Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

TABLE OF CONTENTS:

1. General S1
2. Some Supplementary Detailed Results for Screening Reaction Conditions S1
3. $Fe(OTf)_3$ Catalyzed Alkylation of Carbazole Derivatives via Hydroarylation of Styrenes S2
4.Copies of NMR Spectra S11

1. General

All moisture or oxygen-sensitive reactions were carried out under a nitrogen atmosphere in oven or heat-dried flasks or Schlenk tubes. All commercially available reagents were directly used as received without further purification. All reactions were monitored by thin-layer chromatography (TLC) on gel F_{254} plates using UV light as visualizing agent (if applicable), and a solution of phosphomolybdic acid hydrate (50 g/L) in EtOH followed by heating as developing agents. The products were purified by flash column chromatography on silica gel (200-300 meshes) from the Qingdao Marine Chemical Factory in China.

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Bruker Ascend 500 MHz instrument. Chemical shifts were denoted in ppm (δ), and calibrated by using residual undeuterated solvent ($CHCl_3$ (7.26 ppm) or tetramethylsilane (0.00 ppm)) as internal reference for ^{1}H NMR and the deuterated solvent ($CDCl_3$ (77.16 ppm) or tetramethylsilane (0.00 ppm)) as internal standard for ^{13}C NMR. The coupling constants were reported in Hz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, td = triple doublet, dt = double triplet, m = multiplet. High-resolution mass spectral analysis (HRMS) data were measured on a Thermo Scientific TM Q Exactive PlusTM mass spectrometer by means of the ESI technique.

2. Some Supplementary Detailed Results for Screening Reaction Conditions

In the screening process, it was found that tandem N-alkylation and C-di-alkylation could occur when using a NH-carbazole derivative. However, the yield was only up to 30% and a trail of byproducts was observed on TLC. Thus N-protected carbazoles were finally selected as the substrates to study their C-alkylation reactions.

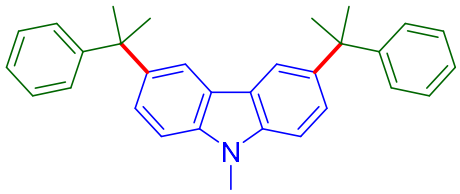
Employing N-methyl-carbazole as the model substrate, some experiments were carried out to try to form the C-mono-alkylated product. Unfortunately, those attempts were failed and the C-di-alkylated product was always obtained even when less than 1 equiv. of alkene was used. This is because the electron-donating property of the newly attached alkyl substituent makes the resulting C-mono-alkylated product more reactive than N-methyl-carbazole itself. Therefore, once the C-mono-alkylated product was formed, it reacted more quickly with alkene than N-methyl-carbazole which led to the formation of C-di-alkylated product.

3. $Fe(OTf)_3$ Catalyzed Alkylation of Carbazole Derivatives via Hydroarylation of Styrenes

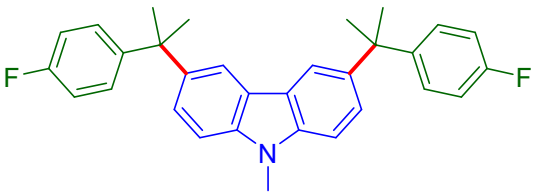
General experimental procedure was described as follows:

To an oven-dried Schlenk tube were sequentially added 9-methylcarbazole or its derivatives (0.25 mmol), iron (III) trifluomethanesulfonate (25.2 mg, 0.05 mmol) and dichloromethane (2.0 mL). The reaction mixture was stirred at room temperature for 5 min. Then, alkene substrate (0.625 mmol, 2.5 equiv) was added to the reaction mixture. The resultant mixture was stirred at room temperature for 0.25–24 h (monitored by TLC until the 9-methylcarbazole or its derivatives had disappeared or the system no longer changed). Then the reaction mixture was quenched with water (10 mL). Following addition of ethyl acetate (AcOEt) (10 mL), the organic layer was separated, and the aqueous phase was extracted with AcOEt (10 mL). The combined organic extracts were washed with H_2O (4 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with an eluent (*n*-hexane/AcOEt (250:1→100:1) to afford the product.

Except for special notes, all the products was obtained following the above general experimental procedure.

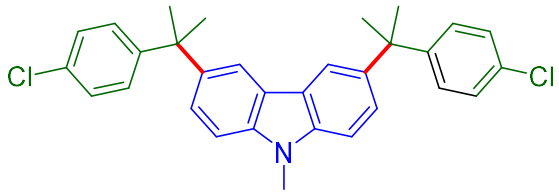
3ab: 

The general experimental procedure was followed to afford product **3ab** as white solid (100.0 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.06 (s, 2H), 7.30–7.19 (m, 12H), 7.17–7.12 (m, 2H), 3.73 (s, 3H), 1.80 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.9, 141.3, 139.7, 128.1, 127.0, 125.7, 125.5, 122.5, 117.6, 108.2, 43.1, 31.5, 29.2. HRMS (ESI) *m/z*: [*M*+H]$^+$ Calcd for $C_{31}H_{32}N$ 418.2529; Found 418.2528.

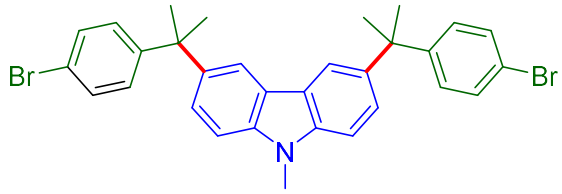
3ac: 

The general experimental procedure was followed to afford product **3ac** as colorless oil (109.3 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.04 (s, 2H), 7.25–7.20 (m, 8H), 6.96–6.90 (m, 4H), 3.77 (s, 3H), 1.79 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 161.0 (d, $^1J_{C-F}$ = 244.4 Hz), 147.6, 141.1, 139.7, 128.5 (d, $^3J_{C-F}$ = 7.6 Hz), 125.6, 122.5, 117.5, 114.7 (d, $^2J_{C-}$

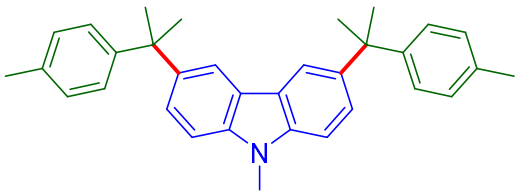
$_F$ = 21.4 Hz), 108.3, 42.7, 31.7, 29.2. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{31}H_{30}F_2N$ 454.2341; Found 454.2339.

3ad: 

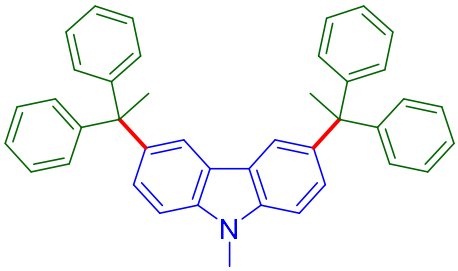
The general experimental procedure was followed to afford product **3ad** as colorless oil (110.3 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.02 (d, J = 1.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.22–7.17 (m, 10H), 3.76 (s, 3H) ,1.78 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 150.4, 140.8, 139.8, 131.3, 128.5, 128.2, 125.6, 122.4, 117.6, 108.3, 42.8, 31.5, 29.2. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{31}H_{30}Cl_2N$ 486.1750; Found 486.1751.

3ae: 

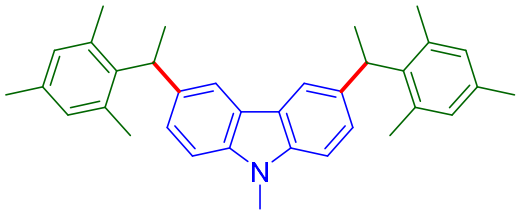
The general experimental procedure was followed to afford product **3ae** as colorless oil (125.1 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.02 (d, J = 1.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 4H), 7.24 (d, J = 8.5 Hz, 2H), 7.20 (dd, J = 8.5, 1.5 Hz, 2H), 7.13 (d, J = 8.5 Hz, 4H), 3.75 (s, 3H) ,1.77 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.0, 140.7, 139.8, 131.1, 128.9, 125.6, 122.4, 119.4, 117.6, 108.3, 42.9, 31.4, 29.2. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{31}H_{30}Br_2N$ 574.0740; Found 574.0728.

3af: 

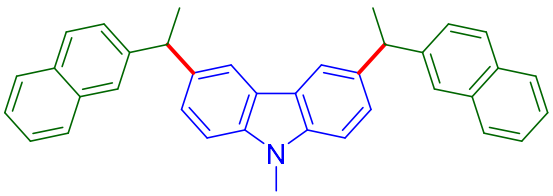
The general experimental procedure was followed to afford product **3af** as colorless oil (103.1 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.07 (d, J = 1.5 Hz, 2H), 7.23 (dd, J = 8.5, 1.5 Hz, 2H), 7.19–7.12 (m, 6H), 7.04 (d, J = 8.5 Hz, 4H), 3.68 (s, 3H), 2.28 (s, 6H) ,1.78 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 149.0, 141.4, 139.7, 134.9, 128.8, 126.9, 125.6, 122.5, 117.6, 108.1, 42.7, 31.6, 29.2, 21.0. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{33}H_{36}N$ 446.2842; Found 446.2843.

3ag: 

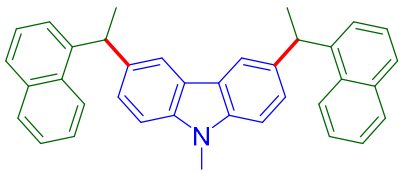
The general experimental procedure was followed to afford product **3ag** as yellow oil (90.5 mg, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.80 (s, 2H), 7.26–7.15 (m, 14H), 7.14–7.09 (m, 10H), 3.72 (s, 3H), 2.27 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 150.0, 139.9, 139.8, 128.9, 127.9, 127.5, 125.9, 122.6, 119.8, 107.8, 52.6, 31.3, 29.2. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{41}H_{36}N$ 542.2842; Found 542.2840.

3ah: 

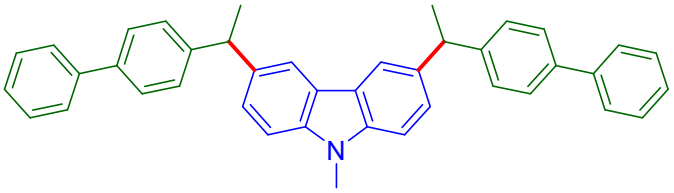
The general experimental procedure was followed to afford product **3ah** as colorless oil (113.7 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.97 (d, J = 4.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 6.86 (s, 4H), 4.84 (q, J = 7.0 Hz, 2H), 3.80 (s, 3H), 2.30 (s, 6H), 2.17 (s, 12H), 1.80 (d, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 141.1, 141.0, 139.6, 136.8, 135.9, 135.34, 135.32, 130.2, 125.3, 122.8, 118.1, 118.0, 108.1, 38.0, 29.2, 21.3, 20.9, 17.60, 17.56. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{40}N$ 474.3155; Found 474.3149.

3ai: 

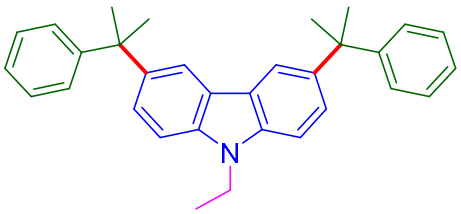
The general experimental procedure was followed to afford product **3ai** as colorless oil (77.7 mg, 63% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.02 (s, 2H), 7.84–7.73 (m, 8H), 7.50–7.42 (m, 4H), 7.40–7.34 (m, 4H), 7.29 (d, J = 8.5 Hz, 2H), 4.53 (q, J = 7.0 Hz, 2H), 3.79 (s, 3H), 1.87 (d, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 145.0, 140.1, 136.9, 133.7, 132.2, 128.0, 127.9, 127.7, 127.2, 126.1, 126.0, 125.4, 125.3, 122.8, 119.1, 108.5, 44.9, 29.2, 22.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{37}H_{32}N$ 490.2529; Found 490.2526.

3aj: 

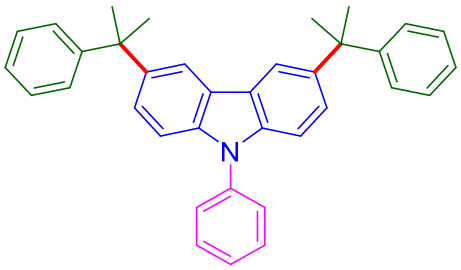
The general experimental procedure was followed to afford product **3aj** as colorless oil (74.4 mg, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.16–8.10 (m, 2H), 7.95 (s, 2H), 7.84–7.80 (m, 2H), 7.75–7.70 (m, 2H), 7.47–7.42 (m, 4H), 7.42–7.35 (m, 4H), 7.28–7.24 (m, 2H), 7.22–7.17 (m, 2H), 5.09 (q, J = 7.0 Hz, 2H), 3.70 (s, 3H), 1.84 (d, J = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 142.7, 142.6, 140.0, 137.32, 137.28, 134.2, 131.9, 128.8, 126.9, 125.94, 125.85, 125.83, 125.6, 125.4, 124.61, 124.59, 124.4, 124.3, 122.9, 119.12, 119.08, 108.5, 40.84, 40.81, 29.2, 23.4, 23.3. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{37}H_{32}N$ 490.2529; Found 490.2528.

3ak: 

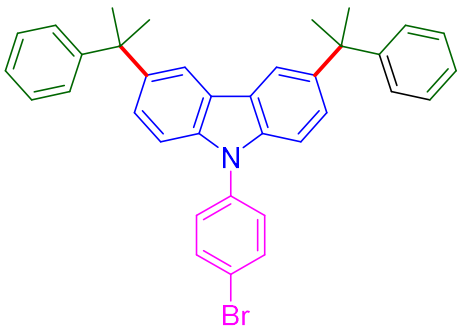
The general experimental procedure was followed to afford product **3ak** as white solid (65.5 mg, 48% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.02 (s, 2H), 7.58 (d, J =7.5 Hz, 4H), 7.53 (d, J = 8.0 Hz, 4H), 7.42 (t, J = 7.8 Hz, 4H), 7.38–7.30 (m, 10H), 4.41 (q, J = 7.0 Hz, 2H), 3.81 (s, 3H), 1.81 (d, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 146.7, 141.2, 140.2, 138.8, 136.9, 128.8, 128.2, 127.20, 127.16, 127.1, 126.0, 122.9, 119.0, 108.5, 44.6, 29.3, 22.6. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{41}H_{36}N$ 542.2842; Found 542.2839.

3bb: 

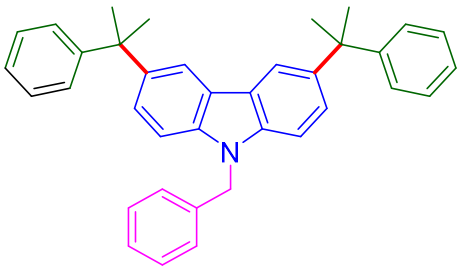
The general experimental procedure was followed to afford product **3bb** as colorless oil (103.4 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.06 (s, 2H), 7.31–7.20 (m, 12H), 7.16 (t, J = 7.0 Hz, 2H), 4.28 (q, J = 7.0 Hz, 2H), 1.80 (s, 12H), 1.39 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.9, 141.2, 138.6, 128.1, 127.0, 125.6, 125.5, 122.6, 117.7, 108.2, 43.1, 37.7, 31.5, 14.1. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{32}H_{34}N$ 432.2686; Found 432.2686.

3cb: 

The general experimental procedure was followed to afford product **3cb** as colorless oil (115.3 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.09 (d, J = 2.0 Hz, 2H), 7.53–7.50 (m, 4H), 7.40–7.35 (m, 1H), 7.31–7.23 (m, 10H), 7.19–7.13 (m, 4H), 1.81 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.7, 142.5, 139.4, 138.1, 129.8, 128.1, 127.2, 127.0, 126.9, 125.9, 125.6, 123.2, 117.6, 109.5, 43.1, 31.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{36}H_{34}N$ 480.2686; Found 480.2684.

3db: 

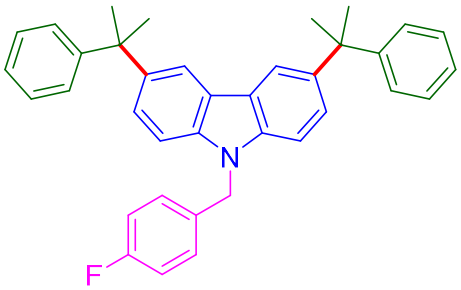
The general experimental procedure was followed to afford product **3db** as colorless oil (56.6 mg, 41% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.08 (d, J = 1.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.30–7.12 (m, 14H), 1.80 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.6, 142.8, 139.1, 137.2, 133.1, 128.4, 128.1, 127.0, 126.1, 125.6, 123.4, 120.5, 117.7, 109.3, 43.1, 31.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{36}H_{33}BrN$ 558.1791; Found 558.1791.

3eb: 

The general experimental procedure was followed to afford product **3eb** as colorless oil (104.8 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.07 (s, 2H), 7.30–7.12 (m, 19H), 5.38 (s, 2H), 1.79 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.8, 141.7, 139.4, 137.6, 128.8, 128.1, 127.5, 127.0, 126.7, 125.8, 125.6, 122.8, 117.7, 108.6, 46.9, 43.1, 31.5. HRMS (ESI)

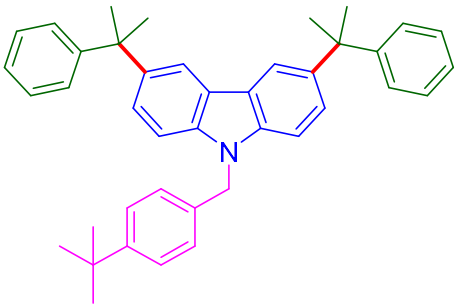
m/z: [*M*+H]$^+$ Calcd for $C_{37}H_{36}N$ 494.2842; Found 494.2838.

3fb:



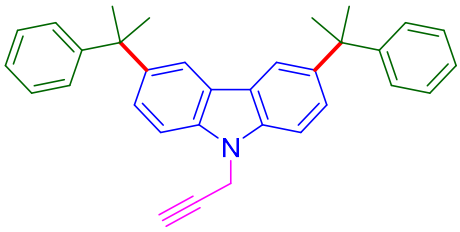
The general experimental procedure was followed to afford product **3fb** as colorless oil (114.5 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.07 (d, J = 1.0 Hz, 2H), 7.30–7.23 (m, 8H), 7.21–7.10 (m, 8H), 6.93 (t, J = 8.5 Hz, 2H), 5.37 (s, 2H), 1.80 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 162.2 (d, $^1J_{C\text{-}F}$ = 247.0 Hz), 151.7, 141.8, 139.2, 133.3, 128.4 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 128.1, 127.0, 125.9, 125.6, 122.8, 117.8, 115.8 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 108.5, 46.2, 43.1, 31.5. HRMS (ESI) *m/z*: [*M*+H]$^+$ Calcd for $C_{37}H_{35}FN$ 512.2748; Found 512.2742.

3gb:



The general experimental procedure was followed to afford product **3gb** as colorless oil (120.4 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.08 (s, 2H), 7.29–7.18 (m, 10H), 7.18–7.10 (m, 6H), 7.04 (d, J = 8.0 Hz, 2H), 5.29 (s, 2H), 1.78 (s, 12H), 1.22 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.7, 150.3, 141.5, 139.4, 134.5, 128.1, 127.0, 126.4, 125.8, 125.7, 125.6, 122.7, 117.6, 108.7, 46.4, 43.0, 34.5, 31.5, 31.4. HRMS (ESI) *m/z*: [*M*+H]$^+$ Calcd for $C_{41}H_{44}N$ 550.3468; Found 550.3469.

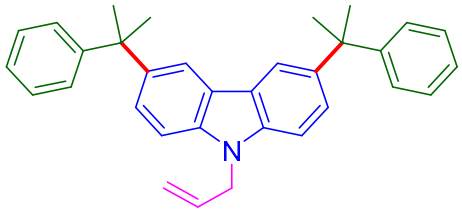
3hb:



The general experimental procedure was followed to afford product **3hb** as colorless oil (95.2 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.04 (d, J = 1.5 Hz, 2H), 7.33–7.14 (m, 14H), 4.94 (d, J = 2.5 Hz, 2H), 2.21 (t, J = 2.5 Hz, 1H), 1.80 (s, 12H). ^{13}C NMR (126 MHz,

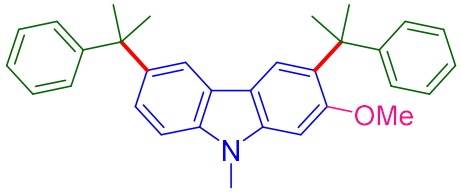
$CDCl_3$): δ (ppm) 151.7, 142.1, 138.6, 128.1, 127.0, 125.9, 125.6, 123.0, 117.9, 108.4, 78.2, 72.3, 43.1, 32.5, 31.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{33}H_{32}N$ 442.2529; Found 442.2528.

3ib:



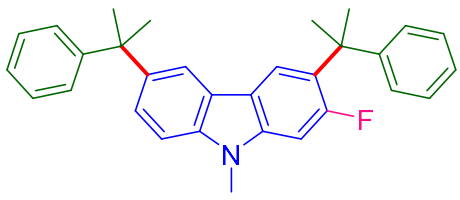
The general experimental procedure was followed to afford product **3ib** as colorless oil (101.5 mg, 92% yield). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.06 (d, J = 1.0 Hz, 2H), 7.30–7.09 (m, 14H), 5.94–5.85 (m, 1H), 5.10 (d, J = 10.5 Hz, 1H), 5.04 (d, J = 17.0 Hz, 1H), 4.74 (d, J = 5.0 Hz, 2H), 1.79 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.8, 141.5, 139.1, 132.8, 128.1, 127.0, 125.7, 125.5, 122.7, 117.6, 116.9, 108.5, 45.5, 43.1, 31.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{33}H_{34}N$ 444.2686; Found 444.2685.

3jb:



The general experimental procedure was followed to afford product **3jb** as white solid (95.1 mg, 85% yield). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.15 (s, 1H), 8.03 (d, J = 1.0 Hz, 1H), 7.33–7.15 (m, 11H), 7.11–7.06 (m, 1H), 6.73 (s, 1H), 3.76 (s, 3H), 3.42 (s, 3H), 1.83 (s, 6H), 1.78 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 157.9, 152.5, 152.0, 141.5, 141.4, 139.3, 131.1, 128.1, 127.6, 127.0, 125.6, 125.5, 124.7, 124.1, 122.9, 118.1, 116.9, 115.6, 107.9, 93.4, 55.8, 43.1, 42.2, 31.6, 30.4, 29.3. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{32}H_{34}NO$ 448.2635; Found 448.2640.

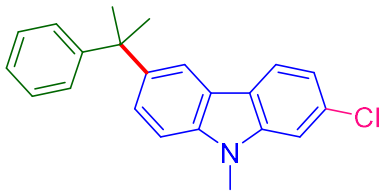
3kb:



The general experimental procedure was followed to afford product **3kb** as colorless oil (102.3 mg, 94% yield). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.15 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 1.5 Hz, 1H), 7.31–7.19 (m, 10H), 7.18–7.12 (m, 2H), 6.88 (d, J = 12.5 Hz, 1H), 3.67 (s, 3H), 1.81 (d, J = 5.5 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 160.8 (d, $^1J_{C\text{-}F}$ = 245.7 Hz), 151.8, 150.9, 142.0, 140.8 (d, $^3J_{C\text{-}F}$ = 12.6 Hz), 139.8, 128.6 (d, $^2J_{C\text{-}F}$ = 13.9 Hz), 128.14, 128.08, 127.0,

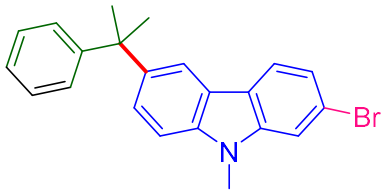
125.8, 125.6, 125.5, 125.2, 122.4, 118.4, 118.3, 117.3, 108.2, 96.7 (d, $^{2}J_{C\text{-}F}$ = 29.0 Hz), 43.1, 41.7, 31.6, 30.4, 29.4. HRMS (ESI) *m/z*: [*M*+H]$^{+}$ Calcd for $C_{31}H_{31}FN$ 436.2435; Found 436.2437.

