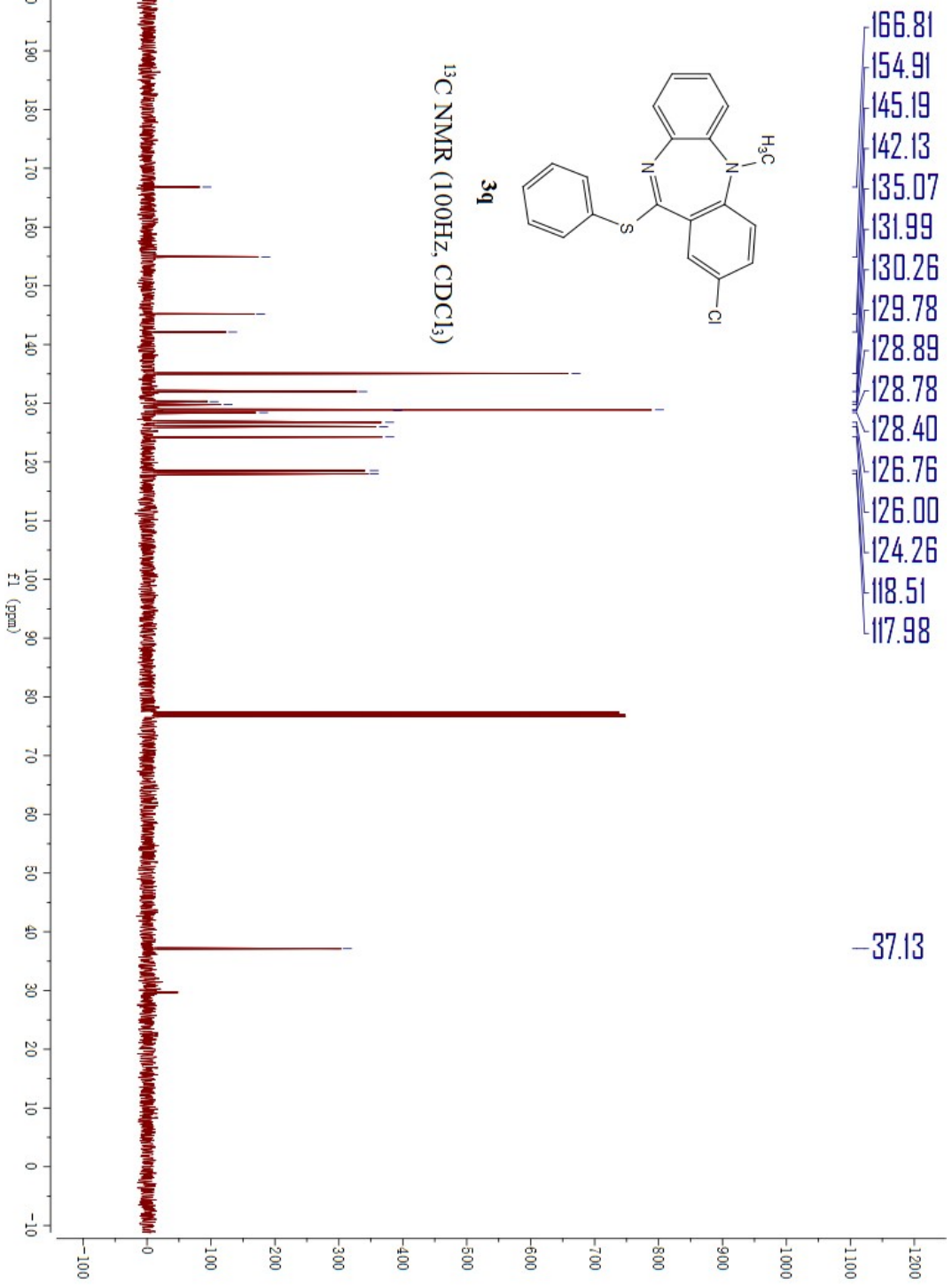
3p. ^{13}C NMR


^{13}C NMR (100Hz, CDCl$_3$)
3p
H_3C
N
N
S
CH_3
168.21
154.01
145.93
142.39
135.08
132.94
132.63
130.86
129.38
128.81
128.67
128.33
126.62
125.74
123.86
117.76
117.13
37.04
20.59
f1 (ppm)

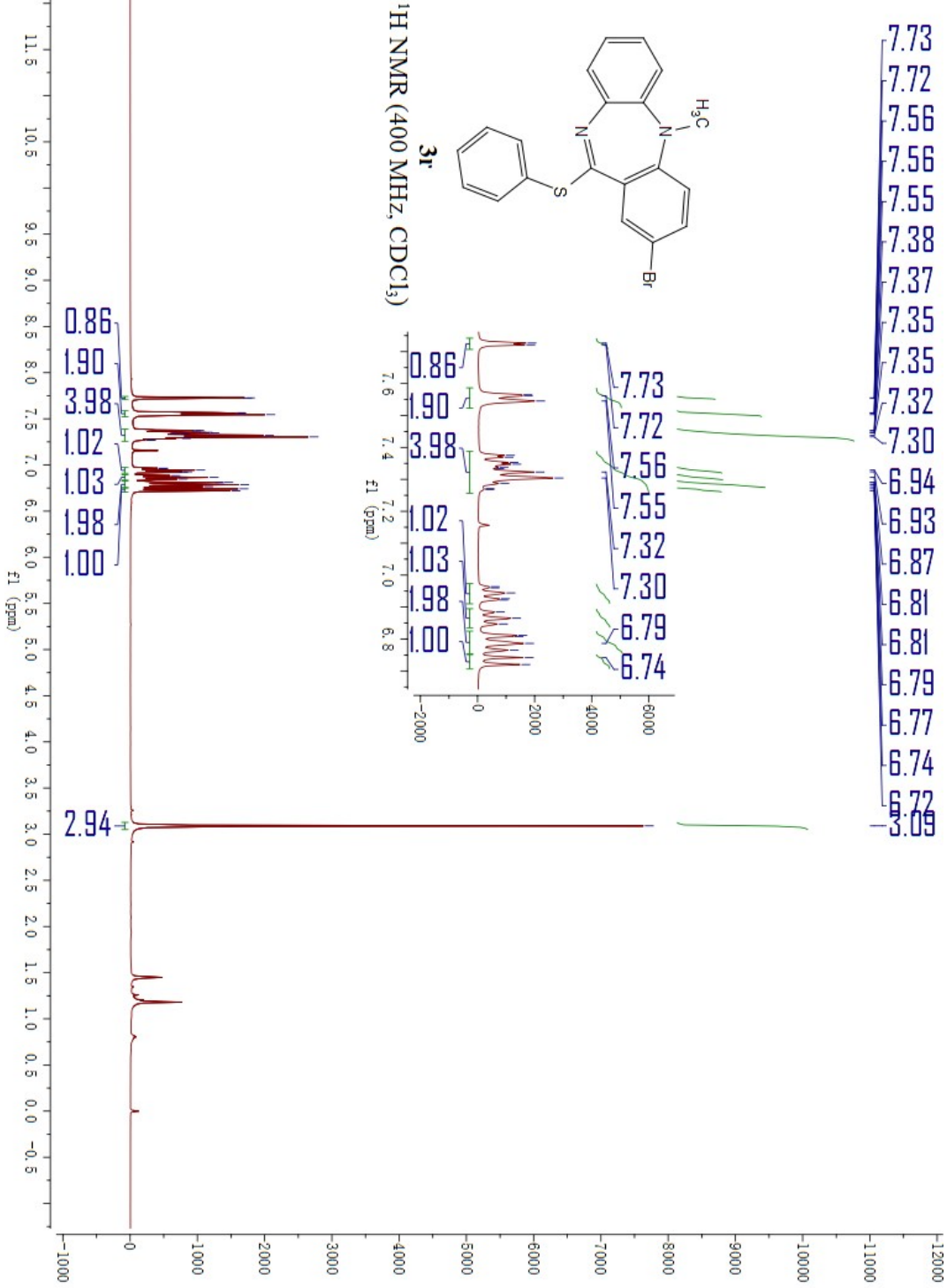
3q. ^{1}H NMR


3q
^{1}H NMR (400 MHz, CDCl$_3$)
H$_3$C
N
N
S
Cl
0.86
1.89
3.03
0.98
1.00
1.01
3.00
2.99
7.59
7.59
7.55
7.33
7.31
6.81
6.79
6.78
f1 (ppm)

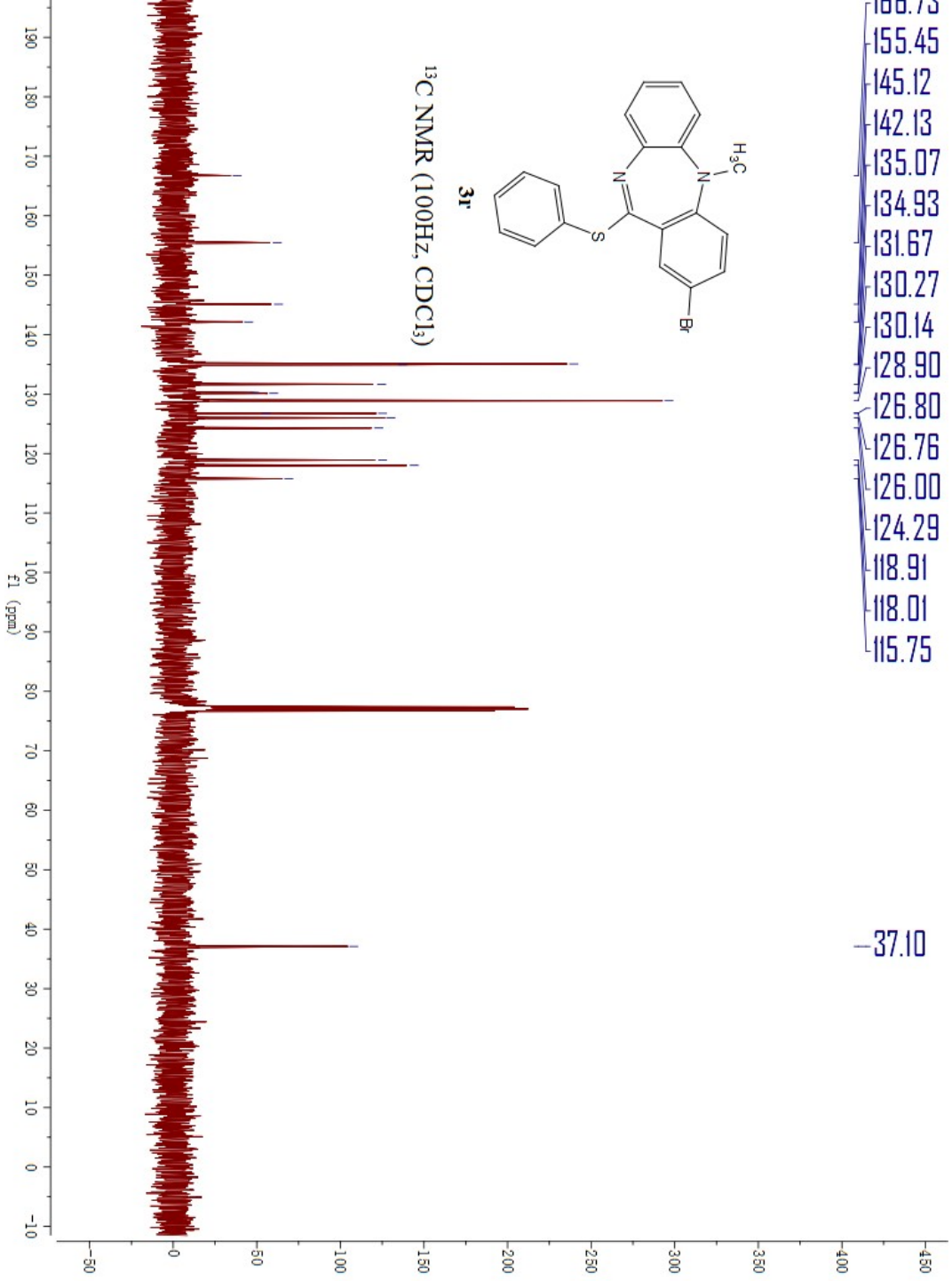
3q. ^{13}C NMR


166.81
154.91
145.19
142.13
135.07
131.99
130.26
129.78
128.89
128.78
128.40
126.76
126.00
124.26
118.51
117.98
37.13
^{13}C NMR (100Hz, CDCl$_3$)
3q
H$_3$C
N
N
S
Cl
f1 (ppm)

