

Supporting Information

Brønsted Acid-Catalyzed One-Pot Tandem Annulation/
[5+2]-Cycloaddition of *o*-Propargyl Alcohol Benzaldehydes with
Alkynes: Regioselective and Stereoselective Synthesis of
Dibenzo[*a,f*]azulen-12-ones

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Table of Contents

1	General Remarks	S2
2	General Procedure for the Synthesis of Substrates and Products	S2-S6
3	Reference	S7
4	Characterization Data of 3a-3ap, 4a-4l, 5a, 6a, 7a, 8a and 9a	S8-S30
5	Crystallographic data of 3a, 5a, 8a and 9a	S31- S34
6	¹H NMR and ¹³C NMR Spectra for Products	S35-S168
7	High resolution mass spectrometry analysis	S169-S171

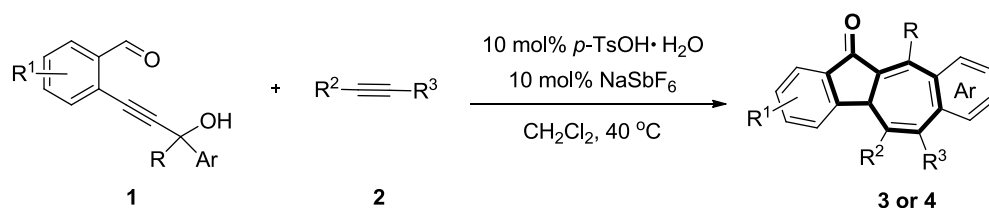
General Remarks

Column chromatography was carried out on silica gel (200-300 meshes). Conversion was monitored by thin layer chromatography (TLC). ^1H NMR spectra were recorded on 400 MHz in chloroform-d and ^{13}C NMR spectra were recorded on 100 MHz in chloroform-d. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1} . All products were further characterized by high resolution mass spectra (HRMS); copies of their ^1H NMR and ^{13}C NMR spectra are provided in the Supporting Information. Dry THF were distilled over CaH_2 , and other commercial solvents were used without further treatment.

Synthetic Procedures and Spectral Data

All starting materials were prepared according to previously reported procedures.^{S1}

General Procedure of dibenzo[a,f]azulen-12-ones **3** or **4**



To a solution of *o*-propargyl alcohol benzaldehydes **1** (0.20 mmol) and alkynes **2** (1.0 equiv) in CH_2Cl_2 (3.0 mL) was added $p\text{-TsOH}\cdot\text{H}_2\text{O}$ (10 mol%) and NaSbF_6 (10 mol%) at $40\text{ }^\circ\text{C}$ for 12 h. When the reaction was completed, the reaction mixture was quenched by addition of saturated aqueous sodium hydrogen carbonate (5 mL) and extracted with ethyl acetate (3 x 15 mL), washed with water, saturated brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford corresponding dibenzo[a,f]azulen-12-ones **3** or **4**.

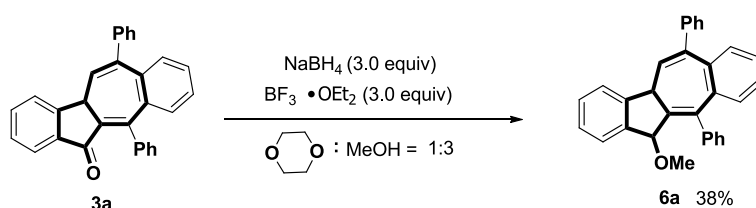
General procedure for the diastereoselective epoxidation of **3a**:^{S2}



To a solution of azulenones **3a** (0.20 mmol) in CH_2Cl_2 (3.0 mL) was added

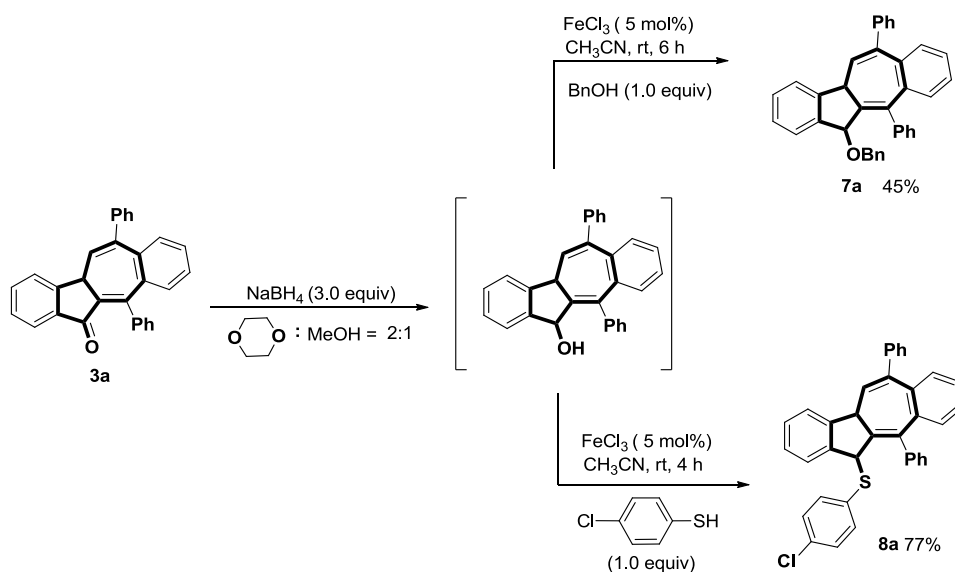
m-CPBA (3.0 equiv) and NaHCO₃ (3.0 equiv.) at room temperature for 24 h. When the reaction was completed, the reaction mixture was quenched by addition of saturated aqueous sodium hyposulfite (5 mL) and extracted with ethyl acetate (3 x 15 mL), washed with water, saturated brine, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford hydroazulenone[b]oxirane **5a** in 81% yield.

General procedure for the allylic methoxylation reaction of **3a**:



To a stirred solution of **3a** (0.2 mmol) in MeOH : dioxane (3 : 1, 3.0 mL), was added NaBH₄ (3.0 equiv, 0.6 mmol) and BF₃·OEt₂ (3.0 equiv, 0.6 mmol) at room temperature for 2 h. When the reaction was considered to be complete, the reaction mixture was quenched by water and extracted with ethyl acetate (3 x 15 mL), washed with water, saturated brine, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford 12-methoxydibenzo[a,f]azulene **6a** in 38% yield.

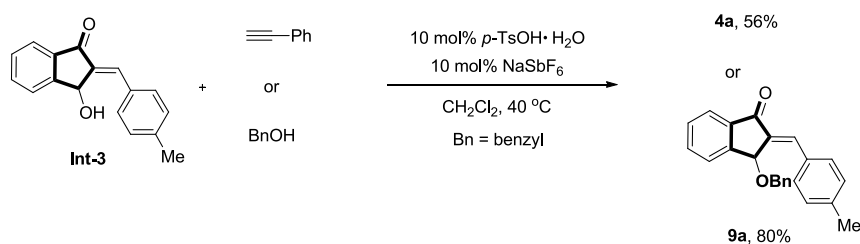
General procedure for the allylic benzyloxylation and thioetherification reactions of **3a**:^{S3}



To a stirred solution of **3a** (0.2 mmol) in MeOH : dioxane (1 : 2, 3.0 mL), was added NaBH₄ (3.0 equiv, 0.6 mmol) at room temperature for 5 h. When the reaction was considered to be complete, the reaction mixture was quenched by water and extracted with ethyl acetate (3 x 15 mL), washed with water, saturated brine, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford 12-hydroxyl dibenzo[a,f]azulene intermediate.

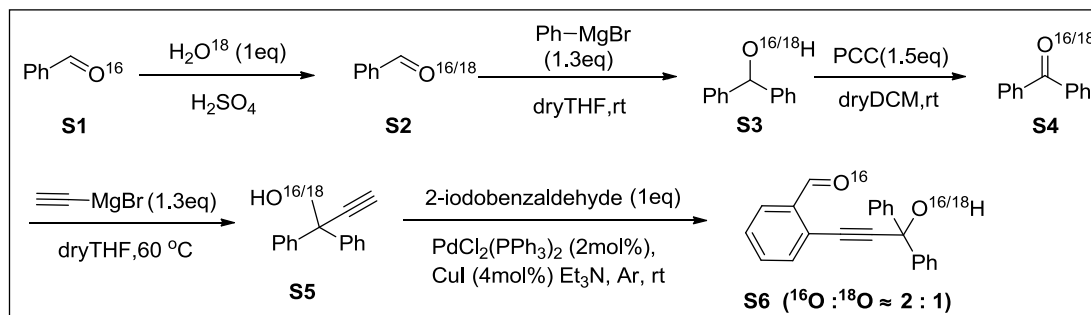
To a solution of 12-hydroxyl dibenzo[a,f]azulene intermediate (0.20 mmol) and BnOH (0.2 mmol, 1.0 equiv) or *p*-chlorothiophenol (0.2 mmol, 1.0 equiv) in CH₃CN (2.0 mL) was added FeCl₃ (5 mol%) at room temperature for 6h or 4h. When the reaction was completed, the reaction mixture was quenched by addition of saturated aqueous ammonium chloride (5 mL) and extracted with ethyl acetate (3 x 15 mL), washed with water, saturated brine, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford 12-benzyloxy dibenzo[a,f]azulene **7a** and 12-(*p*-chlorothiophenyl) dibenzo[a,f]azulene **8a** in 45% and 77% yield, respectively.

General procedure for the [5+2]-cycloaddition reactions and the allylic benzyloxylation of Int-3:^{S4}



To a solution of ethynylbenzene **2a** (1.0 equiv) or BnOH (1.0 equiv) and 3-hydroxy indanones **Int-3** (0.20 mmol) in CH₂Cl₂ (3.0 mL) was added *p*-TsOH·H₂O (10 mol%) and NaSbF₆ (10 mol%) at 40 °C for 12 h. When the reaction was completed, the reaction mixture was quenched by addition of saturated aqueous sodium hydrogen carbonate (5 mL) and extracted with ethyl acetate (3 x 15 mL), washed with water, saturated brine, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford the corresponding **4a** and **9a** in 56% and 80% yield, respectively.

General Procedure of 2-(3-hydroxy-3,3-diphenylprop-1-yn-1-yl)benzaldehyde 1a
(1a-¹⁶O : 1a-¹⁸O ≈ 6 : 1): ^{S5}



To a solution of benzaldehyde **S1** (150 mmol) was added H₂O¹⁸ (1.0 equiv) and H₂SO₄ (30mg) at rt for 12 h. When the reaction was completed, the reaction mixture was quenched by addition of saturated aqueous sodium hydrogen carbonate (5 mL), washed with water, saturated brine, dried over Na₂SO₄. The residue was purified by distillation under reduced pressure to obtain the corresponding **S2**.

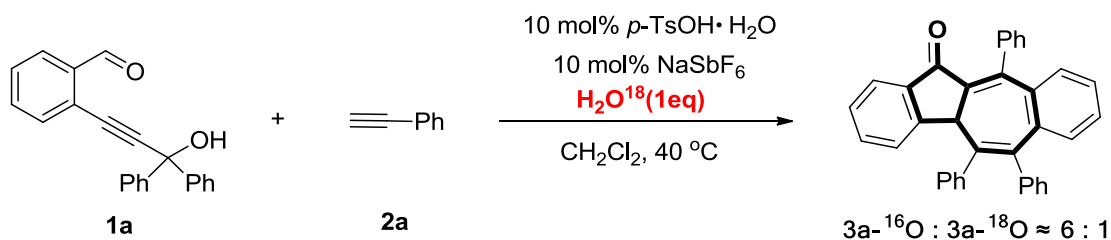
To a solution of benzaldehyde **S2** (50 mmol) in THF (10 mL) was added phenylmagnesium bromide (65 mmol) and the reaction vial was flushed with Ar and the reaction mixture was stirred for 5h. Upon completion, the mixture was quenched with saturated NH₄Cl solution (40 mL), extracted with EtOAc (50 mL×3), washed with water, saturated brine, dried over Na₂SO₄, filtered, and concentrated to get the crude product **S3**.

To a solution of crude product **S3** (40 mmol) in dry CH₂Cl₂ (20 mL) was added PCC (60 mmol) in one portion at rt and then the mixture was stirred at rt for 5 h. Upon completion, the mixture was filtered through a celite plug, concentrated to give the crude product and the residue was purified by chromatography (PE:EA = 20:1) to get the desired substrate benzophenone **S4**.

To a solution of benzophenone **S4** (15 mmol) in THF (20 mL) was added ethynylmagnesium bromide (19 mmol) and the reaction vial was flushed with Ar and the reaction mixture was stirred for 8h at 60°C. Upon completion, the mixture was quenched with saturated NH₄Cl solution (40 mL), extracted with EtOAc (50 mL×3), washed with water, saturated brine, dried over Na₂SO₄, filtered, and concentrated to get the desired substrate 1,1-diphenylprop-2-yn-1-ol **S5**.

To a solution of 2-iodobenzaldehyde (5 mmol) in Et₃N (10 mL) was added PdCl₂(PPh₃)₂ (4 mol %) and CuI (2 mol %) and the reaction vial was flushed with Ar and the reaction mixture was stirred for 5 minutes. A solution of 1,1-diphenylprop-2-yn-1-ol **S5** in Et₃N (5 mL) were then added dropwise through a syringe for 5 minutes. The resulting solution was stirred at room temperature overnight. When the reaction was considered complete as determined by TLC analysis, the mixture was quenched by addition of saturated aqueous ammonium chloride (10 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with water, brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude material was purified by flash column chromatography (PE:EA = 5:1) to give **S6** (substrate **S6** proved to be the inseparable mixture (**S6**-¹⁶O and **S6**-¹⁸O) in an approximate 2 : 1 ratio by high resolution mass spectrometry analysis).

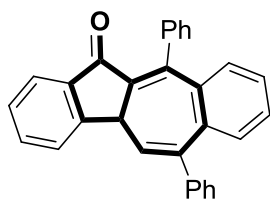
General Procedure of dibenzo[a,f]azulen-12-one **3a (**3a**-¹⁶O : **3a**-¹⁸O ≈ 6 : 1)**



To a solution of 2-(3-hydroxy-3,3-diphenylprop-1-yn-1-yl)benzaldehyde **1a** (0.20 mmol) and phenylacetylene **2a** (1.0 equiv) in CH₂Cl₂ (3.0 mL) was added *p*-TsOH·H₂O (10 mol%) , NaSbF₆ (10 mol%) and H₂O¹⁸ (1.0 equiv) at 40 °C for 12 h. When the reaction was completed, the reaction mixture was quenched by addition of saturated aqueous sodium hydrogen carbonate (5 mL) and extracted with ethyl acetate (3 x 15 mL), washed with water, saturated brine, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford corresponding dibenzo[a,f]azulen-12-one **3a** in 34% yield.

Reference:

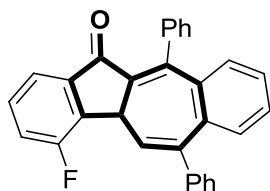
- S1 (a) H.-T. Zhu, X. Dong, L.-J. Wang, M.-J. Zhong, X.-Y. Liu, Y.-M. Liang, *Chem. Commun.* 2012, 48, 10748; (b) H.-T. Zhu, M.-J. Fan, D.-S. Yang, X.-L. Wang, S. Ke, C.-Y. Zhang, Z.-H. Guan, *Org. Chem. Front.* 2015, **2**, 506.
- S2 K.-G. Ji, Y.-W. Shen, X.-Z. Shu, H.-Q. Xiao, Y.-J. Bian, Y.-M. Liang, *Adv. Synth. Catal.* 2008, **350**, 1275.
- S3 X. Zhang, W. Rao, Sally, P. W. H. Chan, *Org. Biomol. Chem.* 2009, **7**, 4186.
- S4 N.-N. Zhou, S.-S. Ning, X.-J. Tong, T.-T. Luo, J. Yang, L.-Q. Li, M.-J. Fan, D.-S. Yang, H.-T. Zhu, *J. Org. Chem.* 2019, **84**, 8497.
- S5 Senkus, M., Brown, W. G. *J. Org. Chem.* 1938, **2**, 569.