3lb:



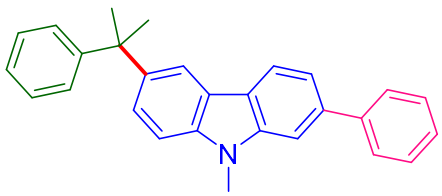
The general experimental procedure was followed to afford product **3lb** as colorless oil (75.4 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.99 (d, *J* = 1.5 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.33 (d, *J* = 1.5 Hz, 1H), 7.30–7.22 (m, 6H), 7.20–7.13 (m, 2H), 3.75 (s, 3H), 1.80 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.5, 142.2, 142.0, 139.6, 131.4, 128.1, 127.0, 126.1, 125.7, 121.9, 121.6, 121.1, 119.3, 117.8, 108.8, 108.4, 43.1, 31.4, 29.3. HRMS (ESI) *m/z*: [*M*+H]$^{+}$ Calcd for $C_{22}H_{21}ClN$ 334.1357; Found 334.1360.

3mb:



The general experimental procedure was followed to afford product **3mb** as colorless oil (82.3 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.00 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 1.5 Hz, 1H), 7.31–7.22 (m, 7H), 7.20–7.14 (m, 1H), 3.75 (s, 3H), 1.79 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.5, 142.22, 142.20, 139.4, 128.1, 127.0, 126.2, 125.7, 122.0, 121.91, 121.86, 121.4, 119.2, 117.8, 111.7, 108.4, 43.1, 31.4, 29.2. HRMS (ESI) *m/z*: [*M*+H]$^{+}$ Calcd for $C_{22}H_{21}BrN$ 378.0852; Found 378.0844.

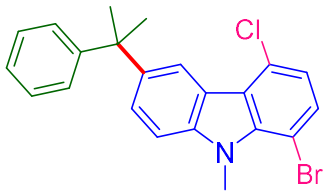
3nb:



The general experimental procedure was followed to afford product **3nb** as colorless oil (90.2 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.09 (d, *J* = 8.0 Hz, 1H), 8.06 (dd, *J* = 1.5, 0.5 Hz, 1H), 7.72 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.55 (d, *J* = 1.0 Hz, 1H), 7.49–7.44 (m, 3H), 7.37–7.32 (m, 1H), 7.31–7.14 (m, 7H), 3.83 (s, 3H), 1.81 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.7, 142.4, 142.0, 141.8, 139.9, 139.1, 128.9, 128.1, 127.7, 127.1, 127.0, 125.8,

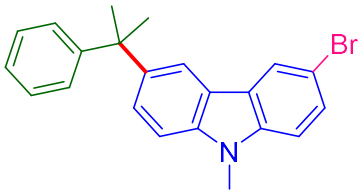
125.6, 122.3, 122.2, 120.6, 118.6, 117.9, 108.2, 107.1, 43.1, 31.5, 29.2. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{26}N$ 376.2060; Found 376.2060.

3ob:



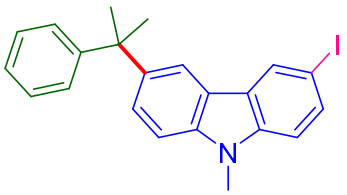
The general experimental procedure was followed to afford product **3ob** as colorless oil (78.1 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.68 (d, J = 1.5 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.30–7.21 (m, 6H), 7.19–7.14 (m, 1H), 6.98 (d, J = 8.5 Hz, 1H), 4.16 (s, 3H), 1.81 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.3, 142.8, 140.4, 138.5, 130.7, 128.1, 127.5, 127.0, 125.7, 123.0, 120.9, 120.1, 108.7, 101.1, 43.1, 32.3, 31.3. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{20}BrClN$ 412.0462; Found 412.0460.

3pb:



The general experimental procedure was followed to afford product **3pb** as colorless oil (90.6 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.16 (d, J = 2.0 Hz, 1H), 7.98 (d, J = 1.5 Hz, 1H), 7.49 (dd, J = 8.8, 1.8 Hz, 1H), 7.30–7.15 (m, 8H), 3.73 (s, 3H), 1.79 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.4, 142.1, 140.0, 139.6, 128.17, 128.15, 126.9, 126.5, 125.7, 124.7, 123.0, 121.3, 117.9, 111.6, 109.9, 108.4, 43.0, 31.4, 29.2. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{21}BrN$ 378.0852; Found 378.0843.

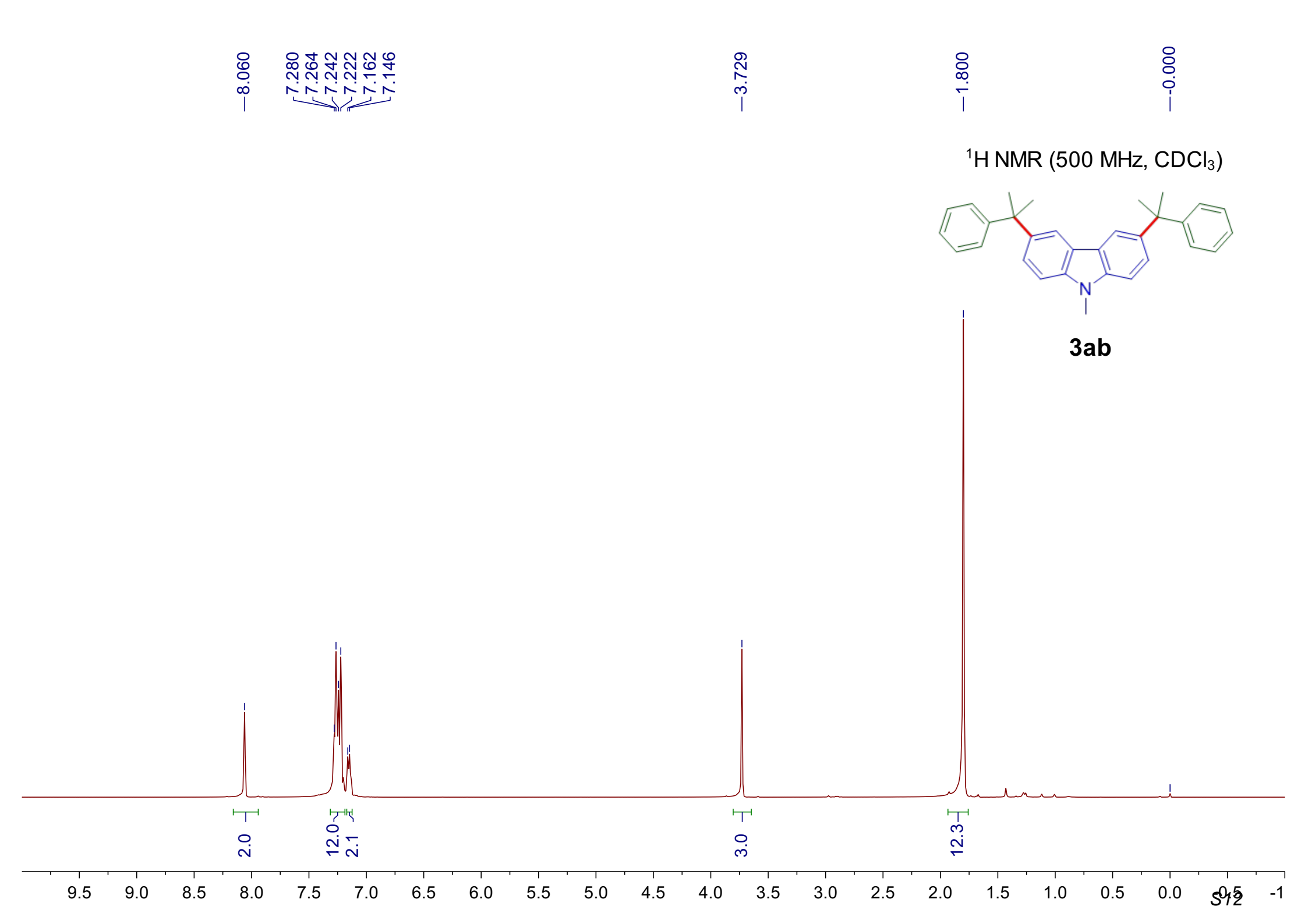
3qb:



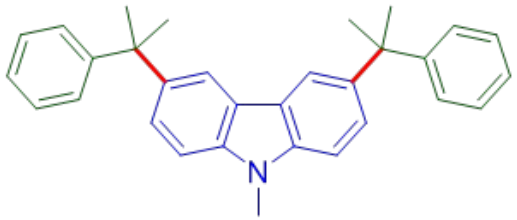
The general experimental procedure was followed to afford product **3qb** as colorless oil (36.8 mg, 35% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.35 (s, 1H), 7.97 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.34–7.21 (m, 6H), 7.20–7.11 (m, 2H), 3.76 (s, 3H), 1.78 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.4, 142.2, 140.5, 139.3, 133.8, 129.2, 128.2, 127.0, 126.5, 125.7, 125.6, 121.1, 117.9, 110.6, 108.4, 81.3, 43.1, 31.4, 29.3. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{21}IN$ 426.0713; Found 426.0713.

4. Copies of NMR Spectra

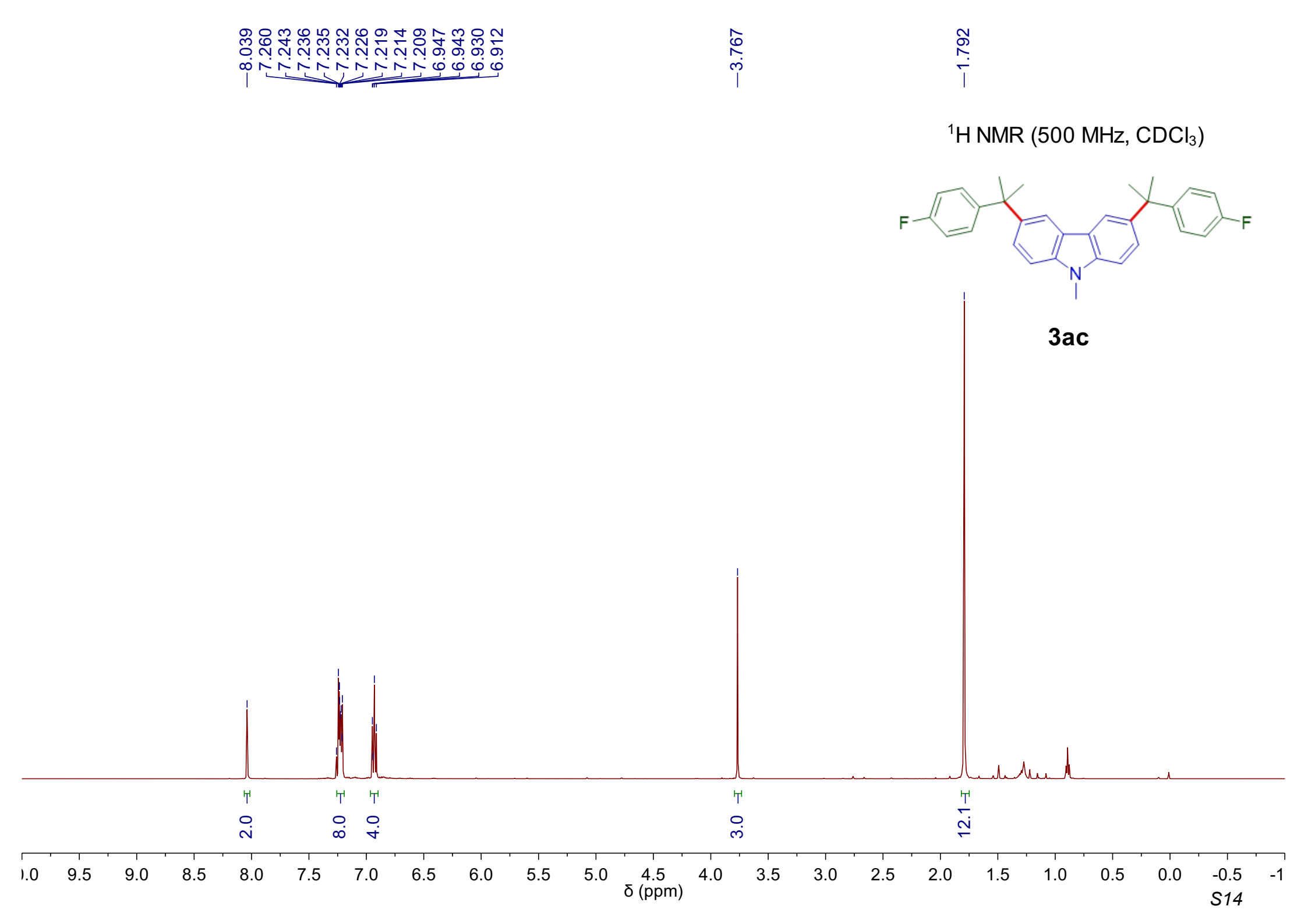
See the next page!


8.060
7.280
7.264
7.242
7.222
7.162
7.146
3.729
1.800
-0.000
^{1}H NMR (500 MHz, $CDCl_3$)
N
3ab
2.0
12.0
2.1
3.0
12.3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1

^{13}C NMR (126 MHz, $CDCl_3$)

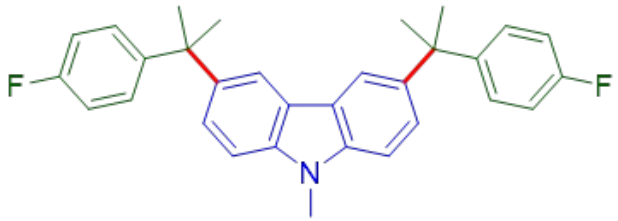


3ab

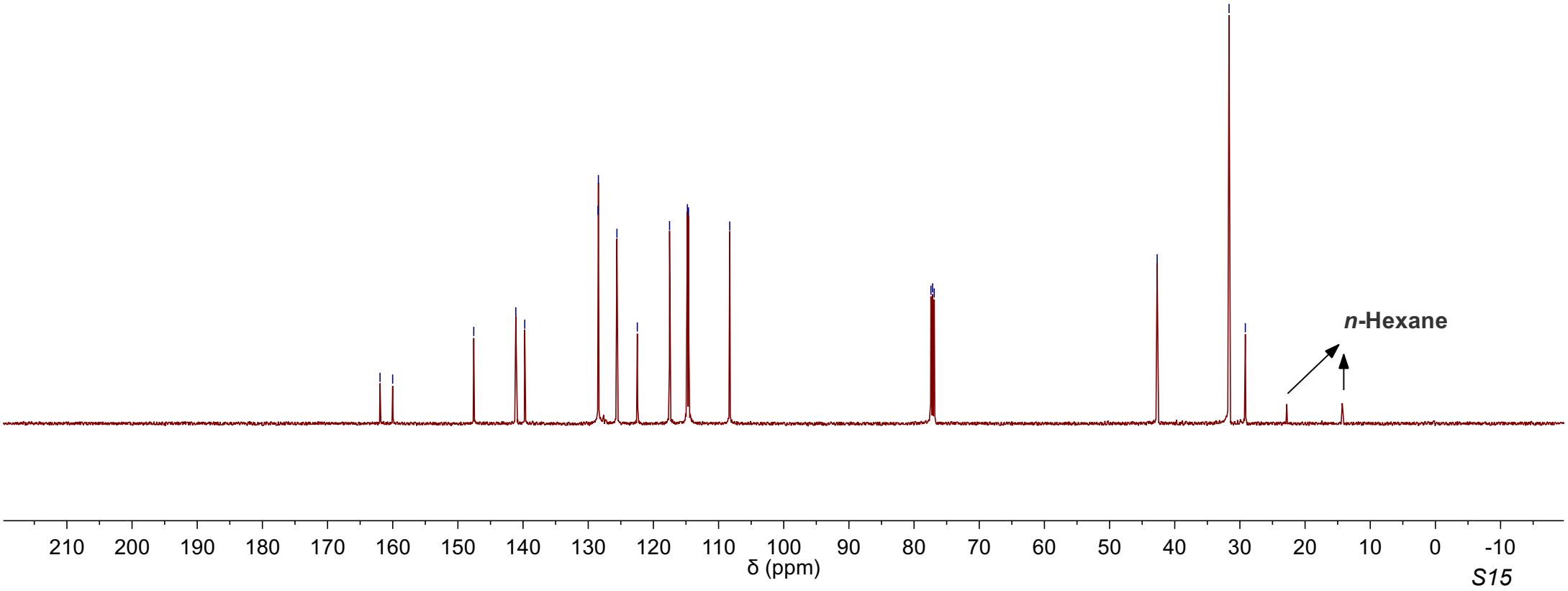

8.039
7.260
7.243
7.236
7.235
7.232
7.226
7.219
7.214
7.209
6.947
6.943
6.930
6.912
3.767
1.792
^{1}H NMR (500 MHz, $CDCl_3$)
F
F
N
3ac
2.0
8.0
4.0
3.0
12.1
δ (ppm)

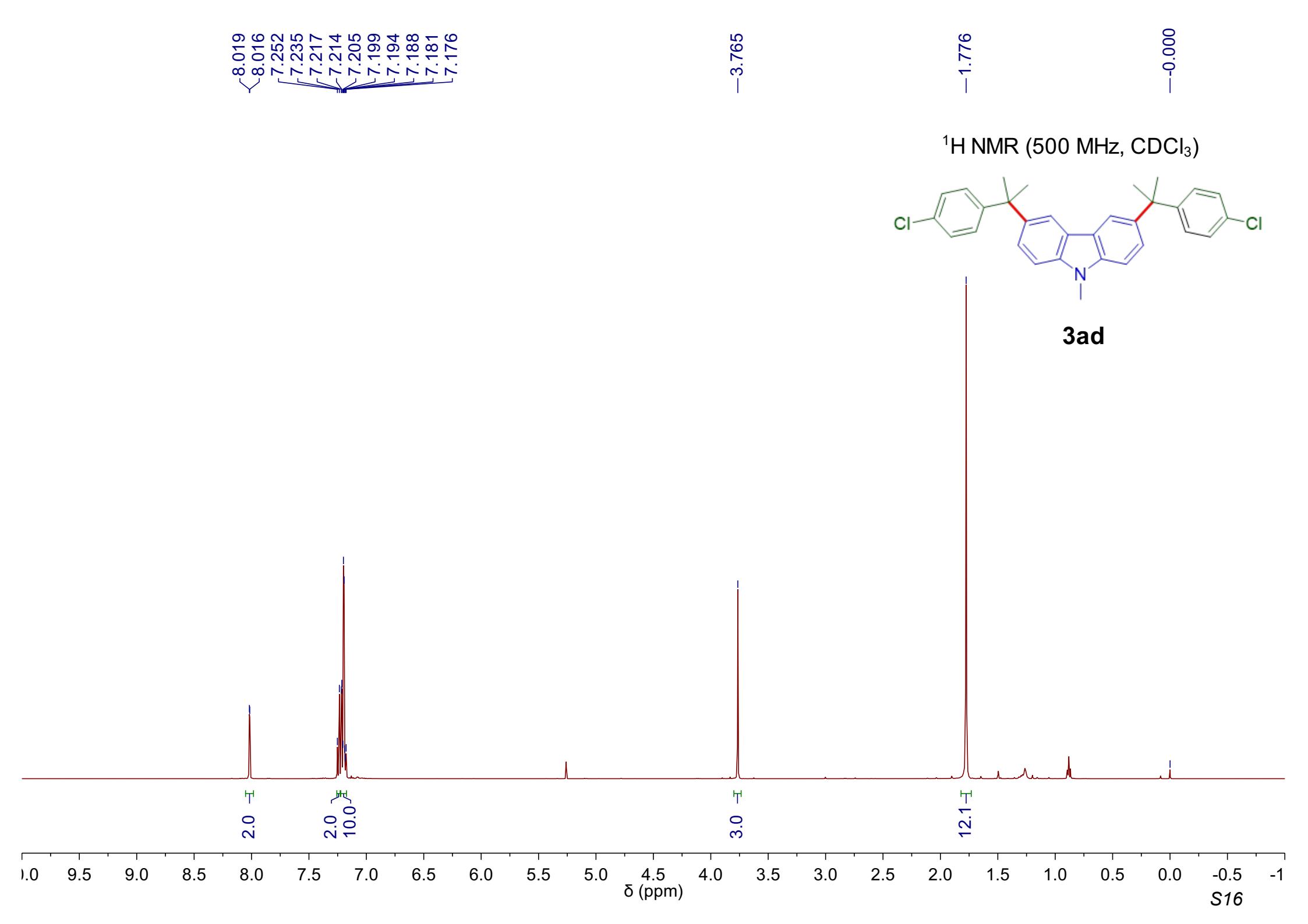
161.95
160.01
147.56
141.11
139.74
128.50
128.44
125.60
122.47
117.52
114.78
114.61
108.29
77.41
77.16
76.91
42.70
31.67
29.17

^{13}C NMR (126 MHz, $CDCl_3$)



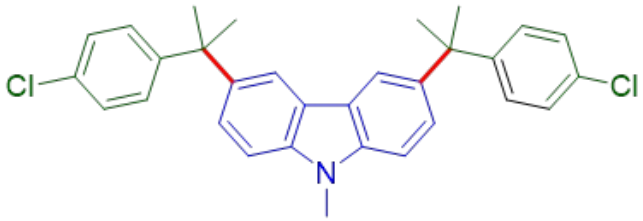
3ac



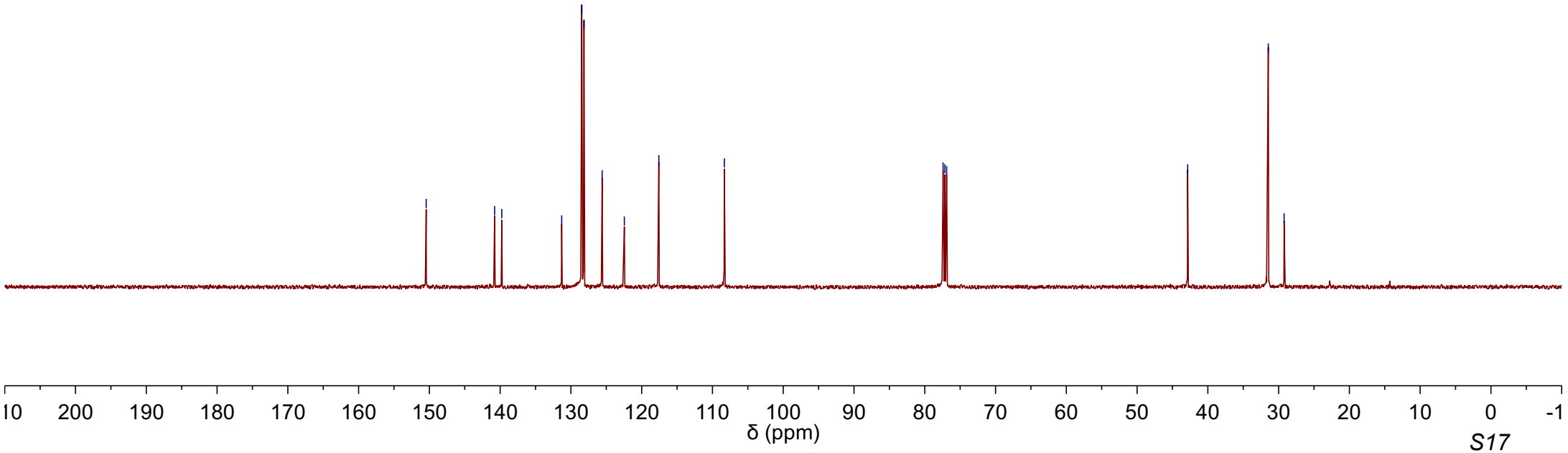

8.019
8.016
7.252
7.235
7.217
7.214
7.205
7.199
7.194
7.188
7.181
7.176
3.765
1.776
0.000
^{1}H NMR (500 MHz, $CDCl_3$)
Cl
Cl
N
3ad
2.0
2.0
10.0
3.0
12.1
δ (ppm)