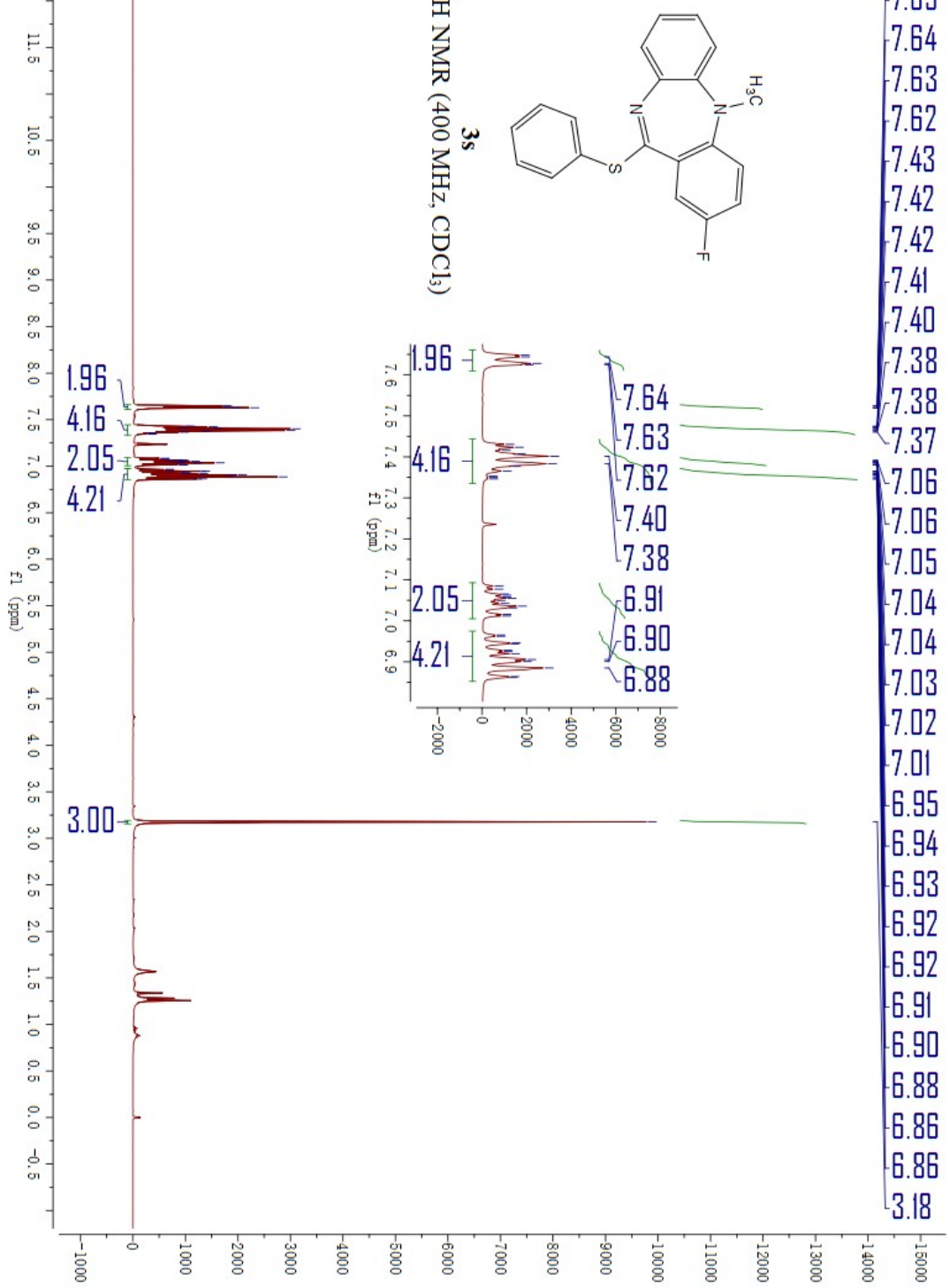
3r. ^{1}H NMR


3r
^{1}H NMR (400 MHz, CDCl$_3$)
H$_3$C
N
N
S
Br
0.86
1.90
3.98
1.02
1.03
1.98
1.00
2.94
7.73
7.72
7.56
7.56
7.55
7.38
7.37
7.35
7.35
7.32
7.30
6.94
6.93
6.87
6.81
6.81
6.79
6.77
6.74
6.72
3.09
f1 (ppm)

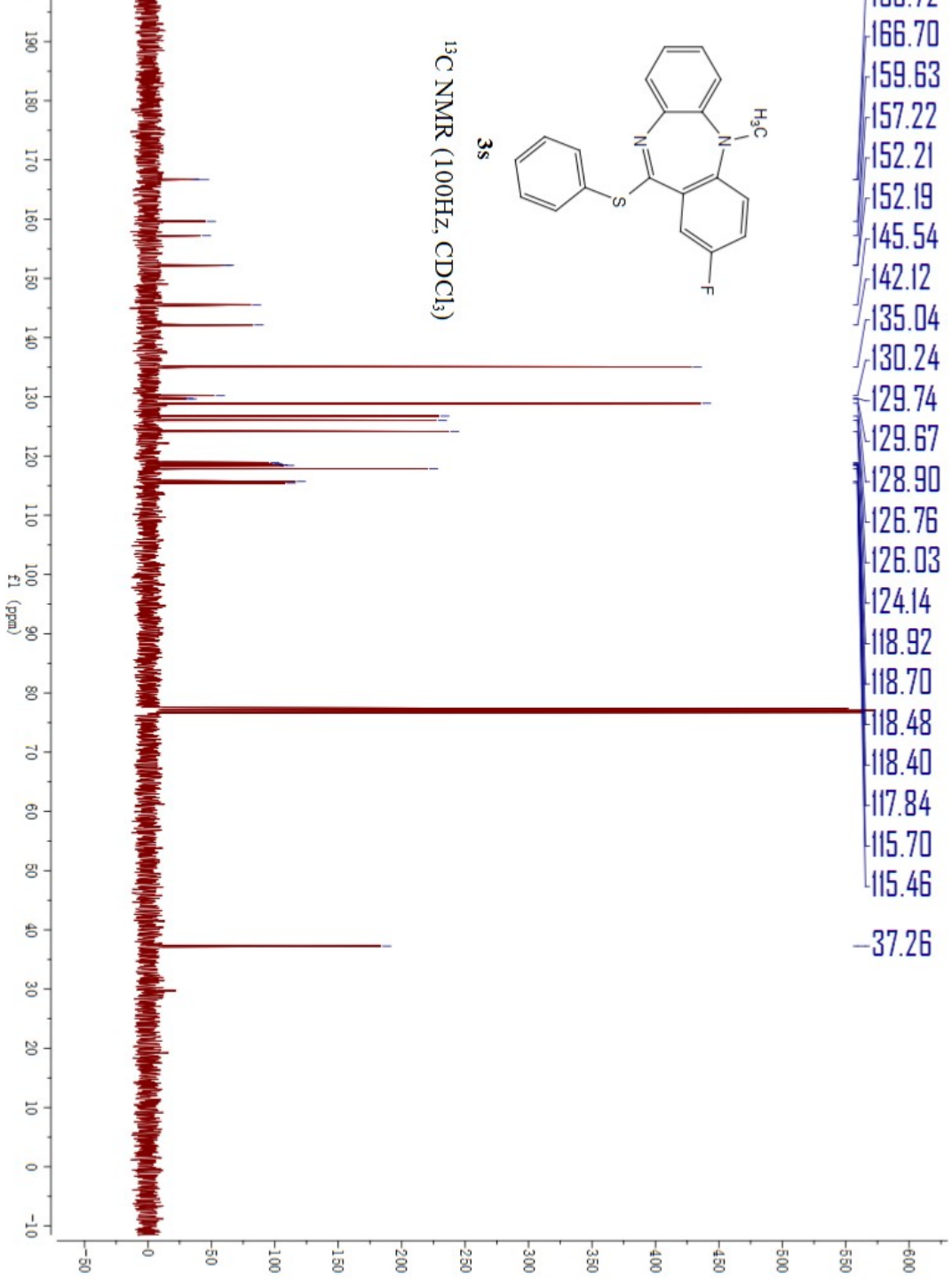
3r. ^{13}C NMR


^{13}C NMR (100Hz, CDCl$_3$)
3r
H$_3$C
N
N
S
Br
166.73
155.45
145.12
142.13
135.07
134.93
131.67
130.27
130.14
128.90
126.80
126.76
126.00
124.29
118.91
118.01
115.75
37.10
f1 (ppm)

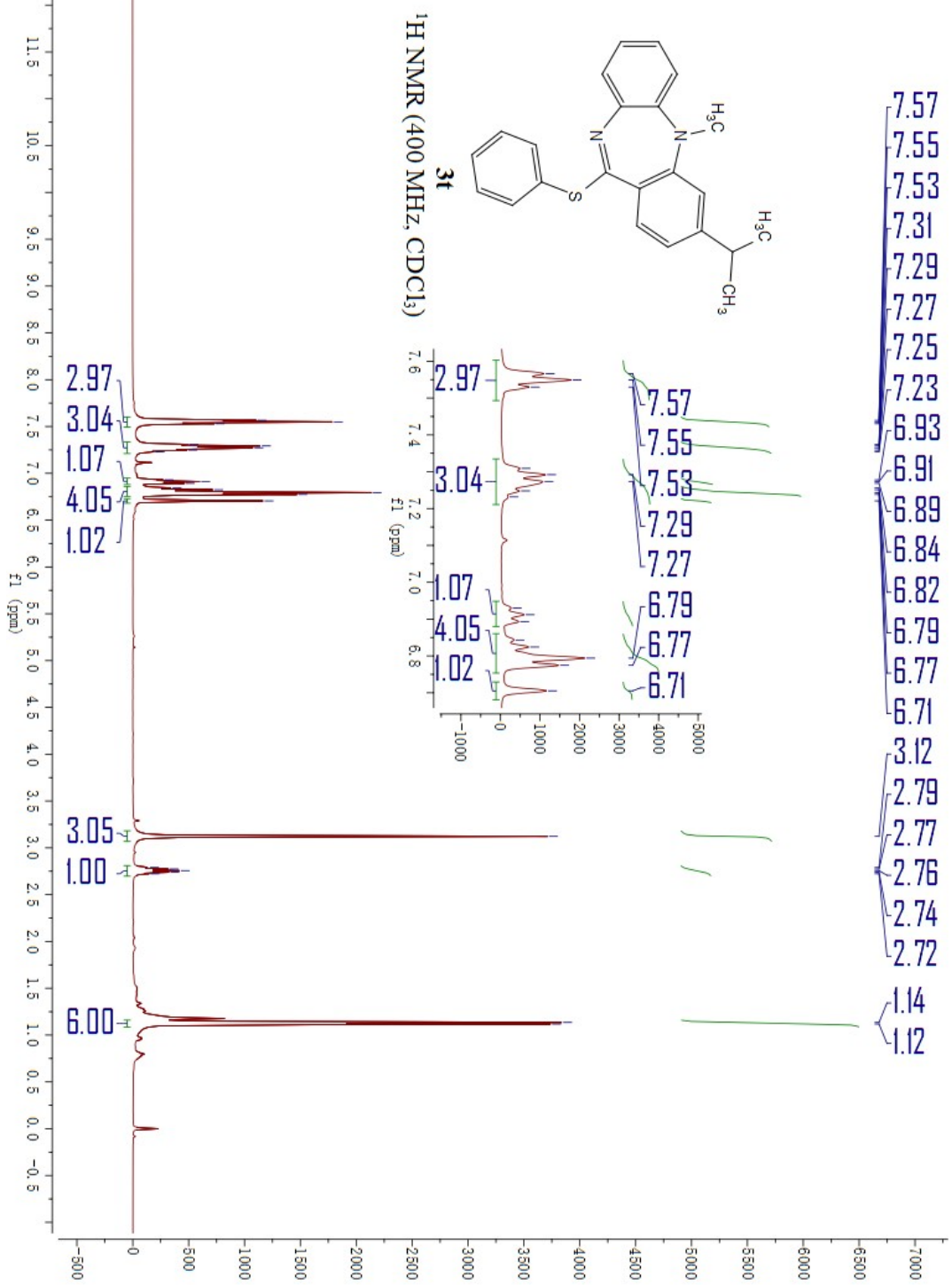
3s. ^{1}H NMR


3s
H NMR (400 MHz, CDCl3)
H3C
N
N
S
F
1.96
4.16
2.05
4.21
3.00
7.64
7.63
7.62
7.40
7.38
6.91
6.90
6.88
3.18
f1 (ppm)