6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3a):

yellow solid (70mg, 89% yield); mp 190–192 °C; $R_f = 0.40$ (PE/EA = 30:1).

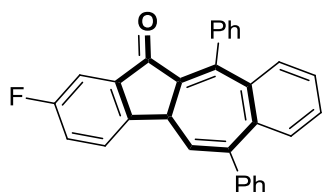
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.6$ Hz, 1H), 7.64 (d, $J = 3.7$ Hz, 2H), 7.46 – 7.38 (m, 4H), 7.35 (d, $J = 7.7$ Hz, 1H), 7.33 – 7.23 (m, 8H), 7.23 – 7.17 (m, 2H), 6.07 (d, $J = 5.0$ Hz, 1H), 3.95 (d, $J = 5.0$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 190.1, 151.6, 145.3, 142.4, 141.0, 140.9, 140.0, 139.6, 139.1, 138.0, 135.0, 134.5, 131.7, 130.8, 130.2, 129.1, 128.9, 128.4, 128.2, 128.1, 128.0, 127.6, 127.5, 126.7, 125.5, 124.1, 42.0. HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{21}\text{O}$ [$\text{M}+\text{H}$] $^+$: 397.1587, found: 397.1585.



4-fluoro-6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3b):

yellow solid (50mg, 61% yield); mp 230–232 °C; $R_f = 0.40$ (PE/EA = 30:1).

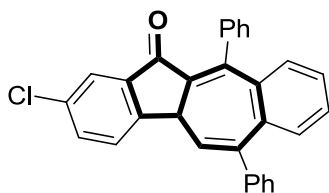
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 (d, $J = 7.5$ Hz, 1H), 7.43 (dd, $J = 7.7, 5.1$ Hz, 4H), 7.38 – 7.24 (m, 10H), 7.22 (dd, $J = 5.3, 2.0$ Hz, 2H), 6.12 (d, $J = 5.0$ Hz, 1H), 4.11 (d, $J = 5.0$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 189.0 (d, $J = 2.5$ Hz), 160.0 (d, $J = 251.4$ Hz), 146.5, 143.0 (d, $J = 4.4$ Hz), 142.4, 141.2, 140.7, 139.6, 138.9, 137.1, 136.9, 132.9, 131.8, 131.0, 130.2 (d, $J = 6.3$ Hz), 130.1, 129.1, 128.4 (d, $J = 3.4$ Hz), 128.1, 127.9, 127.7, 126.9, 121.1 (d, $J = 19.9$ Hz), 120.0 (d, $J = 3.8$ Hz), 39.0. HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{20}\text{FO}$ [$\text{M}+\text{H}$] $^+$: 415.1493, found: 415.1490.



2-fluoro-6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3c):

yellow solid (74mg, 90% yield); mp 240–242 °C; $R_f = 0.40$ (PE/EA = 30:1).

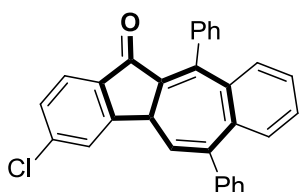
$^1\text{H NMR}$ (400 MHz, acetone) δ 7.87 (dd, $J = 8.4, 4.6$ Hz, 1H), 7.54 (ddd, $J = 9.0, 8.5, 2.6$ Hz, 1H), 7.44 – 7.39 (m, 3H), 7.38 – 7.25 (m, 11H), 7.17 – 7.12 (m, 1H), 6.11 (d, $J = 5.0$ Hz, 1H), 3.90 (d, $J = 5.0$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, acetone) δ 188.9 (d, $J = 3.0$ Hz), 163.6 (d, $J = 246.5$ Hz), 147.9 (d, $J = 2.2$ Hz), 146.1, 143.1, 142.5 (d, $J = 7.3$ Hz), 141.8, 141.5, 140.3, 140.0, 139.0 (d, $J = 1.0$ Hz), 135.2, 132.3, 131.3, 131.1, 129.6, 129.2, 129.0 (d, $J = 8.2$ Hz), 128.8, 128.6, 128.5, 128.4, 127.6, 123.1 (d, $J = 23.7$ Hz), 109.9 (d, $J = 22.2$ Hz), 42.1. HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{20}\text{FO}$ [$\text{M}+\text{H}$] $^+$: 415.1493, found: 415.1488.



2-chloro-6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3d):

Yellow solid (79mg, 92% yield); mp 200-202 °C; $R_f = 0.40$ (PE/EA = 30:1).

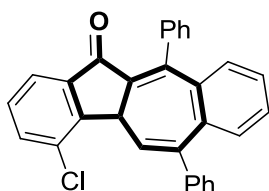
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (d, $J = 1.7$ Hz, 1H), 7.64 – 7.57 (m, 2H), 7.43 (dd, $J = 4.2, 2.3$ Hz, 3H), 7.37 – 7.23 (m, 9H), 7.22 – 7.17 (m, 2H), 6.03 (d, $J = 5.0$ Hz, 1H), 3.93 (d, $J = 5.0$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 188.8, 149.6, 146.2, 142.3, 141.6, 141.2, 140.9, 139.6, 138.9, 137.7, 135.0, 134.6, 133.7, 131.8, 130.8, 130.1, 129.0, 128.5, 128.4, 128.1, 127.8, 127.7, 126.9, 126.8, 124.1, 41.7. HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{20}\text{ClO}$ $[\text{M}+\text{H}]^+$: 431.1197, found: 431.1186.



3-chloro-6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3e):

Yellow solid (74mg, 86% yield); mp 138-140 °C; $R_f = 0.40$ (PE/EA = 30:1).

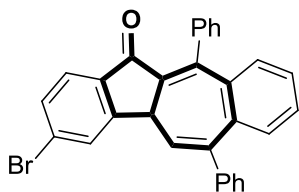
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.1$ Hz, 1H), 7.66 – 7.63 (m, 1H), 7.46 – 7.38 (m, 4H), 7.38 – 7.24 (m, 9H), 7.23 – 7.17 (m, 2H), 6.05 (d, $J = 5.0$ Hz, 1H), 3.94 (d, $J = 5.0$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 188.8, 153.0, 145.3, 142.3, 141.4, 141.2, 140.9, 139.5, 138.9, 138.6, 137.5, 133.4, 131.8, 130.9, 130.1, 129.0, 128.9, 128.5, 128.4, 128.1, 127.8, 126.9, 125.9, 125.4, 41.8. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{23}\text{O}_2$ $[\text{M}+\text{H}]^+$: 427.1693, found: 427.1681.



4-chloro-6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3f):

Yellow solid (58mg, 68% yield); mp 184-186 °C; $R_f = 0.40$ (PE/EA = 30:1).

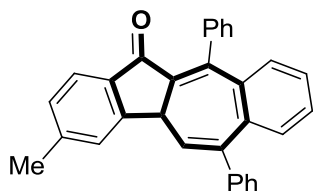
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 – 7.65 (m, 1H), 7.62 (dd, $J = 7.8, 0.9$ Hz, 1H), 7.44 (m, 3H), 7.41 – 7.36 (m, 2H), 7.34 – 7.25 (m, 8H), 7.24 – 7.18 (m, 2H), 6.09 (d, $J = 5.1$ Hz, 1H), 4.04 (d, $J = 5.1$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 189.1, 148.6, 146.4, 142.5, 142.0, 141.0, 140.6, 139.6, 139.0, 137.0, 134.6, 132.8, 132.2, 131.8, 131.0, 130.1, 129.8, 129.1, 128.4, 128.1, 127.8, 127.7, 126.8, 122.6, 41.3. HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{20}\text{ClO}$ $[\text{M}+\text{H}]^+$: 431.1197, found: 431.1187.



3-bromo-6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3g):

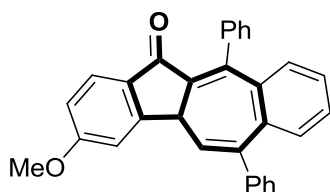
Yellow solid (69mg, 73% yield); mp 162-164 °C; $R_f = 0.40$ (PE/EA = 30:1).

$^1\text{H NMR}$ (400 MHz, acetone) δ 8.09 – 8.05 (m, 1H), 7.69 (dd, $J = 8.1, 1.7$ Hz, 1H), 7.60 (d, $J = 8.1$ Hz, 1H), 7.44 – 7.38 (m, 3H), 7.37 – 7.24 (m, 10H), 7.15 (dd, $J = 7.8, 0.7$ Hz, 1H), 6.16 (d, $J = 5.0$ Hz, 1H), 3.94 (d, $J = 5.0$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, acetone) δ 188.7, 154.0, 146.0, 143.1, 141.8, 141.6, 140.3, 140.0, 139.6, 138.3, 134.6, 132.4, 132.3, 131.3, 131.1, 130.2, 130.0, 129.7, 129.2, 128.8, 128.6, 128.5, 128.4, 127.6, 125.8, 42.4. HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{20}\text{BrO}$ $[\text{M}+\text{H}]^+$: 475.0692, found: 475.0699.

**3-methyl-6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3h):**

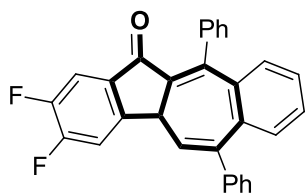
Yellow solid (28mg, 35% yield); mp 160-162 °C; $R_f = 0.40$ (PE/EA = 30:1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 (d, $J = 7.8$ Hz, 1H), 7.46 – 7.40 (m, 4H), 7.37 – 7.23 (m, 10H), 7.23 – 7.19 (m, 2H), 6.07 (d, $J = 5.0$ Hz, 1H), 3.92 (d, $J = 5.0$ Hz, 2H), 2.50 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 189.8, 152.1, 146.3, 144.9, 142.5, 141.2, 140.9, 139.6, 139.3, 138.5, 137.9, 134.6, 131.7, 130.8, 130.2, 129.4, 129.0, 128.4, 128.1, 128.0, 127.6, 127.4, 126.7, 125.9, 124.1, 41.9, 22.4. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$: 411.1743, found: 411.1736.

**3-methoxy-6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3i):**

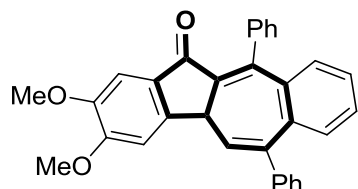
Yellow solid (35mg, 41% yield); mp 174-176 °C; $R_f = 0.30$ (PE/EA = 30:1).

$^1\text{H NMR}$ (400 MHz, acetone) δ 7.61 (d, $J = 8.5$ Hz, 1H), 7.50 – 7.37 (m, 4H), 7.37 – 7.30 (m, 7H), 7.30 – 7.24 (m, 3H), 7.14 (dd, $J = 6.4, 5.7$ Hz, 1H), 7.04 (dd, $J = 8.5, 2.3$ Hz, 1H), 6.15 (d, $J = 5.0$ Hz, 1H), 3.97 (s, 3H), 3.86 (d, $J = 5.0$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, acetone) δ 188.8, 166.5, 155.0, 144.1, 143.2, 142.2, 141.5, 140.2, 139.6, 135.2, 134.0, 132.2, 131.2, 129.6, 129.2, 128.5, 128.4, 128.3, 128.1, 127.5, 126.0, 116.6, 110.2, 56.3, 42.7. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{23}\text{O}_2$ $[\text{M}+\text{H}]^+$: 427.1693, found: 427.1681.

**2,3-difluoro-6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3j):**

yellow solid (71mg, 82% yield); mp 180–182 °C; $R_f = 0.40$ (PE/EA = 30:1).

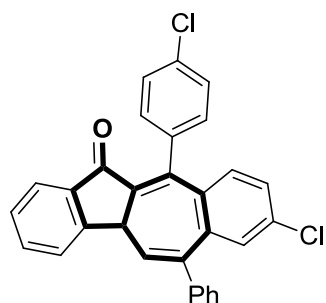
¹H NMR (400 MHz, acetone) δ 7.84 (dd, *J* = 9.9, 6.9 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.44 – 7.38 (m, 3H), 7.38 – 7.30 (m, 7H), 7.30 – 7.24 (m, 3H), 7.14 (m, 1H), 6.14 (d, *J* = 5.0 Hz, 1H), 3.93 (d, *J* = 5.0 Hz, 1H). **¹³C {¹H} NMR (100 MHz, acetone)** δ 187.8 (d, *J* = 2.7 Hz), 155.7 (dd, *J* = 255.6, 14.2 Hz), 152.0 (dd, *J* = 249.8, 14.4 Hz), 149.3 (dd, *J* = 8.2, 2.8 Hz), 146.0, 143.0, 142.0, 141.6, 140.3, 139.8, 138.3, 137.4 (dd, *J* = 5.4, 2.5 Hz), 134.5, 132.4, 131.3, 131.1, 129.7, 129.2, 128.9, 128.6, 128.5, 128.4, 127.7, 115.9 (d, *J* = 18.9 Hz), 112.4 (dd, *J* = 17.9, 1.8 Hz), 42.2 (d, *J* = 1.6 Hz). **HRMS (ESI)** calcd. for C₃₀H₁₈F₂NaO [M+Na]⁺: 455.1218, found: 455.1227.



2,3-dimethoxy-6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3k):

Yellow solid (49mg, 54% yield); mp 136-138 °C; R_f = 0.30 (PE/EA = 20:1).

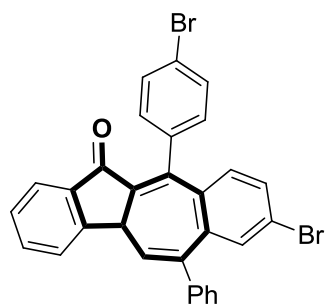
¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.40 (m, 3H), 7.36 – 7.23 (m, 9H), 7.23 – 7.14 (m, 3H), 7.08 (s, 1H), 6.10 (d, *J* = 5.0 Hz, 1H), 4.04 (s, 3H), 3.94 – 3.91 (m, 1H), 3.90 (s, 3H). **¹³C {¹H} NMR (100 MHz, CDCl₃)** δ 189.0, 155.9, 150.0, 146.6, 143.8, 142.5, 141.3, 140.9, 139.5, 139.2, 138.8, 134.5, 133.5, 131.7, 130.8, 130.3, 129.0, 128.4, 128.1, 128.0, 127.6, 127.3, 126.7, 106.5, 105.0, 56.5, 56.3, 41.8. **HRMS (ESI)** calcd. for C₃₂H₂₅O₃ [M+H]⁺: 457.1798, found: 457.1793.



8-chloro-11-(4-chlorophenyl)-6-phenyldibenzo[a,f]azulen-12(4bH)-one (3l):

Yellow solid (42mg, 45% yield); mp 236-238 °C; R_f = 0.40 (PE/EA = 30:1).

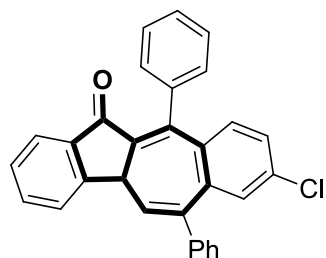
¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.67 (m, 2H), 7.48 – 7.38 (m, 3H), 7.38 – 7.28 (m, 4H), 7.27 – 7.17 (m, 5H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.09 (d, *J* = 5.0 Hz, 1H), 3.95 (d, *J* = 5.0 Hz, 1H). **¹³C {¹H} NMR (100 MHz, CDCl₃)** δ 190.0, 151.3, 143.0, 141.6, 141.3, 140.1, 140.0, 139.2, 138.4, 137.0, 135.5, 135.4, 134.6, 133.8, 133.1, 131.7, 130.5, 128.9, 128.7, 128.5, 128.4, 128.0, 127.3, 125.6, 124.3, 42.0. **HRMS (ESI)** calcd. for C₃₀H₁₉Cl₂O [M+H]⁺: 465.0807, found: 465.0803.