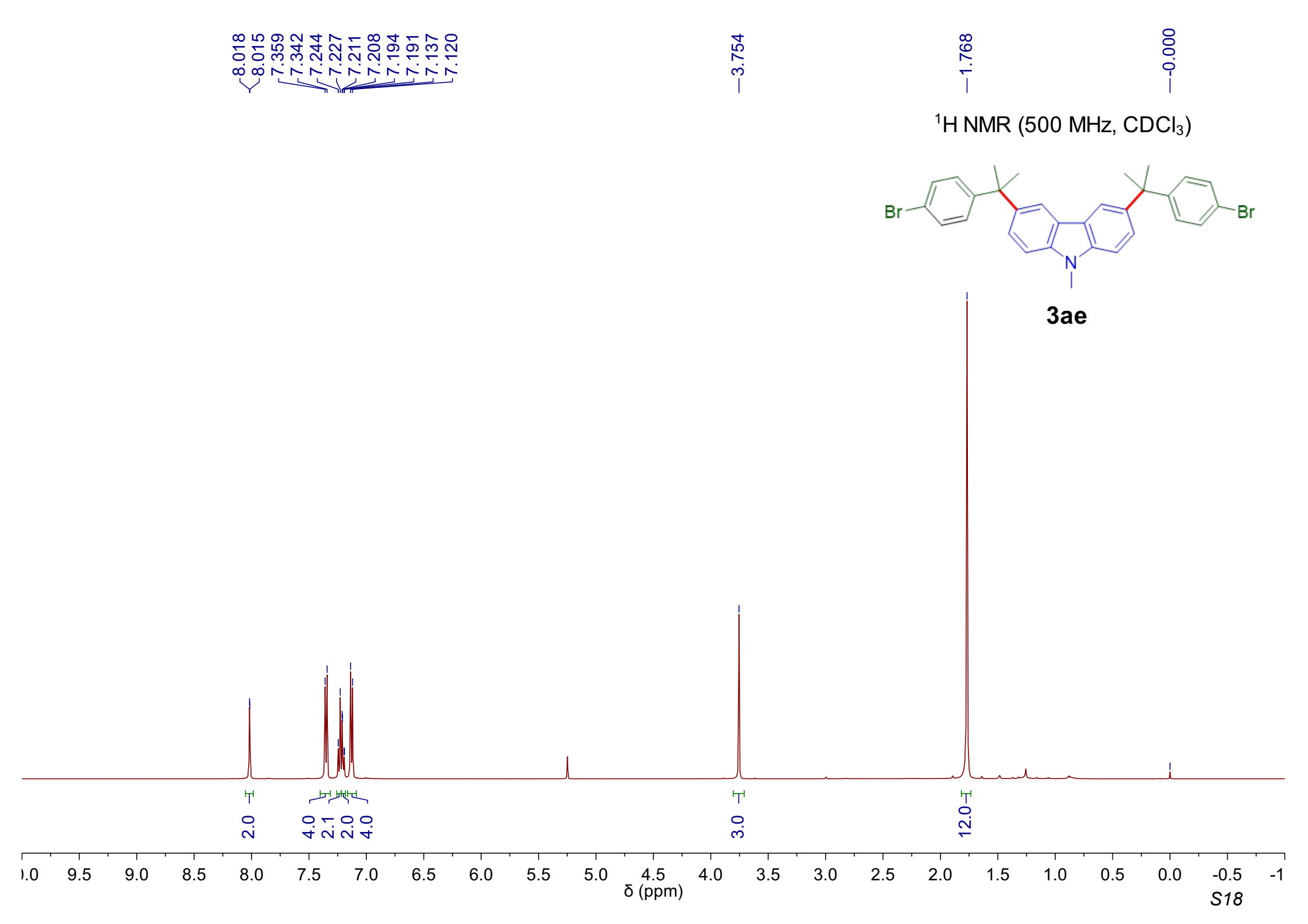
150.45
140.78
139.77
131.30
128.47
128.15
125.59
122.45
117.58
108.32
77.41
77.16
76.91
42.85
31.46
29.22

^{13}C NMR (126 MHz, $CDCl_3$)



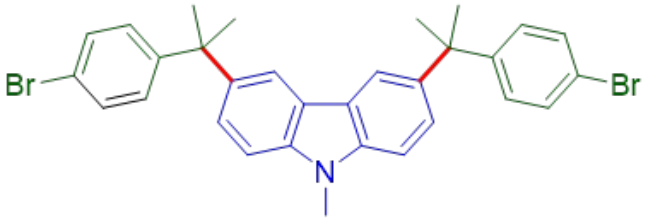
3ad



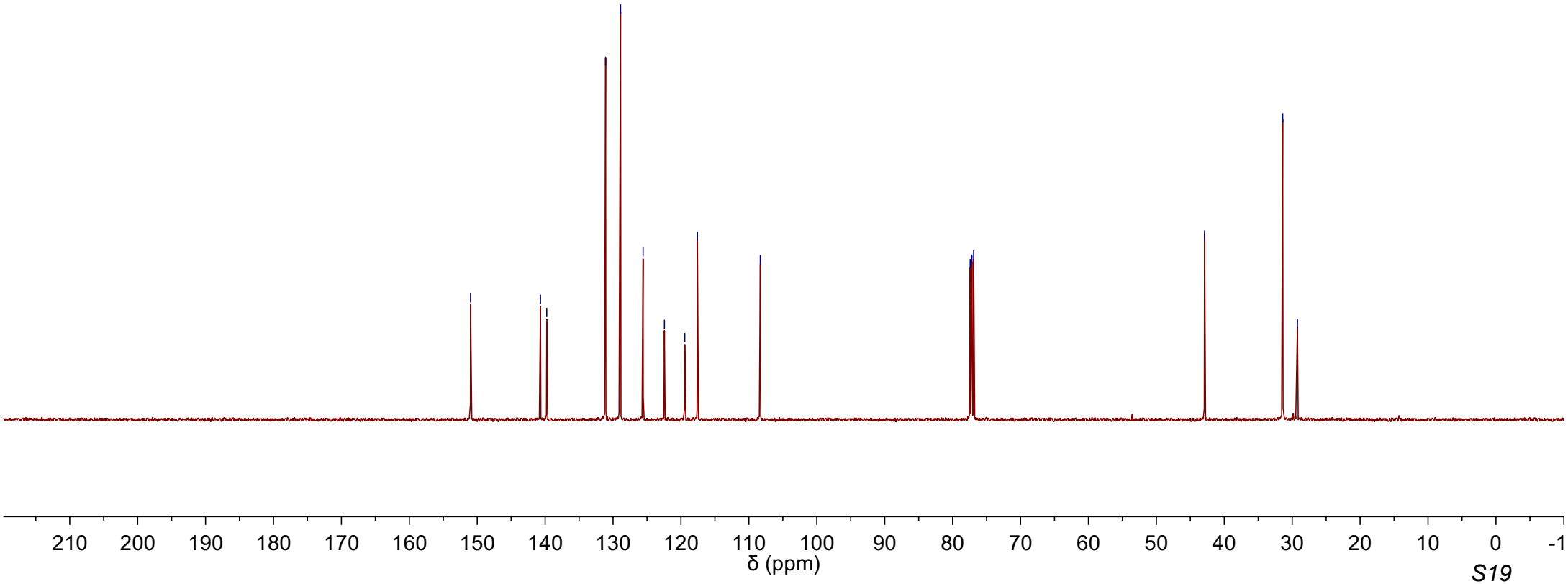

8.018
8.015
7.359
7.342
7.244
7.227
7.211
7.208
7.194
7.191
7.137
7.120
3.754
1.768
0.000
^{1}H NMR (500 MHz, $CDCl_3$)
Br
Br
N
3ae
2.0
4.0
2.1
2.0
4.0
3.0
12.0
δ (ppm)

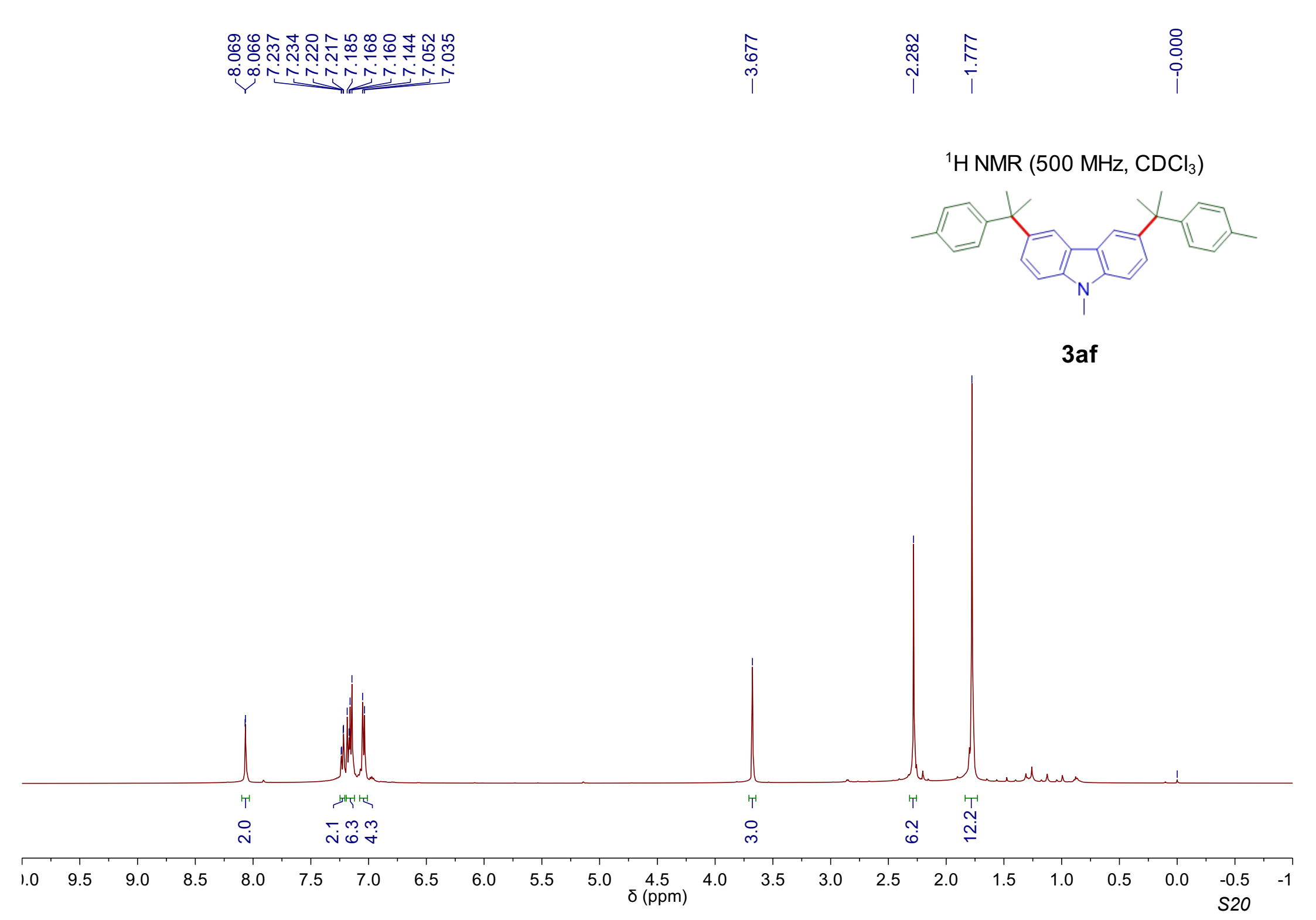
150.98
140.68
139.76
131.10
128.90
125.58
122.44
119.44
117.58
108.32
77.41
77.16
76.91
42.91
31.40
29.23

^{13}C NMR (126 MHz, $CDCl_3$)



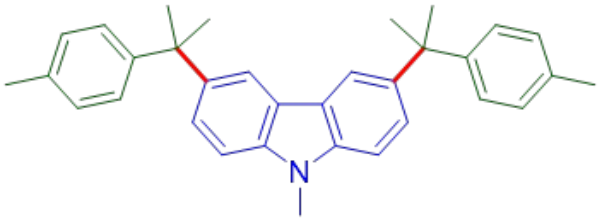
3ae



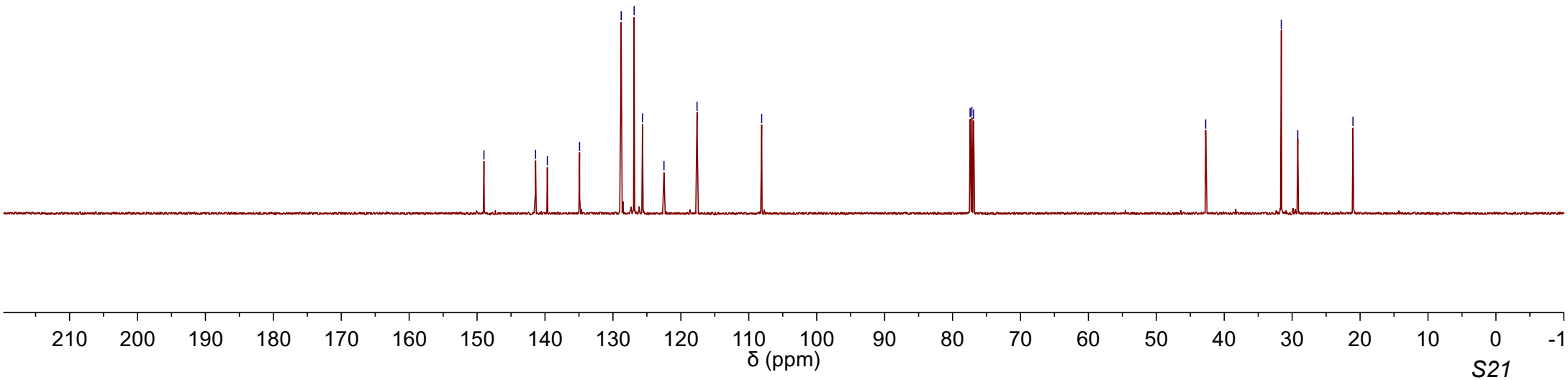

8.069
8.066
7.237
7.234
7.220
7.217
7.185
7.168
7.160
7.144
7.052
7.035
3.677
2.282
1.777
0.000
^{1}H NMR (500 MHz, $CDCl_3$)
N
3af
2.0
2.1
6.3
4.3
3.0
6.2
12.2
δ (ppm)

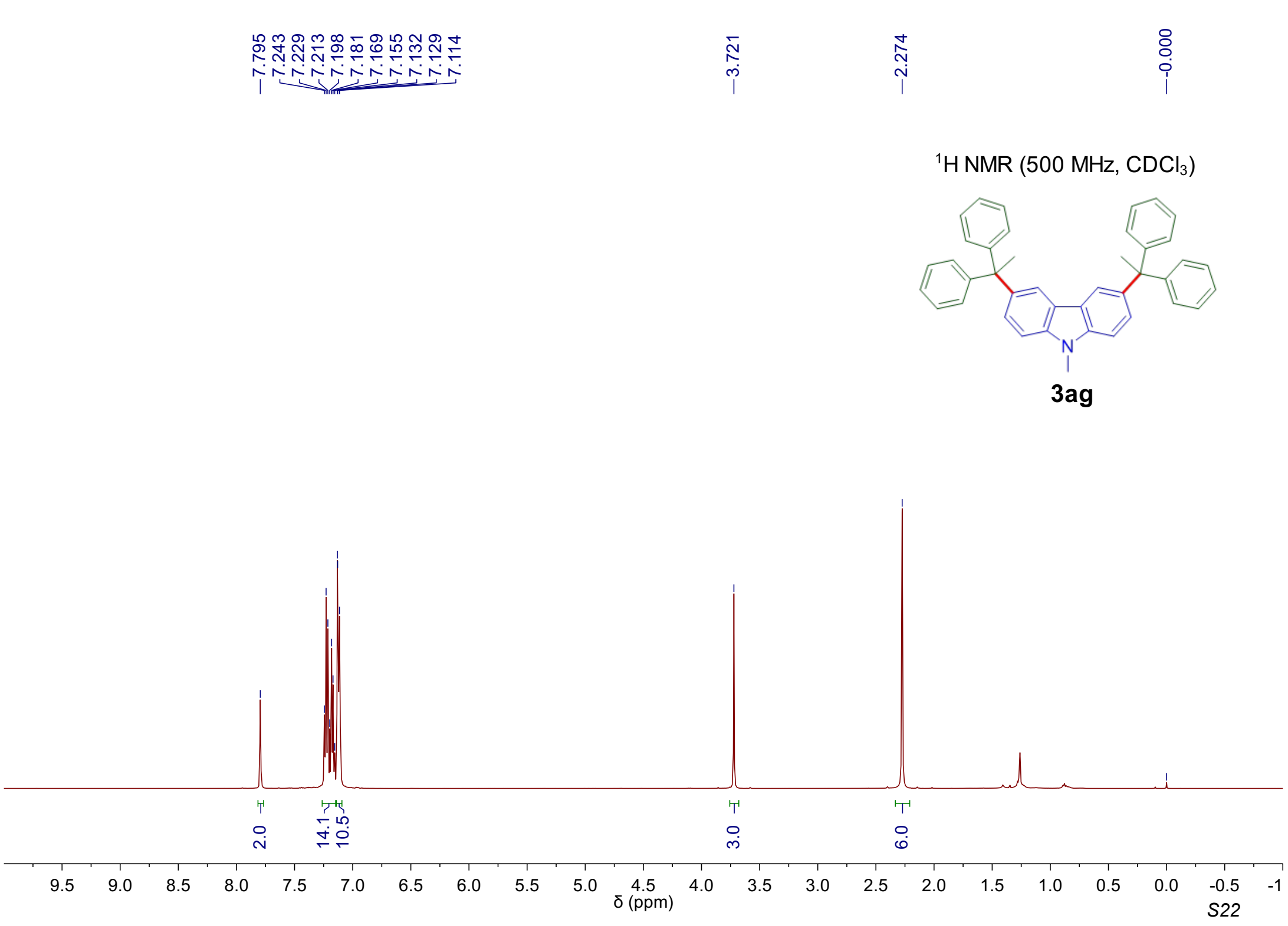
148.99
141.39
139.66
134.92
128.79
126.88
125.64
122.49
117.62
108.10
77.41
77.16
76.91
42.73
31.60
29.17
21.05

^{13}C NMR (126 MHz, $CDCl_3$)



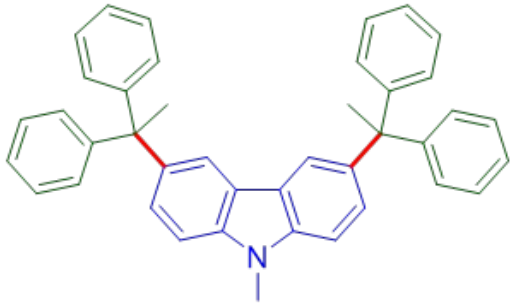
3af



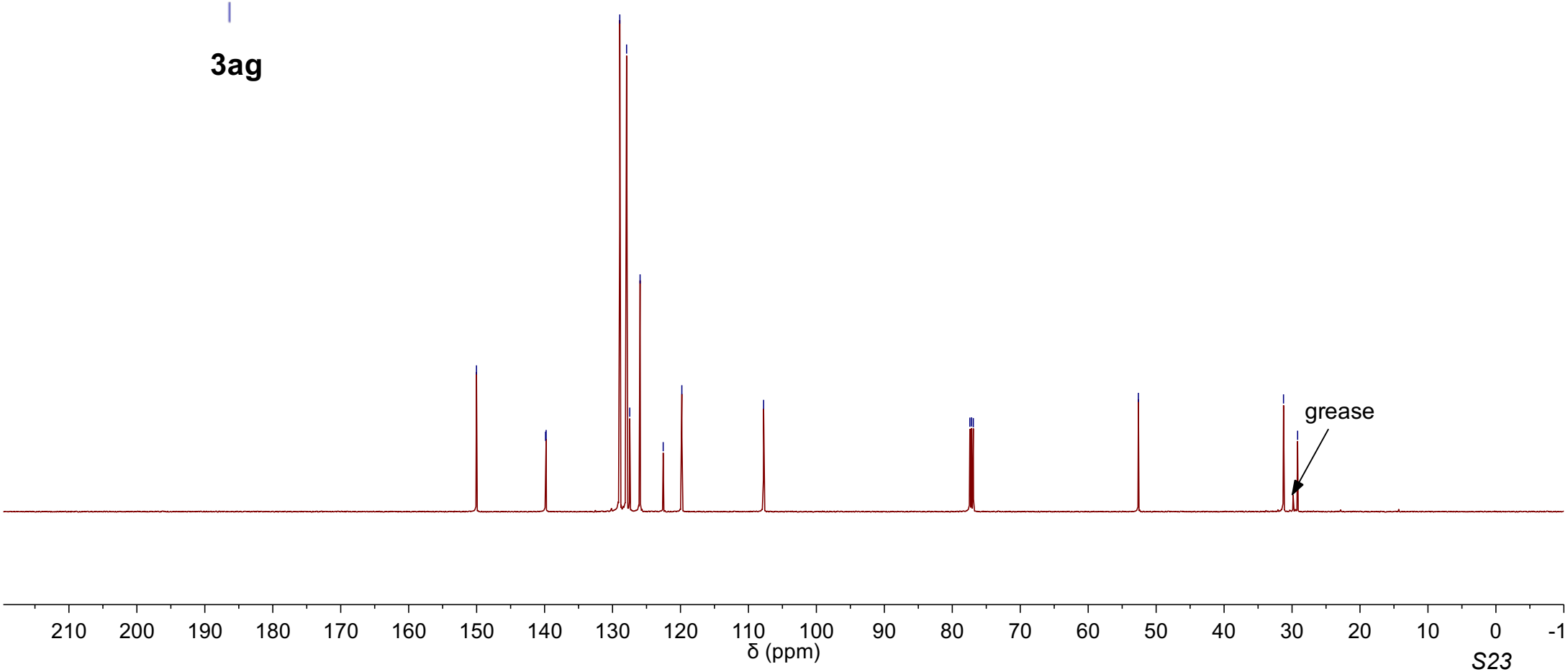

7.795
7.243
7.229
7.213
7.198
7.181
7.169
7.155
7.132
7.129
7.114
3.721
2.274
-0.000
^{1}H NMR (500 MHz, $CDCl_3$)
N
3ag
2.0
14.1
10.5
3.0
6.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
δ (ppm)