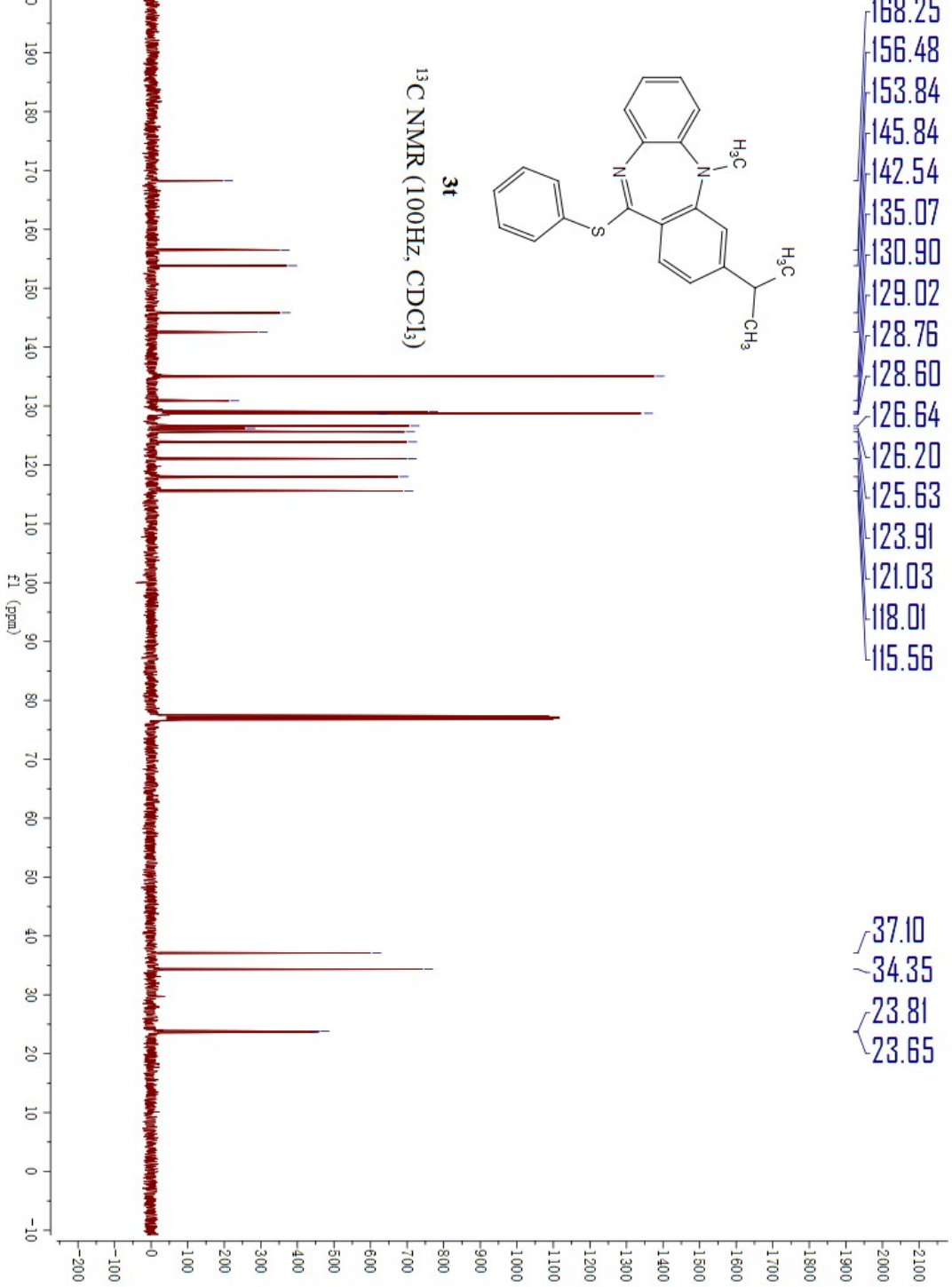
3s. ^{13}C NMR


3s
^{13}C NMR (100Hz, CDCl$_3$)
166.70
159.63
157.22
152.21
152.19
145.54
142.12
135.04
130.24
129.74
129.67
128.90
126.76
126.03
124.14
118.92
118.70
118.48
118.40
117.84
115.70
115.46
37.26
f1 (ppm)

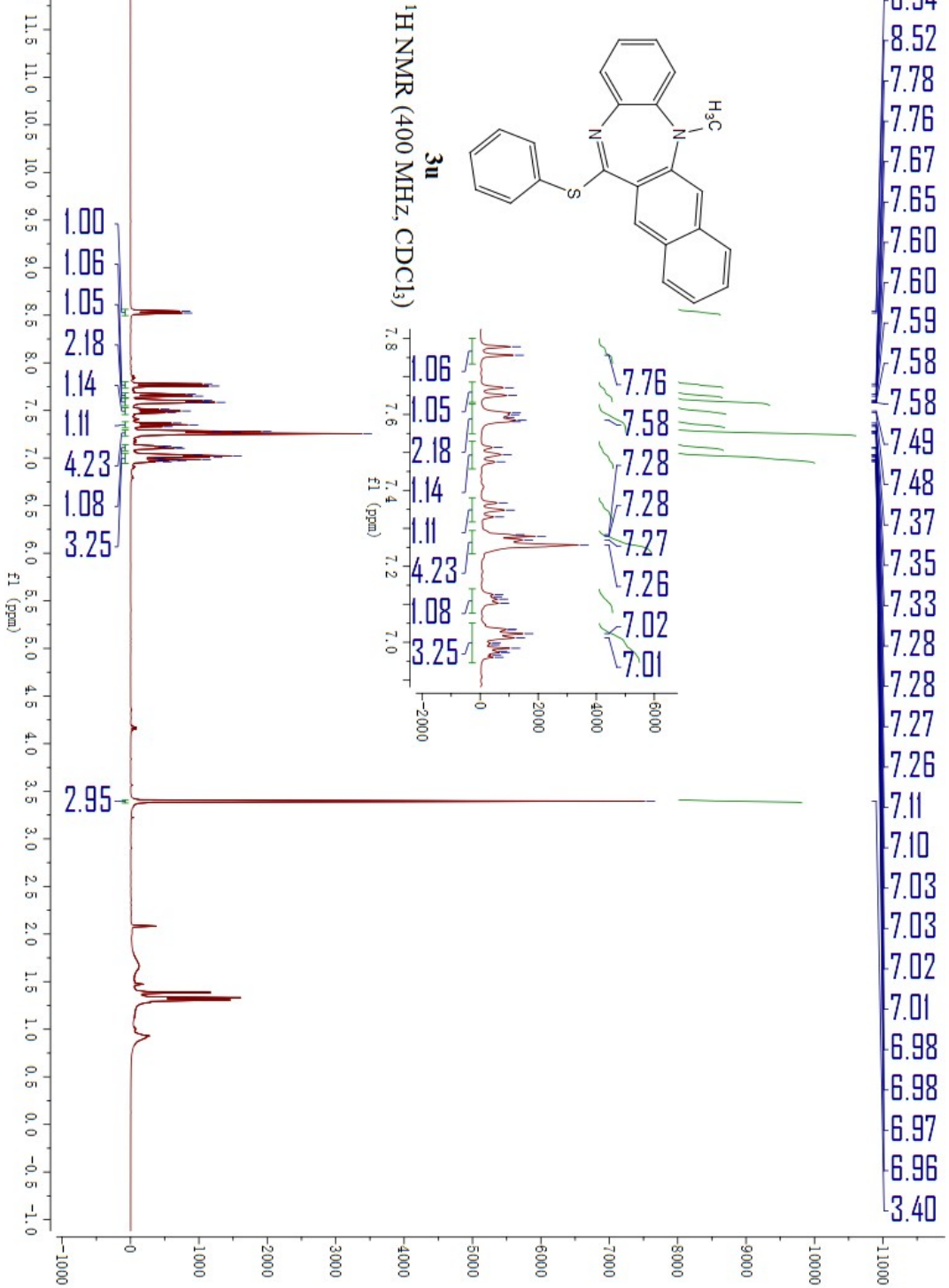
3t. ^{1}H NMR


3t
^{1}H NMR (400 MHz, CDCl$_3$)
2.97
3.04
1.07
4.05
1.02
3.05
1.00
6.00
7.57
7.55
7.53
7.31
7.29
7.27
7.25
7.23
6.93
6.91
6.89
6.84
6.82
6.79
6.77
6.71
3.12
2.79
2.77
2.76
2.74
2.72
1.14
1.12
f1 (ppm)

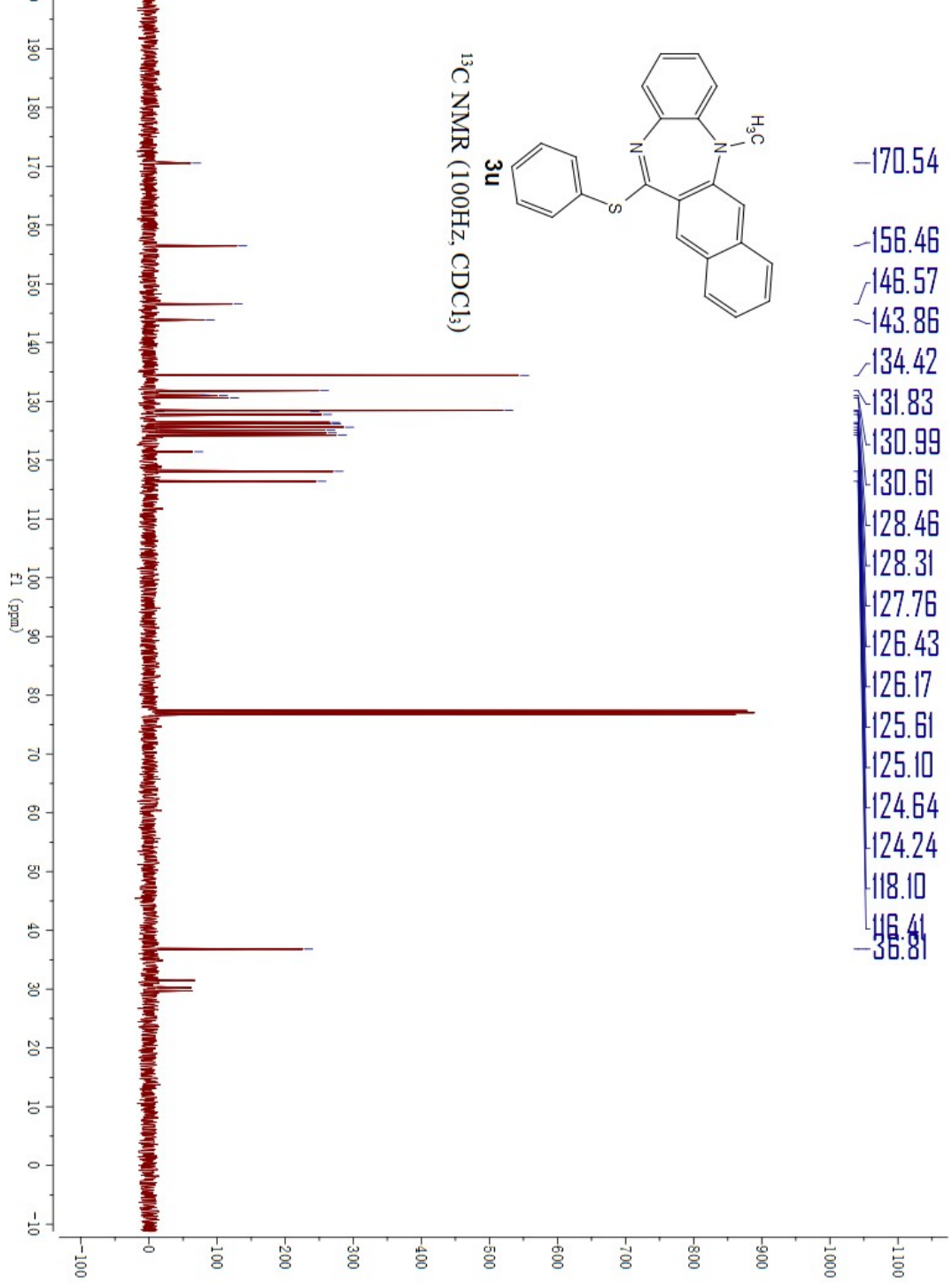
3t. ^{13}C NMR


3t
^{13}C NMR (100Hz, CDCl$_3$)
f1 (ppm)
168.25
156.48
153.84
145.84
142.54
135.07
130.90
129.02
128.76
128.60
126.64
126.20
125.63
123.91
121.03
118.01
115.56
37.10
34.35
23.81
23.65

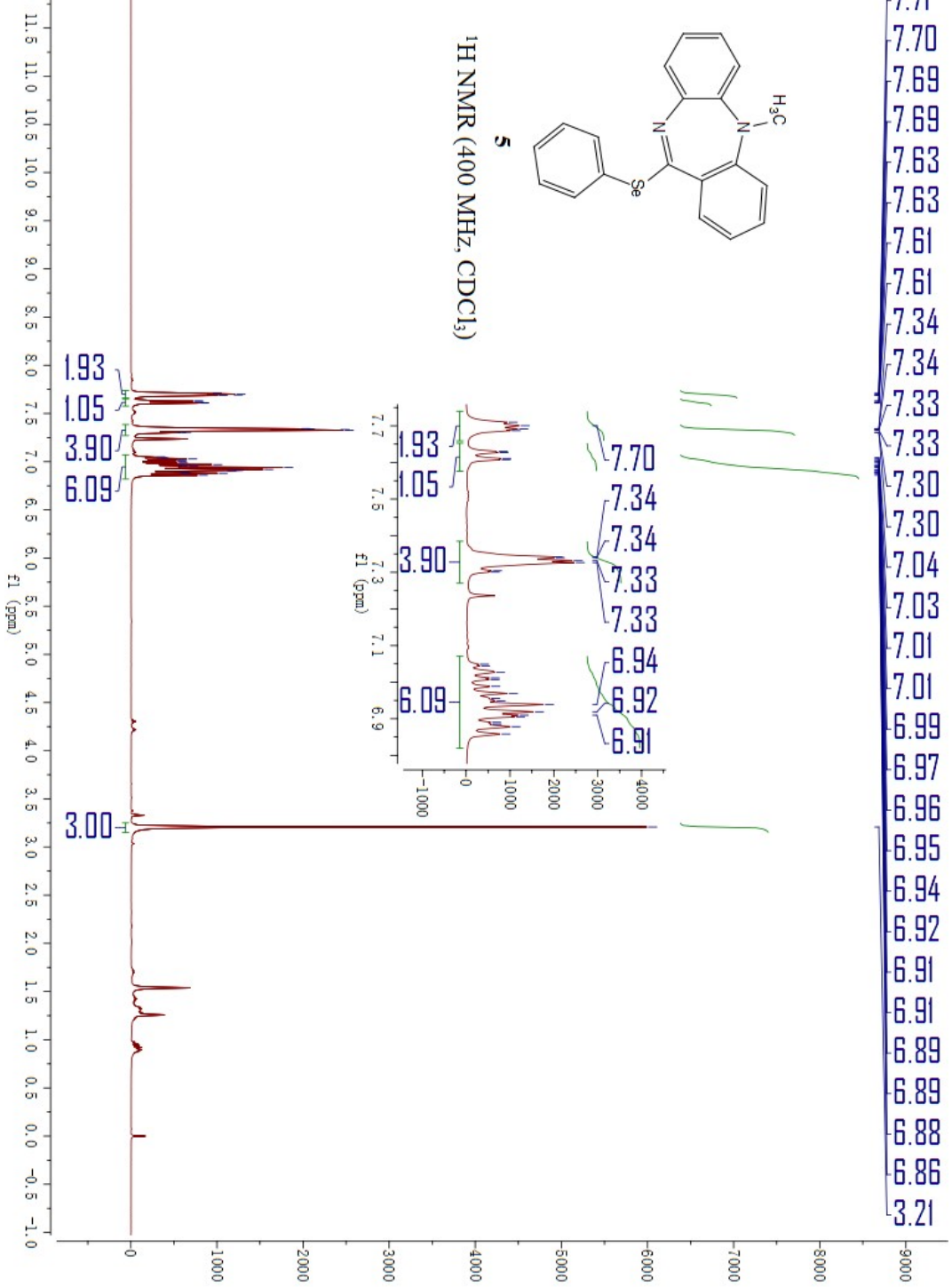
3u. ^{1}H NMR


3u
^{1}H NMR (400 MHz, CDCl$_3$)
H$_3$C
N
N
S
1.00
1.06
1.05
2.18
1.14
1.11
4.23
1.08
3.25
2.95
7.76
7.58
7.28
7.28
7.27
7.26
7.02
7.01
7.49
7.48
7.37
7.35
7.33
7.28
7.28
7.27
7.26
7.11
7.10
7.03
7.03
7.02
7.01
6.98
6.98
6.97
6.96
3.40
f1 (ppm)