8-bromo-11-(4-bromophenyl)-6-phenyldibenzo[a,f]azulen-12(4bH)-one (3m):

Yellow solid (60mg, 54% yield); mp 154-156 °C; $R_f = 0.40$ (PE/EA = 30:1).

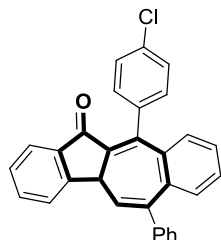
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.7$ Hz, 1H), 7.68 (m, 2H), 7.56 (t, $J = 5.3$ Hz, 2H), 7.50 (d, $J = 2.1$ Hz, 1H), 7.47 – 7.42 (m, 1H), 7.37 – 7.29 (m, 4H), 7.26 – 7.22 (m, 2H), 7.17 – 7.11 (m, 2H), 7.03 (d, $J = 8.6$ Hz, 1H), 6.09 (d, $J = 5.0$ Hz, 1H), 3.94 (d, $J = 5.0$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.0, 151.3, 143.0, 141.5, 141.4, 140.0, 139.8, 139.5, 138.5, 137.4, 135.5, 135.4, 133.4, 133.2, 131.9, 131.4, 130.1, 128.9, 128.7, 128.4, 128.1, 125.6, 124.3, 122.9, 122.2, 42.0. HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{19}\text{Br}_2\text{O}$ $[\text{M}+\text{H}]^+$: 552.9797, found: 552.9792.



8-chloro-6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3n):

Yellow solid (28mg, 33% yield); mp 86-88 °C; $R_f = 0.40$ (PE/EA = 30:1).

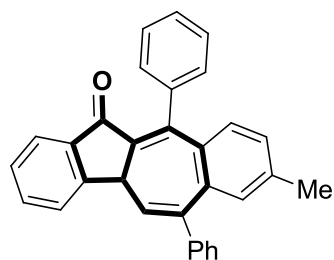
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.6$ Hz, 1H), 7.71 – 7.64 (m, 2H), 7.46 – 7.41 (m, 4H), 7.37 – 7.30 (m, 4H), 7.30 – 7.24 (m, 4H), 7.20 – 7.12 (m, 2H), 6.10 (d, $J = 5.0$ Hz, 1H), 3.96 (d, $J = 5.0$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.0, 151.3, 144.4, 141.7, 141.2, 140.1, 140.0, 139.6, 138.7, 138.1, 135.5, 135.2, 133.6, 133.3, 130.3, 130.2, 128.9, 128.6, 128.5, 128.3, 128.2, 128.0, 127.1, 125.6, 124.3, 42.0. HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{20}\text{ClO}$ $[\text{M}+\text{H}]^+$: 431.1197, found: 431.1187.



11-(4-chlorophenyl)-6-phenyldibenzo[a,f]azulen-12(4bH)-one (3n'):

Yellow solid (39mg, 45% yield); mp 181-183 °C; $R_f = 0.40$ (PE/EA = 30:1).

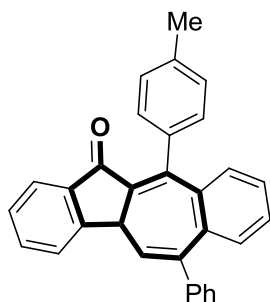
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 – 7.74 (m, 1H), 7.70 – 7.62 (m, 2H), 7.48 – 7.35 (m, 4H), 7.34 – 7.20 (m, 9H), 7.19 – 7.14 (m, 1H), 6.07 (d, $J = 5.0$ Hz, 1H), 3.96 (d, $J = 5.0$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.2, 151.6, 143.9, 141.0, 140.6, 139.9, 139.7, 138.3, 137.5, 135.3, 134.5, 134.3, 131.7, 131.7, 130.9, 129.0, 128.4, 128.3, 128.3, 127.8, 127.7, 126.9, 125.6, 124.2, 42.0. HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{20}\text{ClO}$ $[\text{M}+\text{H}]^+$: 431.1197, found: 431.1193.



8-methyl-6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3o):

Yellow solid (37mg, 45% yield); mp 105-107 °C; $R_f = 0.40$ (PE/EA = 30:1).

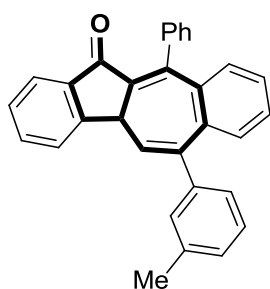
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (d, $J = 7.6$ Hz, 1H), 7.68 – 7.62 (m, 2H), 7.47 – 7.39 (m, 4H), 7.36 – 7.23 (m, 7H), 7.17 (d, $J = 7.5$ Hz, 1H), 7.10 (d, $J = 8.2$ Hz, 1H), 7.03 (dd, $J = 8.2, 1.3$ Hz, 1H), 6.05 (d, $J = 5.0$ Hz, 1H), 3.96 (d, $J = 5.0$ Hz, 1H), 2.29 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.2, 151.6, 145.6, 142.6, 140.9, 140.2, 139.6, 139.3, 138.5, 137.7, 137.2, 134.9, 134.3, 131.8, 131.0, 130.2, 129.0, 128.4, 128.2, 128.1, 128.0, 127.9, 127.5, 125.5, 124.1, 42.1, 21.5. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$: 411.1743, found: 431.1746.



6-phenyl-11-(p-tolyl)dibenzo[a,f]azulen-12(4bH)-one (3o'):

Yellow solid (33mg, 40% yield); mp 70-72 °C; $R_f = 0.40$ (PE/EA = 30:1).

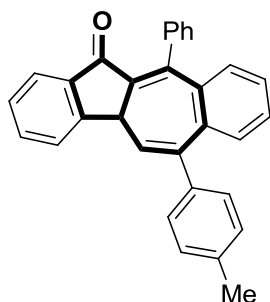
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 – 7.74 (m, 1H), 7.67 – 7.63 (m, 2H), 7.45 – 7.39 (m, 1H), 7.37 – 7.21 (m, 11H), 7.21 – 7.15 (m, 2H), 6.07 (d, $J = 5.0$ Hz, 1H), 3.95 (d, $J = 5.0$ Hz, 1H), 2.43 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.2, 151.6, 145.7, 142.5, 141.3, 140.9, 140.2, 139.7, 138.1, 137.9, 136.3, 135.0, 134.6, 131.9, 130.7, 130.2, 129.0, 128.8, 128.4, 128.1, 127.6, 127.5, 126.7, 125.5, 124.2, 42.1, 21.6. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$: 411.1743, found: 431.1740.



11-phenyl-6-(m-tolyl)dibenzo[a,f]azulen-12(4bH)-one (3p):

Yellow solid (52mg, 64% yield); mp 200-202 °C; $R_f = 0.40$ (PE/EA = 30:1).

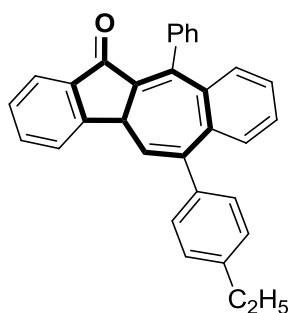
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.6$ Hz, 1H), 7.66 (dd, $J = 4.7, 0.9$ Hz, 2H), 7.46 – 7.39 (m, 4H), 7.36 (d, $J = 7.7$ Hz, 1H), 7.24 (m, 6H), 7.12 – 7.01 (m, 3H), 6.06 (d, $J = 5.0$ Hz, 1H), 3.95 (d, $J = 5.0$ Hz, 1H), 2.33 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.2, 151.6, 145.3, 142.4, 141.1, 141.0, 140.1, 139.7, 139.2, 138.0, 137.9, 135.0, 134.3, 131.7, 130.8, 130.2, 129.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.5, 126.7, 126.2, 125.6, 124.2, 42.0, 21.5. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$: 411.1743, found: 411.1751.



11-phenyl-6-(p-tolyl)dibenzo[a,f]azulen-12(4bH)-one (3q):

Yellow solid (37mg, 45% yield); mp 218-220 °C; $R_f = 0.40$ (PE/EA = 30:1).

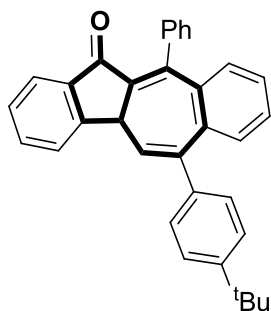
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (dd, $J = 8.0, 4.7$ Hz, 1H), 7.68 – 7.65 (m, 2H), 7.46 – 7.40 (m, 4H), 7.37 (d, $J = 7.7$ Hz, 1H), 7.31 – 7.23 (m, 4H), 7.22 – 7.08 (m, 6H), 6.05 (d, $J = 5.0$ Hz, 1H), 3.95 (d, $J = 5.0$ Hz, 1H), 2.35 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.3, 151.7, 145.3, 141.1, 140.8, 140.1, 139.8, 139.7, 139.2, 137.4, 135.0, 133.9, 131.7, 130.8, 130.2, 129.3, 129.1, 128.9, 128.7, 128.3, 128.2, 128.1, 128.0, 127.5, 126.7, 125.6, 124.2, 42.1, 21.3. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$: 411.1743, found: 411.1734.



6-(4-ethylphenyl)-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3r):

Yellow solid (55mg, 65% yield); mp 194-196 °C; $R_f = 0.40$ (PE/EA = 30:1).

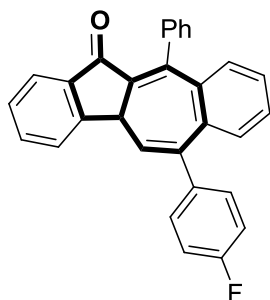
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.5$ Hz, 1H), 7.66 (dd, $J = 4.8, 1.0$ Hz, 2H), 7.46 – 7.36 (m, 5H), 7.31 – 7.23 (m, 3H), 7.22 – 7.11 (m, 6H), 6.06 (d, $J = 5.0$ Hz, 1H), 3.96 (d, $J = 5.0$ Hz, 1H), 2.65 (q, $J = 7.6$ Hz, 2H), 1.24 (t, $J = 7.6$ Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.3, 151.7, 145.3, 143.8, 141.1, 140.8, 140.1, 140.0, 139.8, 139.2, 138.1, 135.0, 133.9, 131.7, 130.8, 130.2, 128.9, 128.2, 128.1, 128.0, 127.9, 127.5, 126.7, 125.6, 124.2, 42.0, 28.7, 15.7. HRMS (ESI) calcd. for $\text{C}_{32}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}]^+$: 425.1900, found: 425.1906.



6-(4-(tert-butyl)phenyl)-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3s):

Yellow solid (60mg, 67% yield); mp 118-120 °C; $R_f = 0.40$ (PE/EA = 30:1).

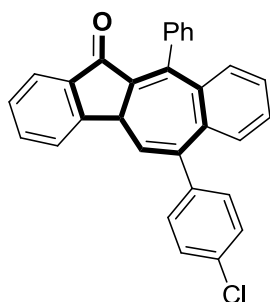
¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 3.7 Hz, 2H), 7.45 – 7.39 (m, 5H), 7.34 – 7.23 (m, 6H), 7.22 – 7.17 (m, 3H), 6.07 (d, *J* = 5.0 Hz, 1H), 3.96 (d, *J* = 5.0 Hz, 1H), 1.32 (s, 9H). **¹³C {¹H} NMR (100 MHz, CDCl₃)** δ 190.2, 151.7, 150.7, 145.3, 141.1, 140.7, 140.1, 139.7, 139.5, 139.2, 138.1, 135.0, 134.0, 131.7, 130.9, 130.2, 128.6, 128.2, 128.1, 128.0, 127.5, 126.7, 125.6, 125.3, 124.2, 42.0, 34.7, 31.5. **HRMS (ESI)** calcd. for C₃₄H₂₉O [M+H]⁺: 453.2213, found: 453.2211.



6-(4-fluorophenyl)-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3t):

Yellow solid (43mg, 52% yield); mp 204-206 °C; R_f = 0.40 (PE/EA = 30:1).

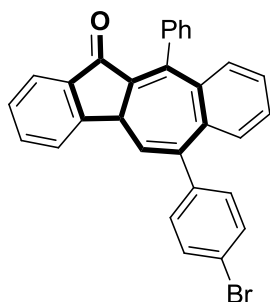
¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.47 – 7.41 (m, 4H), 7.31 – 7.20 (m, 8H), 7.05 – 6.97 (m, 2H), 6.04 (d, *J* = 5.0 Hz, 1H), 3.96 (d, *J* = 5.0 Hz, 1H). **¹³C {¹H} NMR (100 MHz, CDCl₃)** δ 190.2, 162.5 (d, *J* = 246.9 Hz), 151.5, 145.3, 141.1, 140.1, 139.9, 139.5, 139.1, 138.6 (d, *J* = 3.4 Hz), 138.1, 135.1, 134.4, 131.9, 130.6 (d, *J* = 4.1 Hz), 130.2, 128.3 (d, *J* = 4.8 Hz), 128.1, 127.7, 126.9, 125.5, 124.2, 115.3 (d, *J* = 21.4 Hz), 42.0. **HRMS (ESI)** calcd. for C₃₀H₁₉FN₁O [M+H]⁺: 437.1312, found: 437.1310.



6-(4-chlorophenyl)-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3u):

Yellow solid (63mg, 73% yield); mp 190-192 °C; R_f = 0.40 (PE/EA = 30:1).

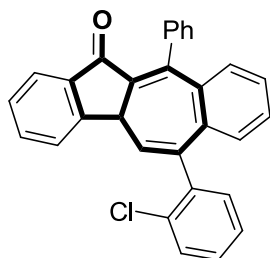
¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.47 – 7.40 (m, 4H), 7.33 – 7.24 (m, 6H), 7.21 (m, 4H), 6.07 (d, *J* = 5.0 Hz, 1H), 3.96 (d, *J* = 5.0 Hz, 1H). **¹³C {¹H} NMR (100 MHz, CDCl₃)** δ 190.1, 151.4, 145.4, 141.1, 140.9, 140.1, 139.8, 139.2, 139.0, 138.0, 135.1, 134.8, 133.6, 131.9, 130.6, 130.3, 130.2, 128.6, 128.3, 128.3, 128.1, 127.7, 127.0, 125.5, 124.2, 42.0. **HRMS (ESI)** calcd. for C₃₀H₂₀ClO [M+H]⁺: 431.1197, found: 431.1208.



6-(4-bromophenyl)-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3v):

Yellow solid (59mg, 63% yield); mp 192-194 °C; $R_f = 0.40$ (PE/EA = 30:1).

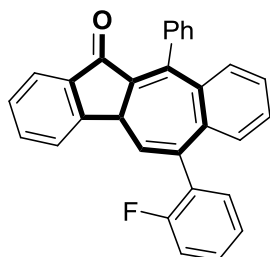
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.7$ Hz, 1H), 7.70 – 7.61 (m, 2H), 7.47 – 7.38 (m, 6H), 7.34 – 7.19 (m, 6H), 7.17 – 7.09 (m, 2H), 6.07 (d, $J = 5.0$ Hz, 1H), 3.95 (d, $J = 5.0$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 190.1, 151.3, 145.3, 141.4, 141.1, 140.1, 139.9, 139.1, 139.0, 138.0, 135.1, 134.8, 131.9, 131.6, 130.6, 130.5, 130.2, 128.3, 128.2, 128.1, 127.7, 127.0, 125.5, 124.2, 121.8, 42.0. **HRMS (ESI)** calcd. for $\text{C}_{30}\text{H}_{20}\text{BrO}$ $[\text{M}+\text{H}]^+$: 475.0692, found: 475.0695.