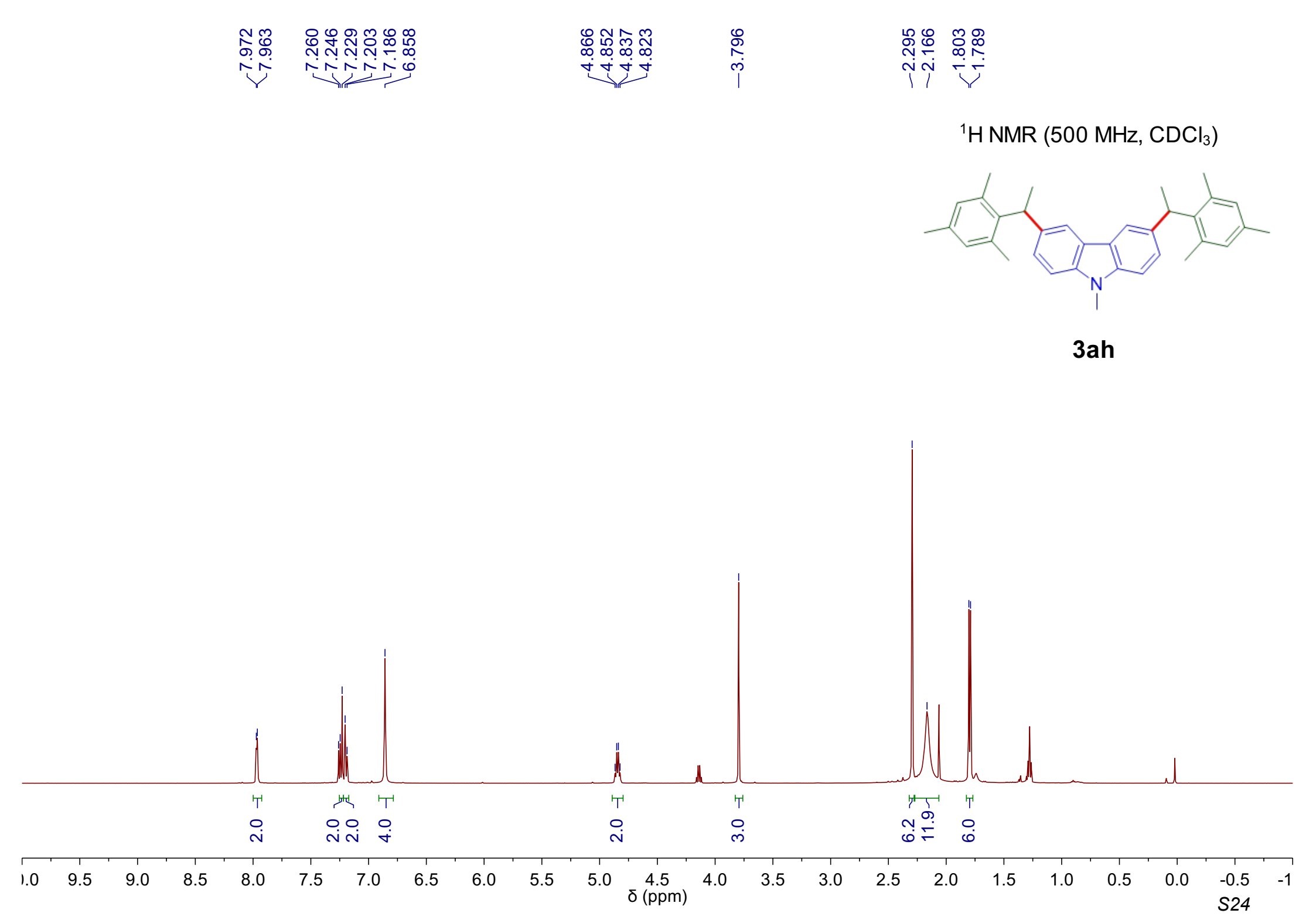
150.02
139.86
139.77
128.93
127.93
127.47
125.94
122.55
119.80
107.77
77.41
77.16
76.91
52.61
31.26
29.18

^{13}C NMR (126 MHz, $CDCl_3$)

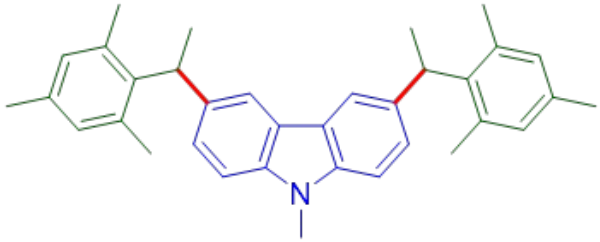


3ag



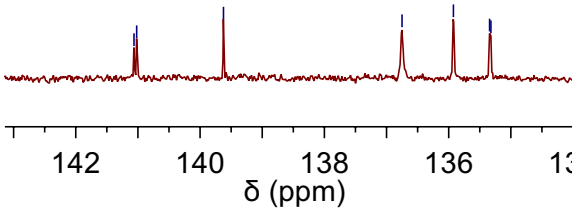

7.972
7.963
7.260
7.246
7.229
7.203
7.186
6.858
4.866
4.852
4.837
4.823
3.796
2.295
2.166
1.803
1.789
^{1}H NMR (500 MHz, $CDCl_3$)
N
3ah
2.0
2.0
2.0
4.0
2.0
3.0
6.2
11.9
6.0
δ (ppm)

^{13}C NMR (126 MHz, $CDCl_3$)



3ah

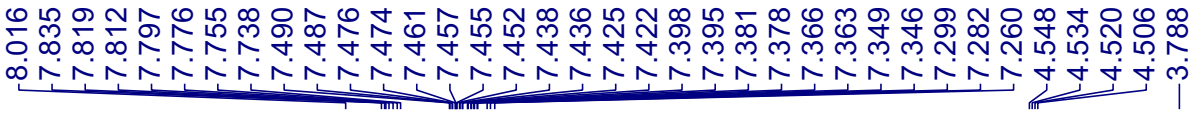
141.06
141.02
139.62
136.75
135.92
135.34
135.32
130.17
125.31
122.76
118.10
118.05
108.12
77.41
77.16
76.91
37.95
29.25
21.30
20.91
17.60
17.56



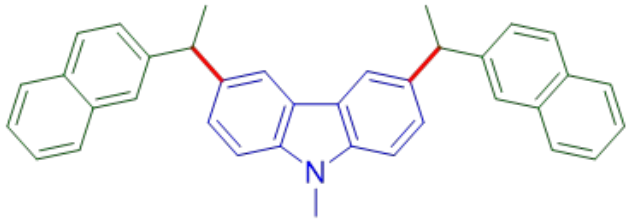
ethyl acetate

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

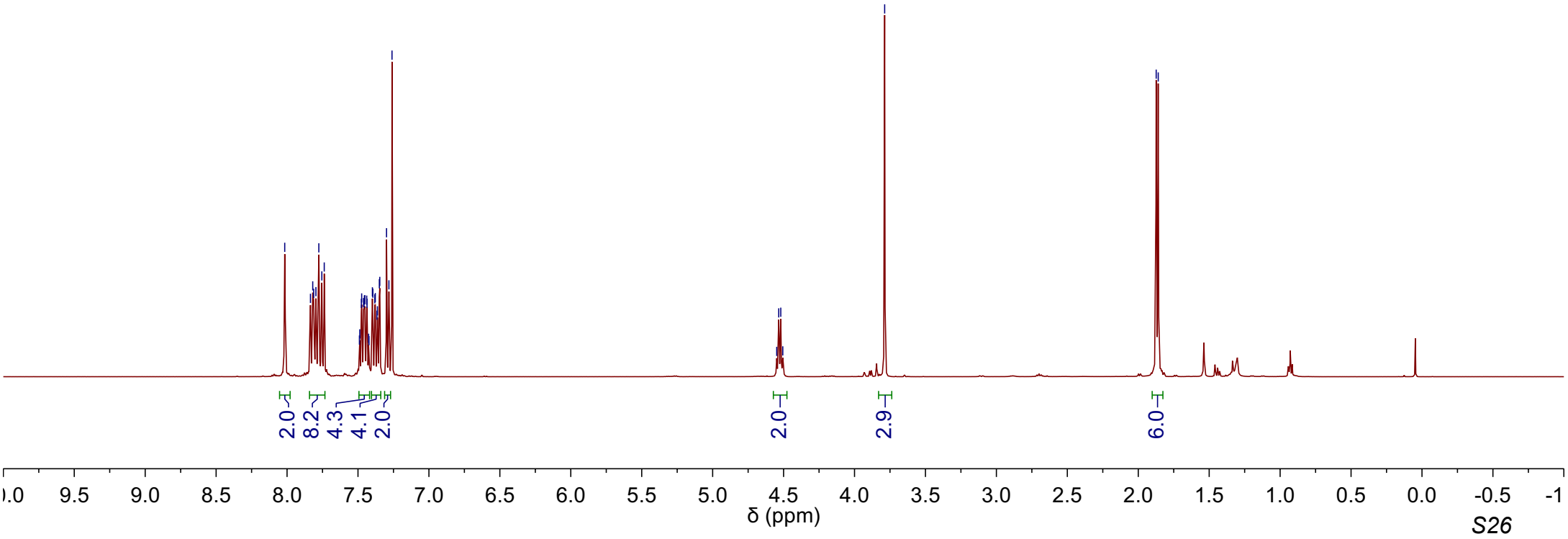
δ (ppm)



^{1}H NMR (500 MHz, $CDCl_3$)

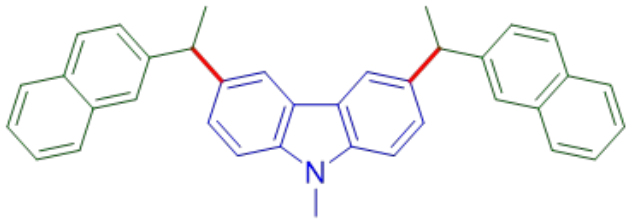


3ai

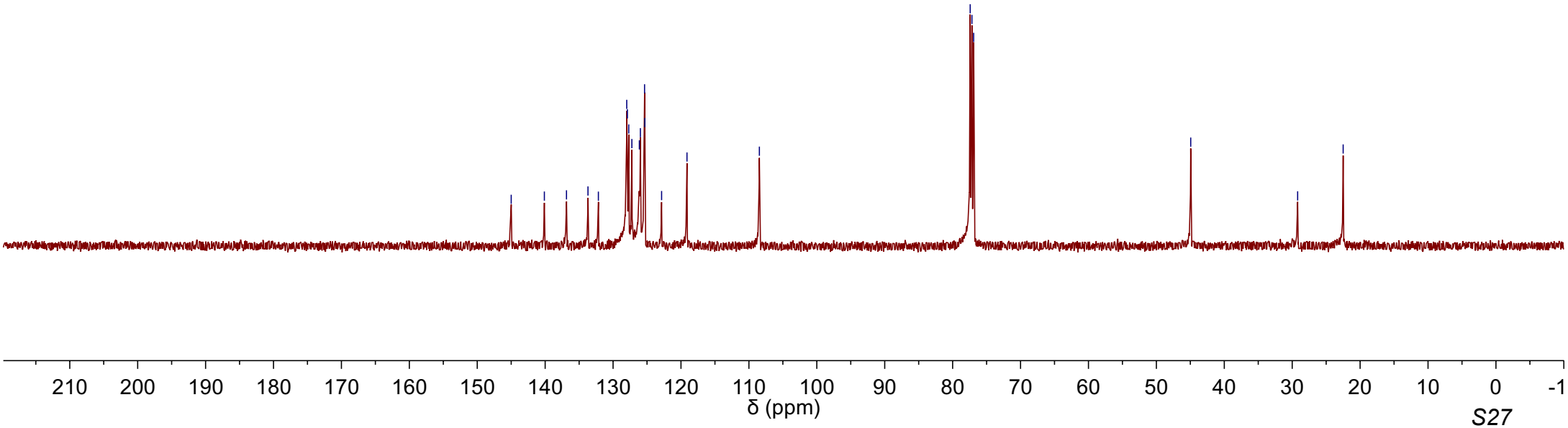


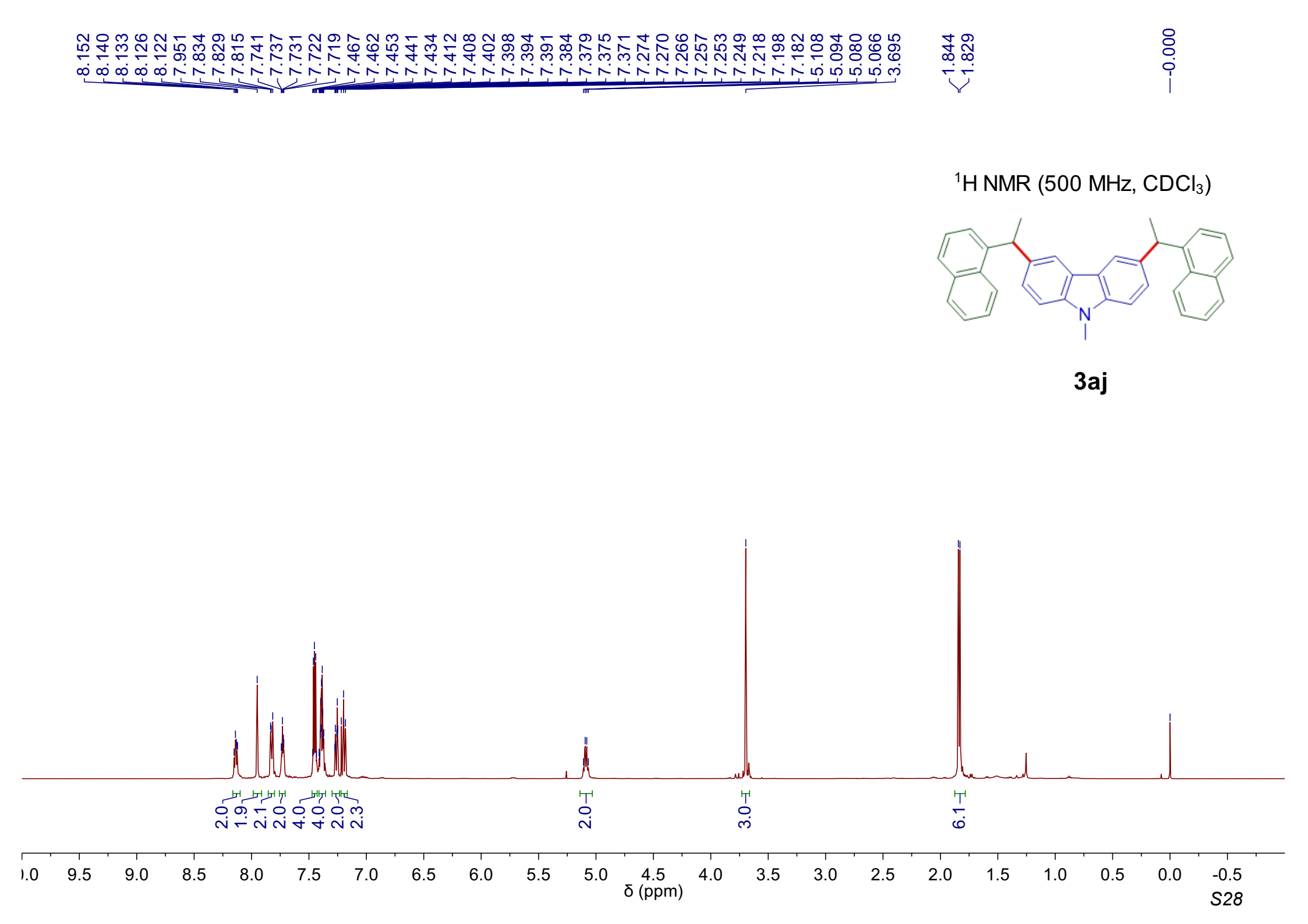
145.00
140.12
136.86
133.69
132.16
127.99
127.89
127.69
127.23
126.13
125.98
125.36
125.33
122.85
119.12
108.46
77.41
77.16
76.91
44.94
29.20
22.50

^{13}C NMR (126 MHz, $CDCl_3$)

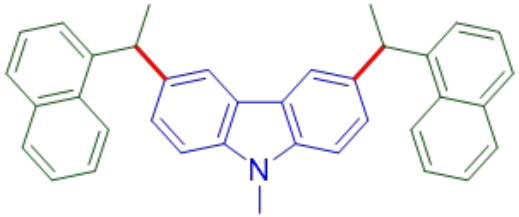


3ai

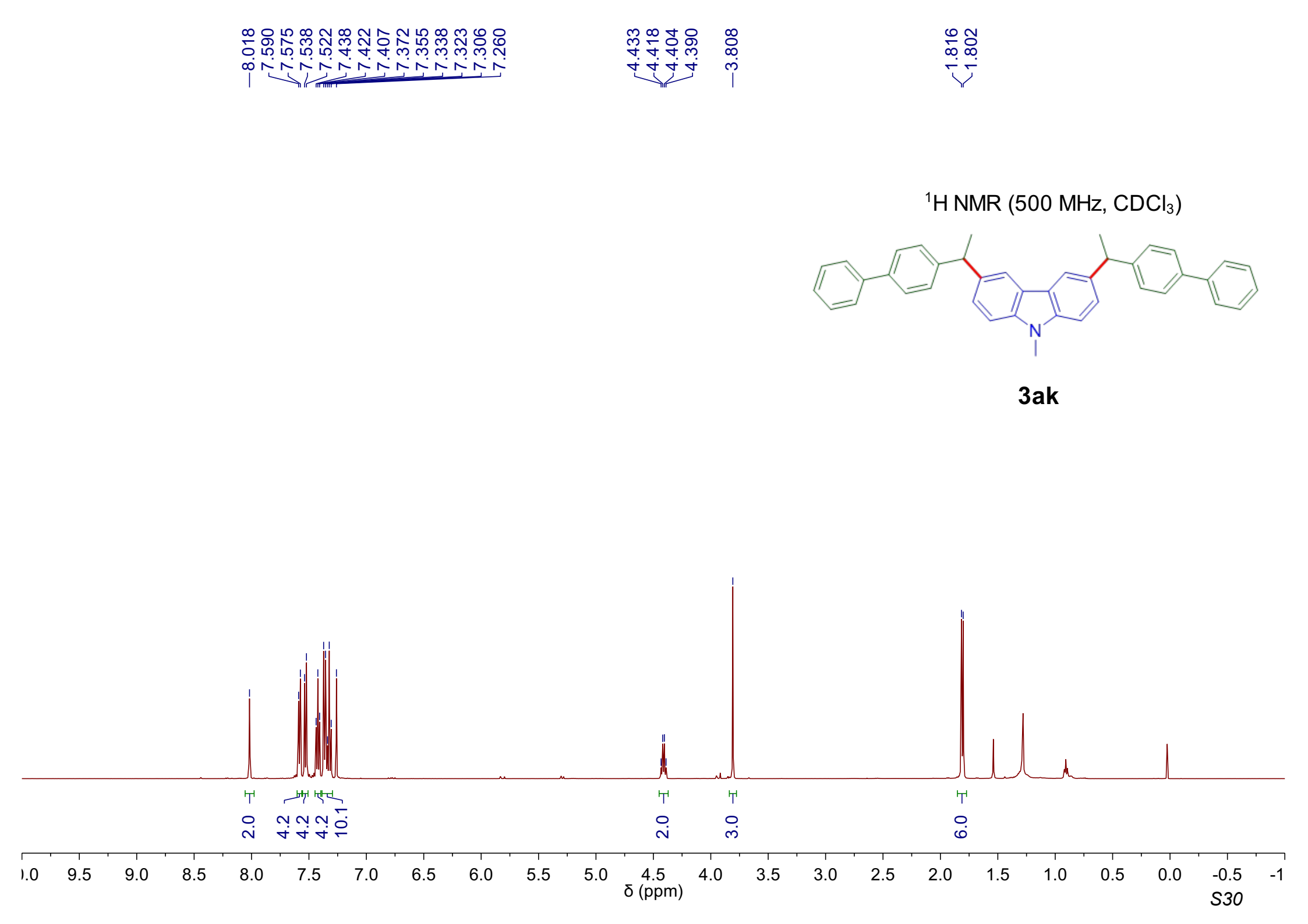



8.152
8.140
8.133
8.126
8.122
7.951
7.834
7.829
7.815
7.741
7.737
7.731
7.722
7.719
7.467
7.462
7.453
7.441
7.434
7.412
7.408
7.402
7.398
7.394
7.391
7.384
7.379
7.375
7.371
7.274
7.270
7.266
7.257
7.253
7.249
7.218
7.198
7.182
5.108
5.094
5.080
5.066
3.695
1.844
1.829
-0.000
1H NMR (500 MHz, CDCl3)
N
3aj
2.0
1.9
2.1
2.0
4.0
4.0
2.0
2.3
2.0
3.0
6.1
δ (ppm)

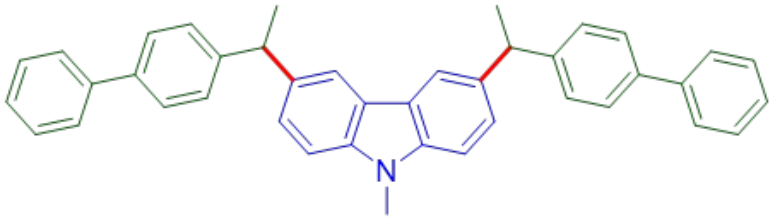
^{13}C NMR (126 MHz, $CDCl_3$)



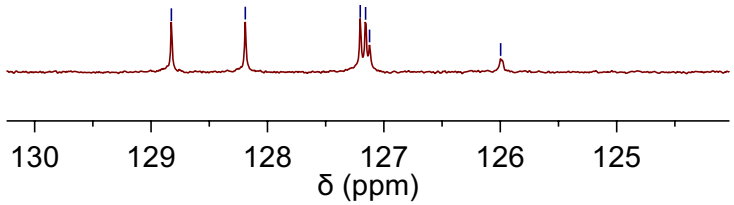
3aj

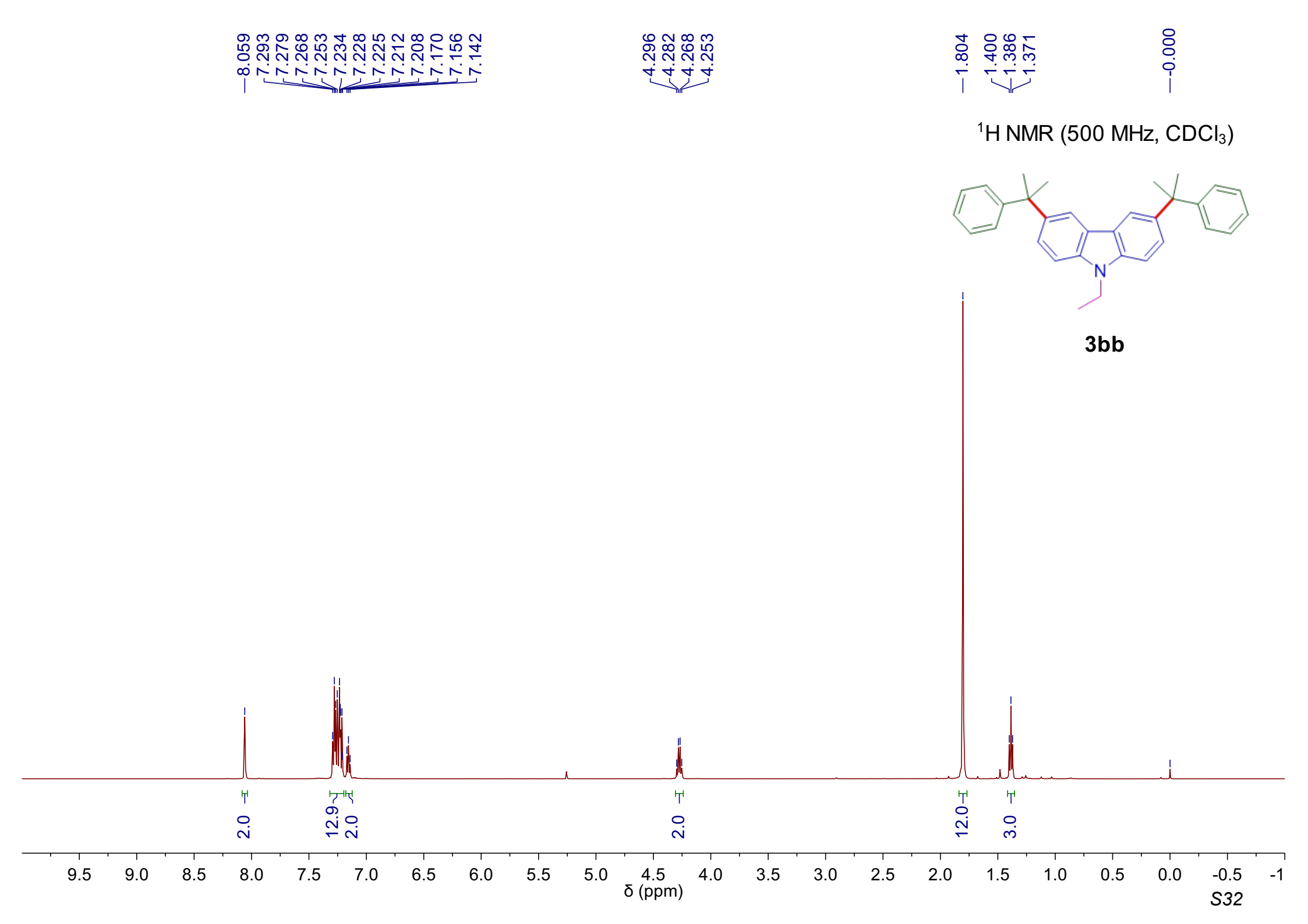

8.018
7.590
7.575
7.538
7.522
7.438
7.422
7.407
7.372
7.355
7.338
7.323
7.306
7.260
4.433
4.418
4.404
4.390
3.808
1.816
1.802
^{1}H NMR (500 MHz, CDCl$_3$)
N
3ak
2.0
4.2
4.2
4.2
10.1
2.0
3.0
6.0
δ (ppm)