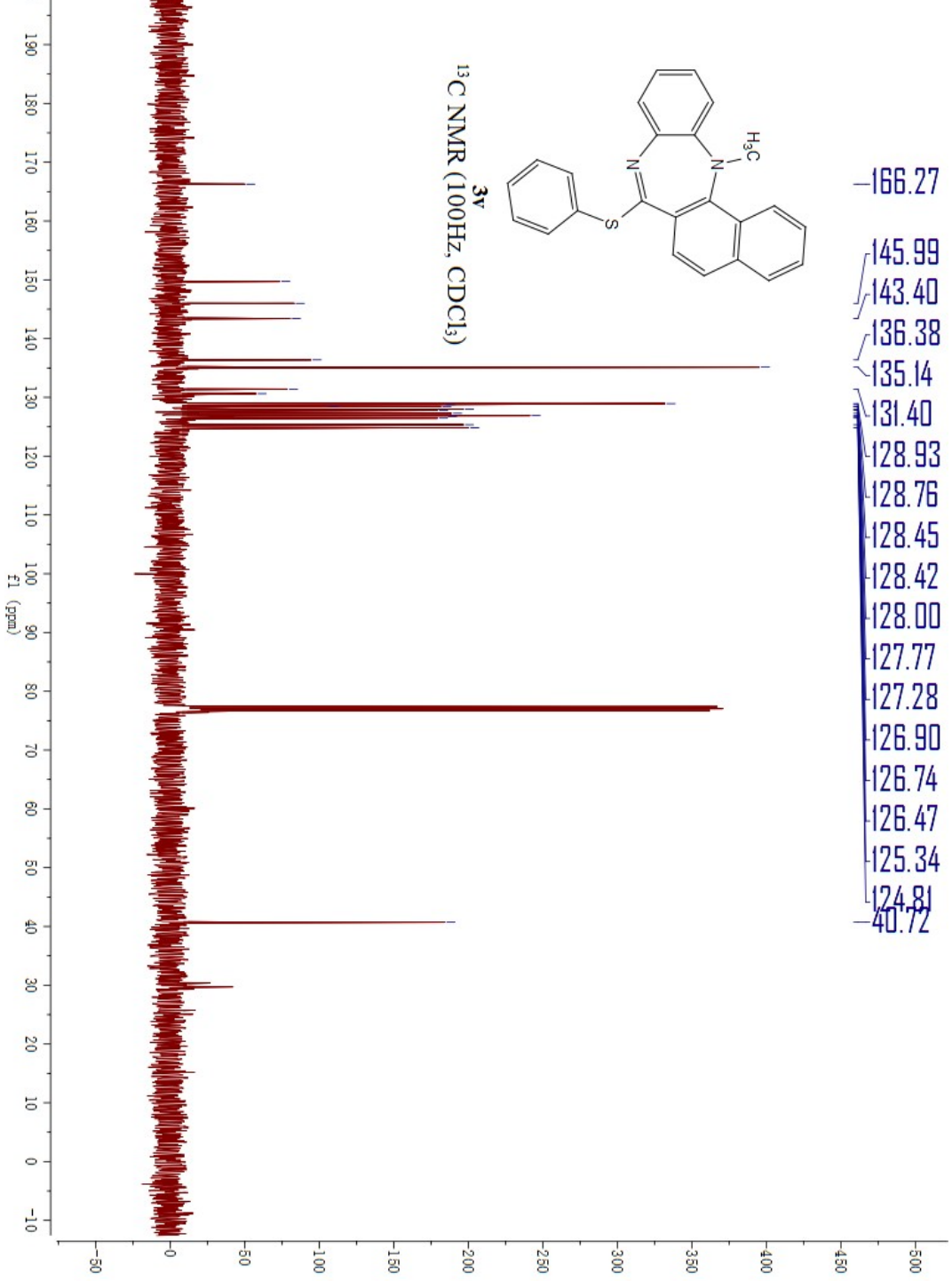
3u. ^{13}C NMR


3u
^{13}C NMR (100Hz, CDCl$_3$)
H$_3$C
N
N
S
170.54
156.46
146.57
143.86
134.42
131.83
130.99
130.61
128.46
128.31
127.76
126.43
126.17
125.61
125.10
124.64
124.24
118.10
116.41
36.81
f1 (ppm)

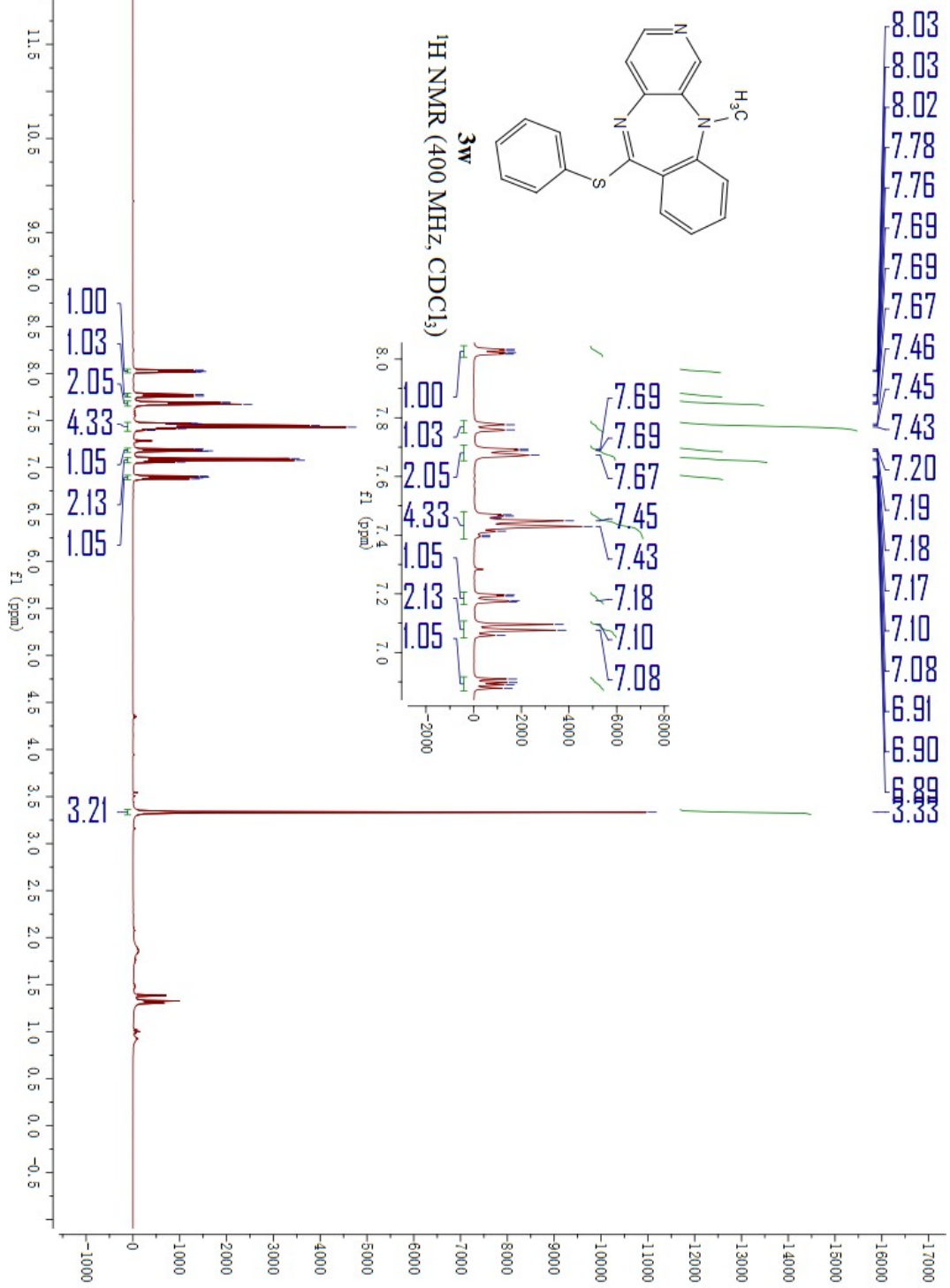
3v. ^{1}H NMR


5
^{1}H NMR (400 MHz, CDCl$_3$)
1.93
1.05
3.90
6.09
3.00
7.70
7.34
7.34
7.33
7.33
6.94
6.92
6.91
f1 (ppm)

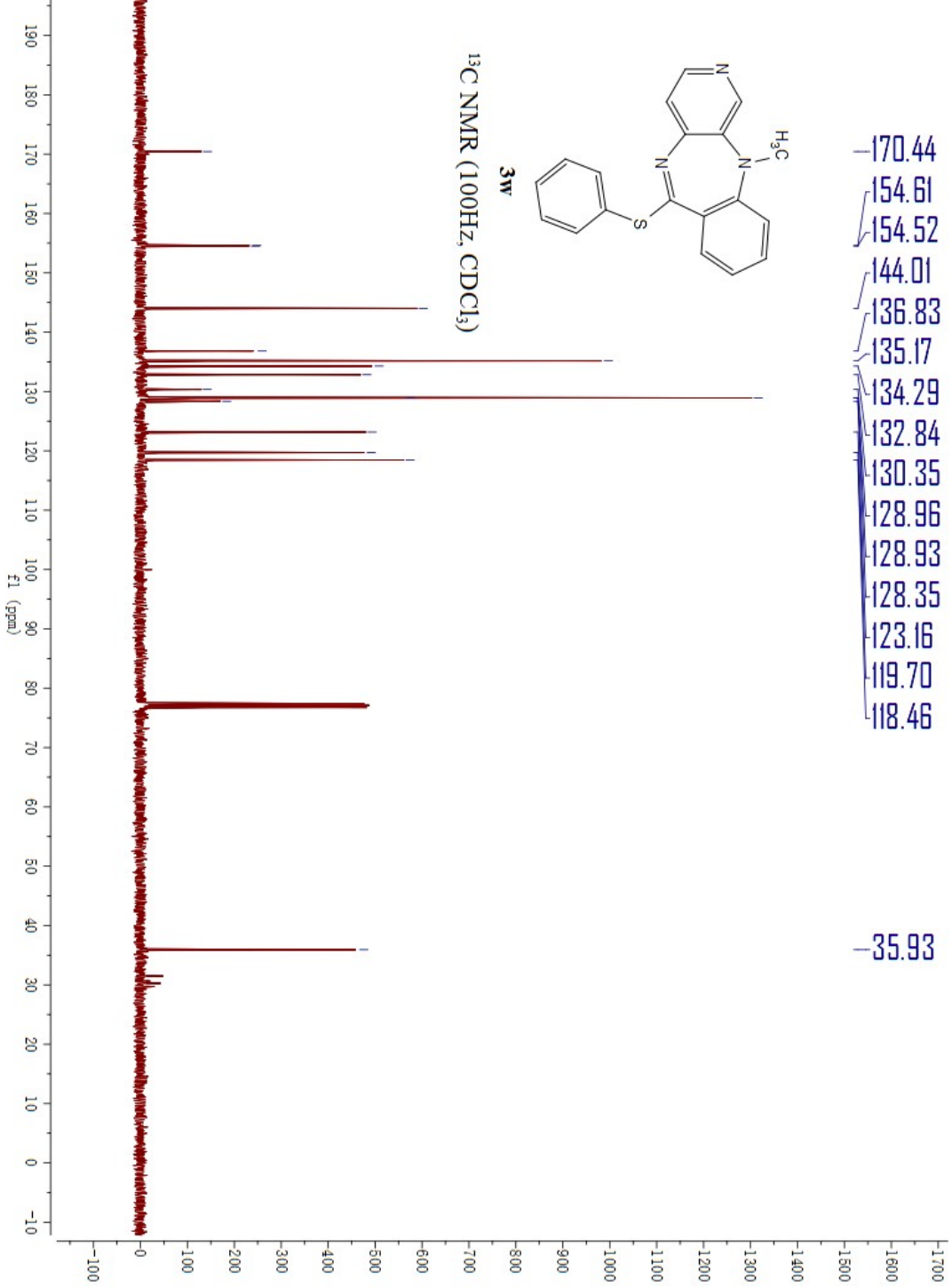
3v. ^{13}C NMR


3v
13C NMR (100Hz, CDCl3)
H3C
N
N
S
166.27
145.99
143.40
136.38
135.14
131.40
128.93
128.76
128.45
128.42
128.00
127.77
127.28
126.90
126.74
126.47
125.34
124.81
40.72
f1 (ppm)