6-(2-chlorophenyl)-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3w):

Yellow solid (66mg, 77% yield); mp 166-168 °C; $R_f = 0.40$ (PE/EA = 30:1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.6$ Hz, 1H), 7.64 (dd, $J = 4.8, 1.0$ Hz, 2H), 7.45 – 7.38 (m, 4H), 7.36 – 7.25 (m, 5H), 7.26 – 7.11 (m, 5H), 6.01 (d, $J = 4.7$ Hz, 1H), 4.05 (d, $J = 4.6$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 190.2, 151.2, 146.0, 140.9, 140.6, 140.1, 139.5, 139.3, 137.4, 137.2, 135.0, 133.8, 132.3, 132.1, 130.1, 130.0, 129.2, 128.9, 128.2, 128.1, 128.0, 127.9, 126.8, 126.6, 125.5, 124.2, 41.8. **HRMS (ESI)** calcd. for $\text{C}_{30}\text{H}_{20}\text{ClO}$ $[\text{M}+\text{H}]^+$: 431.1197, found: 431.1194.

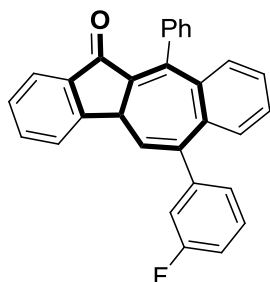


6-(2-fluorophenyl)-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3x):

Yellow solid (53mg, 65% yield); mp 158-160 °C; $R_f = 0.40$ (PE/EA = 30:1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.7$ Hz, 1H), 7.68 – 7.63 (m, 2H), 7.46 – 7.39 (m, 4H), 7.35 (td, $J = 7.6, 1.8$ Hz, 1H), 7.32 – 7.24 (m, 5H), 7.23 – 7.18 (m, 2H), 7.14 (td, $J = 7.5, 1.2$ Hz, 1H), 7.05 – 6.96 (m, 1H), 6.09 (d, $J = 4.8$ Hz, 1H), 4.02 (d, $J = 4.8$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 190.1, 160.2 (d, $J = 248.4$ Hz),

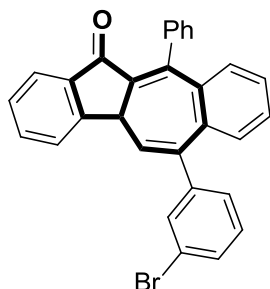
151.3, 145.7, 140.3, 140.1, 139.6, 139.3, 137.7, 137.3, 135.4, 135.1, 132.0, 131.6 (d, $J = 3.3$ Hz), 130.1, 130.0, 129.9, 129.6 (d, $J = 8.2$ Hz), 129.2, 128.2 (d, $J = 1.5$ Hz), 128.0, 127.8, 126.7, 125.6, 124.2 (d, $J = 3.7$ Hz), 116.0 (d, $J = 22.1$ Hz), 42.0. **HRMS (ESI)** calcd. for $C_{30}H_{20}FO$ $[M+H]^+$: 415.1493, found: 415.1495.



6-(3-fluorophenyl)-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3y):

Yellow solid (65mg, 79% yield); mp 178-180 °C; $R_f = 0.40$ (PE/EA = 30:1).

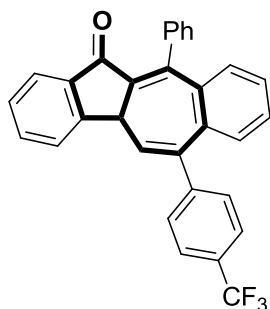
1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, $J = 7.7$ Hz, 1H), 7.66 (dd, $J = 6.3, 1.1$ Hz, 2H), 7.47 – 7.40 (m, 4H), 7.34 (d, $J = 7.5$ Hz, 1H), 7.31 – 7.19 (m, 6H), 7.06 – 7.02 (m, 1H), 7.01 – 6.93 (m, 2H), 6.10 (d, $J = 5.0$ Hz, 1H), 3.97 (d, $J = 5.0$ Hz, 1H). ^{13}C { 1H } NMR (100 MHz, $CDCl_3$) δ 190.1, 162.9 (d, $J = 245.9$ Hz), 151.3, 145.4, 144.6 (d, $J = 7.6$ Hz), 141.1, 140.1, 139.9 (d, $J = 2.2$ Hz), 139.0 (d, $J = 6.3$ Hz), 138.0, 135.2 (d, $J = 12.3$ Hz), 131.9, 130.6, 130.2, 129.9 (d, $J = 8.4$ Hz), 128.3 (d, $J = 2.9$ Hz), 128.1, 127.7, 127.0, 125.55, 124.7 (d, $J = 2.8$ Hz), 124.2, 115.8 (d, $J = 21.9$ Hz), 114.5 (d, $J = 21.2$ Hz), 42.0. **HRMS (ESI)** calcd. for $C_{30}H_{20}FO$ $[M+H]^+$: 415.1493, found: 415.1489.



6-(3-bromophenyl)-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3z):

Yellow solid (63mg, 67% yield); mp 194-196 °C; $R_f = 0.40$ (PE/EA = 30:1).

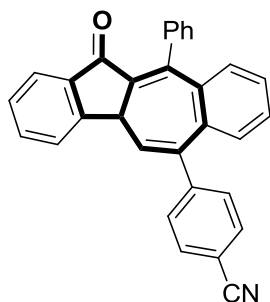
1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, $J = 7.7$ Hz, 1H), 7.67 (dd, $J = 6.2, 1.1$ Hz, 2H), 7.48 – 7.39 (m, 6H), 7.32 – 7.20 (m, 6H), 7.18 (m, 2H), 6.09 (d, $J = 5.0$ Hz, 1H), 3.97 (d, $J = 5.0$ Hz, 1H). ^{13}C { 1H } NMR (100 MHz, $CDCl_3$) δ 190.0, 151.3, 145.4, 144.5, 141.1, 140.0, 139.7, 139.0, 138.9, 137.9, 135.4, 135.2, 131.9, 131.8, 130.7, 130.6, 130.2, 129.9, 128.3, 128.2, 128.1, 127.8, 127.7, 127.1, 125.6, 124.3, 122.6, 42.0. **HRMS (ESI)** calcd. for $C_{30}H_{20}BrO$ $[M+H]^+$: 475.0692, found: 475.0691.



11-phenyl-6-(4-(trifluoromethyl)phenyl)dibenzo[a,f]azulen-12(4bH)-one (3aa):

Yellow solid (43mg, 46% yield); mp 116-118 °C; $R_f = 0.40$ (PE/EA = 30:1).

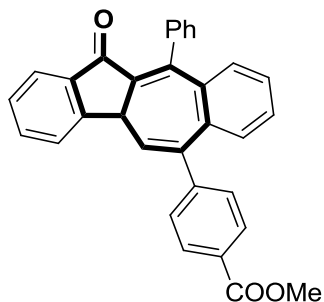
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 (d, $J = 7.7$ Hz, 1H), 7.71 – 7.64 (m, 2H), 7.57 (d, $J = 8.2$ Hz, 2H), 7.46 – 7.42 (m, 3H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.31 – 7.21 (m, 7H), 6.15 (d, $J = 5.0$ Hz, 1H), 4.00 (d, $J = 5.0$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 190.0, 151.2, 146.1, 145.5, 141.2, 140.1, 139.9, 139.0, 138.8, 137.9, 136.0, 135.2, 132.0, 130.6, 129.7 (q, $J = 33$ Hz), 128.1, 127.8, 127.2, 125.5, 125.4 (q, $J = 3.8$ Hz), 124.3, 124.2 (q, $J = 270.4$ Hz), 42.1. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{20}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 465.1461, found: 465.1467.



4-(12-oxo-11-phenyl-4b,12-dihydrodibenzo[a,f]azulen-6-yl)benzonitrile (3ab):

Yellow solid (30mg, 36% yield); mp 150-152 °C; $R_f = 0.40$ (PE/EA = 30:1).

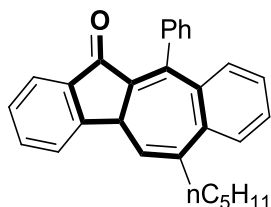
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 (d, $J = 7.6$ Hz, 1H), 7.72 – 7.59 (m, 4H), 7.47 – 7.42 (m, 3H), 7.40 – 7.36 (m, 2H), 7.30 – 7.23 (m, 8H), 6.17 (d, $J = 5.1$ Hz, 1H), 4.01 (d, $J = 5.1$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 190.0, 151.0, 146.9, 145.5, 141.2, 139.6, 138.8, 138.3, 137.9, 136.8, 135.3, 132.3, 132.1, 130.5, 130.1, 129.6, 128.4, 128.2, 127.9, 127.4, 125.5, 124.4, 118.9, 111.4, 42.2. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$: 422.1539, found: 422.1545.



methyl 4-(12-oxo-11-phenyl-4b,12-dihydrodibenzo[a,f]azulen-6-yl)benzoate (3ac):

Yellow solid (47mg, 52% yield); mp 198-200 °C; $R_f = 0.30$ (PE/EA = 30:1).

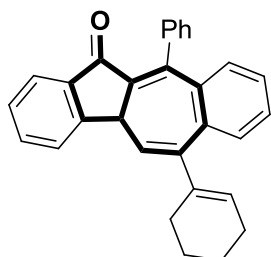
^1H NMR (400 MHz, CDCl_3) δ 8.01 – 7.96 (m, 2H), 7.77 (d, J = 7.6 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.47 – 7.41 (m, 4H), 7.37 – 7.32 (m, 2H), 7.32 – 7.26 (m, 4H), 7.26 – 7.21 (m, 2H), 6.17 (d, J = 5.1 Hz, 1H), 4.00 (d, J = 5.0 Hz, 1H), 3.91 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.0, 167.0, 151.3, 146.9, 140.2, 139.0, 138.9, 135.9, 135.2, 131.9, 130.6, 130.2, 129.8, 129.3, 128.9, 128.3, 128.2, 128.1, 127.7, 127.1, 125.6, 124.3, 52.3, 42.1. HRMS (ESI) calcd. for $\text{C}_{32}\text{H}_{23}\text{O}_3$ $[\text{M}+\text{H}]^+$: 455.1642, found: 455.1645.



6-pentyl-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3ad):

Yellow solid (31mg, 40% yield); mp 172-174 °C; R_f = 0.40 (PE/EA = 30:1).

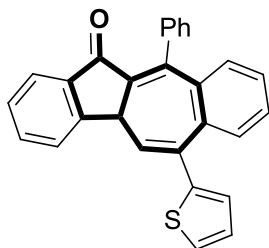
^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 7.6 Hz, 1H), 7.64 (ddd, J = 9.8, 8.4, 4.5 Hz, 2H), 7.55 (dd, J = 7.6, 0.7 Hz, 1H), 7.45 – 7.33 (m, 5H), 7.22 – 7.12 (m, 4H), 5.78 (d, J = 4.7 Hz, 1H), 3.80 (d, J = 4.2 Hz, 1H), 2.87 – 2.77 (m, 1H), 2.47 – 2.27 (m, 1H), 1.40 – 1.11 (m, 6H), 0.80 (t, J = 7.1 Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.5, 151.9, 145.1, 140.4, 140.1, 139.8, 139.4, 139.0, 138.6, 135.0, 133.3, 132.2, 130.0, 128.1, 128.0, 127.9, 127.1, 126.2, 125.5, 124.1, 41.5, 36.2, 31.3, 28.7, 22.5, 14.1. HRMS (ESI) calcd. for $\text{C}_{29}\text{H}_{27}\text{O}$ $[\text{M}+\text{H}]^+$: 391.2056, found: 391.2054.



6-(cyclohex-1-en-1-yl)-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3ae):

Yellow solid (46mg, 58% yield); mp 192-194 °C; R_f = 0.40 (PE/EA = 30:1).

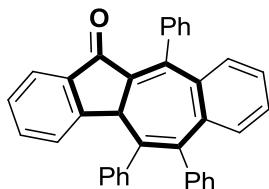
^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, J = 7.6 Hz, 1H), 7.65 – 7.55 (m, 3H), 7.44 – 7.36 (m, 4H), 7.35 – 7.28 (m, 1H), 7.26 – 7.20 (m, 2H), 7.15 (dtd, J = 9.4, 8.0, 1.4 Hz, 2H), 5.86 (d, J = 5.0 Hz, 1H), 5.81 (s, 1H), 3.83 (d, J = 5.0 Hz, 1H), 2.12 (dd, J = 13.9, 5.1 Hz, 3H), 1.89 (d, J = 18.4 Hz, 1H), 1.62 (ddd, J = 20.8, 14.5, 8.5 Hz, 5H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.5, 151.9, 145.2, 143.0, 140.9, 140.1, 139.2, 138.8, 138.7, 138.5, 134.9, 131.7, 131.5, 130.2, 130.0, 128.1, 128.0, 127.9, 127.3, 126.3, 125.6, 124.1, 41.7, 28.3, 25.9, 23.1, 22.3. HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}]^+$: 401.1900, found: 401.1896.



11-phenyl-6-(thiophen-2-yl)dibenzo[a,f]azulen-12(4bH)-one(3af):

Yellow solid (35mg, 44% yield); mp 202-204 °C; $R_f = 0.30$ (PE/EA = 30:1).

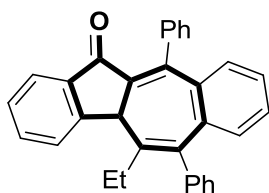
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.6$ Hz, 1H), 7.70 – 7.60 (m, 2H), 7.56 – 7.51 (m, 1H), 7.46 – 7.39 (m, 4H), 7.33 – 7.19 (m, 6H), 7.16 (dd, $J = 3.0, 1.2$ Hz, 1H), 7.00 (dd, $J = 5.0, 1.3$ Hz, 1H), 6.16 (d, $J = 5.1$ Hz, 1H), 3.93 (t, $J = 12.2$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 190.2, 151.5, 145.3, 143.2, 140.7, 140.1, 139.3, 139.1, 138.3, 135.4, 135.1, 133.7, 131.7, 130.3, 130.2, 128.3, 128.2, 128.1, 128.0, 127.6, 126.9, 125.6, 125.5, 124.2, 123.0, 41.9. HRMS (ESI) calcd. for $\text{C}_{28}\text{H}_{19}\text{OS}$ $[\text{M}+\text{H}]^+$: 403.1151, found: 403.1148.



5,6,11-triphenyldibenzo[a,f]azulen-12(4bH)-one (3ag):

Yellow solid (73mg, 77% yield); mp 228-230 °C; $R_f = 0.30$ (PE/EA = 30:1).

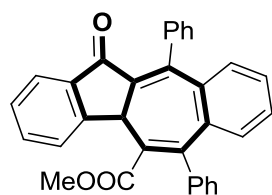
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56 (d, $J = 7.6$ Hz, 1H), 7.51 – 7.43 (m, 3H), 7.40 – 7.30 (m, 5H), 7.28 – 7.21 (m, 2H), 7.21 – 7.12 (m, 2H), 7.11 – 6.94 (m, 6H), 6.79 (s, 4H), 4.16 (s, 1H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 190.2, 149.7, 145.0, 143.8, 142.3, 141.1, 141.0, 140.4, 139.5, 138.8, 138.5, 137.0, 133.5, 131.3, 130.9, 130.3, 128.3, 128.2, 127.8, 127.7, 127.6, 127.1, 126.4, 126.3, 126.3, 123.8, 47.1. HRMS (ESI) calcd. for $\text{C}_{36}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}]^+$: 473.1900, found: 473.1895.



5-ethyl-6,11-diphenyldibenzo[a,f]azulen-12(4bH)-one (3ah):

Yellow solid (57mg, 68% yield); mp 148-150 °C; $R_f = 0.30$ (PE/EA = 30:1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (d, $J = 7.7$ Hz, 1H), 7.65 – 7.59 (m, 2H), 7.45 (m, 4H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.33 – 7.27 (m, 3H), 7.23 – 7.12 (m, 5H), 7.08 (ddd, $J = 8.3, 6.5, 1.6$ Hz, 1H), 3.92 (s, 1H), 2.06 (dq, $J = 15.1, 7.5$ Hz, 1H), 1.86 (dq, $J = 14.5, 7.3$ Hz, 1H), 0.46 (t, $J = 7.4$ Hz, 3H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 190.1, 149.5, 145.0, 143.9, 142.8, 141.7, 141.6, 139.8, 139.6, 138.8, 135.6, 133.9, 131.0, 130.9, 130.3, 130.0, 128.4, 128.3, 128.2, 128.1, 127.7, 127.6, 126.8, 125.7, 124.3, 46.1, 24.7, 15.7. HRMS (ESI) calcd. for $\text{C}_{32}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}]^+$: 425.1900, found: 425.1897.