^{13}C NMR (126 MHz, $CDCl_3$)

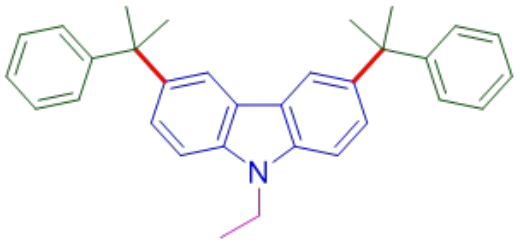


3ak

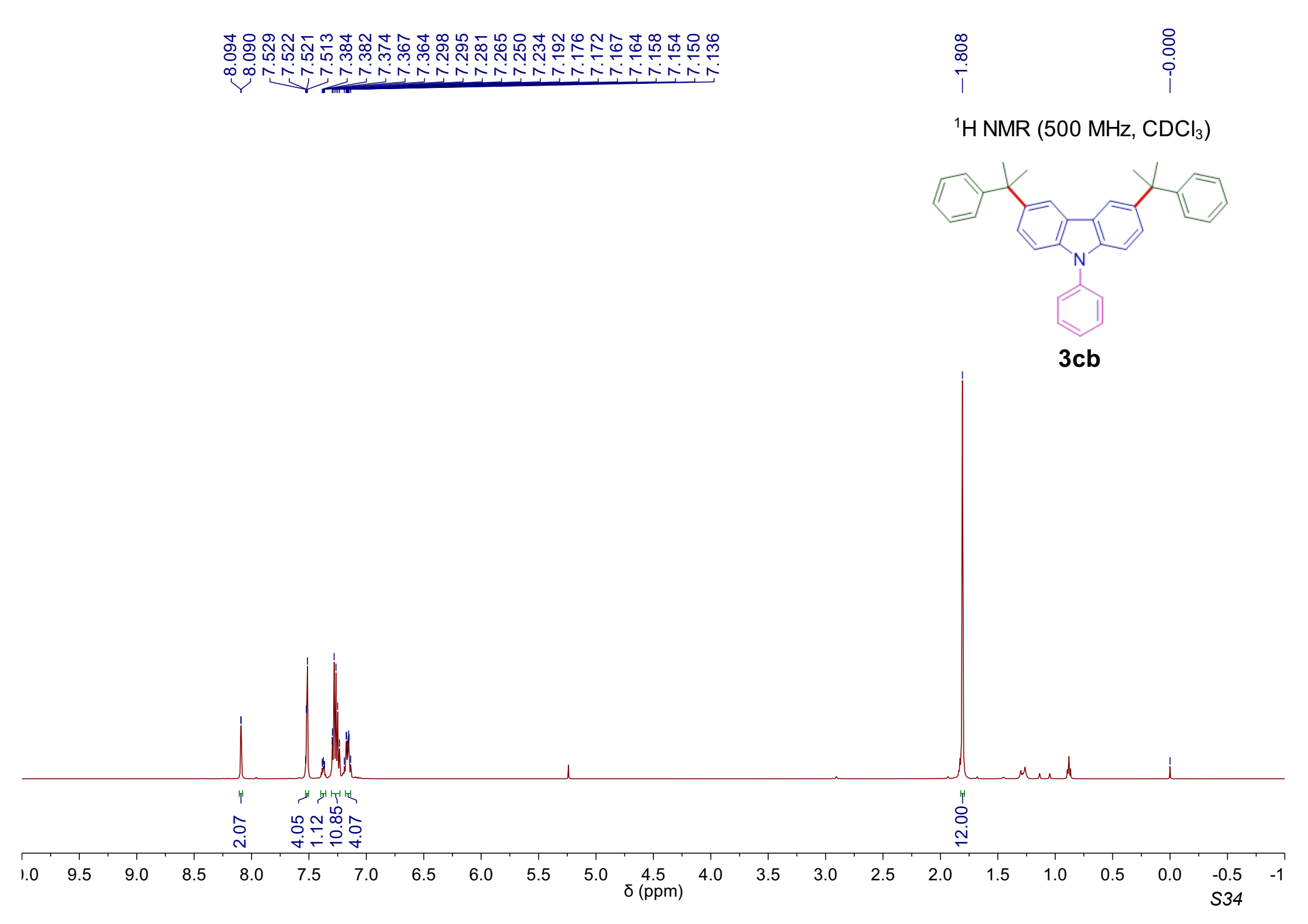



8.059
7.293
7.279
7.268
7.253
7.234
7.228
7.225
7.212
7.208
7.170
7.156
7.142
4.296
4.282
4.268
4.253
1.804
1.400
1.386
1.371
0.000
1H NMR (500 MHz, CDCl3)
N
3bb
2.0
12.9
2.0
2.0
12.0
3.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
δ (ppm)

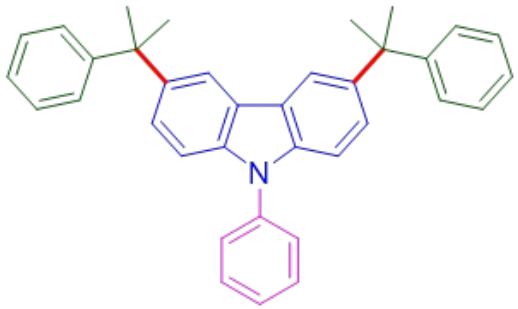
^{13}C NMR (126 MHz, $CDCl_3$)



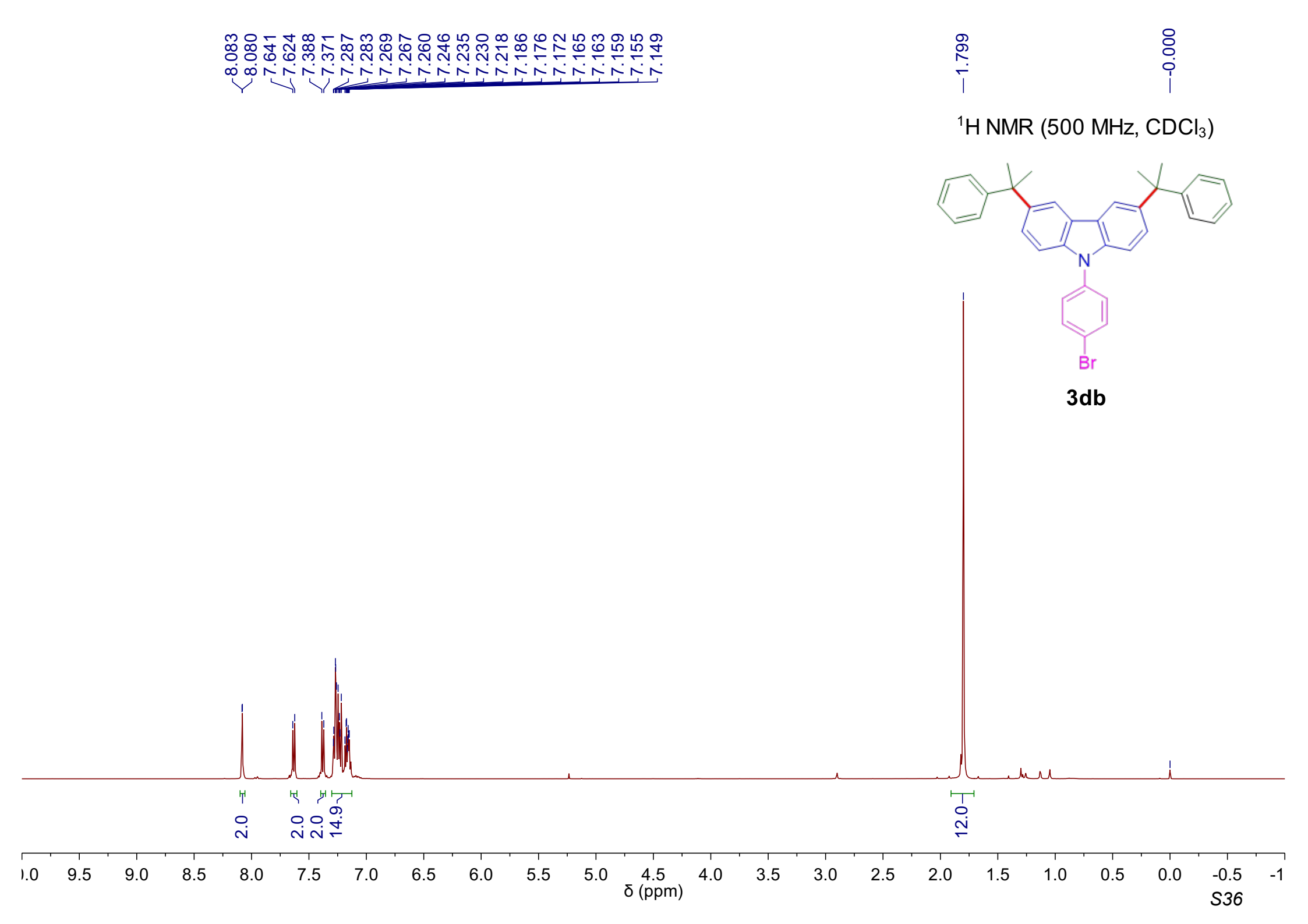
3bb


8.094
8.090
7.529
7.522
7.521
7.513
7.384
7.382
7.374
7.367
7.364
7.298
7.295
7.281
7.265
7.250
7.234
7.192
7.176
7.172
7.167
7.164
7.158
7.154
7.150
7.136
1.808
0.000
1H NMR (500 MHz, CDCl3)
N
3cb
2.07
4.05
1.12
10.85
4.07
12.00
δ (ppm)

^{13}C NMR (126 MHz, $CDCl_3$)

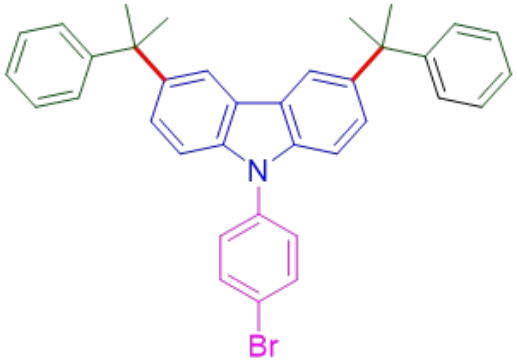


3cb

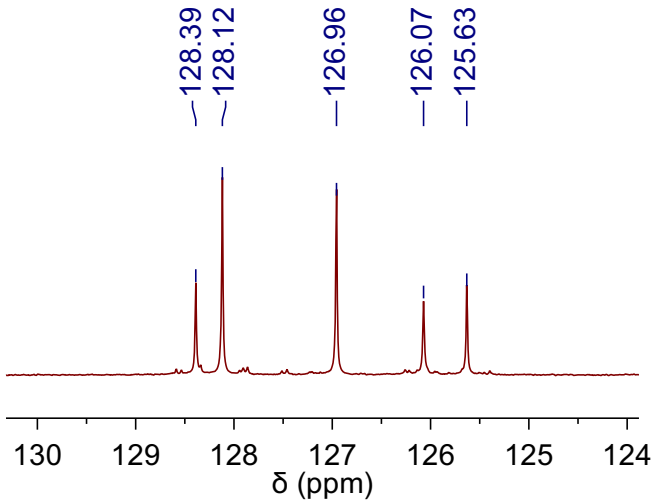

8.083
8.080
7.641
7.624
7.388
7.371
7.287
7.283
7.269
7.267
7.260
7.246
7.235
7.230
7.218
7.186
7.176
7.172
7.165
7.163
7.159
7.155
7.149
1.799
0.000
^{1}H NMR (500 MHz, $CDCl_3$)
N
Br
3db
2.0
2.0
2.0
14.9
12.0
δ (ppm)

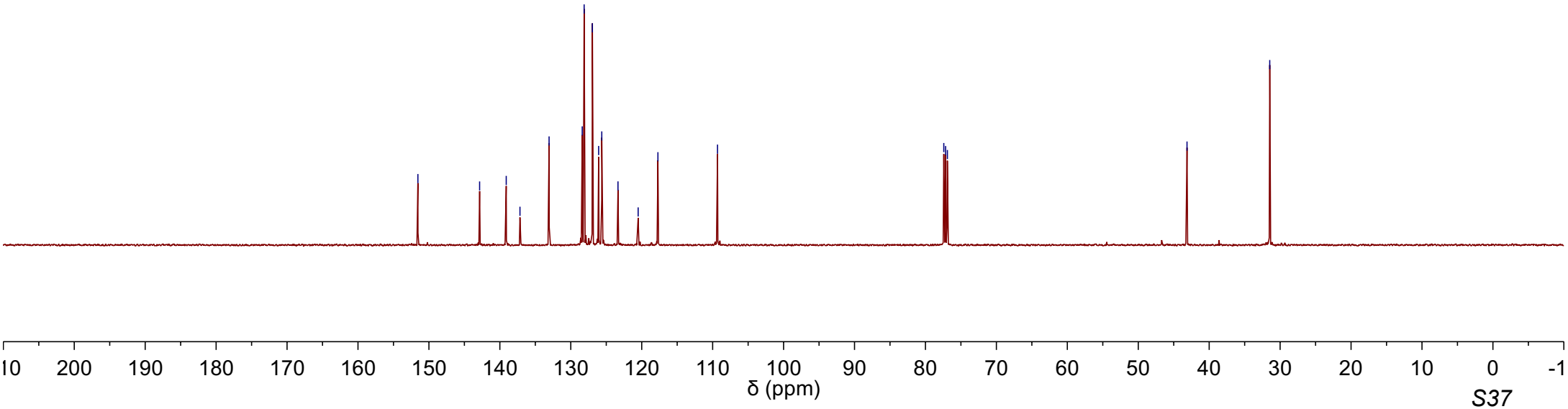
151.55
142.85
139.10
137.16
133.06
128.39
128.12
126.96
126.07
125.63
123.35
120.50
117.72
109.31
77.41
77.16
76.91
43.13
31.46

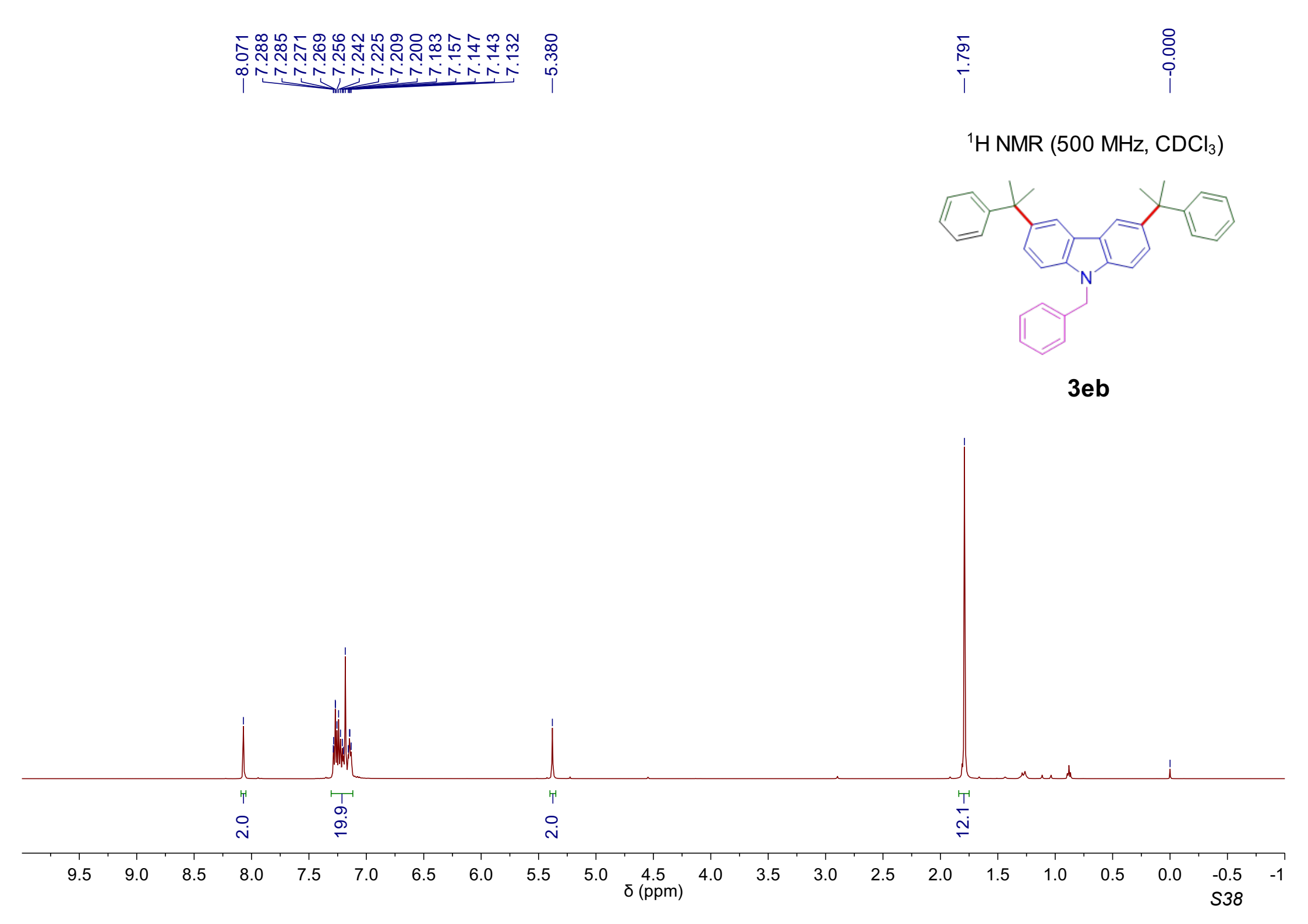
^{13}C NMR (126 MHz, $CDCl_3$)



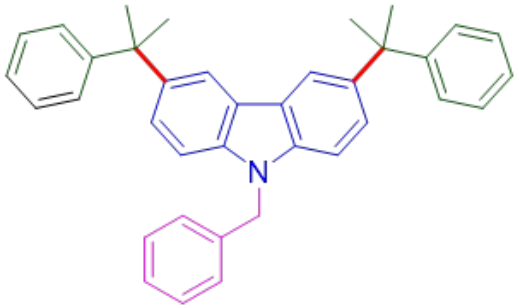
3db



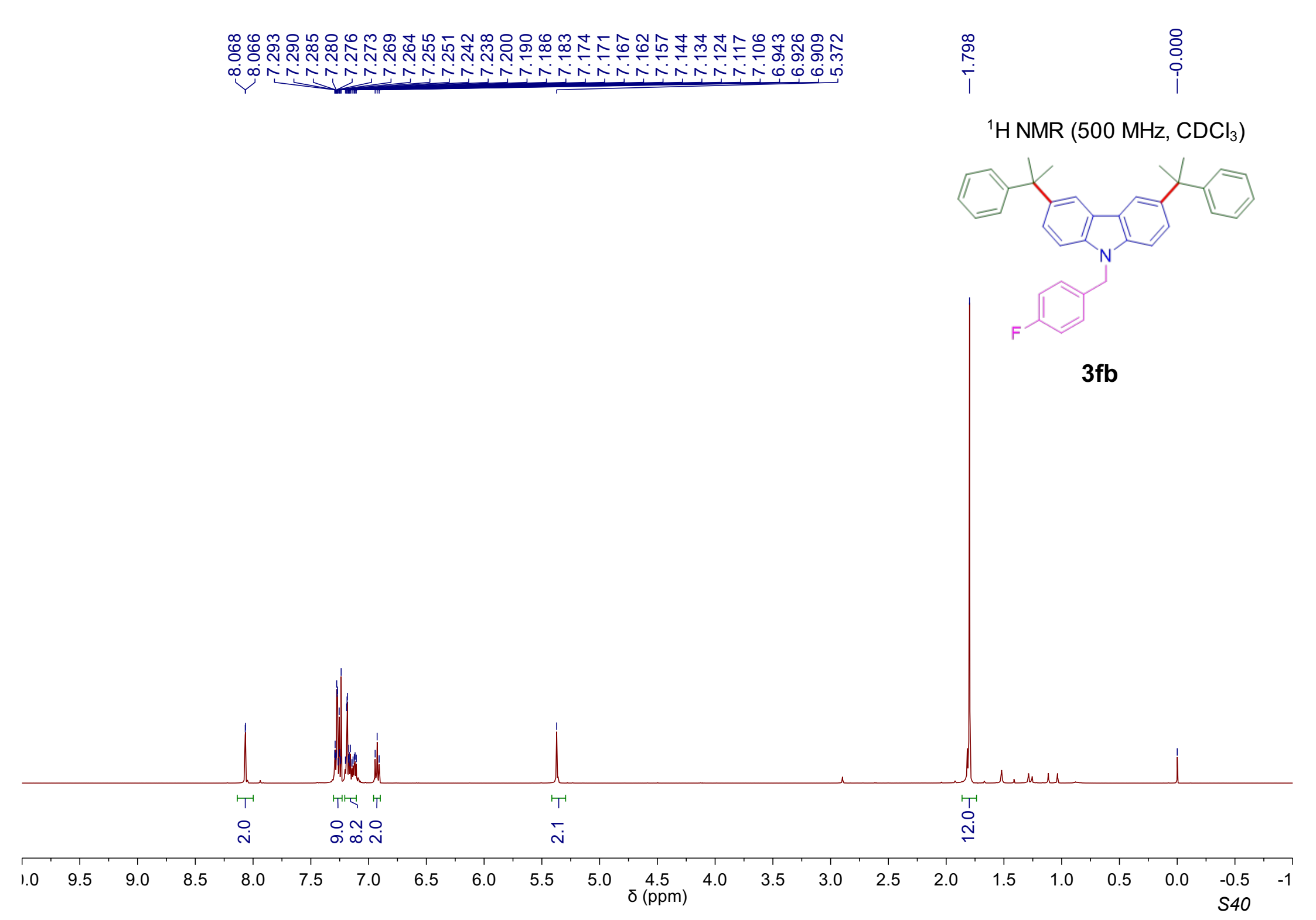



8.071
7.288
7.285
7.271
7.269
7.256
7.242
7.225
7.209
7.200
7.183
7.157
7.147
7.143
7.132
5.380
1.791
0.000
^{1}H NMR (500 MHz, $CDCl_3$)
N
3eb
2.0
19.9
2.0
12.1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
δ (ppm)

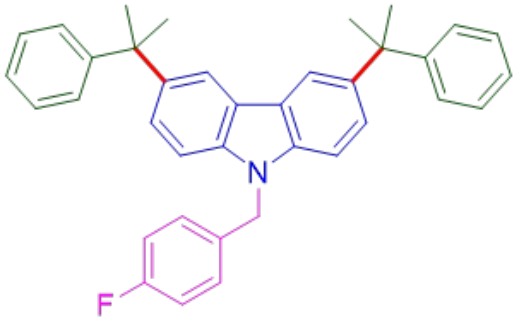
^{13}C NMR (126 MHz, $CDCl_3$)