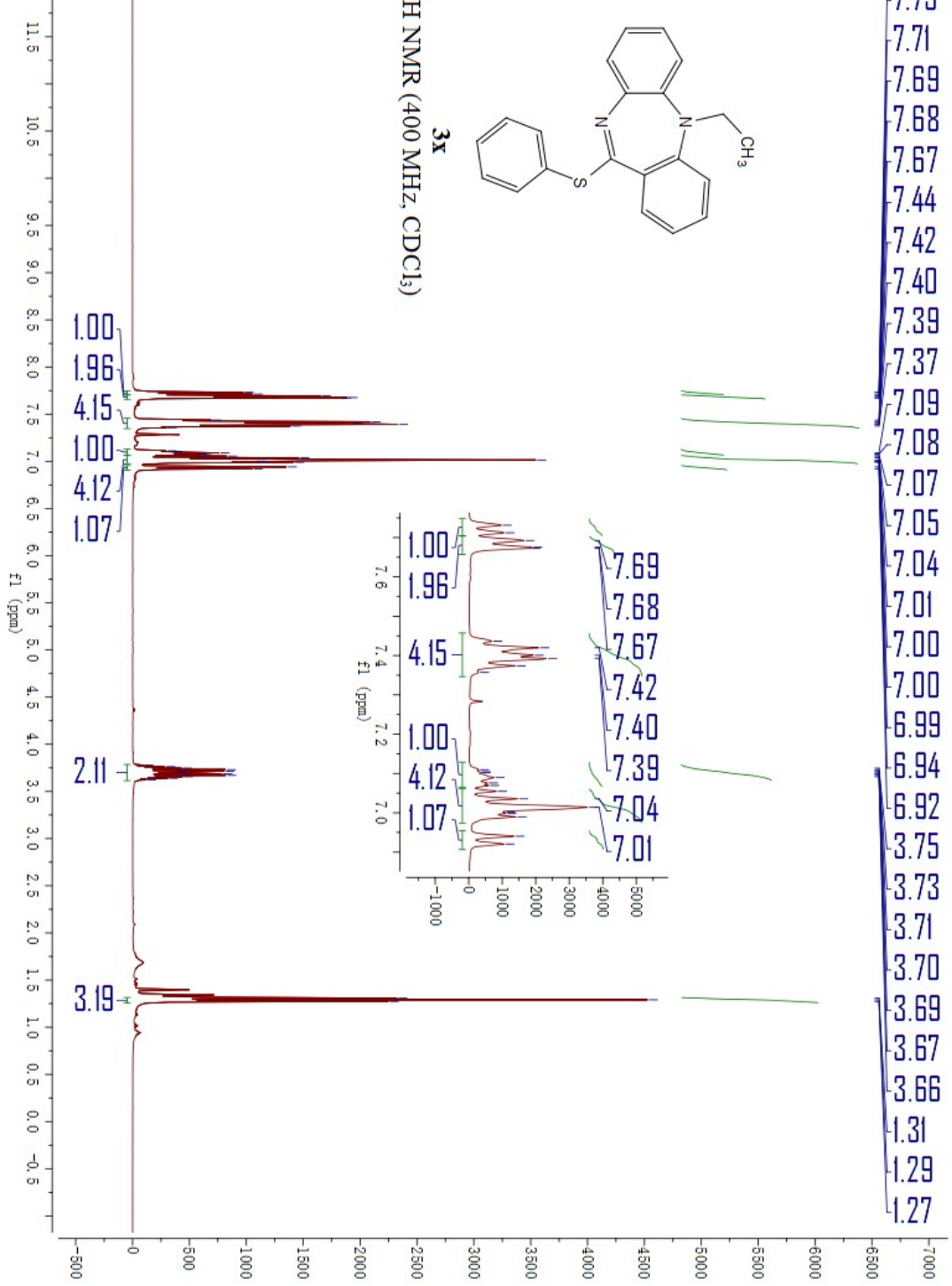
3w. ^{1}H NMR


3w
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
1.03
2.05
4.33
1.05
2.13
1.05
3.21
8.03
8.03
8.02
7.78
7.76
7.69
7.69
7.67
7.46
7.45
7.43
7.20
7.19
7.18
7.17
7.10
7.08
6.91
6.90
6.89
3.33
f1 (ppm)

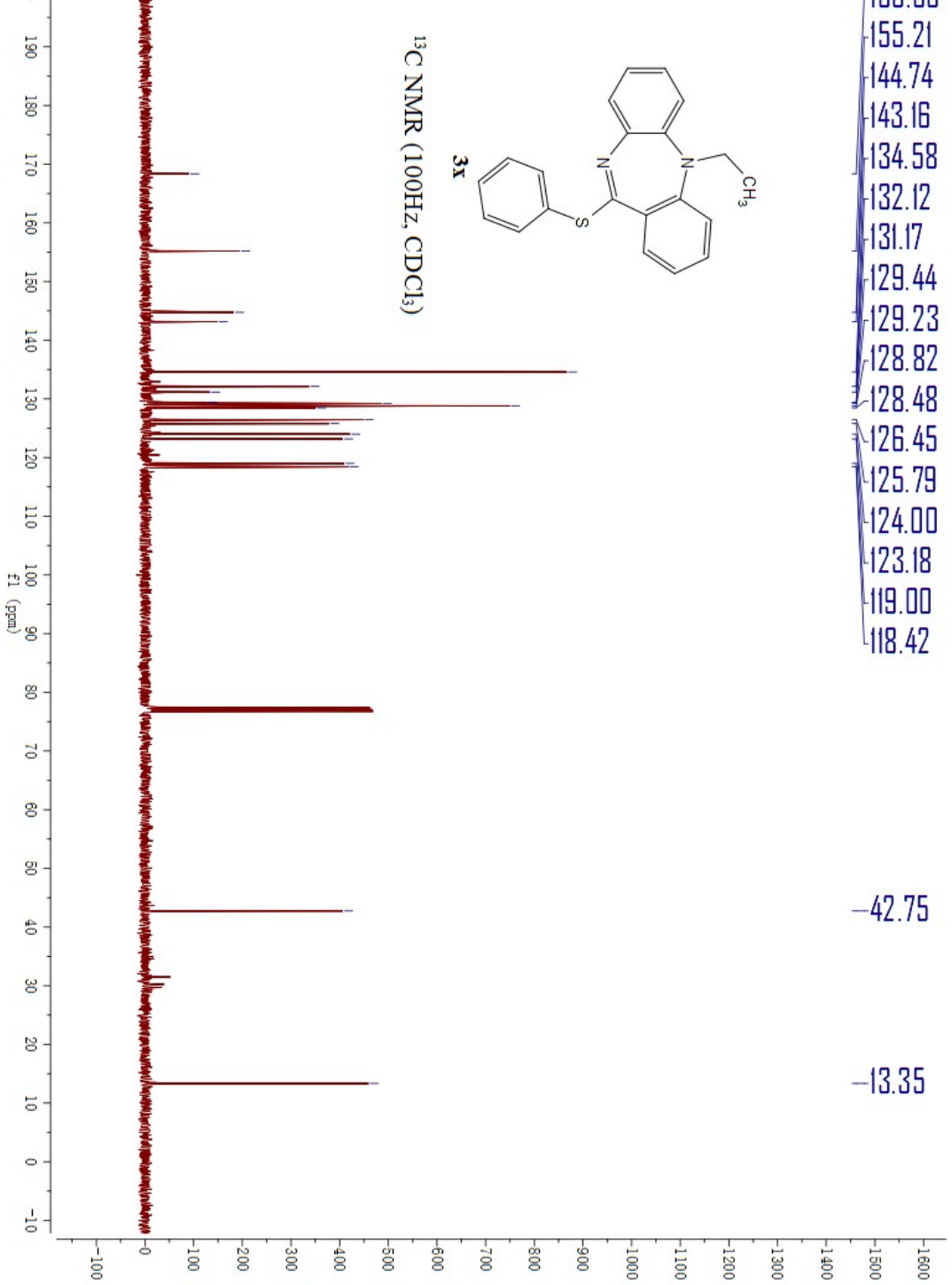
3w. ^{13}C NMR


^{13}C NMR (100Hz, CDCl$_3$)
3w
170.44
154.61
154.52
144.01
136.83
135.17
134.29
132.84
130.35
128.96
128.93
128.35
123.16
119.70
118.46
35.93
f1 (ppm)

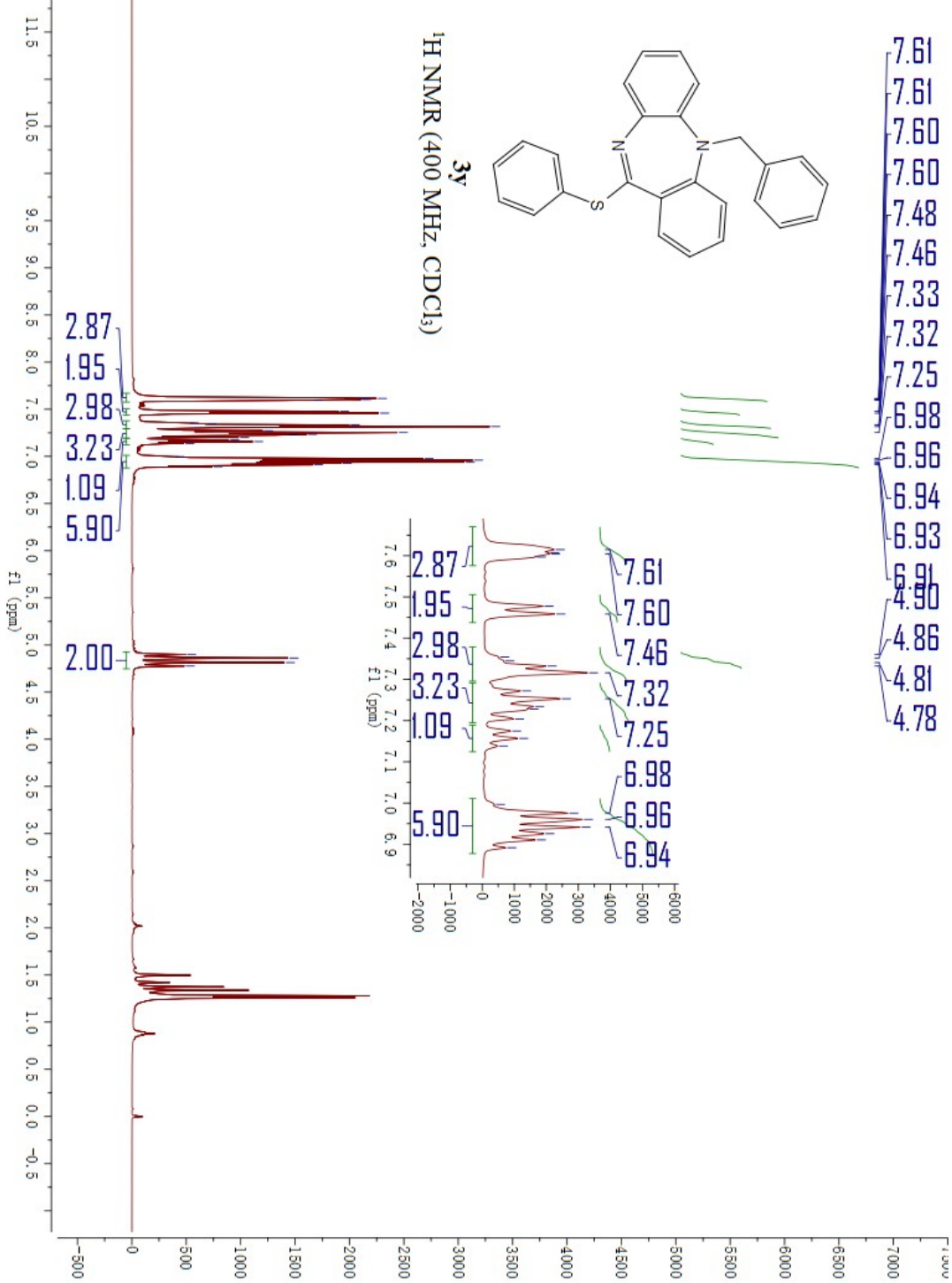
3x. ^{1}H NMR


3x
H NMR (400 MHz, CDCl3)
CH3
S
N
N
1.00
1.96
4.15
1.00
4.12
1.07
2.11
3.19
7.69
7.68
7.67
7.42
7.40
7.39
7.04
7.01
f1 (ppm)