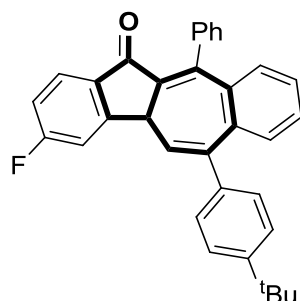


methyl 12-oxo-6,11-diphenyl-4b,12-dihydrodibenzo[a,f]azulene-5-carboxylate (3ai):

Yellow solid (41mg, 45% yield); mp 124-126 °C; $R_f = 0.30$ (PE/EA = 30:1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (d, $J = 7.6$ Hz, 1H), 7.67 – 7.57 (m, 2H), 7.46 (dd, $J = 5.2, 1.9$ Hz, 3H), 7.31 (m, 5H), 7.28 – 7.19 (m, 8H), 4.10 (s, 1H), 2.93 (s, 3H).

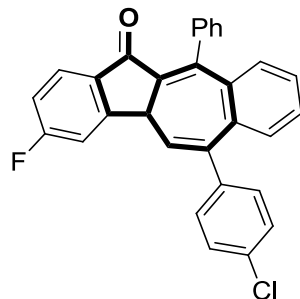
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 189.6, 166.9, 147.7, 141.0, 140.5, 140.4, 139.6, 138.7, 134.1, 131.5, 131.4, 130.2, 130.1, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 127.3, 124.0, 51.4, 43.3. HRMS (ESI) calcd. for $\text{C}_{32}\text{H}_{23}\text{O}_3$ $[\text{M}+\text{H}]^+$: 455.1642, found: 455.1644.



6-(4-(tert-butyl)phenyl)-3-fluoro-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3aj):

Yellow solid (39mg, 42% yield); mp 182-184 °C; $R_f = 0.40$ (PE/EA = 30:1).

$^1\text{H NMR}$ (400 MHz, acetone) δ 7.74 (dd, $J = 8.4, 5.4$ Hz, 1H), 7.60 (dd, $J = 8.7, 2.3$ Hz, 1H), 7.43 – 7.25 (m, 13H), 7.16 (d, $J = 7.9$ Hz, 1H), 6.14 (d, $J = 5.0$ Hz, 1H), 3.93 (d, $J = 5.0$ Hz, 1H), 1.31 (s, 9H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, acetone) δ 188.2, 167.9 (d, $J = 253.2$ Hz), 155.2 (d, $J = 10.1$ Hz), 151.3, 145.4, 141.9, 141.5, 140.4, 140.2, 140.0, 138.8, 137.2 (d, $J = 1.9$ Hz), 134.0, 132.2, 131.3, 131.1, 129.3, 128.7, 128.6, 128.4, 127.6, 126.9, 126.8, 126.1, 116.9 (d, $J = 23.9$ Hz), 113.6 (d, $J = 22.9$ Hz), 42.6 (d, $J = 2.1$ Hz), 35.1, 31.9. HRMS (ESI) calcd. for $\text{C}_{34}\text{H}_{28}\text{FO}$ $[\text{M}+\text{H}]^+$: 471.2119, found: 471.2113.

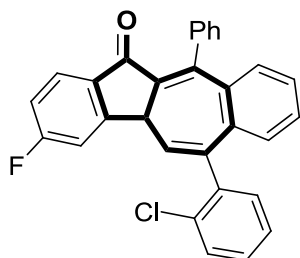


6-(4-chlorophenyl)-3-fluoro-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3ak):

Yellow solid (57mg, 64% yield); mp 118-120 °C; $R_f = 0.40$ (PE/EA = 30:1).

$^1\text{H NMR}$ (400 MHz, acetone) δ 7.74 (dd, $J = 8.4, 5.4$ Hz, 1H), 7.60 (dd, $J = 8.8, 2.2$ Hz, 1H), 7.44 – 7.34 (m, 8H), 7.34 – 7.25 (m, 5H), 7.18 – 7.12 (m, 1H), 6.19 (d, $J =$

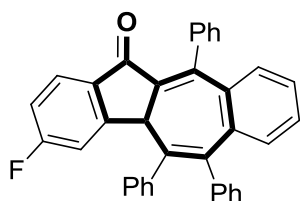
5.0 Hz, 1H), 3.94 (d, $J = 5.0$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, acetone) δ 188.2, 167.9 (d, $J = 253.3$ Hz), 155.0 (d, $J = 10.0$ Hz), 145.5, 141.9 (d, $J = 10.3$ Hz), 140.4, 140.0, 139.8, 138.7, 137.2 (d, $J = 1.7$ Hz), 135.2, 133.9, 132.4, 131.3, 131.2 (d, $J = 4.3$ Hz), 129.3, 128.8, 128.6, 128.5, 127.8, 126.9, 126.8, 117.0 (d, $J = 23.9$ Hz), 113.7 (d, $J = 22.9$ Hz), 42.6 (d, $J = 2.1$ Hz). HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{19}\text{ClFO}$ $[\text{M}+\text{H}]^+$: 449.1103, found: 449.1106.



6-(2-chlorophenyl)-3-fluoro-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3al):

Yellow solid (55mg, 62% yield); mp 124-126 °C; $R_f = 0.40$ (PE/EA = 30:1).

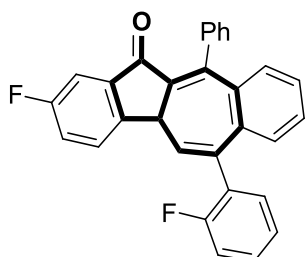
^1H NMR (400 MHz, acetone) δ 7.75 (dd, $J = 8.4, 5.4$ Hz, 1H), 7.68 (d, $J = 6.8$ Hz, 1H), 7.58 (m, 1H), 7.48 – 7.37 (m, 6H), 7.34 – 7.19 (m, 5H), 7.19 – 7.06 (m, 2H), 6.08 (d, $J = 4.7$ Hz, 1H), 4.04 (d, $J = 4.7$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, acetone) δ 188.2, 167.9 (d, $J = 253.3$ Hz), 154.8 (d, $J = 10.1$ Hz), 146.0, 141.5 (d, $J = 7.5$ Hz), 140.4, 140.1, 138.2, 137.4, 137.2 (d, $J = 2.0$ Hz), 134.0, 133.3, 132.8, 131.0, 130.6, 130.4, 129.4, 128.8, 128.7, 128.6, 128.1, 127.4, 126.9, 126.8, 117.0 (d, $J = 23.9$ Hz), 113.5 (d, $J = 22.9$ Hz), 42.4 (d, $J = 2.1$ Hz). HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{19}\text{ClFO}$ $[\text{M}+\text{H}]^+$: 449.1103, found: 449.1119.



3-fluoro-5,6,11-triphenyldibenzo[a,f]azulen-12(4bH)-one (3am):

Yellow solid (64mg, 66% yield); mp 216-218 °C; $R_f = 0.30$ (PE/EA = 30:1).

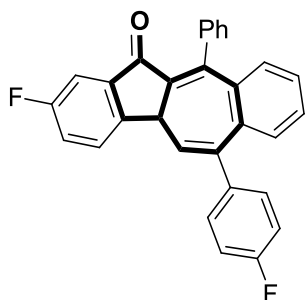
^1H NMR (400 MHz, acetone) δ 7.53 – 7.50 (m, 1H), 7.45 (dd, $J = 5.1, 1.9$ Hz, 3H), 7.42 – 7.23 (m, 7H), 7.22 – 7.17 (m, 1H), 7.07 (m, 8H), 6.84 (t, $J = 7.1$ Hz, 2H), 4.16 (s, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, acetone) δ 188.2, 166.7 (d, $J = 252.2$ Hz), 153.4 (d, $J = 10.4$ Hz), 145.2, 143.9, 143.1, 141.8, 141.1, 140.1, 139.7, 139.4, 138.2 (d, $J = 1.9$ Hz), 137.7 131.9, 131.6, 131.4, 131.1, 128.8 (d, $J = 1.1$ Hz), 128.5, 128.4, 127.8, 127.2 (d, $J = 2.8$ Hz), 126.3, 126.2, 116.3 (dd, $J = 23.5, 7.5$ Hz), 47.6 (d, $J = 2.1$ Hz). HRMS (ESI) calcd. for $\text{C}_{36}\text{H}_{24}\text{FO}$ $[\text{M}+\text{H}]^+$: 491.1806, found: 491.1820.



2-fluoro-6-(2-fluorophenyl)-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3an):

Yellow solid (65mg, 76% yield); mp 132-134 °C; $R_f = 0.40$ (PE/EA = 30:1).

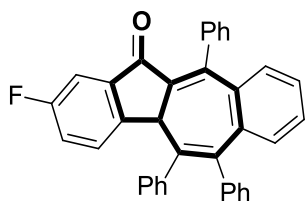
$^1\text{H NMR}$ (400 MHz, acetone) δ 7.86 (dd, $J = 8.4, 4.6$ Hz, 1H), 7.58 – 7.49 (m, 2H), 7.45 – 7.20 (m, 10H), 7.18 – 7.01 (m, 3H), 6.12 (d, $J = 4.9$ Hz, 1H), 3.97 (d, $J = 4.8$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, acetone) δ 188.8 (d, $J = 3.1$ Hz), 163.7 (d, $J = 246.5$ Hz), 160.8 (d, $J = 246.8$ Hz), 147.7 (d, $J = 2.2$ Hz), 146.3, 142.5 (d, $J = 7.3$ Hz), 142.9, 140.9, 140.4 (d, $J = 0.7$ Hz), 140.1, 138.8 (d, $J = 1.1$ Hz), 136.2, 132.6 (d, $J = 4.0$ Hz), 130.9, 130.8 (d, $J = 8.3$ Hz), 130.7, 130.5, 129.6 (d, $J = 0.9$ Hz), 128.9 (d, $J = 8.2$ Hz), 128.8, 128.6, 127.5, 125.3 (d, $J = 3.7$ Hz), 123.3, 123.1, 116.5 (d, $J = 22.0$ Hz), 109.9 (d, $J = 22.2$ Hz), 42.1. **HRMS (ESI)** calcd. for $\text{C}_{30}\text{H}_{19}\text{F}_2\text{O}$ $[\text{M}+\text{H}]^+$: 433.1398, found: 433.1395.



2-fluoro-6-(4-fluorophenyl)-11-phenyldibenzo[a,f]azulen-12(4bH)-one (3ao):

Yellow solid (48mg, 56% yield); mp 172-174 °C; $R_f = 0.40$ (PE/EA = 30:1).

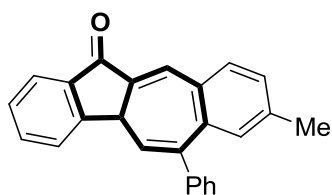
$^1\text{H NMR}$ (400 MHz, acetone) δ 7.88 (dd, $J = 8.4, 4.6$ Hz, 1H), 7.55 (ddd, $J = 9.1, 8.5, 2.6$ Hz, 1H), 7.44 – 7.25 (m, 11H), 7.15 (m, 4.8 Hz, 3H), 6.12 (d, $J = 5.0$ Hz, 1H), 3.92 (d, $J = 5.0$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, acetone) δ 188.9 (d, $J = 3.0$ Hz), 163.5 (dd, $J = 245.8, 45.9$ Hz), 147.9 (d, $J = 2.2$ Hz), 146.1, 142.5 (d, $J = 7.3$ Hz), 141.9, 140.5, 140.2, 140.0, 139.5 (d, $J = 3.3$ Hz), 139.1, 135.3, 132.4, 131.7, 131.6, 131.2, 131.1, 129.1, 129.0, 128.8, 128.6 (d, $J = 3.2$ Hz), 127.7, 123.3, 123.1, 115.9 (d, $J = 21.6$ Hz), 109.9 (d, $J = 22.2$ Hz), 42.2. **HRMS (ESI)** calcd. for $\text{C}_{30}\text{H}_{19}\text{F}_2\text{O}$ $[\text{M}+\text{H}]^+$: 433.1398, found: 433.1413.



2-fluoro-5,6,11-triphenyldibenzo[a,f]azulen-12(4bH)-one (3ap):

Yellow solid (64mg, 65% yield); mp 228-230 °C; $R_f = 0.30$ (PE/EA = 30:1).

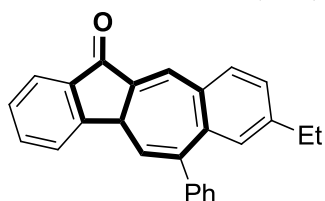
$^1\text{H NMR}$ (400 MHz, acetone) δ 7.69 (dd, $J = 8.4, 4.7$ Hz, 1H), 7.52 – 7.42 (m, 4H), 7.40 – 7.16 (m, 8H), 7.15 – 6.97 (m, 7H), 6.84 (m, 2H), 4.13 (s, 1H). ^{13}C { ^1H } NMR (100 MHz, acetone) δ 188.8 (d, $J = 3.0$ Hz), 163.1 (d, $J = 246.5$ Hz), 146.3 (d, $J = 2.2$ Hz), 145.6, 144.5, 143.5 (d, $J = 7.3$ Hz), 143.2, 141.9, 141.1, 140.5, 139.7, 139.5, 137.6, 131.9, 131.8, 131.7, 131.6, 131.4, 131.0, 128.8 (d, $J = 1.9$ Hz), 128.6, 128.4, 127.8, 127.2 (d, $J = 1.2$ Hz), 127.1, 121.5 (d, $J = 23.7$ Hz), 109.4 (d, $J = 22.1$ Hz), 47.2. **HRMS (ESI)** calcd. for $\text{C}_{36}\text{H}_{24}\text{FO}$ $[\text{M}+\text{H}]^+$: 491.1806, found: 491.1799.



8-methyl-6-phenyldibenzo[a,f]azulen-12(4bH)-one (4a):

Yellow solid (31mg, 46% yield); mp 66-68 °C; $R_f = 0.30$ (PE/EA = 30:1).

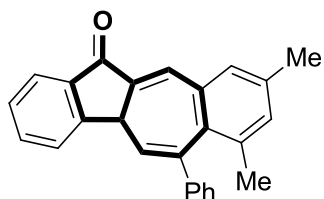
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.88 (d, $J = 7.7$ Hz, 1H), 7.76 – 7.64 (m, 3H), 7.51 (d, $J = 7.9$ Hz, 1H), 7.44 (dt, $J = 11.6, 5.8$ Hz, 1H), 7.29 – 7.23 (m, 3H), 7.21 – 7.15 (m, 3H), 7.08 (s, 1H), 5.96 (d, $J = 4.4$ Hz, 1H), 4.05 (d, $J = 3.8$ Hz, 1H), 2.29 (s, 3H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 191.5, 152.4, 143.5, 141.9, 139.6, 138.0, 135.3, 133.5, 132.7, 132.6, 131.7, 131.2, 129.2, 128.6, 128.3, 128.2, 127.5, 125.8, 124.2, 40.7, 21.6. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{19}\text{O}$ [$\text{M}+\text{H}$] $^+$: 335.1430, found: 335.1429.



8-ethyl-6-phenyldibenzo[a,f]azulen-12(4bH)-one (4b):

Yellow solid (37mg, 53% yield); mp 60-62 °C; $R_f = 0.30$ (PE/EA = 30:1).