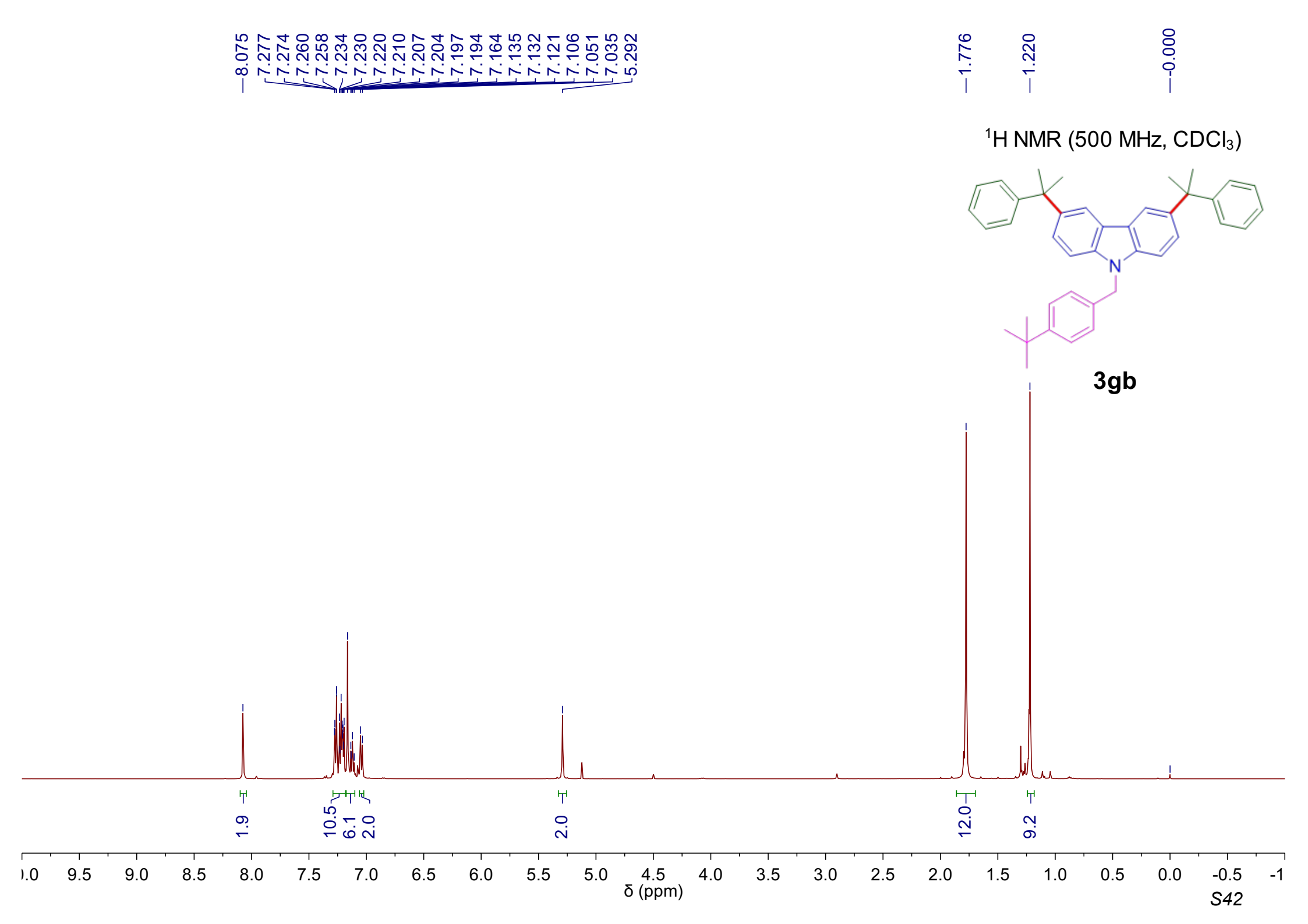
3eb


8.068
8.066
7.293
7.290
7.285
7.280
7.276
7.273
7.269
7.264
7.255
7.251
7.242
7.238
7.200
7.190
7.186
7.183
7.174
7.171
7.167
7.162
7.157
7.144
7.134
7.124
7.117
7.106
6.943
6.926
6.909
5.372
1.798
0.000
^{1}H NMR (500 MHz, $CDCl_3$)
N
F
3fb
2.0
9.0
8.2
2.0
2.1
12.0
δ (ppm)

^{13}C NMR (126 MHz, $CDCl_3$)

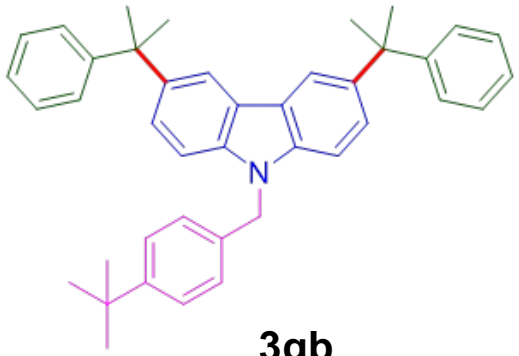


3fb

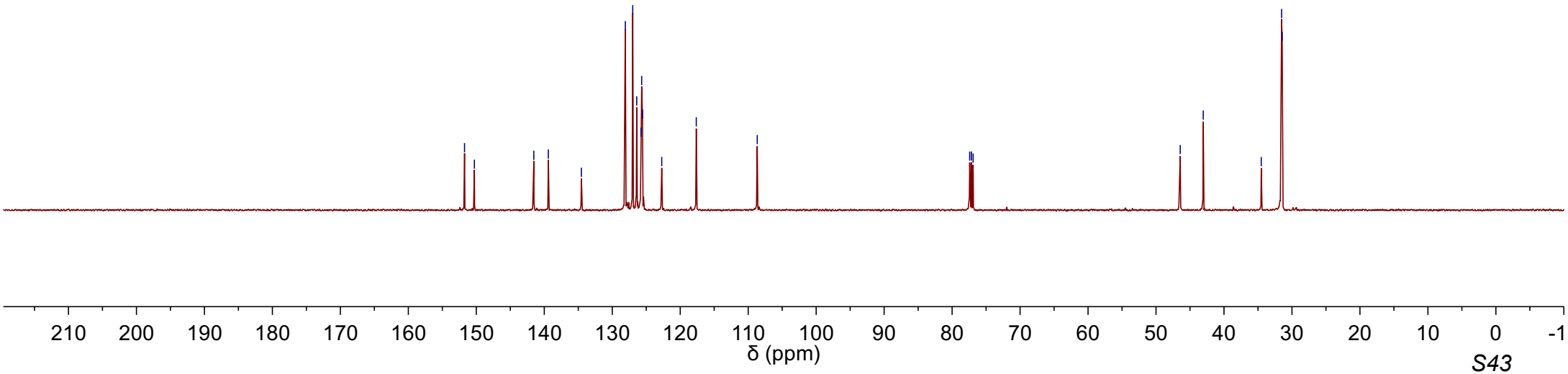

8.075
7.277
7.274
7.260
7.258
7.234
7.230
7.220
7.210
7.207
7.204
7.197
7.194
7.164
7.135
7.132
7.121
7.106
7.051
7.035
5.292
1.776
1.220
0.000
1H NMR (500 MHz, CDCl3)
N
3gb
1.9
10.5
6.1
2.0
2.0
12.0
9.2
δ (ppm)

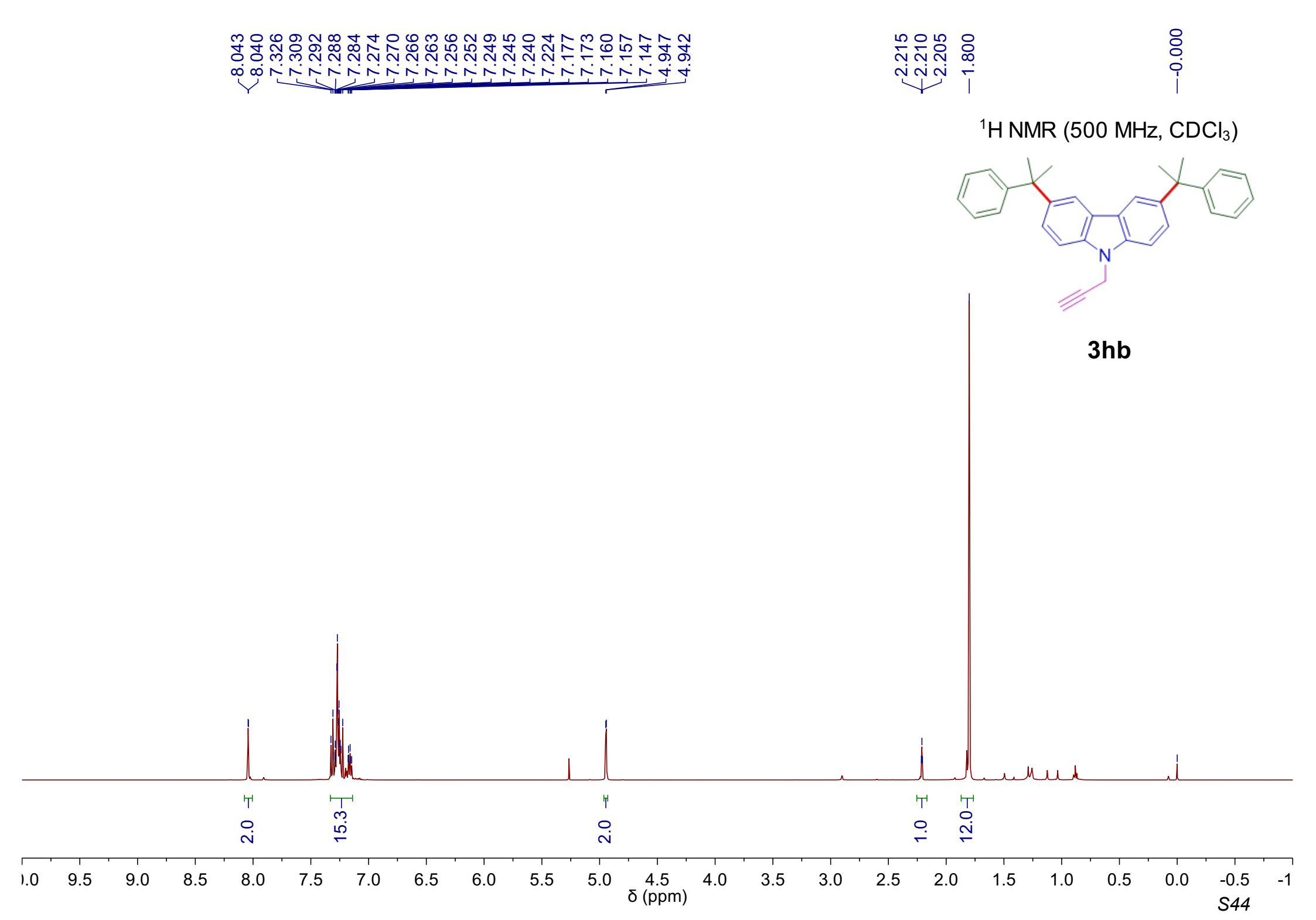
151.73
150.28
141.54
139.40
134.54
128.08
126.99
126.40
125.78
125.67
125.55
122.72
117.64
108.67
77.42
77.16
76.91
46.44
43.05
34.52
31.53
31.44

^{13}C NMR (126 MHz, $CDCl_3$)

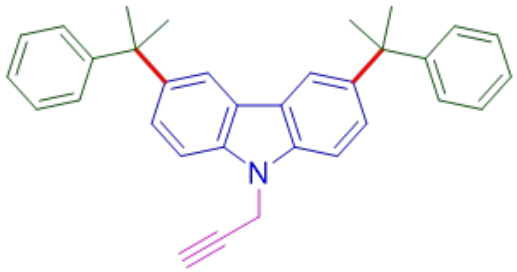


3gb




8.043
8.040
7.326
7.309
7.292
7.288
7.284
7.274
7.270
7.266
7.263
7.256
7.252
7.249
7.245
7.240
7.224
7.177
7.173
7.160
7.157
7.147
4.947
4.942
2.215
2.210
2.205
1.800
-0.000
^{1}H NMR (500 MHz, $CDCl_3$)
N
3hb
2.0
15.3
2.0
1.0
12.0
δ (ppm)

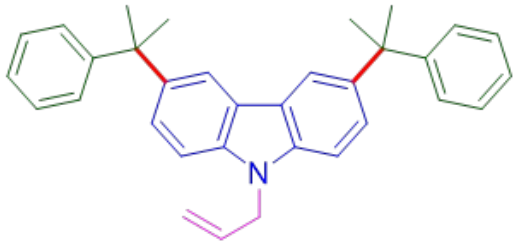
^{13}C NMR (126 MHz, $CDCl_3$)



3hb

8.064
8.062
7.278
7.263
7.242
7.228
7.211
7.194
7.191
7.179
7.162
7.143
7.129
7.115
5.938
5.928
5.917
5.907
5.894
5.883
5.873
5.863
5.107
5.086
5.059
5.025
4.745
4.735
1.787
0.000

^{1}H NMR (500 MHz, $CDCl_3$)



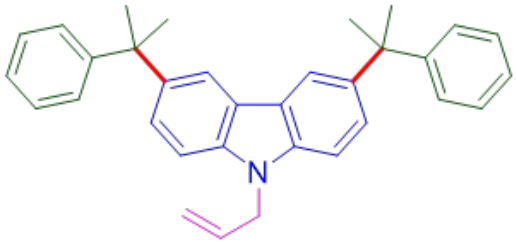
3ib

2.0
14.6
1.0
1.0
1.0
2.0
12.1

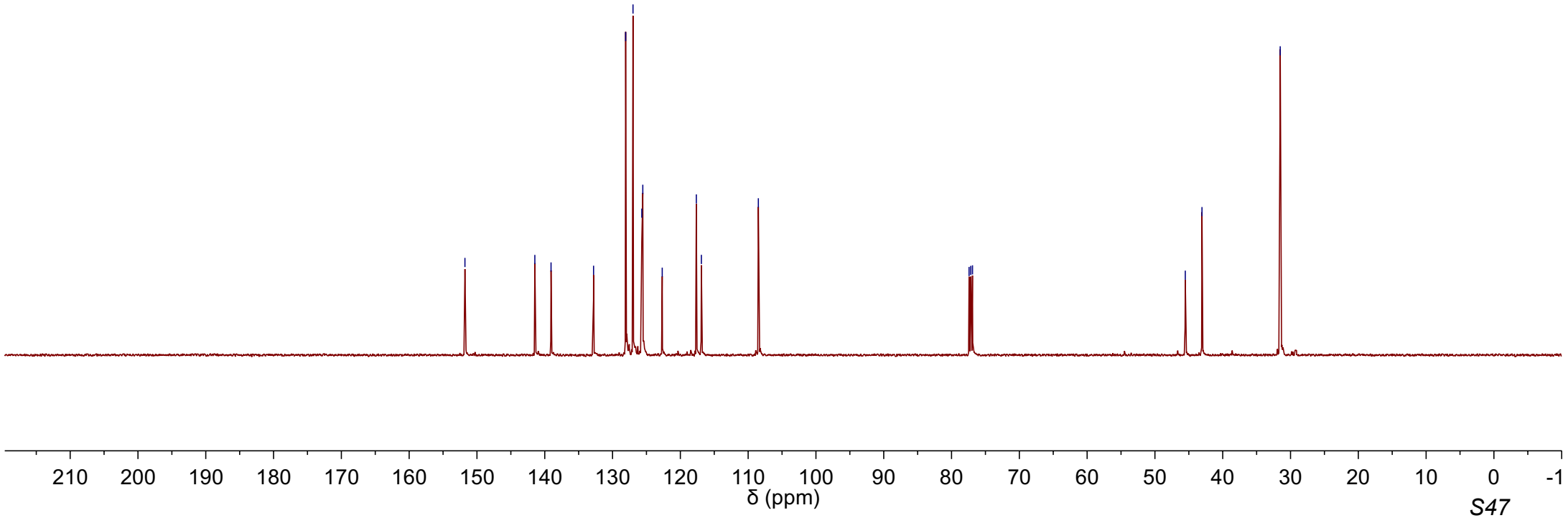
δ (ppm)

151.77
141.46
139.07
132.80
128.07
126.98
125.68
125.54
122.67
117.64
116.90
108.49
77.41
77.16
76.91
45.52
43.06
31.52

^{13}C NMR (126 MHz, $CDCl_3$)

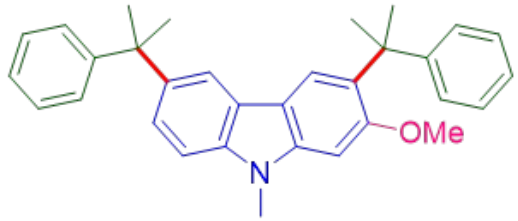


3ib

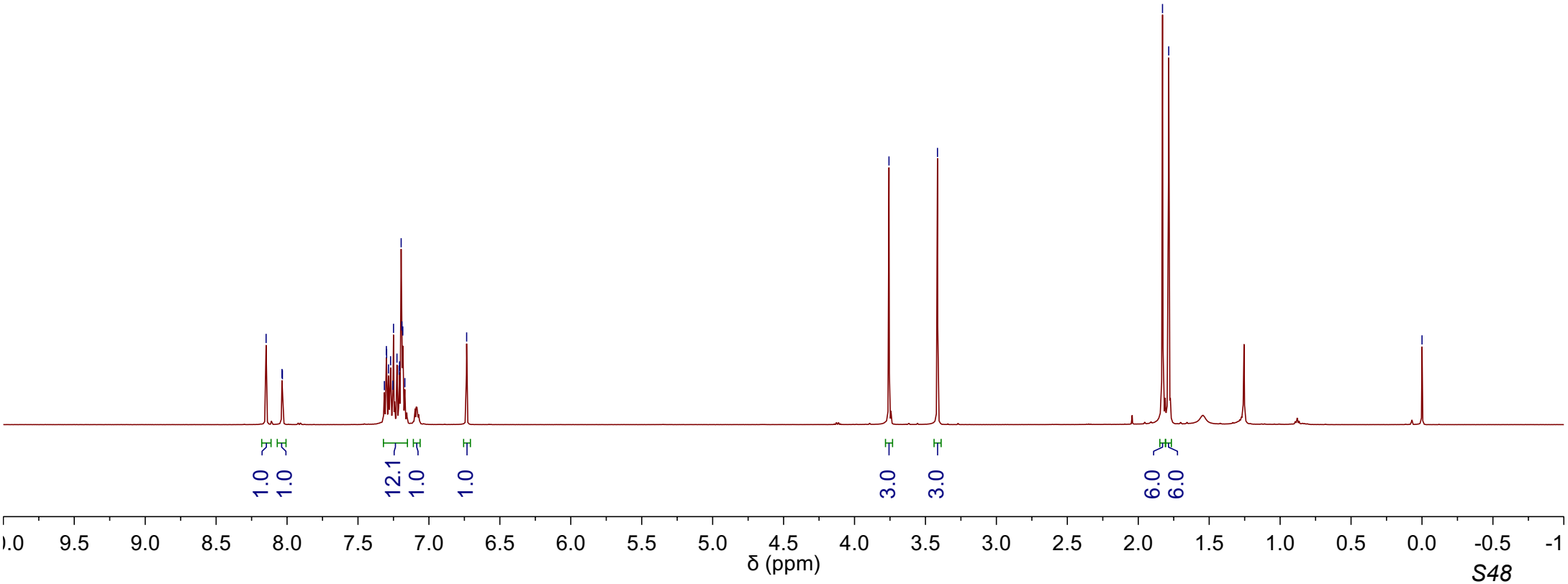


8.148
8.035
8.033
7.314
7.300
7.298
7.285
7.270
7.254
7.249
7.225
7.210
7.207
7.196
7.190
7.184
7.170
6.734
3.757
3.415
1.829
1.785
0.000

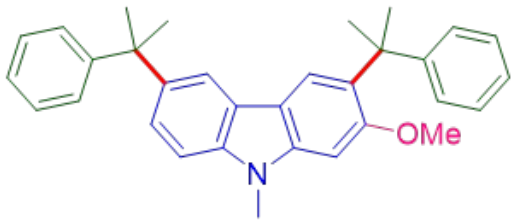
^{1}H NMR (500 MHz, $CDCl_3$)



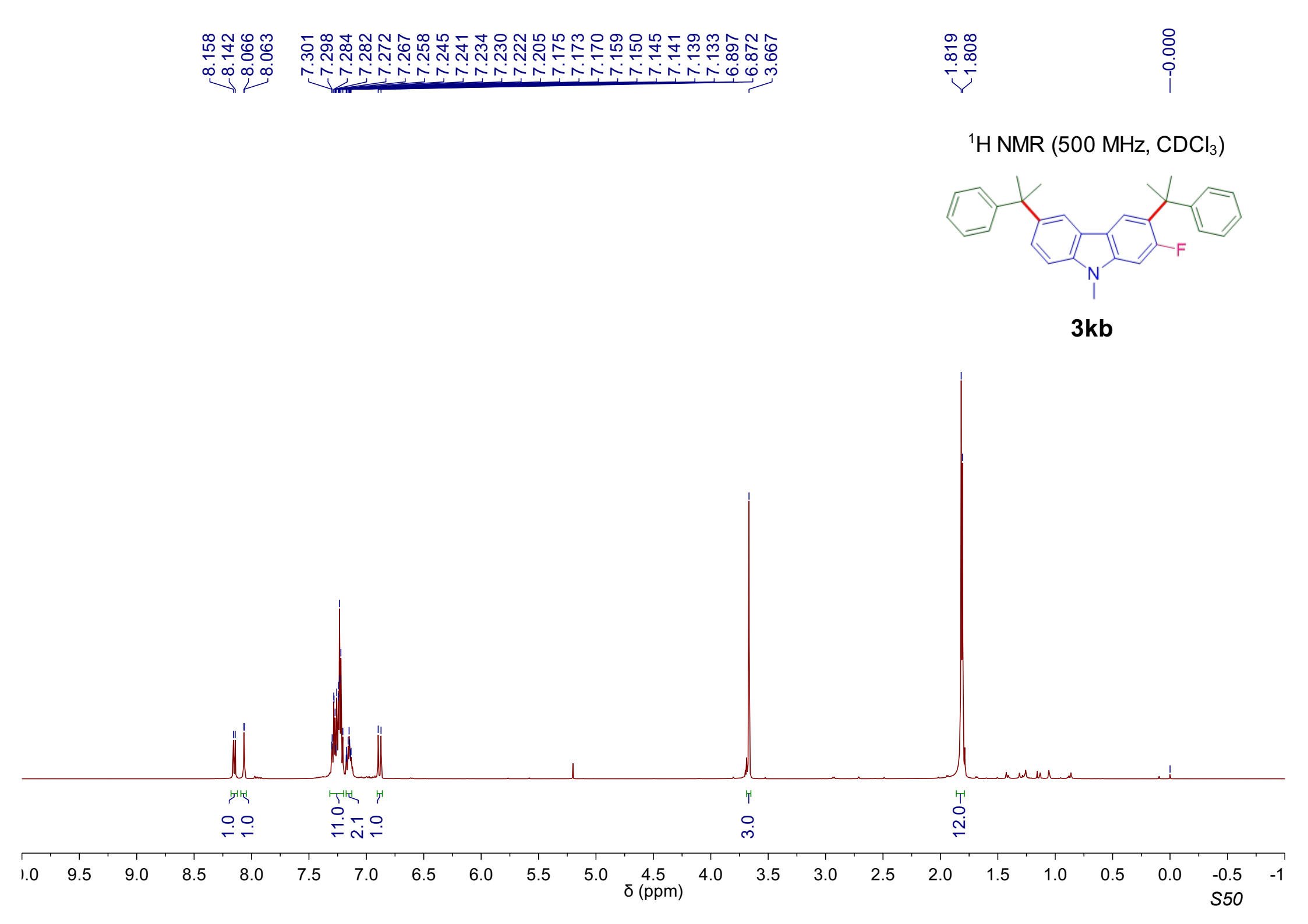
3jb



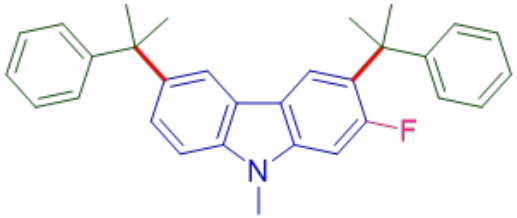
^{13}C NMR (126 MHz, $CDCl_3$)