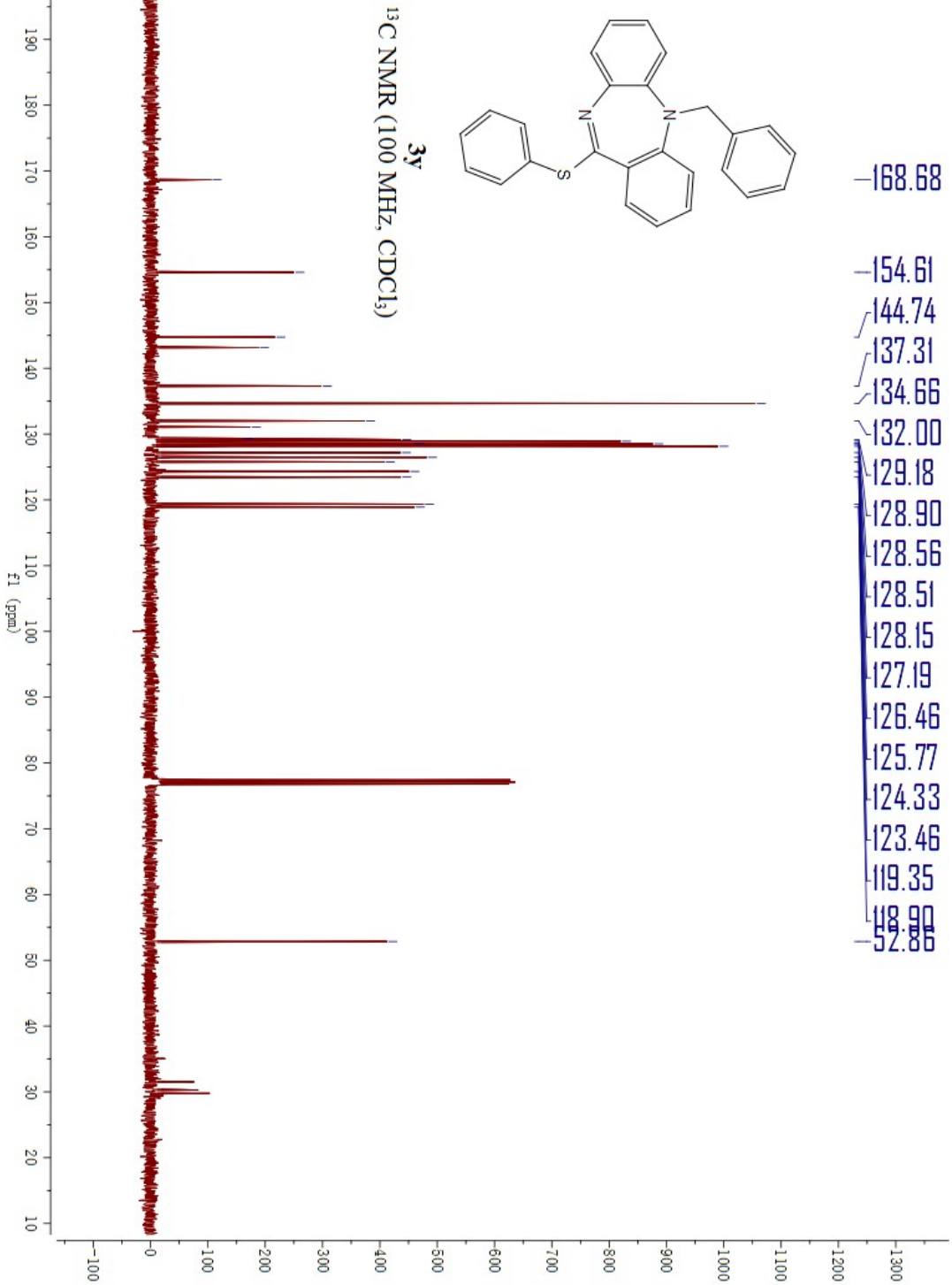
3x. ^{13}C NMR


^{13}C NMR (100Hz, CDCl$_3$)
3x
155.21
144.74
143.16
134.58
132.12
131.17
129.44
129.23
128.82
128.48
126.45
125.79
124.00
123.18
119.00
118.42
42.75
13.35
f1 (ppm)

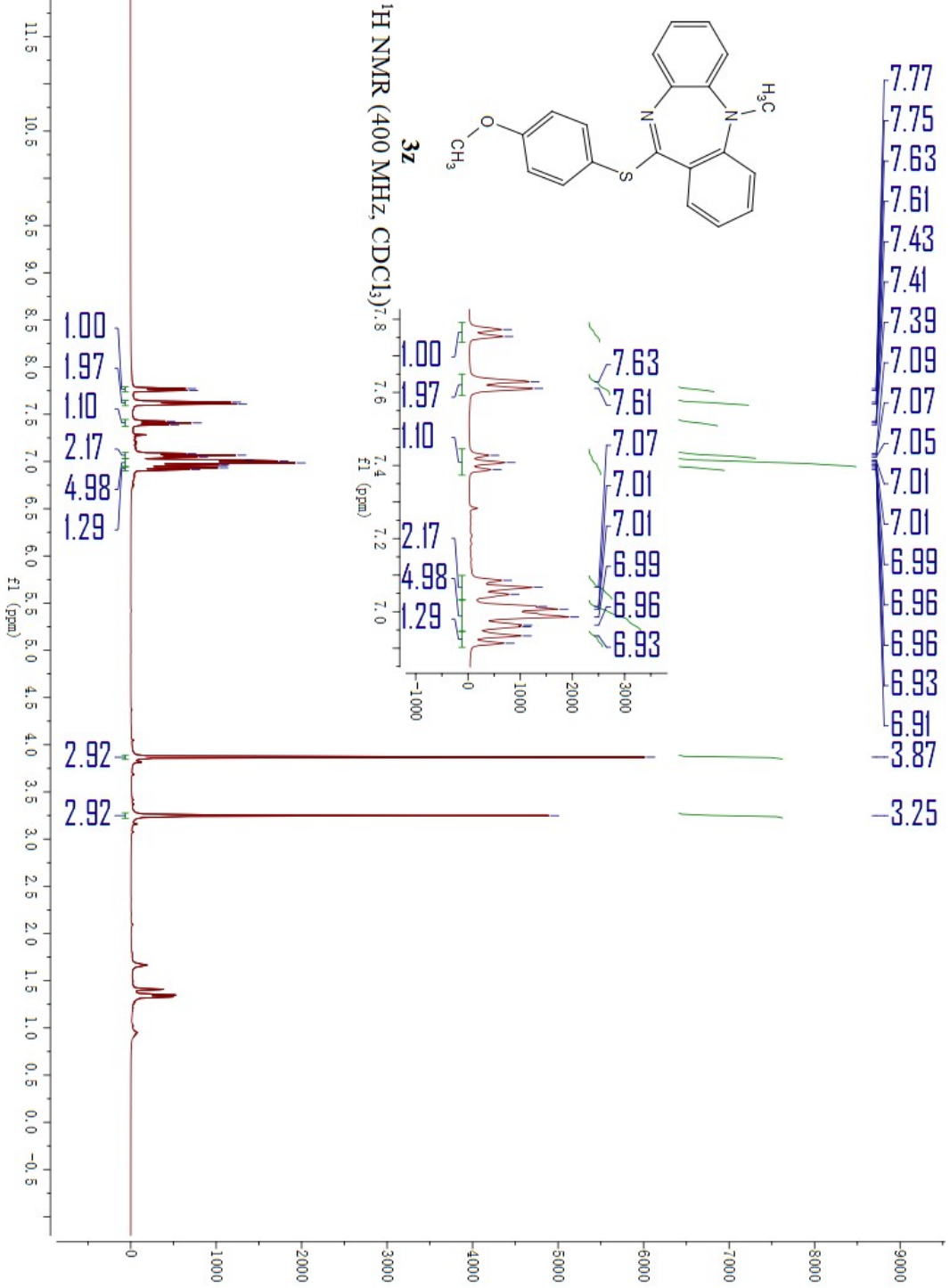
3y. ^{1}H NMR


3y
^{1}H NMR (400 MHz, CDCl$_3$)
N
N
S
2.87
1.95
2.98
3.23
1.09
5.90
2.00
7.61
7.61
7.60
7.60
7.48
7.46
7.33
7.32
7.25
6.98
6.96
6.94
6.93
6.91
4.90
4.86
4.81
4.78
f1 (ppm)

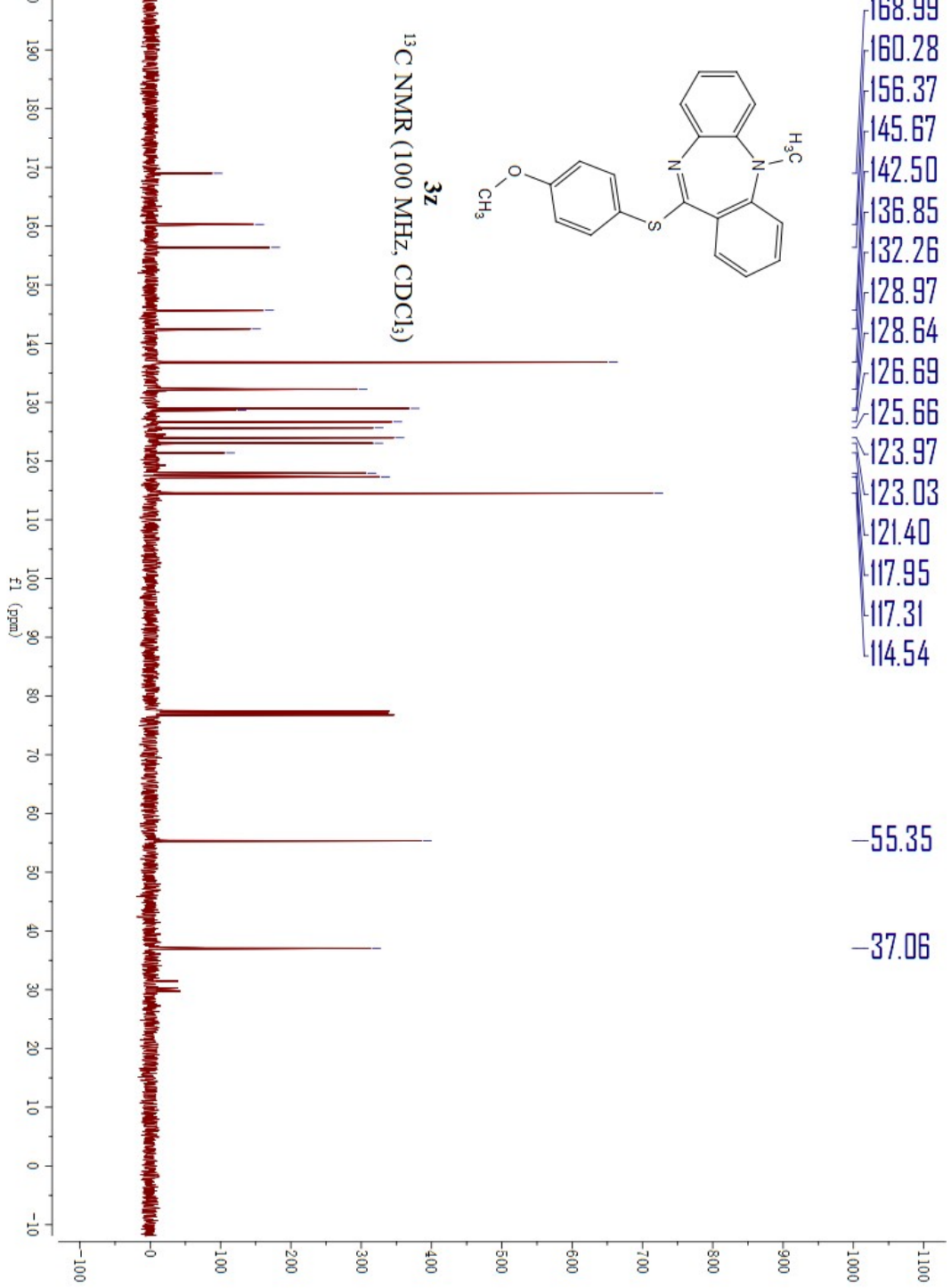
3y. ^{13}C NMR


3y
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)
168.68
154.61
144.74
137.31
134.66
132.00
129.18
128.90
128.56
128.51
128.15
127.19
126.46
125.77
124.33
123.46
119.35
52.86