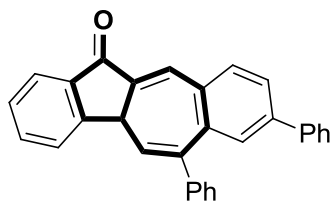
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.88 (d, $J = 7.7$ Hz, 1H), 7.75 (d, $J = 1.7$ Hz, 1H), 7.73 – 7.62 (m, 2H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.47 – 7.41 (m, 1H), 7.30 – 7.15 (m, 6H), 7.10 (d, $J = 1.4$ Hz, 1H), 5.97 (d, $J = 4.4$ Hz, 1H), 4.07 (d, $J = 3.7$ Hz, 1H), 2.58 (q, $J = 7.6$ Hz, 2H), 1.15 (t, $J = 7.6$ Hz, 3H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 191.5, 152.4, 144.2, 143.5, 141.9, 141.3, 139.6, 135.3, 133.7, 132.6, 131.8, 131.6, 131.3, 129.2, 128.2, 127.5, 127.3, 125.7, 124.2, 40.7, 28.9, 15.5. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{21}\text{O}$ [$\text{M}+\text{H}$] $^+$: 349.1587, found: 349.1583.



7,9-dimethyl-6-phenyldibenzo[a,f]azulen-12(4bH)-one (4c):

Yellow solid (36mg, 52% yield); mp 121-123 °C; $R_f = 0.30$ (PE/EA = 30:1).

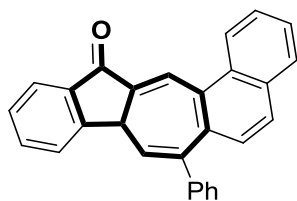
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 (d, $J = 7.7$ Hz, 1H), 7.75 – 7.64 (m, 3H), 7.48 – 7.42 (m, 1H), 7.31 – 7.28 (m, 1H), 7.22 – 7.14 (m, 3H), 7.00 (dd, $J = 7.9, 1.5$ Hz, 3H), 6.02 (d, $J = 5.4$ Hz, 1H), 3.97 – 3.89 (m, 1H), 2.41 (s, 3H), 1.90 (s, 3H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 191.6, 152.3, 143.8, 143.3, 140.2, 139.3, 139.1, 137.1, 136.5, 136.1, 135.3, 134.0, 132.4, 131.7, 131.6, 129.0, 128.4, 128.3, 128.2, 127.1, 126.9, 126.0, 125.9, 124.3, 41.0, 22.6, 21.2. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{21}\text{O}$ [$\text{M}+\text{H}$] $^+$: 349.1587, found: 349.1586.



6,8-diphenyldibenzo[a,f]azulen-12(4bH)-one (4d):

Yellow solid (27mg, 34% yield); mp 99-101 °C; $R_f = 0.30$ (PE/EA = 30:1).

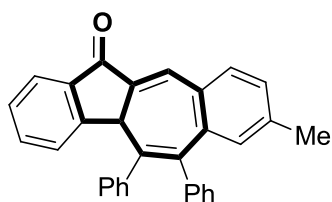
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.7$ Hz, 1H), 7.71 (d, $J = 1.6$ Hz, 1H), 7.66 – 7.56 (m, 3H), 7.52 (dd, $J = 8.1, 1.9$ Hz, 1H), 7.42 (d, $J = 1.7$ Hz, 1H), 7.38 (dd, $J = 10.8, 3.8$ Hz, 3H), 7.28 (t, $J = 7.4$ Hz, 2H), 7.25 – 7.10 (m, 6H), 5.93 (d, $J = 4.4$ Hz, 1H), 4.04 (d, $J = 3.6$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 191.4, 152.4, 143.3, 142.1, 141.9, 140.4, 140.2, 140.0, 139.0, 135.4, 135.1, 133.0, 132.3, 130.9, 130.8, 129.2, 128.9, 128.4, 128.3, 127.9, 127.6, 127.2, 126.2, 125.8, 124.3, 40.8. HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{21}\text{O}$ $[\text{M}+\text{H}]^+$: 397.1587, found: 397.1591.



7-phenylbenzo[a]naphtho[1,2-f]azulen-13(8aH)-one (4e):

Yellow solid (29mg, 39% yield); mp 70-72 °C; $R_f = 0.30$ (PE/EA = 30:1).

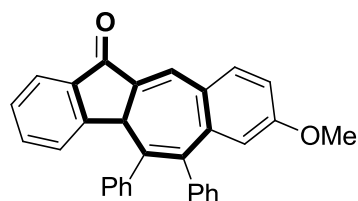
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.50 (d, $J = 1.5$ Hz, 1H), 8.43 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 7.7$ Hz, 1H), 7.89 – 7.84 (m, 1H), 7.78 – 7.46 (m, 7H), 7.38 – 7.33 (m, 1H), 7.31 – 7.23 (m, 3H), 7.22 – 7.14 (m, 2H), 6.06 (d, $J = 4.5$ Hz, 1H), 3.97 (d, $J = 4.6$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 191.2, 152.3, 143.1, 142.1, 142.0, 139.2, 138.0, 135.5, 134.5, 132.9, 132.4, 132.3, 129.3, 129.2, 128.7, 128.4, 128.3, 128.0, 127.6, 127.4, 127.0, 125.9, 125.5, 124.9, 124.4, 40.9. HRMS (ESI) calcd. for $\text{C}_{28}\text{H}_{19}\text{O}$ $[\text{M}+\text{H}]^+$: 371.1430, found: 371.1426.



8-methyl-5,6-diphenyldibenzo[a,f]azulen-12(4bH)-one (4f):

Yellow solid (34mg, 41% yield); mp 90-92 °C; $R_f = 0.30$ (PE/EA = 30:1).

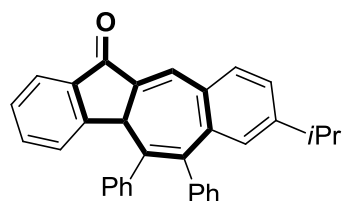
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85 (d, $J = 1.5$ Hz, 1H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.55 (d, $J = 7.9$ Hz, 1H), 7.32 – 7.10 (m, 6H), 7.08 – 6.96 (m, 3H), 6.95 – 6.90 (m, 2H), 6.80 (s, 4H), 4.14 (s, 1H), 2.28 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 191.3, 150.6, 143.2, 142.8, 142.7, 140.8, 139.8, 139.3, 138.1, 137.6, 133.7, 133.1, 132.8, 130.9, 130.7, 130.4, 128.8, 128.1, 127.6, 127.5, 127.1, 126.3, 126.1, 123.8, 45.3, 21.7. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$: 411.1743, found: 411.1732.



8-methoxy-5,6-diphenyldibenzo[a,f]azulen-12(4bH)-one (4g):

Yellow solid (30mg, 35% yield); mp 87-89 °C; $R_f = 0.20$ (PE/EA = 30:1).

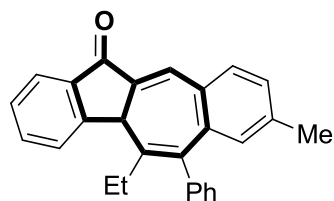
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.84 (d, $J = 1.5$ Hz, 1H), 7.73 (d, $J = 7.5$ Hz, 1H), 7.59 (d, $J = 8.6$ Hz, 1H), 7.29 – 7.14 (m, 4H), 7.08 – 6.90 (m, 7H), 6.87 – 6.76 (m, 4H), 4.17 (s, 1H), 3.69 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 191.3, 159.0, 150.5, 142.8, 142.7, 139.3, 133.6, 132.8, 130.6, 130.4, 129.0, 128.7, 127.7, 127.6, 127.1, 126.4, 126.2, 123.7, 117.1, 113.9, 55.4, 45.3. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{23}\text{O}_2$ $[\text{M}+\text{H}]^+$: 427.1693, found: 427.1690.



8-isopropyl-5,6-diphenyldibenzo[a,f]azulen-12(4bH)-one (4h):

Yellow solid (37mg, 42% yield); mp 98-100 °C; $R_f = 0.30$ (PE/EA = 30:1).

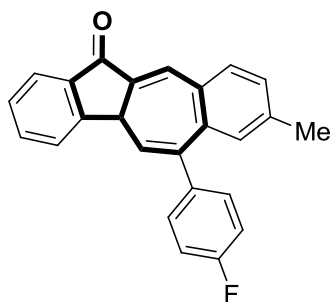
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86 (d, $J = 1.6$ Hz, 1H), 7.73 (d, $J = 7.6$ Hz, 1H), 7.59 (d, $J = 8.1$ Hz, 1H), 7.31 – 7.17 (m, 5H), 7.15 (d, $J = 1.6$ Hz, 1H), 7.07 – 6.90 (m, 6H), 6.80 (s, 4H), 4.17 (s, 1H), 2.82 (dt, $J = 13.8, 6.9$ Hz, 1H), 1.16 (d, $J = 6.9$ Hz, 3H), 1.12 (d, $J = 6.9$ Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 191.4, 150.7, 148.8, 142.9, 142.8, 142.6, 141.0, 139.8, 139.4, 137.9, 133.7, 133.5, 131.1, 130.8, 130.7, 130.4, 128.8, 127.6, 127.4, 127.1, 126.3, 126.2, 125.3, 123.8, 45.3, 34.1, 23.8, 23.7. HRMS (ESI) calcd. for $\text{C}_{33}\text{H}_{27}\text{O}$ $[\text{M}+\text{H}]^+$: 439.2056, found: 439.2052.



5-ethyl-8-methyl-6-phenyldibenzo[a,f]azulen-12(4bH)-one (4i):

Yellow solid (22mg, 30% yield); mp 74-76 °C; $R_f = 0.30$ (PE/EA = 30:1).

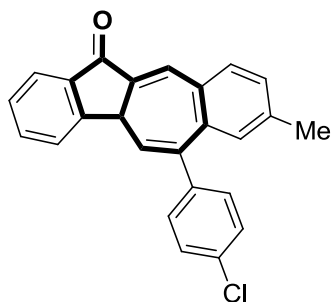
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (d, $J = 7.6$ Hz, 1H), 7.73 (d, $J = 1.5$ Hz, 1H), 7.67 – 7.64 (m, 2H), 7.53 – 7.43 (m, 2H), 7.35 – 7.22 (m, 4H), 7.07 (dd, $J = 7.9, 1.2$ Hz, 2H), 6.95 (s, 1H), 3.86 (s, 1H), 2.23 (s, 3H), 2.18 – 1.98 (m, 2H), 0.31 (t, $J = 7.4$ Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 191.1, 150.5, 143.6, 143.1, 143.0, 141.7, 140.5, 137.9, 135.9, 134.3, 132.9, 132.7, 131.0, 130.5, 130.3, 128.3, 128.2, 128.0, 127.5, 126.7, 124.4, 44.6, 25.2, 21.7, 15.4. HRMS (ESI) calcd. for $\text{C}_{27}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$: 363.1743, found: 363.1740.



6-(4-fluorophenyl)-8-methyldibenzo[a,f]azulen-12(4bH)-one (4j):

Yellow solid (28mg, 40% yield); mp 77-79 °C; $R_f = 0.30$ (PE/EA = 30:1).

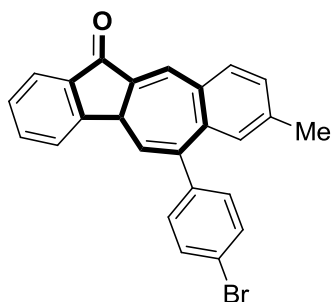
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.6$ Hz, 1H), 7.69 – 7.57 (m, 3H), 7.47 – 7.34 (m, 2H), 7.13 (d, $J = 7.8$ Hz, 1H), 7.09 – 7.02 (m, 2H), 6.97 (s, 1H), 6.89 (t, $J = 8.7$ Hz, 2H), 5.85 (d, $J = 4.4$ Hz, 1H), 3.97 (d, $J = 3.9$ Hz, 1H), 2.23 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.3, 161.3 (d, $J = 246.6$ Hz), 151.2, 140.2, 139.7, 138.4 (d, $J = 3.4$ Hz), 138.3, 137.9, 136.9, 134.2, 132.4, 131.5, 131.3, 130.6, 130.0, 129.7, 129.6, 127.5, 127.1, 124.6, 123.1, 114.0 (d, $J = 21.4$ Hz), 39.5, 20.5. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{18}\text{FO}$ $[\text{M}+\text{H}]^+$: 353.1336, found: 353.1338.



6-(4-chlorophenyl)-8-methyldibenzo[a,f]azulen-12(4bH)-one (4k):

Yellow solid (27mg, 37% yield); mp 75-75 °C; $R_f = 0.30$ (PE/EA = 30:1).

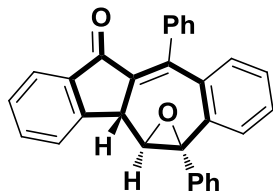
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.88 (dd, $J = 7.2, 3.3$ Hz, 1H), 7.75 – 7.65 (m, 3H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.49 – 7.44 (m, 1H), 7.27 – 7.23 (m, 2H), 7.21 (dd, $J = 7.9, 1.0$ Hz, 1H), 7.14 – 7.08 (m, 2H), 7.02 (d, $J = 8.6$ Hz, 1H), 5.95 (d, $J = 4.4$ Hz, 1H), 4.04 (dd, $J = 4.3, 1.4$ Hz, 1H), 2.31 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 191.2, 152.1, 141.8, 141.1, 140.6, 139.0, 138.9, 138.0, 135.2, 133.4, 133.3, 132.8, 132.2, 131.6, 131.0, 130.2, 128.6, 128.3, 128.2, 125.6, 124.1, 40.5, 21.4. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{18}\text{ClO}$ $[\text{M}+\text{H}]^+$: 369.1041, found: 369.1038.



6-(4-bromophenyl)-8-methyldibenzo[a,f]azulen-12(4bH)-one (4l):

Yellow solid (35mg, 43% yield); mp 75-77 °C; $R_f = 0.30$ (PE/EA = 30:1).

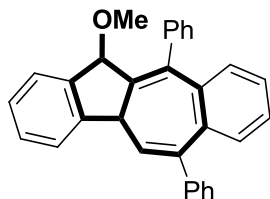
^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 7.7$ Hz, 1H), 7.75 – 7.65 (m, 3H), 7.53 – 7.50 (m, 1H), 7.50 – 7.44 (m, 1H), 7.43 – 7.38 (m, 2H), 7.21 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.08 – 7.01 (m, 3H), 5.95 (d, $J = 4.4$ Hz, 1H), 4.04 (dd, $J = 4.4, 1.5$ Hz, 1H), 2.31 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 191.4, 152.2, 142.4, 140.8, 139.0, 138.2, 135.4, 133.6, 133.0, 132.4, 131.8, 131.4, 131.2, 130.8, 128.8, 128.3, 125.7, 124.3, 121.6, 40.7, 21.6. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{18}\text{BrO}$ $[\text{M}+\text{H}]^+$: 413.0536, found: 413.0533



1a,6-diphenyl-11b,11c-dihydrodibenzo[2,3:6,7]azuleno[4,5-b]oxiren-7(1aH)-one (5a):

Yellow solid (67mg, 81% yield); mp 98-100°C; $R_f = 0.30$ (PE/EA = 20:1).

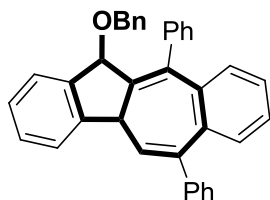
^1H NMR (400 MHz, CDCl_3) δ 7.73 (m, 2H), 7.65 (m, 2H), 7.50 – 7.41 (m, 4H), 7.39 – 7.32 (m, 3H), 7.32 – 7.20 (m, 4H), 7.17 – 7.11 (m, 2H), 7.05 – 6.99 (m, 1H), 3.90 (d, $J = 6.2$ Hz, 1H), 3.42 (dd, $J = 6.1, 3.4$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 191.1, 149.3, 148.5, 140.6, 139.8, 138.6, 138.4, 137.3, 135.2, 132.0, 131.6, 129.7, 129.6, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 125.9, 124.6, 72.2, 60.8, 47.4. HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$: 413.1536, found: 413.1542.