3jb

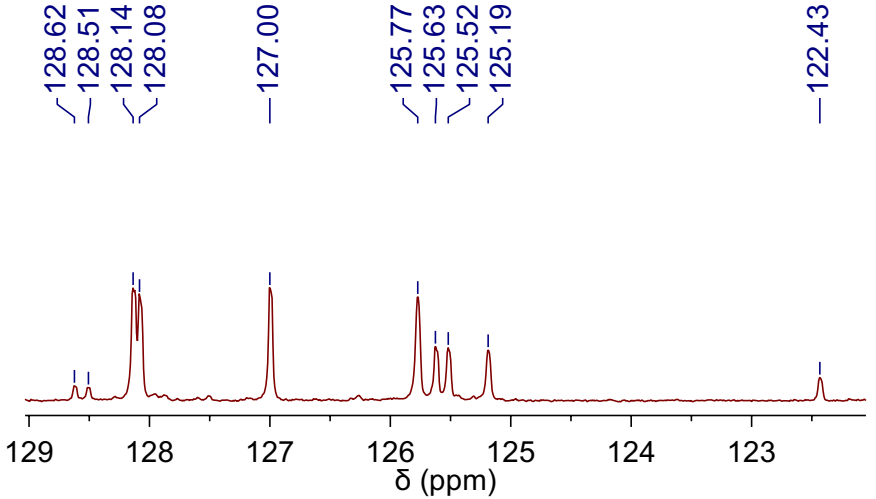

8.158
8.142
8.066
8.063
7.301
7.298
7.284
7.282
7.272
7.267
7.258
7.245
7.241
7.234
7.230
7.222
7.205
7.175
7.173
7.170
7.159
7.150
7.145
7.141
7.139
7.133
6.897
6.872
3.667
1.819
1.808
0.000
1H NMR (500 MHz, CDCl3)
F
N
3kb
1.0
1.0
11.0
2.1
1.0
3.0
12.0
δ (ppm)

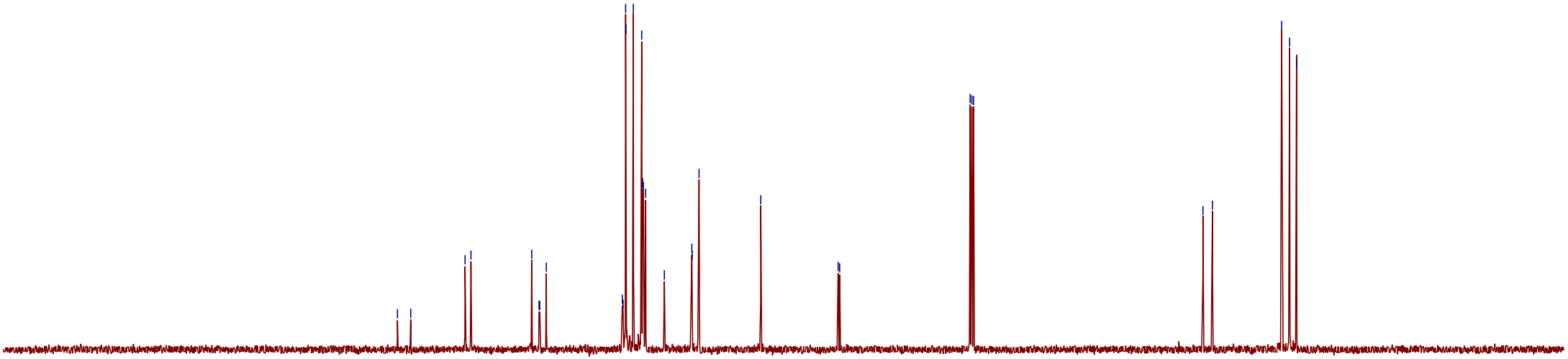
^{13}C NMR (126 MHz, $CDCl_3$)



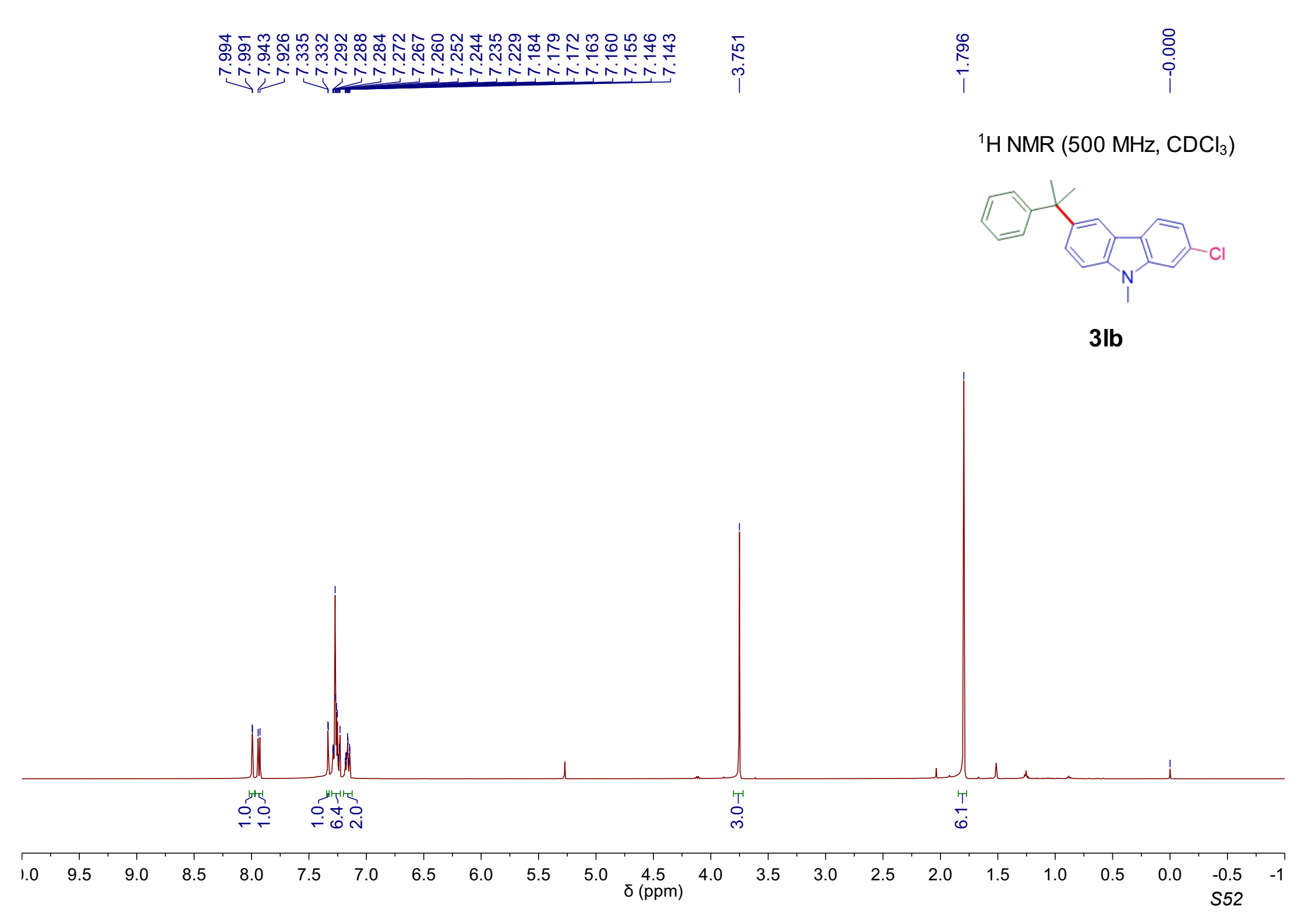
3kb

161.73
159.78
151.77
150.91
141.96
140.88
140.78
139.81
128.62
128.51
128.14
128.08
127.00
125.77
125.63
125.52
125.19
122.43
118.39
118.34
117.33
108.23
96.85
96.62
77.41
77.16
76.91
43.13
41.74
31.55
30.38
29.35



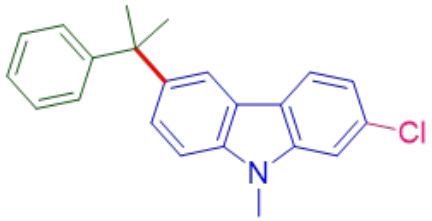


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

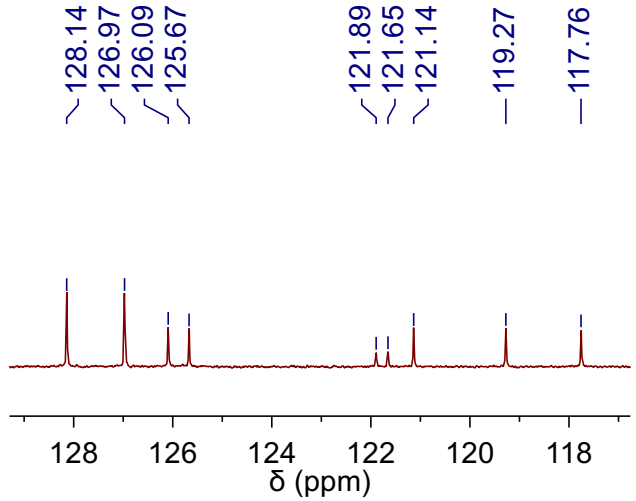

7.994
7.991
7.943
7.926
7.335
7.332
7.292
7.288
7.284
7.272
7.267
7.260
7.252
7.244
7.235
7.229
7.184
7.179
7.172
7.163
7.160
7.155
7.146
7.143
3.751
1.796
0.000
1H NMR (500 MHz, CDCl3)
Cl
N
3lb
1.0
1.0
1.0
6.4
2.0
3.0
6.1
δ (ppm)

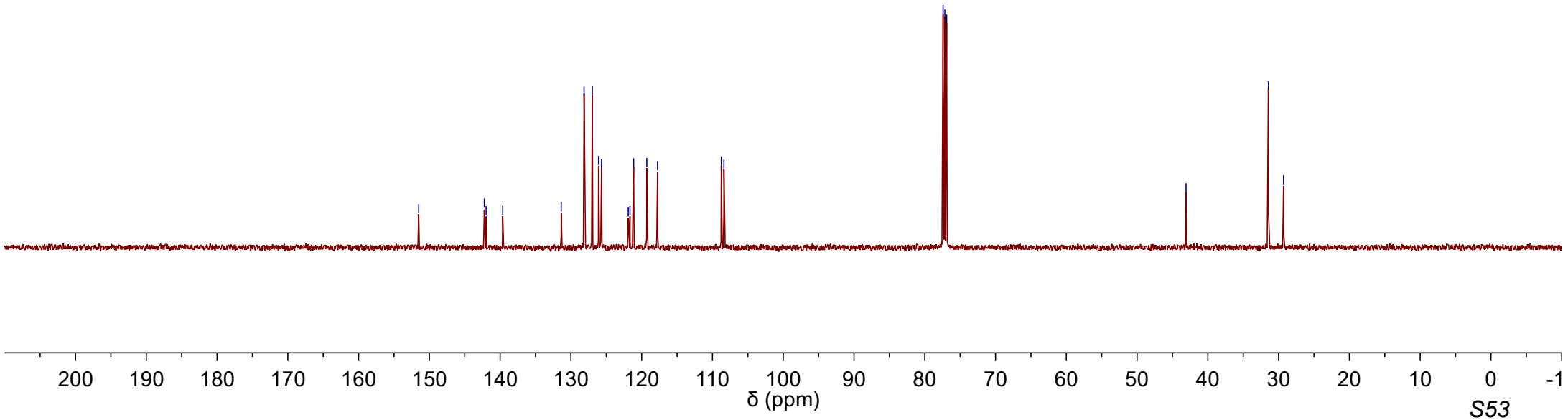
151.50
142.23
141.98
139.63
131.37
128.14
126.97
126.09
125.67
121.89
121.65
121.14
119.27
117.76
108.75
108.38
77.41
77.16
76.91
43.09
31.44
29.30

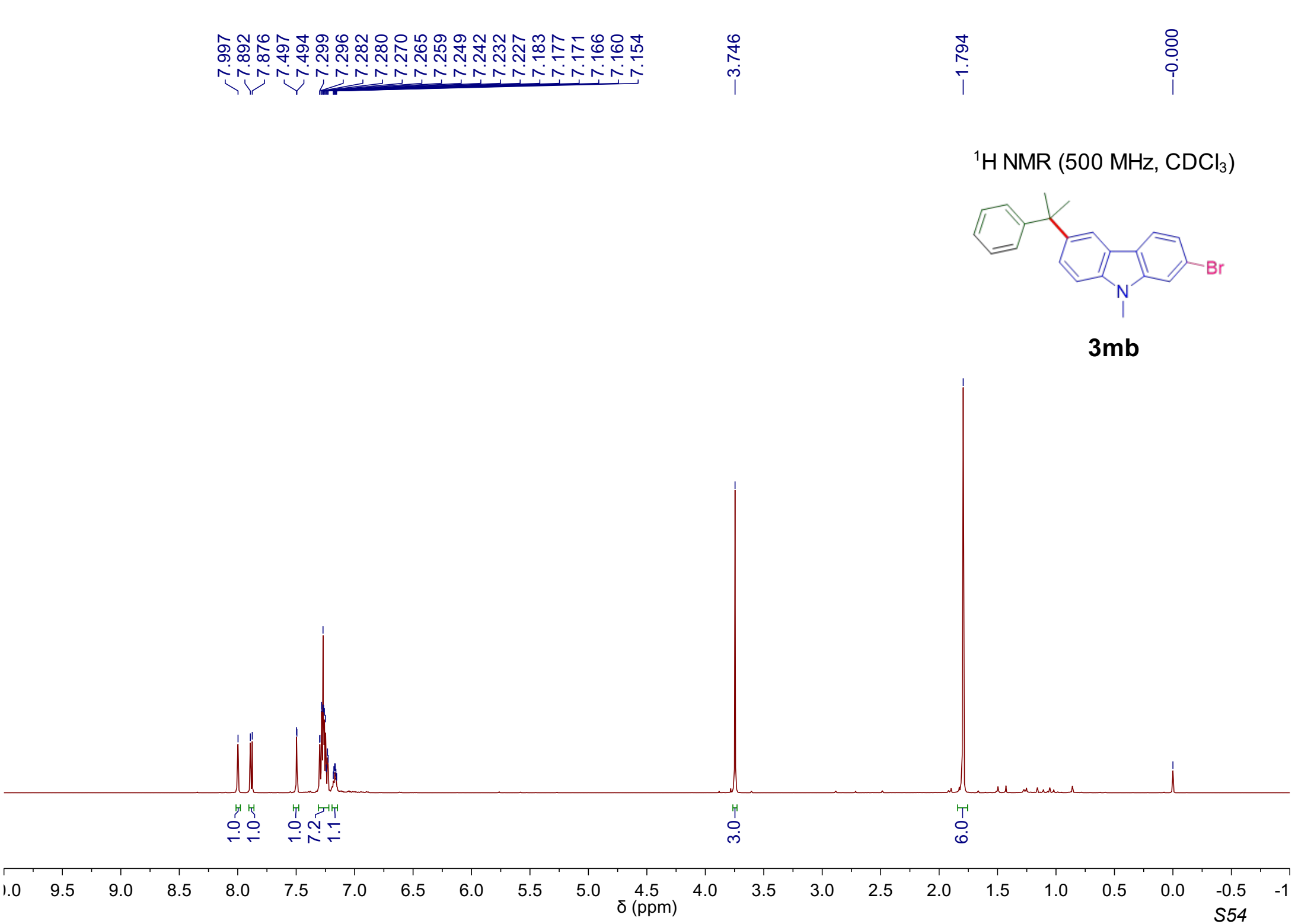
^{13}C NMR (126 MHz, $CDCl_3$)



3lb

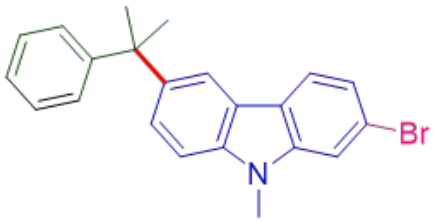




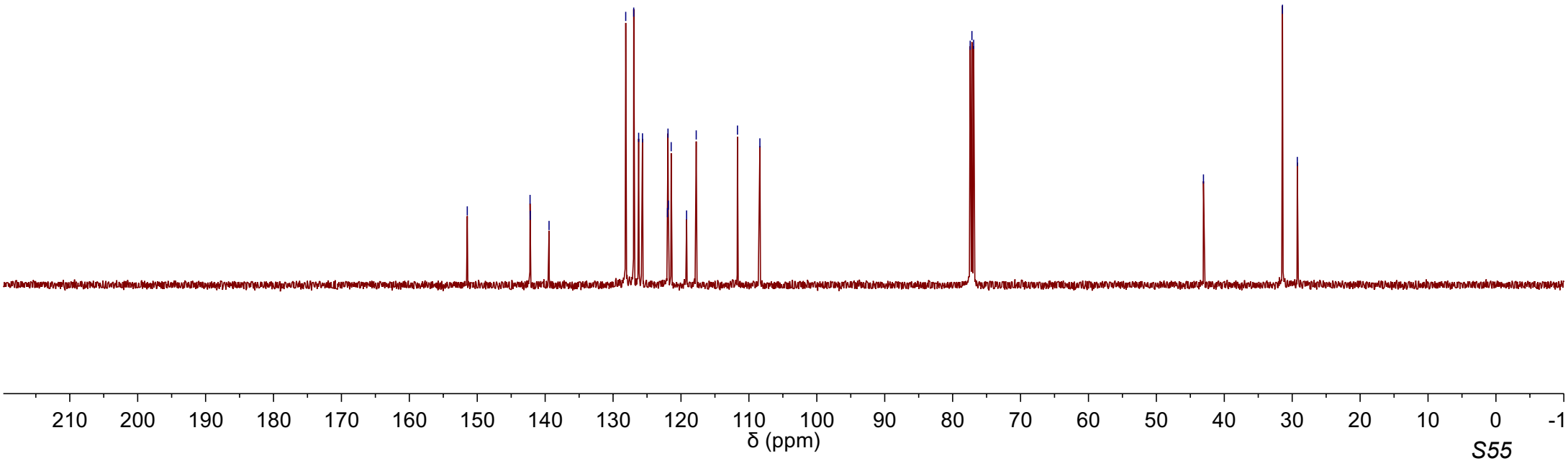

7.997
7.892
7.876
7.497
7.494
7.299
7.296
7.282
7.280
7.270
7.265
7.259
7.249
7.242
7.232
7.227
7.183
7.177
7.171
7.166
7.160
7.154
3.746
1.794
-0.000
1H NMR (500 MHz, CDCl3)
Br
N
3mb
1.0
1.0
1.0
7.2
1.1
3.0
6.0
δ (ppm)

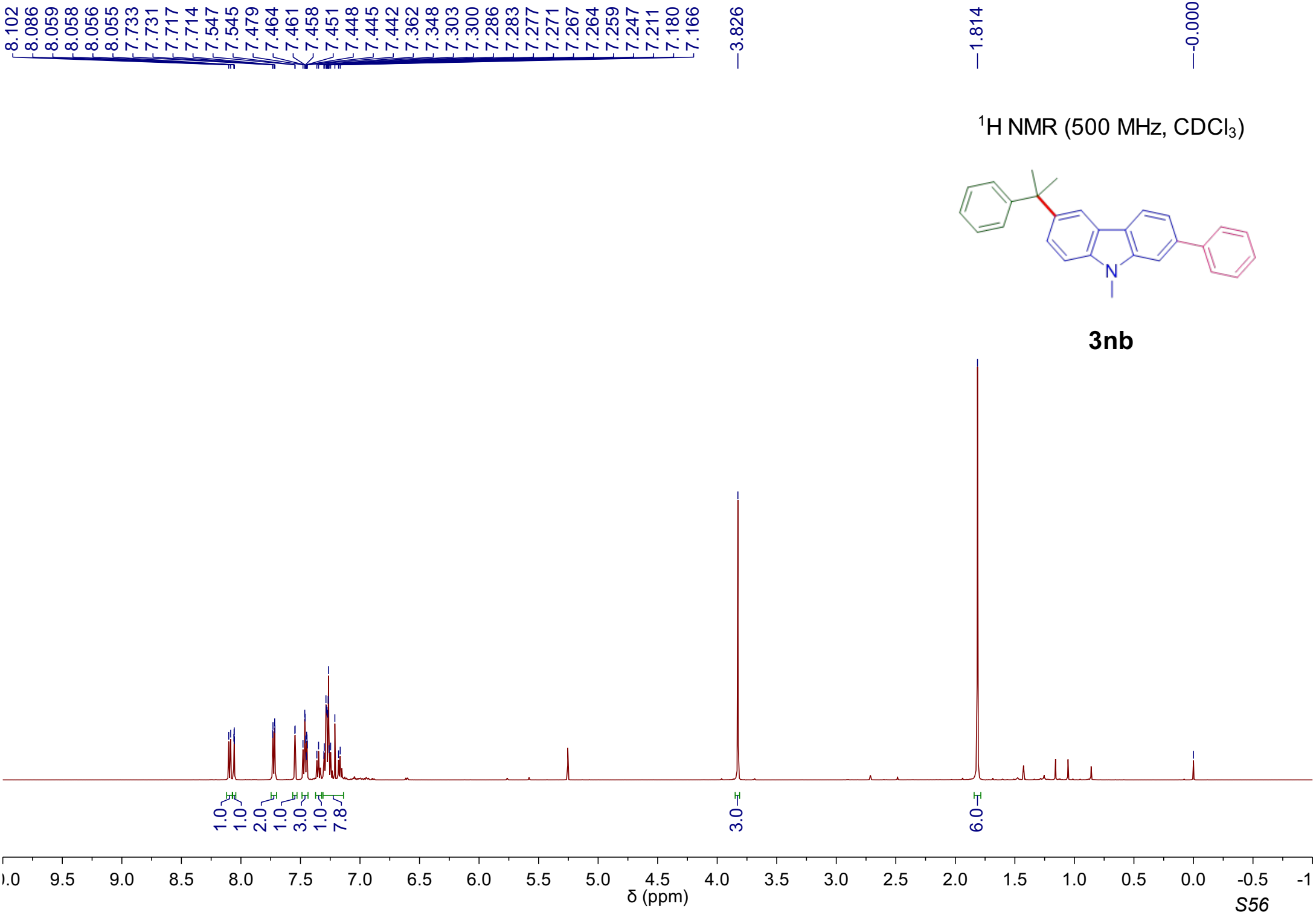
151.47
142.22
142.20
139.43
128.14
126.96
126.23
125.67
121.99
121.91
121.86
121.44
119.18
117.76
111.68
108.38
77.41
77.16
76.91
43.07
31.43
29.25

^{13}C NMR (126 MHz, $CDCl_3$)

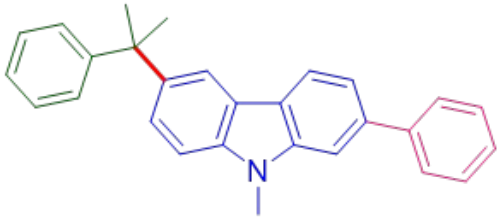


3mb



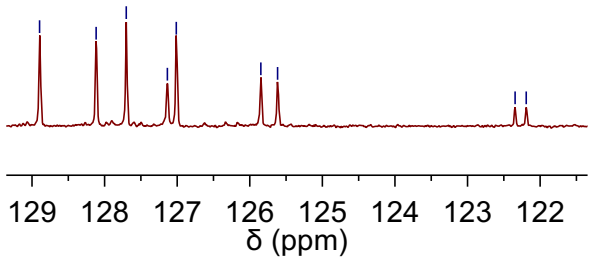

8.102
8.086
8.059
8.058
8.056
8.055
7.733
7.731
7.717
7.714
7.547
7.545
7.479
7.464
7.461
7.458
7.451
7.448
7.445
7.442
7.362
7.348
7.303
7.300
7.286
7.283
7.277
7.271
7.267
7.264
7.259
7.247
7.211
7.180
7.166
3.826
1.814
0.000
1H NMR (500 MHz, CDCl3)
N
3nb
1.0
1.0
2.0
1.0
3.0
1.0
7.8
3.0
6.0
δ (ppm)