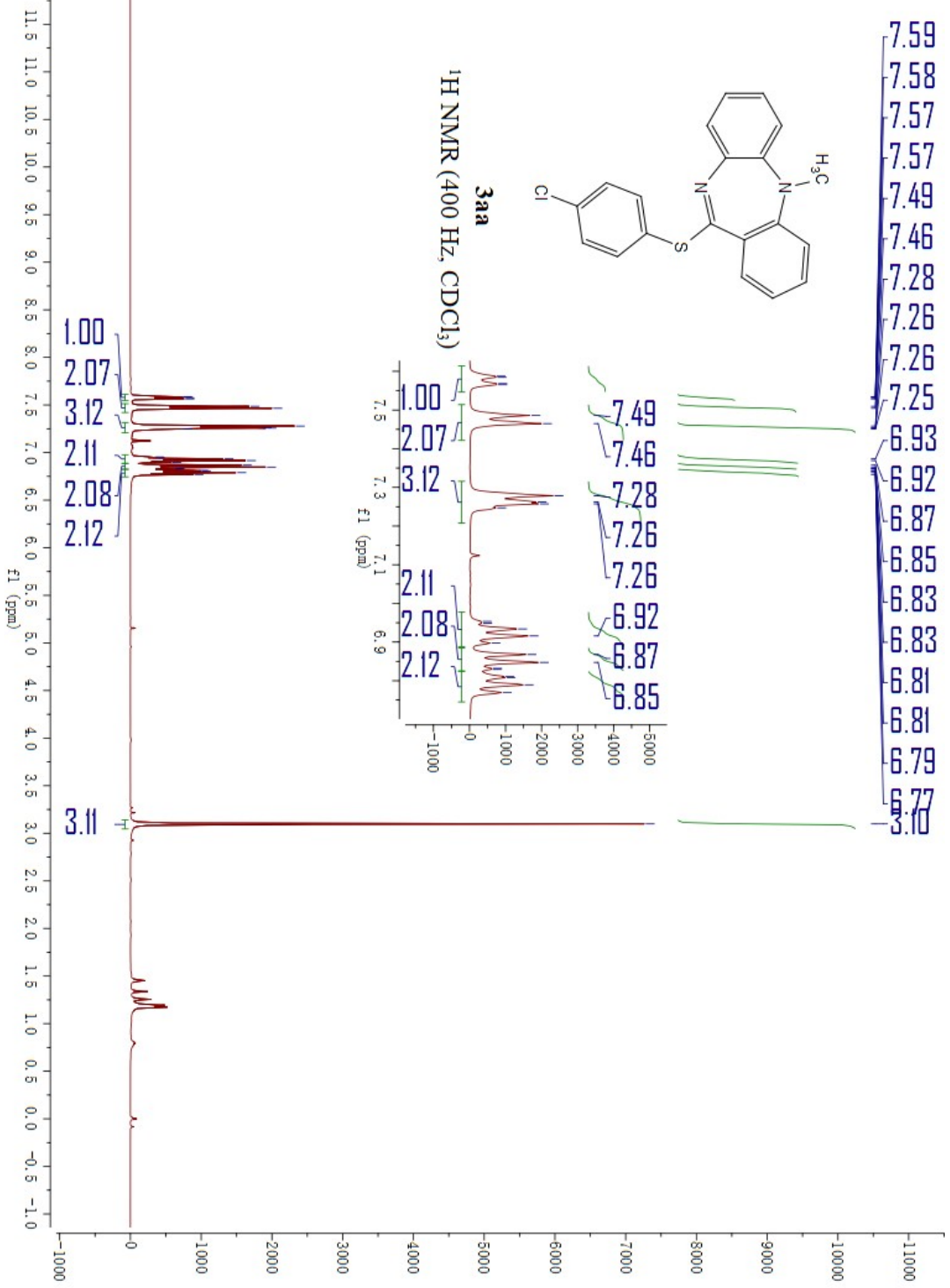
3z. ^{1}H NMR


3z
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
1.97
1.10
2.17
4.98
1.29
2.92
2.92
7.77
7.75
7.63
7.61
7.43
7.41
7.39
7.09
7.07
7.05
7.01
7.01
7.01
6.99
6.96
6.96
6.93
6.91
3.87
3.25
f1 (ppm)

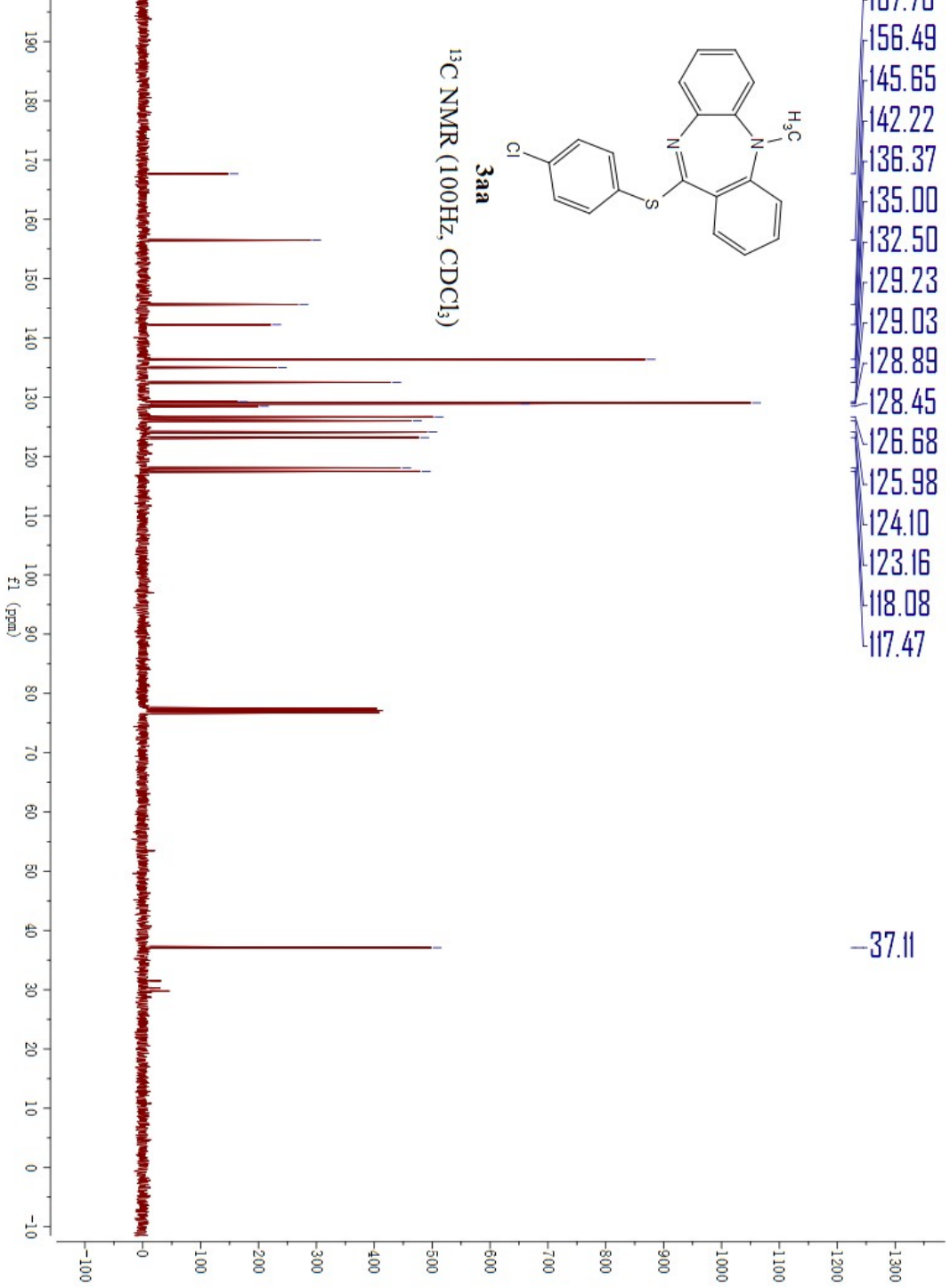
3z. ^{13}C NMR


3z
13C NMR (100 MHz, CDCl3)
f1 (ppm)
168.99
160.28
156.37
145.67
142.50
136.85
132.26
128.97
128.64
126.69
125.66
123.97
123.03
121.40
117.95
117.31
114.54
55.35
37.06

3aa. ^{1}H NMR

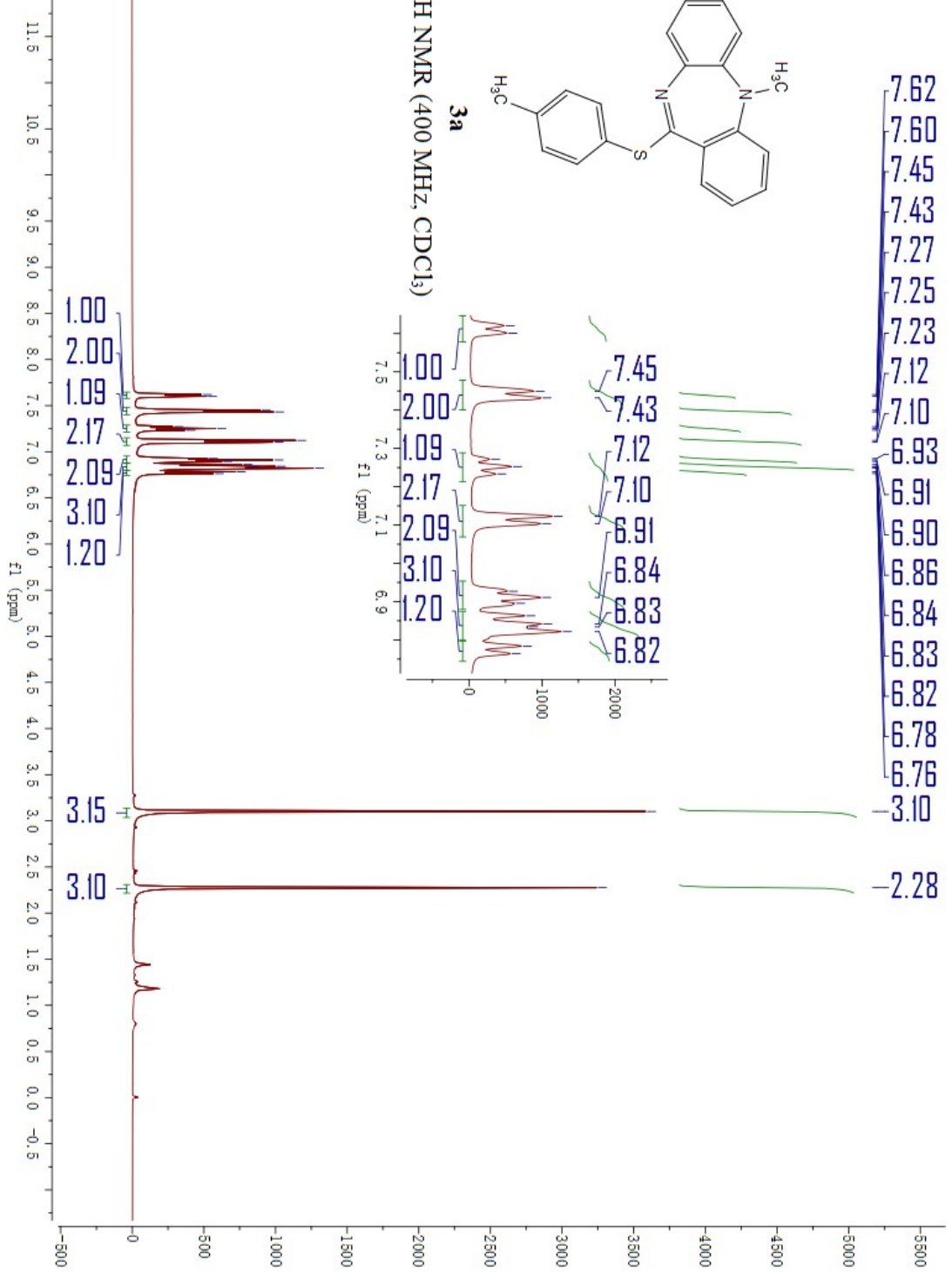

3aa
^{1}H NMR (400 Hz, CDCl$_3$)
Cl
S
N
N
H$_3$C
1.00
2.07
3.12
2.11
2.08
2.12
3.11
7.59
7.58
7.57
7.57
7.49
7.46
7.28
7.26
7.26
7.25
6.93
6.92
6.87
6.85
6.83
6.83
6.81
6.81
6.79
6.77
3.10
f1 (ppm)

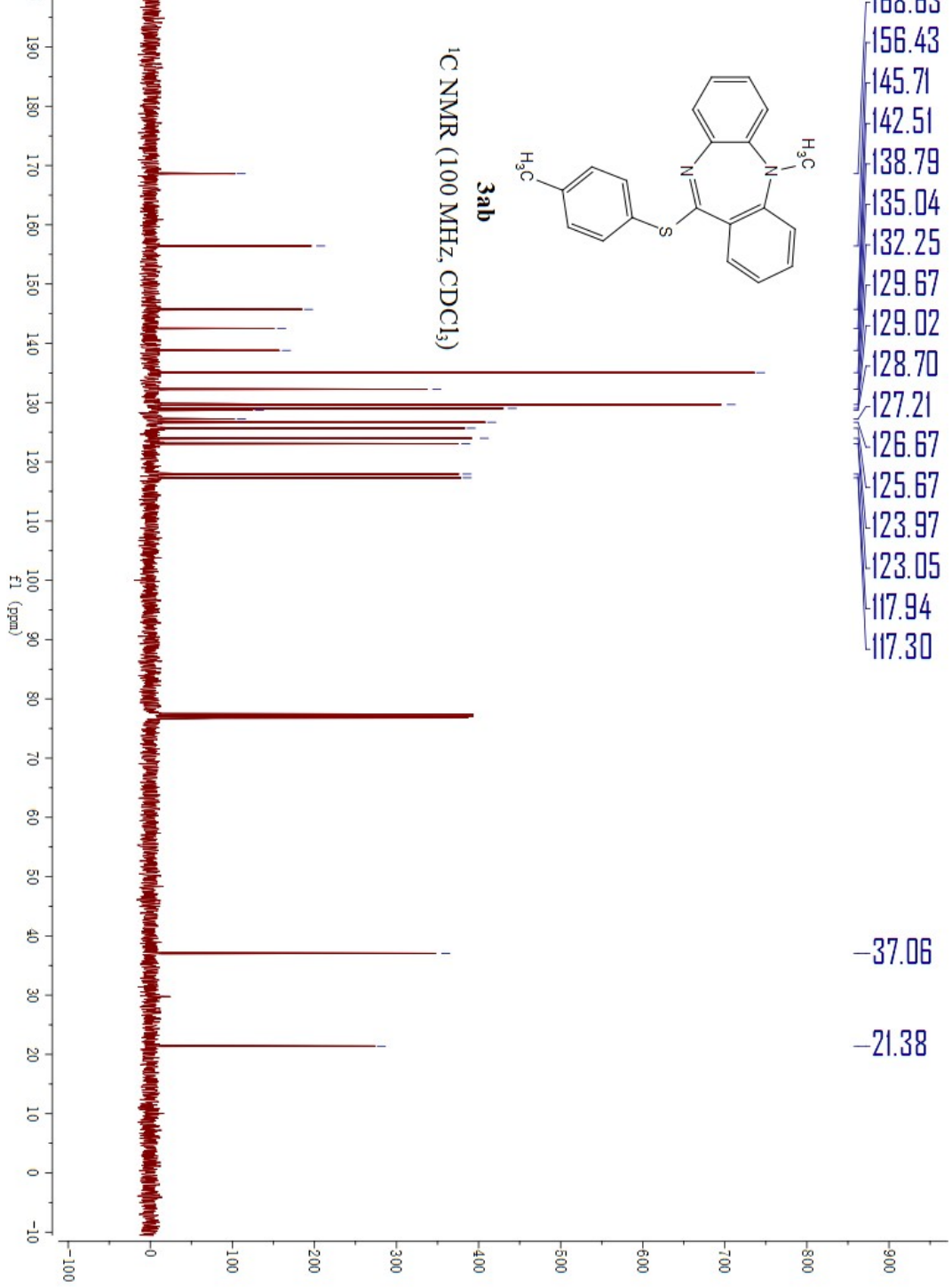
3aa. ^{13}C NMR


3aa
^{13}C NMR (100Hz, CDCl$_3$)
Cl
S
N
N
H$_3$C
156.49
145.65
142.22
136.37
135.00
132.50
129.23
129.03
128.89
128.45
126.68
125.98
124.10
123.16
118.08
117.47
37.11
f1 (ppm)