12-methoxy-6,11-diphenyl-4b,12-dihydrodibenzo[a,f]azulene (6a):

Yellow solid (31mg, 38% yield); mp 108-110 °C; $R_f = 0.4$ (PE/EA = 20:1).

^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.38 (m, 5H), 7.37 – 7.25 (m, 10H), 7.20 – 7.13 (m, 3H), 6.08 (d, $J = 5.1$ Hz, 1H), 5.98 (s, 1H), 3.74 (d, $J = 5.1$ Hz, 1H), 2.73 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.5, 143.9, 143.1, 141.8, 141.7, 141.6, 139.6, 139.0, 137.9, 134.7, 130.8, 129.8, 129.7, 129.4, 129.2, 128.5, 128.3, 127.8, 127.3, 127.2, 126.3, 125.7, 125.6, 124.7, 81.8, 52.7, 46.0, 29.9. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}]^+$: 413.1900, found: 413.1905.

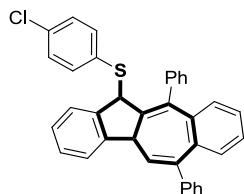


12-(benzyloxy)-6,11-diphenyl-4b,12-dihydrodibenzo[a,f]azulene (7a):

Yellow solid (44mg, 45% yield); mp 202-204 °C; $R_f = 0.40$ (PE/EA = 30:1).

^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, $J = 7.5$ Hz, 1H), 7.45 – 7.39 (m, 4H), 7.39 – 7.22 (m, 12H), 7.21 – 7.14 (m, 3H), 7.11 – 7.05 (m, 3H), 6.75 (dd, $J = 7.3, 2.3$ Hz, 1H), 6.21 (s, 1H), 6.15 (d, $J = 5.2$ Hz, 1H), 4.05 (d, $J = 10.7$ Hz, 1H), 3.79 (dd, $J = 7.9, 5.8$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.4, 144.4, 143.0, 142.0, 141.9,

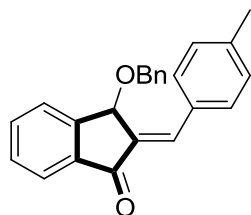
141.8, 139.7, 139.1, 138.8, 137.8, 134.8, 130.7, 130.0, 129.8, 129.7, 129.2, 128.7, 128.3, 128.1, 128.1, 127.8, 127.3, 127.2, 126.3, 125.8, 124.8, 80.9, 67.4, 46.2. **HRMS (ESI)** calcd. for C₃₇H₂₉O [M+H]⁺: 489.2213, found: 489.2215.



6,11-diphenyl-4b,12-dihydrodibenzo[a,f]azulen-12-yl)sulfane (8a):

Yellow solid (80mg, 77% yield); mp 156-158 °C; R_f = 0.40 (PE/EA = 30:1).

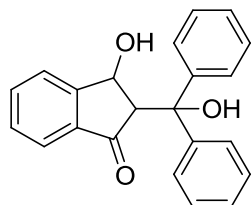
¹H NMR (400 MHz, CDCl₃) δ 7.47 (t, *J* = 7.5 Hz, 3H), 7.42 – 7.26 (m, 10H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.17 – 7.08 (m, 4H), 6.53 (d, *J* = 8.5 Hz, 2H), 6.38 (d, *J* = 8.5 Hz, 2H), 5.61 (s, 1H), 4.64 (d, *J* = 5.5 Hz, 1H), 3.52 (d, *J* = 5.5 Hz, 1H). **¹³C {¹H} NMR (100 MHz, CDCl₃)** δ 144.6, 144.5, 143.4, 142.9, 141.8, 141.7, 139.2, 138.8, 138.1, 137.7, 137.6, 136.1, 135.0, 133.1, 130.7, 130.1, 129.9, 129.4, 128.8, 128.7, 128.6, 128.5, 128.2, 128.1, 127.9, 127.7, 127.3, 127.2, 126.2, 125.6, 125.5, 124.5, 55.9, 46.5. **HRMS (ESI)** calcd. for C₃₆H₂₆ClS [M+H]⁺: 525.1438, found: 525.1445.



(E)-3-(benzyloxy)-2-(4-methylbenzylidene)-2,3-dihydro-1H-inden-1-one (9a):

Yellow solid (54 mg, 80% yield); mp 101-102 °C; R_f = 0.50 (PE/EA = 10:1).

¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.92 (m, 3H), 7.89 (d, *J* = 1.6 Hz, 1H), 7.84 – 7.82 (m, 1H), 7.75 – 7.71 (m, 1H), 7.58 – 7.54 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.20 (m, 3H), 7.06 – 7.04 (m, 2H), 6.18 (s, 1H), 4.15 (d, *J* = 10.3 Hz, 1H), 3.88 (d, *J* = 10.3 Hz, 1H), 2.42 (s, 3H). **¹³C {¹H} NMR (100 MHz, CDCl₃)** δ 192.5, 149.0, 141.4, 139.2, 138.9, 137.9, 135.3, 132.6, 132.4, 131.5, 130.0, 129.9, 128.4, 128.3, 127.8, 126.4, 123.9, 74.8, 65.3, 21.8. **HRMS (ESI)** calcd. for C₂₄H₂₁O₂ [M+H]⁺: 341.1536, found: 341.1545.

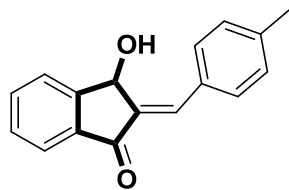


3-hydroxy-2-(hydroxydiphenylmethyl)-2,3-dihydro-1H-inden-1-one (Int-2):

yellow solid (7.3 mg, 11% yield); mp 138–140 °C; R_f = 0.20 (PE/EA = 5:1).

¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.69-7.64 (m, 1H), 7.64-7.60 (m, 1H), 7.50 -7.43 (m, 3H), 7.38-7.32 (m, 2H), 7.31-7.21 (m, 6H), 5.36 (t, *J* = 4.0 Hz, 1H), 4.05 (s, 1H), 3.62 (d, *J* = 4.2 Hz, 1H), 1.68 (d, *J* = 4.0 Hz, 1H). **¹³C {¹H} NMR (100 MHz, CDCl₃)** δ 202.9, 152.8, 145.5, 144.7, 136.3, 135.7, 129.5, 128.6, 128.5,

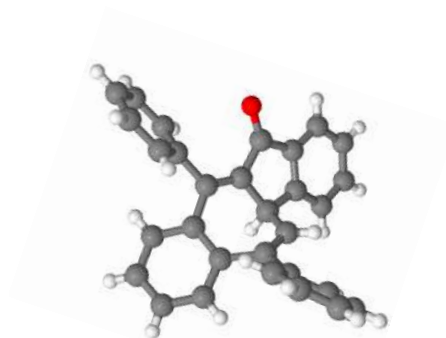
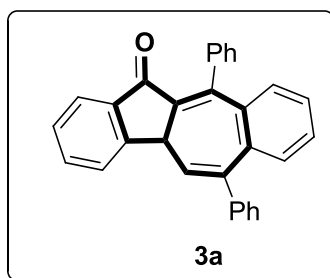
127.7, 127.6, 126.8, 126.7, 125.9, 123.3, 79.5, 71.6, 67.6. **HRMS (ESI)** calcd. for $C_{22}H_{18}NaO_3$ $[M+Na]^+$: 353.1148, found: 353.1133.



3-hydroxy-2-(4-methylbenzylidene)-2,3-dihydro-1H-inden-1-one (Int-3):

Yellow solid (19mg, 37% yield); mp 159-161 °C; R_f = 0.30 (PE/EA = 5:1).

1H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 4H), 7.73 – 7.66 (m, 1H), 7.62 (d, J = 1.4 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.31 – 7.24 (m, 2H), 5.93 – 5.91 (m, 1H), 2.41 (s, 3H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ 192.7, 151.6, 141.3, 138.0, 137.3, 136.4, 135.4, 132.2, 131.2, 129.9, 129.8, 126.2, 123.9, 69.0, 21.8. **HRMS (ESI)** calcd. for $C_{17}H_{15}O_2$ $[M+H]^+$: 251.1067, found: 251.1065.



X-ray structure of **3a**

Thermal ellipsoids drawn at the 35% probability level
CH₂Cl₂ : PE = 1:2 as solvent system for crystal growth

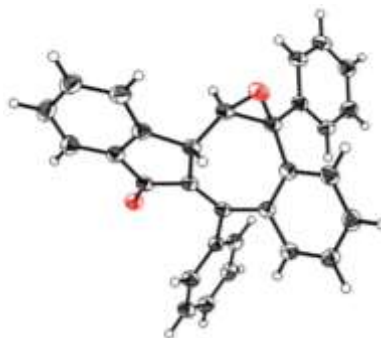
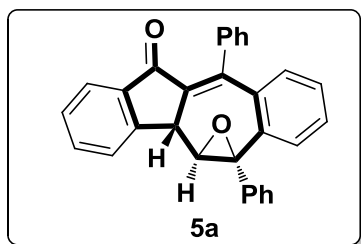
Datablock:

Bond precision:	C-C = 0.0089 Å	Wavelength=0.71073
Cell:	a=26.580(7) b=9.356(3) c=20.482(5)	
	alpha=90 beta=125.071(4) gamma=90	
Temperature:	296 K	

	Calculated	Reported
Volume	4169(2)	4168.9(18)
Space group	C 2/c	C2/c
Hall group	-C 2yc	?
Moiety formula	C30 H20 O	?
Sum formula	C30 H20 O	C30 H20 O
Mr	396.46	396.46
Dx,g cm-3	1.263	1.263
Z	8	8
Mu (mm-1)	0.075	0.075
F000	1664.0	1664.0
F000'	1664.67	
h,k,lmax	31,11,24	31,11,24
Nref	3708	3703
Tmin,Tmax	0.978,0.990	0.977,0.990
Tmin'	0.977	

Correction method= # Reported T Limits: Tmin=0.977 Tmax=0.990
AbsCorr = NONE

Data completeness= 0.999	Theta(max)= 25.100
R(reflections)= 0.0776(1437)	wR2(reflections)= 0.2496(3703)
S = 0.998	Npar= 280

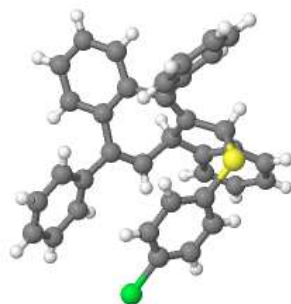
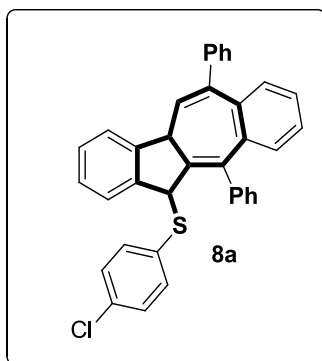


X-ray structure of **5a**

Thermal ellipsoids drawn at the 35% probability level
 CH₃OH: PE = 1:1 as solvent system for crystal growth

Datablock:

Bond precision:	C-C = 0.0020 Å	Wavelength=1.54184
Cell:	a=11.0409(4) b=15.3931(4) c=13.0070(7)	
	alpha=90 beta=105.945(4) gamma=90	
Temperature:	180 K	
	Calculated	Reported
Volume	2125.54(15)	2125.54(15)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C30 H20 O2	?
Sum formula	C30 H20 O2	C30 H20 O2
Mr	412.46	412.46
Dx, g cm ⁻³	1.289	1.289
Z	4	4
Mu (mm ⁻¹)	0.624	0.624
F000	864.0	864.0
F000'	866.46	
h, k, lmax	13, 19, 16	13, 19, 16
Nref	4460	4274
Tmin, Tmax		
Tmin'		
Correction method=	Not given	
Data completeness=	0.958	Theta(max)= 76.528
R(reflections)=	0.0444(3720)	wR2(reflections)= 0.1257(4274)
S =	1.053	Npar= 290

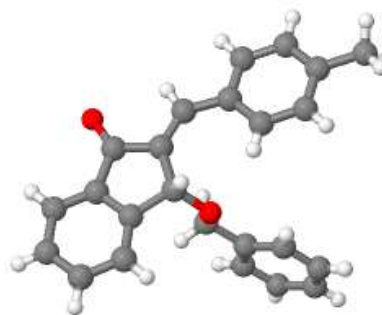
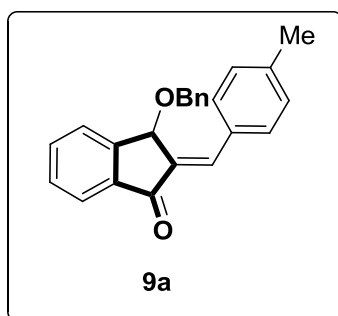


X-ray structure of **8a**

Thermal ellipsoids drawn at the 35% probability level
 CH_2Cl_2 : PE = 1:2 as solvent system for crystal growth

Datablock:

Bond precision:	C-C = 0.0039 Å	Wavelength=0.71073
Cell:	a=13.7240 (7) b=11.3771 (7) c=17.129 (1)	
	alpha=90 beta=96.235 (5) gamma=90	
Temperature:	293 K	
	Calculated	Reported
Volume	2658.7 (3)	2658.7 (3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C ₃₆ H ₂₅ Cl S	C ₃₆ H ₂₅ Cl S
Sum formula	C ₃₆ H ₂₅ Cl S	C ₃₆ H ₂₅ Cl S
Mr	525.07	525.07
Dx, g cm ⁻³	1.312	1.312
Z	4	4
Mu (mm ⁻¹)	0.247	0.247
F000	1096.0	1096.0
F000'	1097.45	
h, k, lmax	16, 14, 21	16, 14, 21
Nref	5219	5208
Tmin, Tmax	0.957, 0.966	0.892, 1.000
Tmin'	0.949	
Correction method=	# Reported T Limits: Tmin=0.892 Tmax=1.000	
AbsCorr =	MULTI-SCAN	
Data completeness=	0.998	Theta (max)= 26.022
R(reflections)=	0.0547 (3300)	wR2(reflections)= 0.1326 (5208)
S =	1.056	Npar= 343