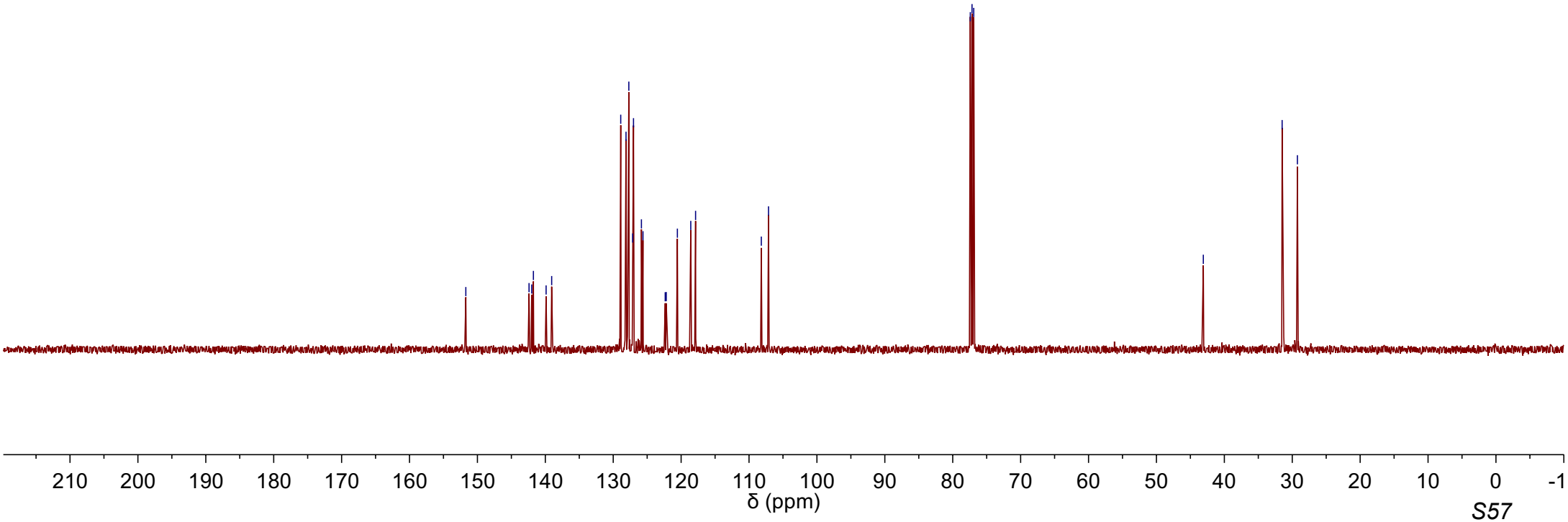
^{13}C NMR (126 MHz, $CDCl_3$)

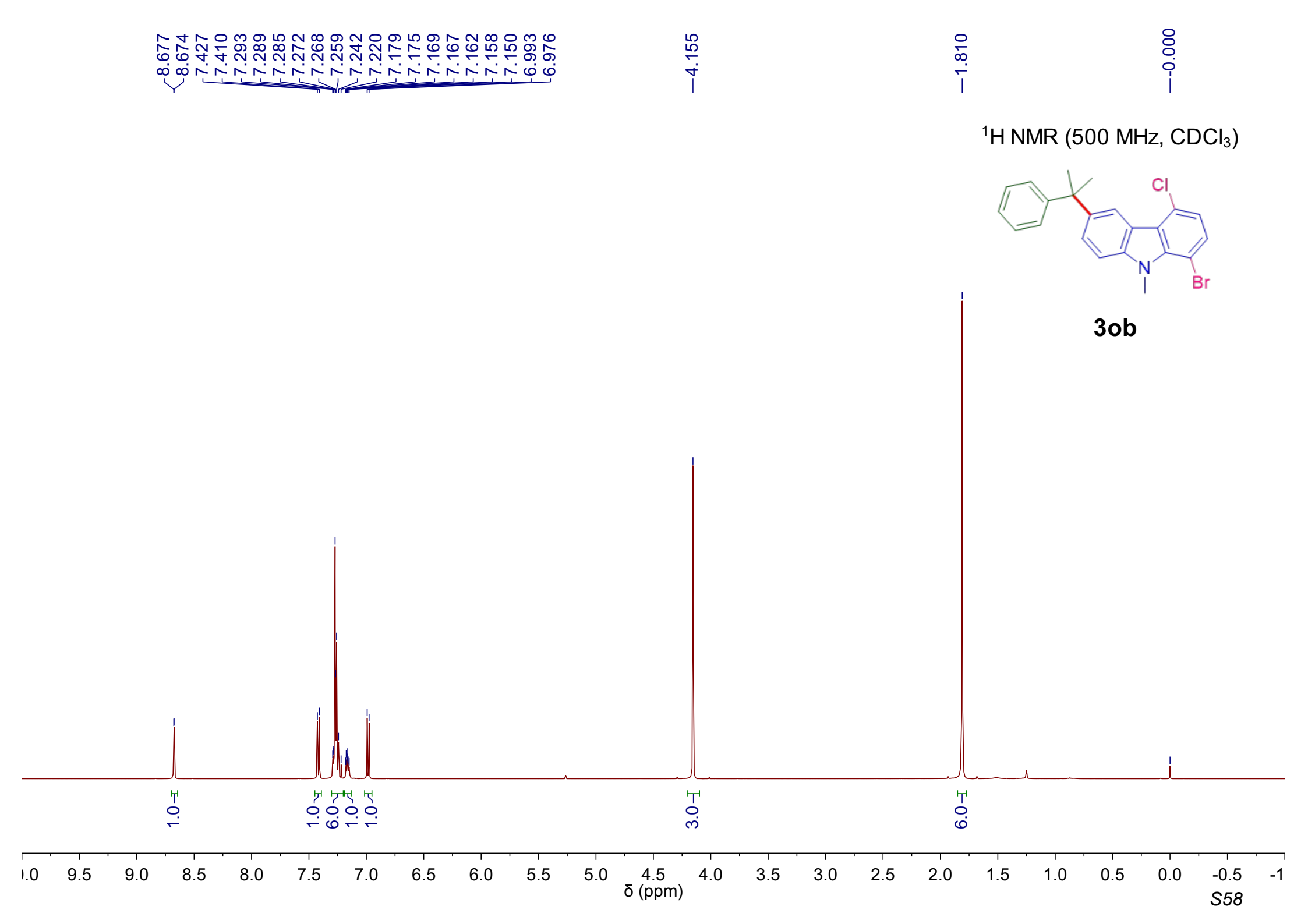


3nb

151.71
142.40
142.01
141.75
139.88
139.06
128.89
128.12
127.70
127.13
127.01
125.85
125.62
122.34
122.19
120.55
118.58
117.87
108.19
107.13
77.41
77.16
76.91
43.10
31.49
29.24

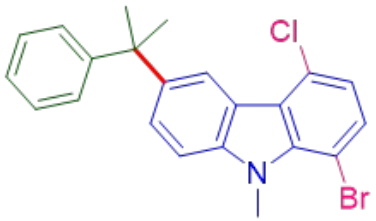




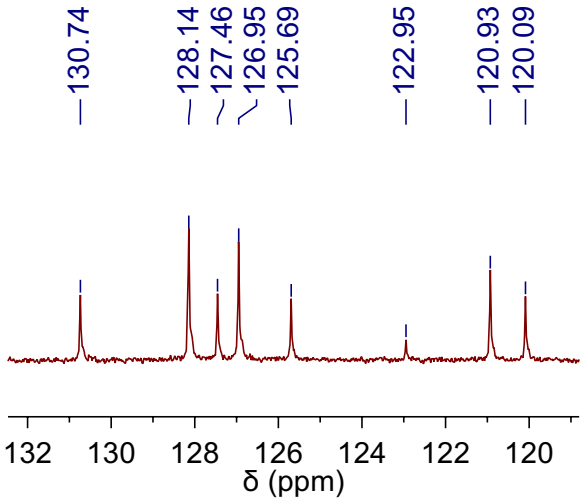

8.677
8.674
7.427
7.410
7.293
7.289
7.285
7.272
7.268
7.259
7.242
7.220
7.179
7.175
7.169
7.167
7.162
7.158
7.150
6.993
6.976
4.155
1.810
0.000
1H NMR (500 MHz, CDCl3)
Cl
N
Br
3ob
1.0
1.0
6.0
1.0
1.0
3.0
6.0
δ (ppm)

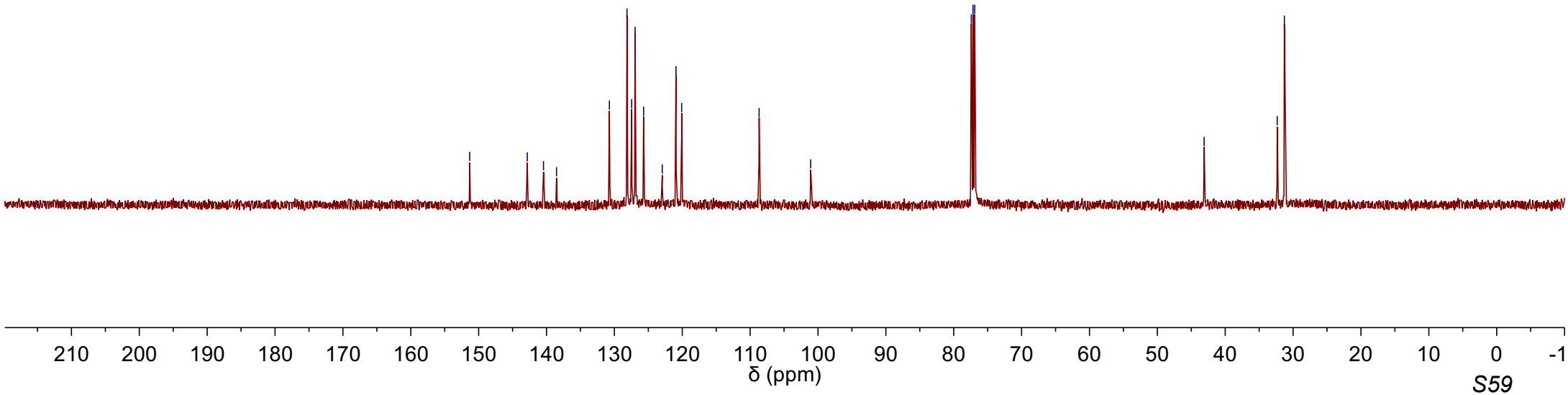
151.32
142.84
140.44
138.53
130.74
128.14
127.46
126.95
125.69
122.95
120.93
120.09
108.68
101.08
77.41
77.16
76.91
43.11
32.34
31.29

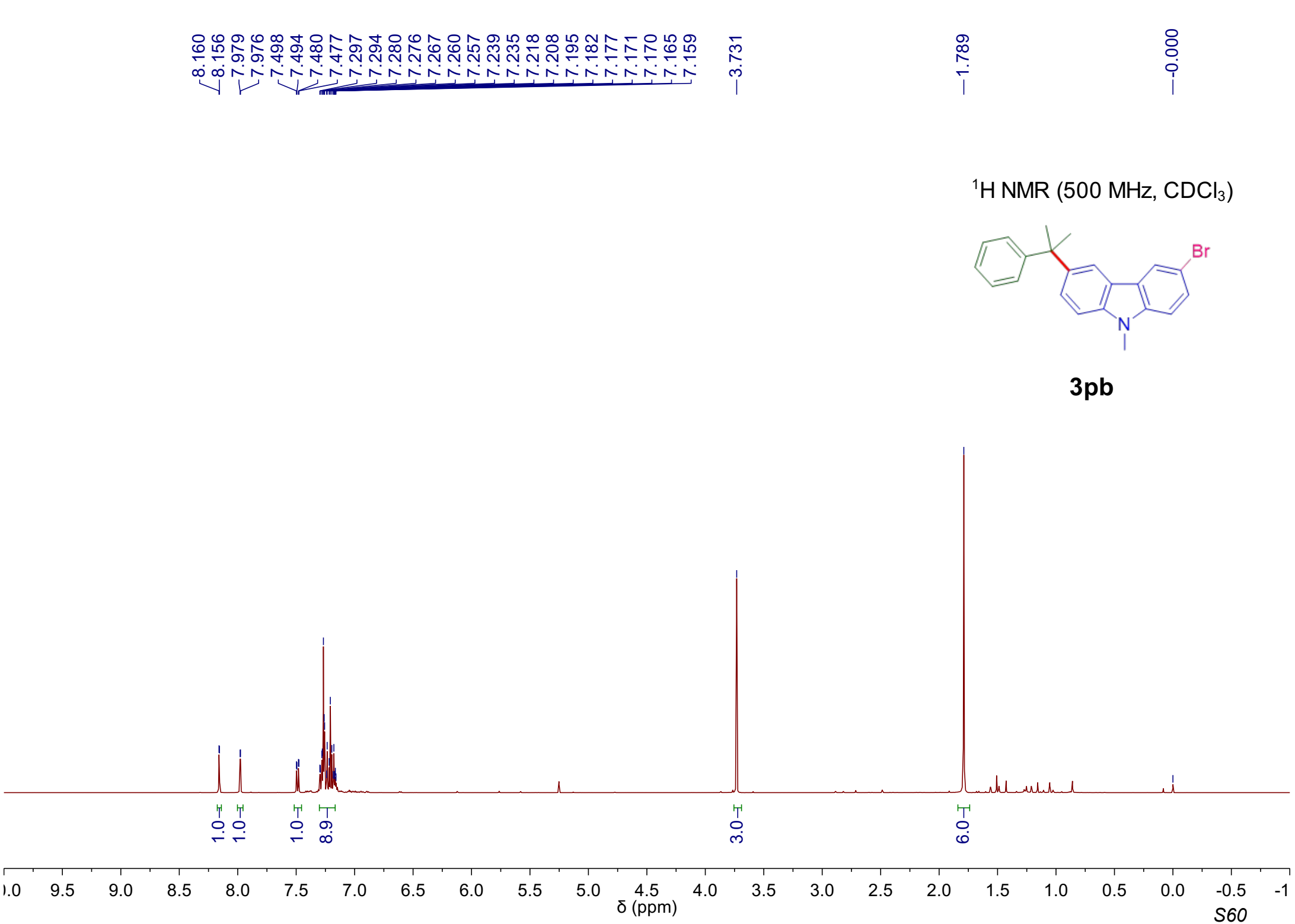
^{13}C NMR (126 MHz, $CDCl_3$)



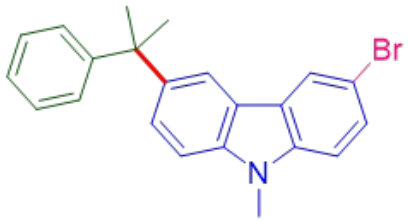
3ob





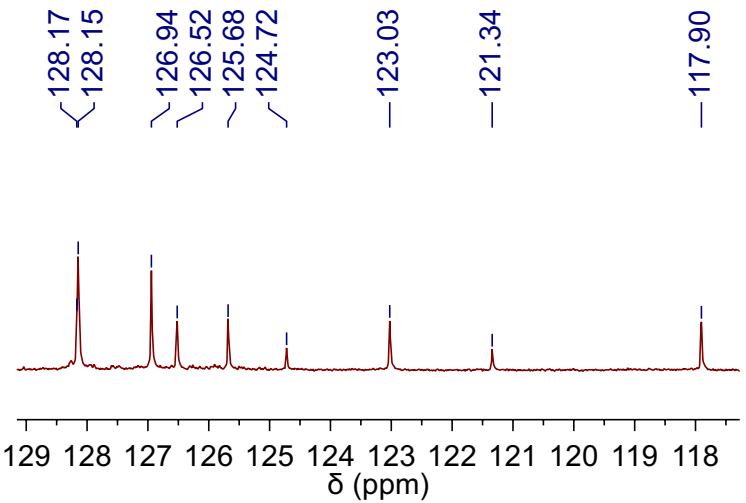

8.160
8.156
7.979
7.976
7.498
7.494
7.480
7.477
7.297
7.294
7.280
7.276
7.267
7.260
7.257
7.239
7.235
7.218
7.208
7.195
7.182
7.177
7.171
7.170
7.165
7.159
3.731
1.789
-0.000
1H NMR (500 MHz, CDCl3)
Br
N
3pb
1.0
1.0
1.0
8.9
3.0
6.0
δ (ppm)

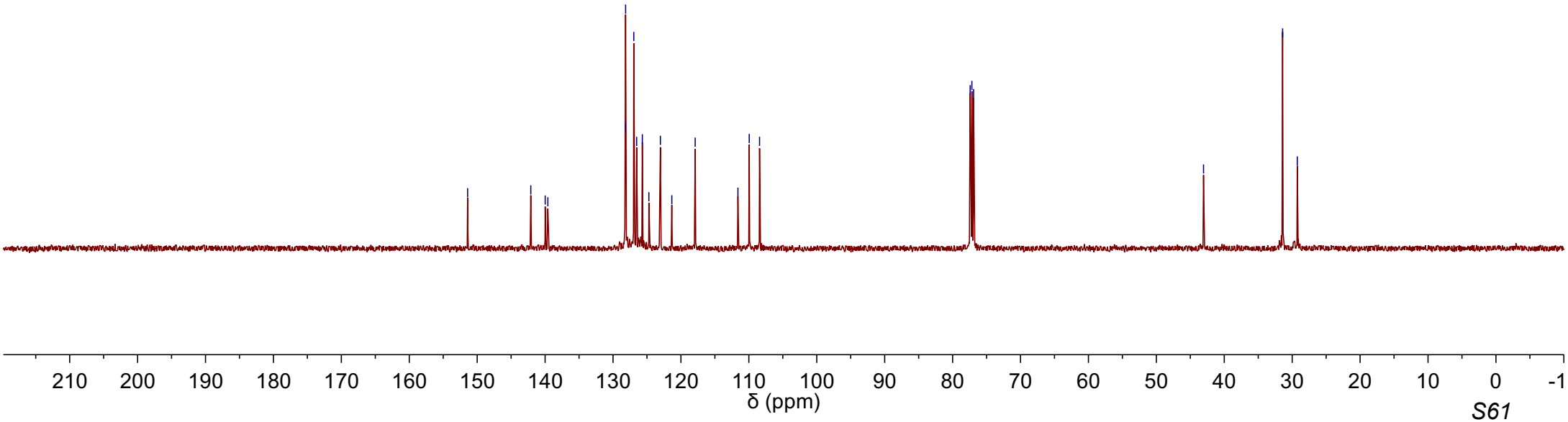
^{13}C NMR (126 MHz, $CDCl_3$)

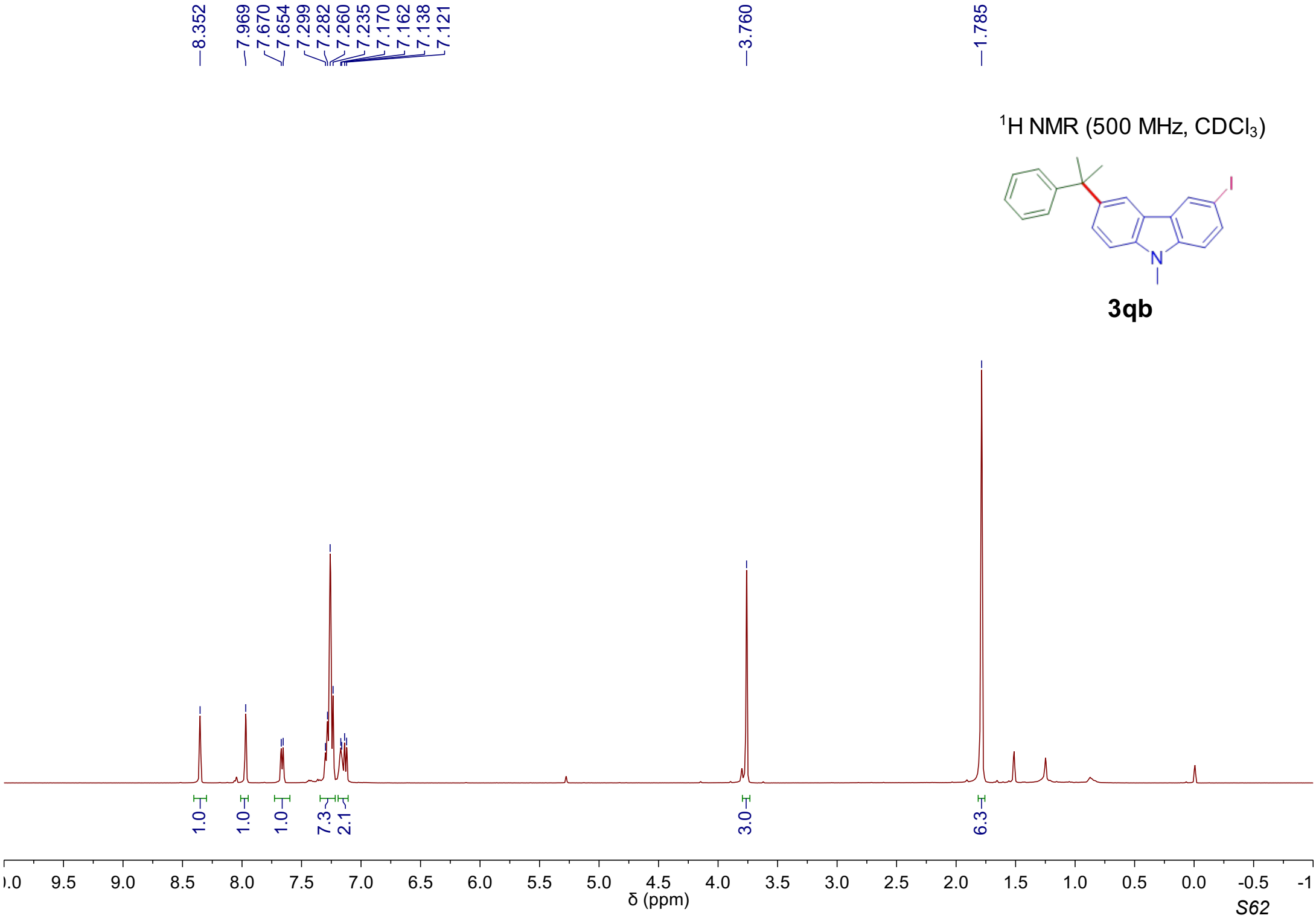


3pb

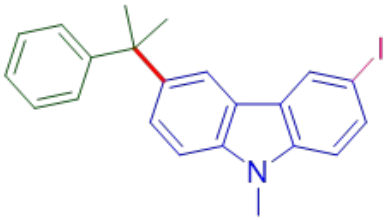
151.41
142.11
139.99
139.59
128.17
128.15
126.94
126.52
125.68
124.72
123.03
121.34
117.90
111.61
109.94
108.42
77.41
77.16
76.91
43.05
31.41
29.25






8.352
7.969
7.670
7.654
7.299
7.282
7.260
7.235
7.170
7.162
7.138
7.121
3.760
1.785
1H NMR (500 MHz, CDCl3)
I
N
3qb
1.0
1.0
1.0
7.3
2.1
3.0
6.3
δ (ppm)

^{13}C NMR (126 MHz, $CDCl_3$)



3qb

151.44
142.24
140.54
139.33
133.75
129.16
128.15
126.96
126.51
125.69
125.56
121.14
117.94
110.61
108.36
81.26
77.41
77.16
76.91
43.09
31.43
29.28