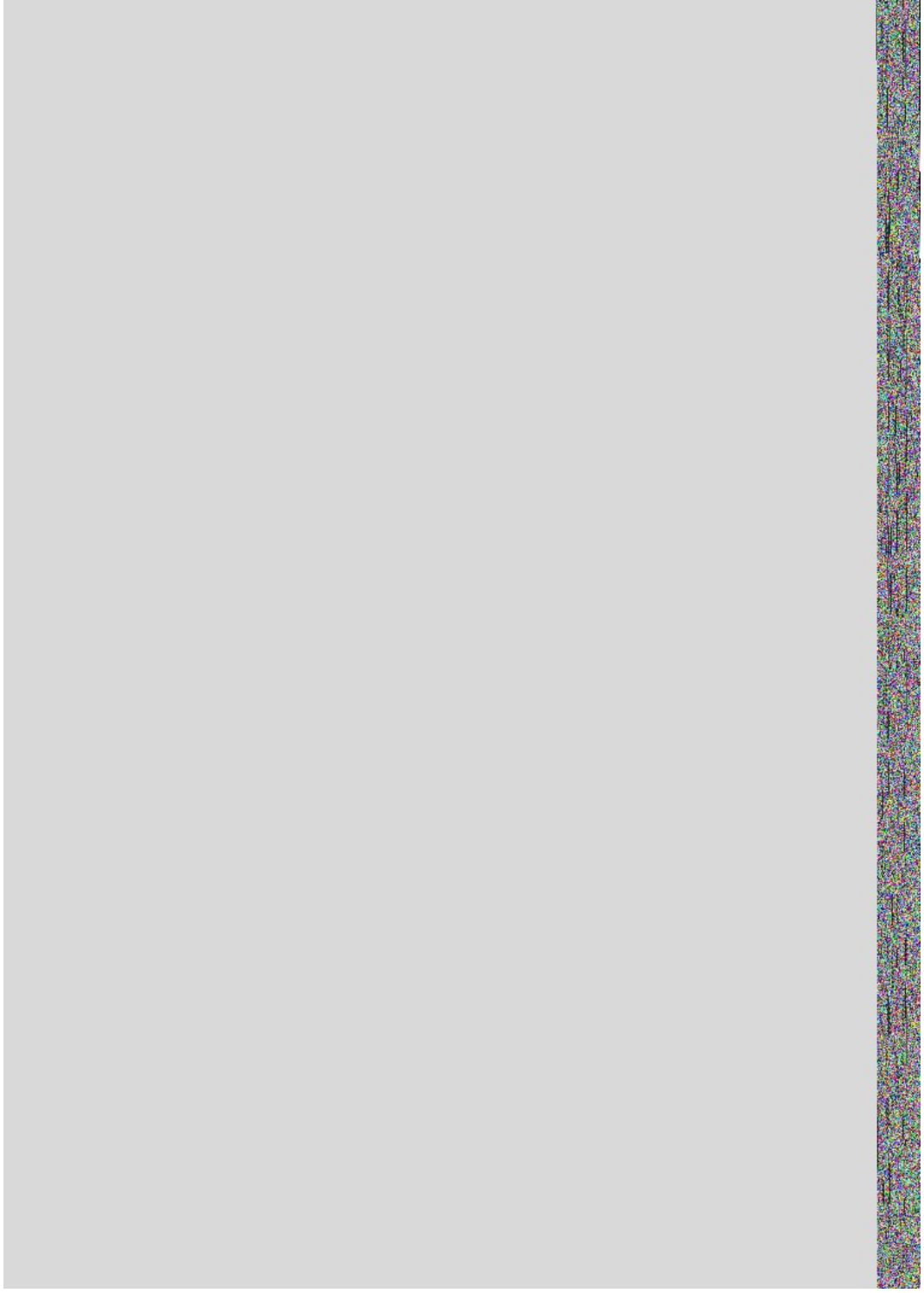
3ab. ^{1}H NMR

3ab. ^{13}C NMR

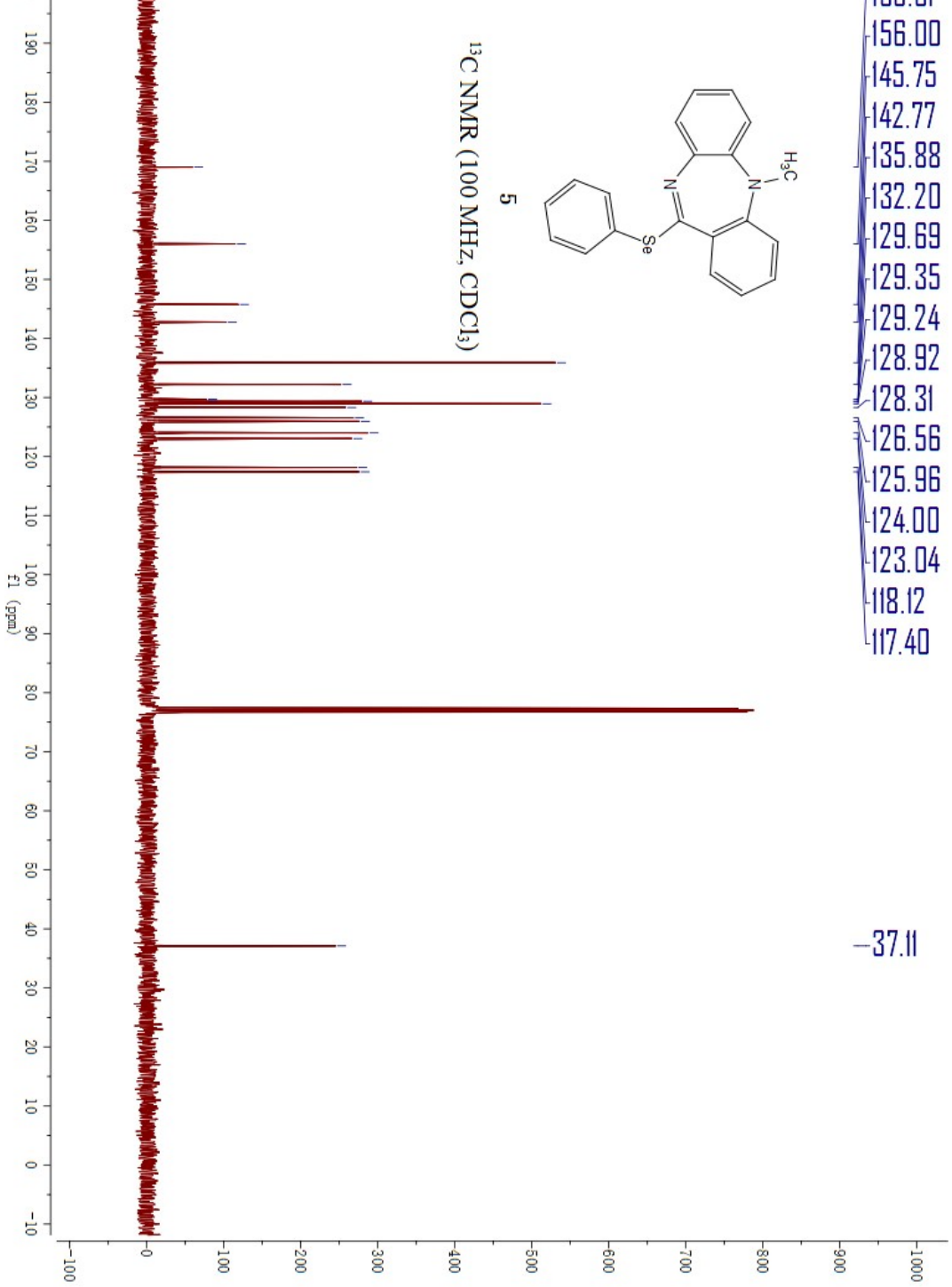

3a
H NMR (400 MHz, CDCl3)
H3C
H3C
N
N
S
1.00
2.00
1.09
2.17
2.09
3.10
1.20
3.15
3.10
7.62
7.60
7.45
7.43
7.27
7.25
7.23
7.12
7.10
6.93
6.91
6.90
6.86
6.84
6.83
6.82
6.78
6.76
3.10
2.28
f1 (ppm)


3ab
^{1}C NMR (100 MHz, CDCl$_3$)
H$_3$C
H$_3$C
N
N
S
168.63
156.43
145.71
142.51
138.79
135.04
132.25
129.67
129.02
128.70
127.21
126.67
125.67
123.97
123.05
117.94
117.30
37.06
21.38
f1 (ppm)

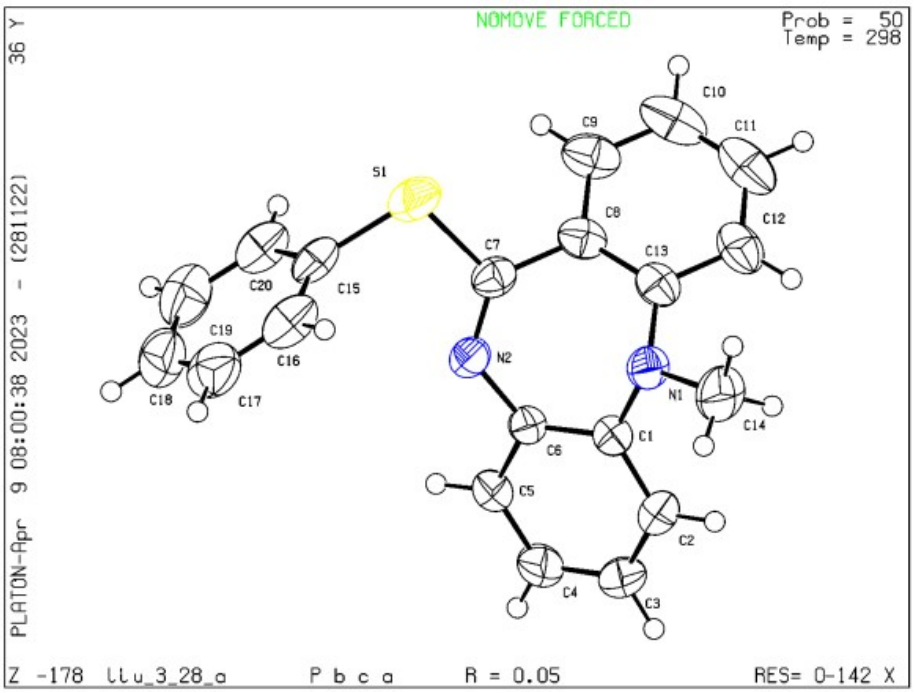
5. ^{1}H NMR



5. ^{13}C NMR



10. XRD data of the compound 3a



Crystal data and structure refinement for liuyi-3-28_auto (CCDC: 2183505).

Identification code	liuyi-3-28_auto
Empirical formula	$C_{20}H_{16}N_2S$
Formula weight	316.41
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 8.3581(7) A alpha = 90 deg. b = 15.8178(11) A beta = 90 deg. c = 24.7199(17) A gamma = 90 deg.
Volume	3268.1(4) $Å^3$
Z, Calculated density	8, 1.286 Mg/m^3
Absorption coefficient	0.199 mm^{-1}
F(000)	1328
Crystal size	0.170 × 0.160 × 0.140 mm
Limiting indices	$-9 \le h \le 6$, $-18 \le k \le 17$, $-20 \le l \le 29$
Reflections collected / unique	8265 / 2891 [$R_{(int)}$ = 0.0249]
Completeness to theta = 25.099	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.48236
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2891 / 0 / 209
Goodness-of-fit on F^2	1.066
Final R indexes [I> 2sigma(I)]	R_1 = 0.0468, wR_2 = 0.1087
R indices (all data)	R_1 = 0.0661, wR_2 = 0.1173
Extinction coefficient	n/a
Largest diff. peak and hole	0.152 and -0.259 e. $Å^{-3}$