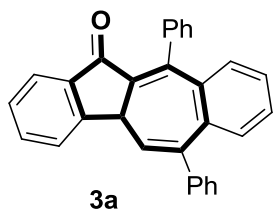


X-ray structure of **9a**

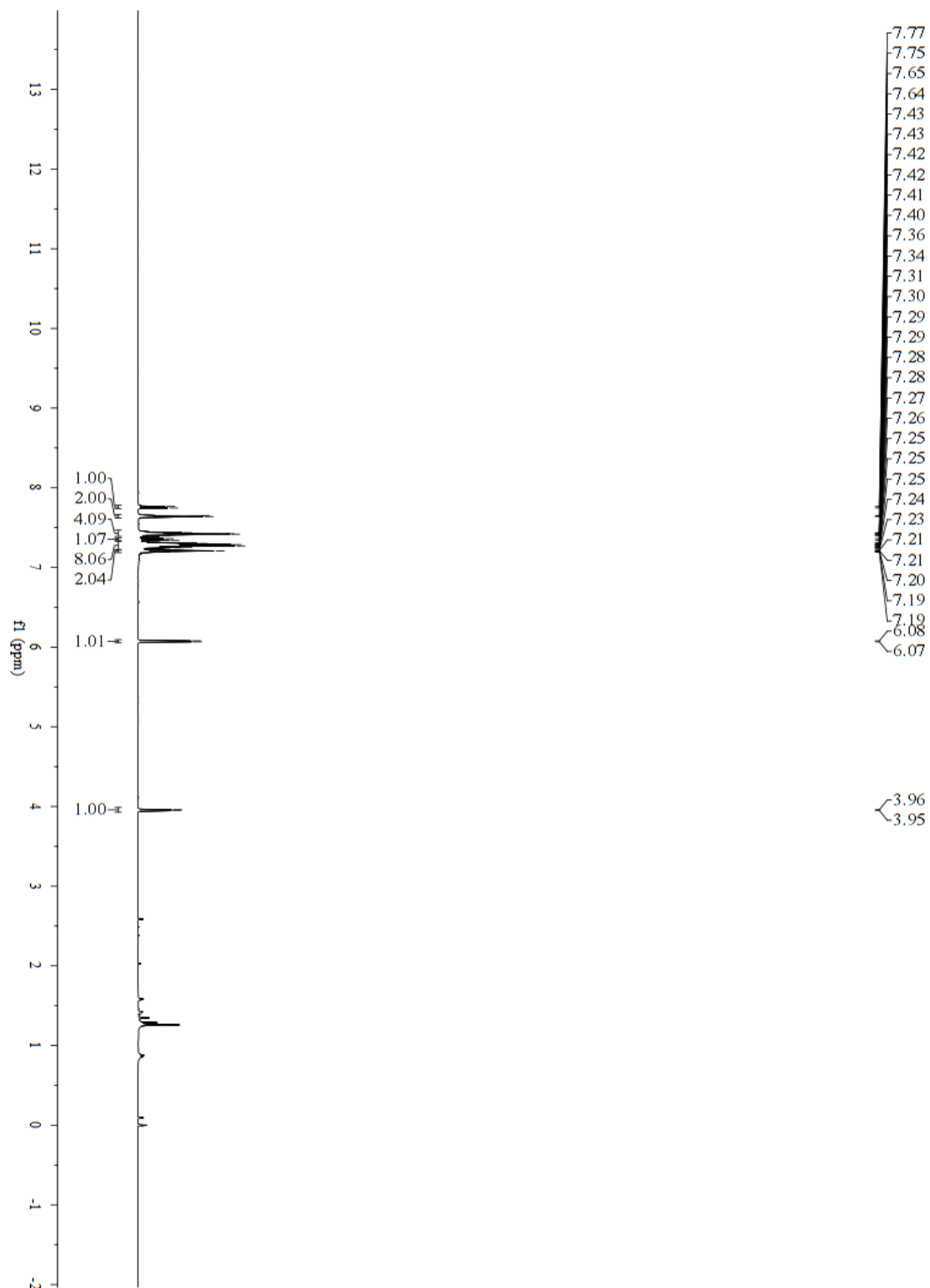
Thermal ellipsoids drawn at the 35% probability level
 CH₂Cl₂ : PE = 1:2 as solvent system for crystal growth

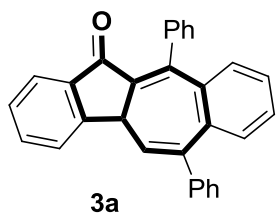
Datablock:

Bond precision:	C-C = 0.0022 Å	Wavelength=0.71073
Cell:	a=11.0194(5) b=12.1077(6) c=14.8611(7)	
	alpha=90 beta=111.464(1) gamma=90	
Temperature:	293 K	
	Calculated	Reported
Volume	1845.25(15)	1845.25(15)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C ₂₄ H ₂₀ O ₂	C ₂₄ H ₂₀ O ₂
Sum formula	C ₂₄ H ₂₀ O ₂	C ₂₄ H ₂₀ O ₂
Mr	340.40	340.40
Dx, g cm ⁻³	1.225	1.225
Z	4	4
Mu (mm ⁻¹)	0.077	0.077
F000	720.0	720.0
F000'	720.32	
h,k,lmax	14,15,19	14,15,19
Nref	4249	4230
Tmin,Tmax	0.973,0.976	0.683,0.746
Tmin'	0.973	
Correction method=	# Reported T Limits: Tmin=0.683 Tmax=0.746	
AbsCorr =	MULTI-SCAN	
Data completeness=	0.996	Theta(max)= 27.555
R(reflections)=	0.0498(3229)	wR2(reflections)= 0.1375(4230)
S =	1.036	Npar= 236

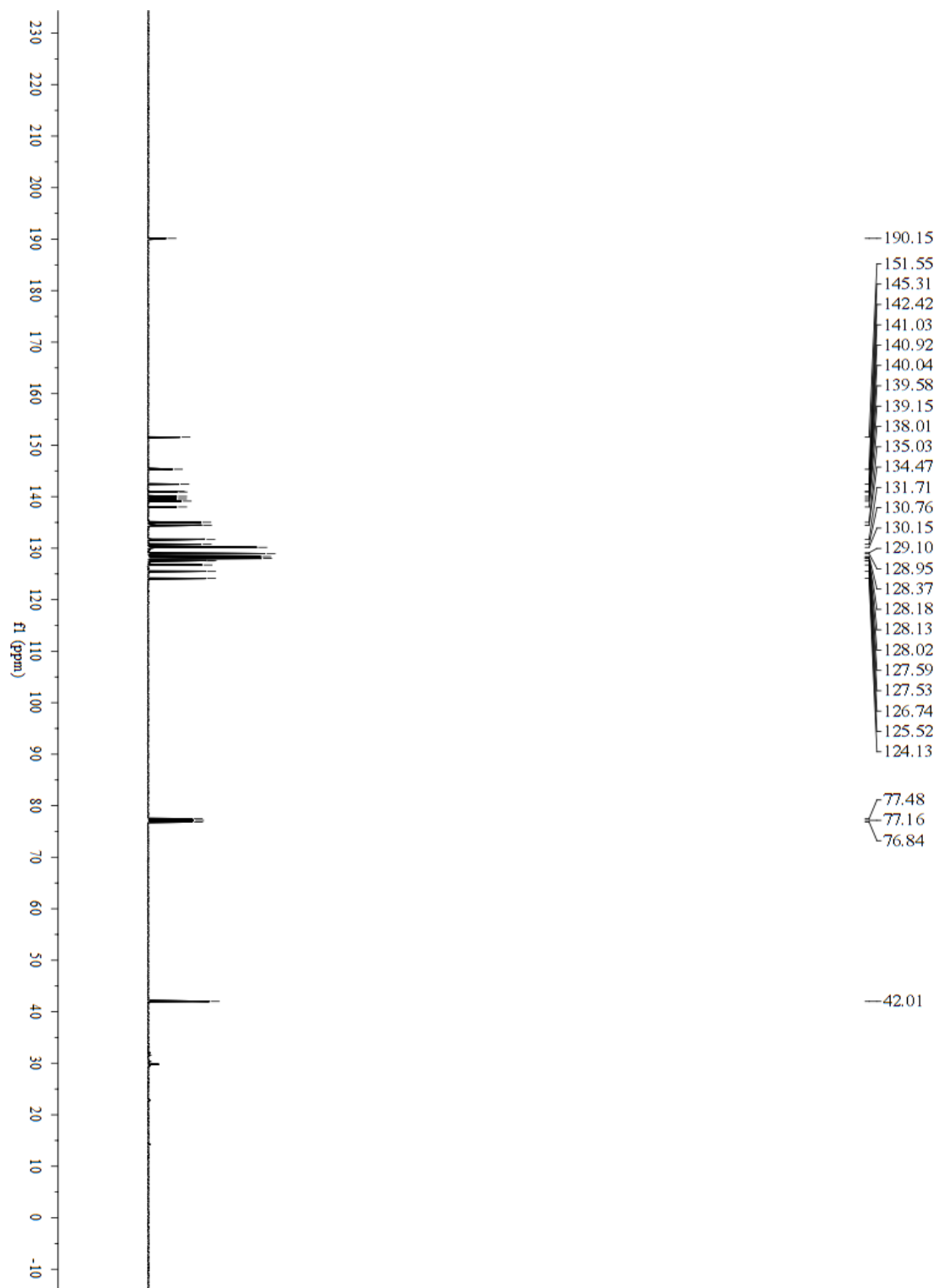


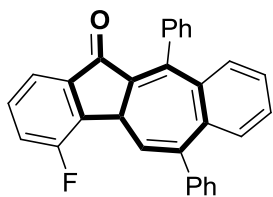
$^1\text{H NMR}$ (400 MHz, CDCl_3)





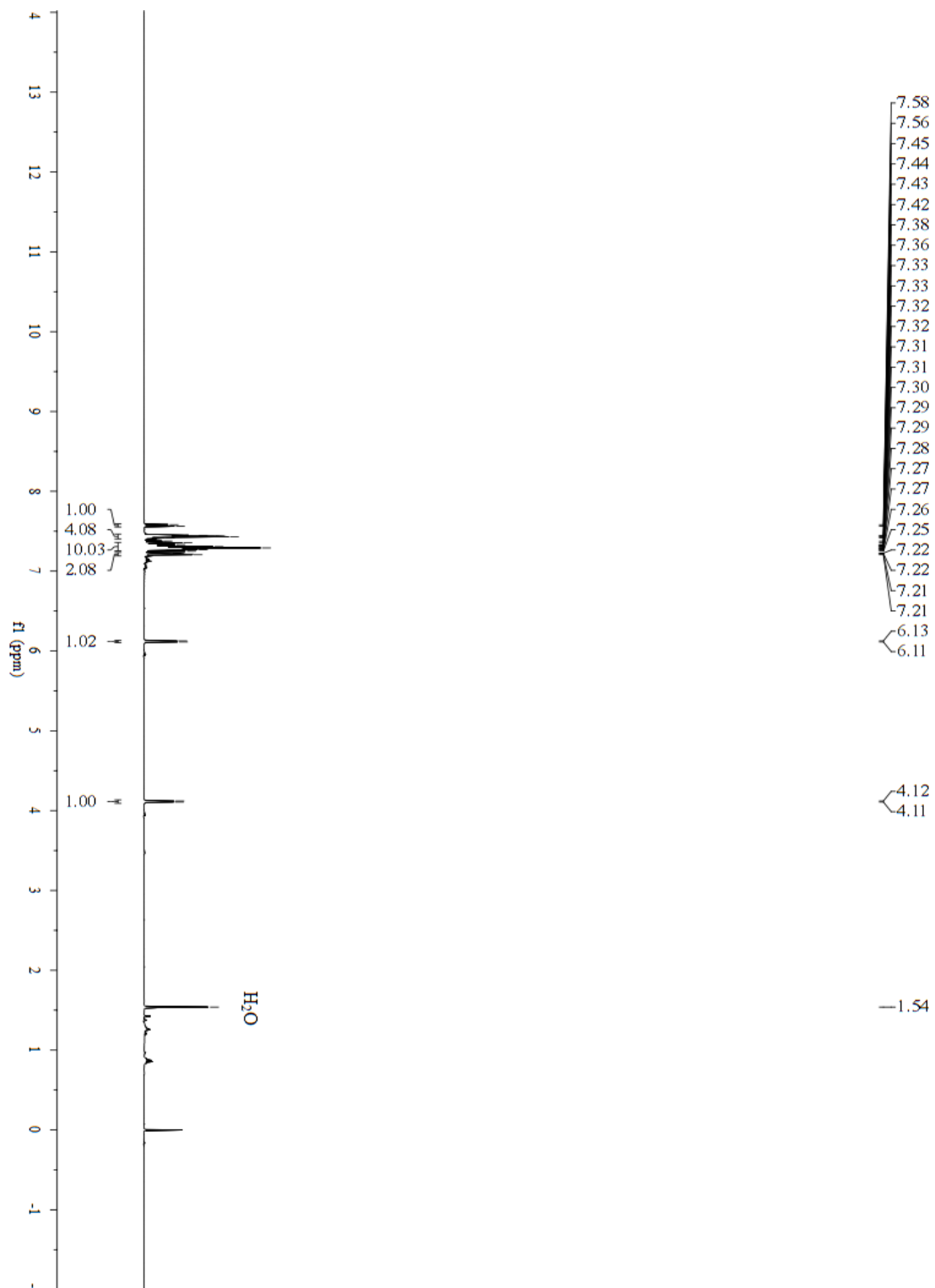
^{13}C NMR (100 MHz, CDCl_3)

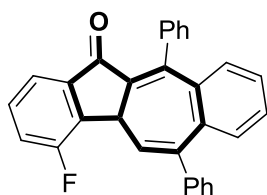




3b

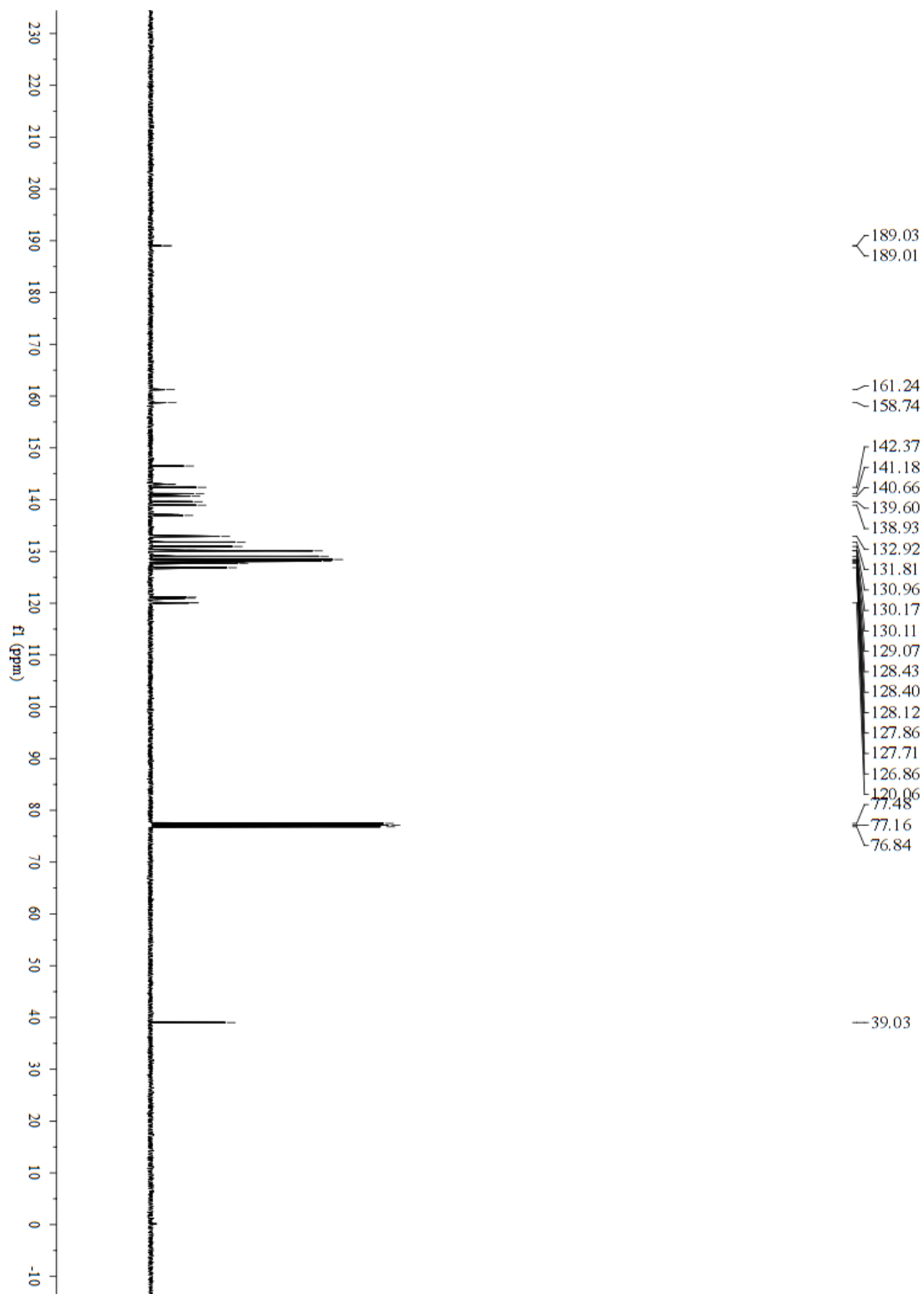
$^1\text{H NMR}$ (400 MHz, CDCl_3)

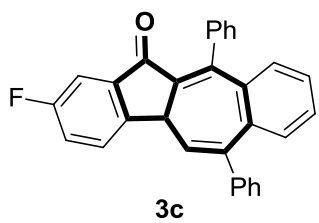




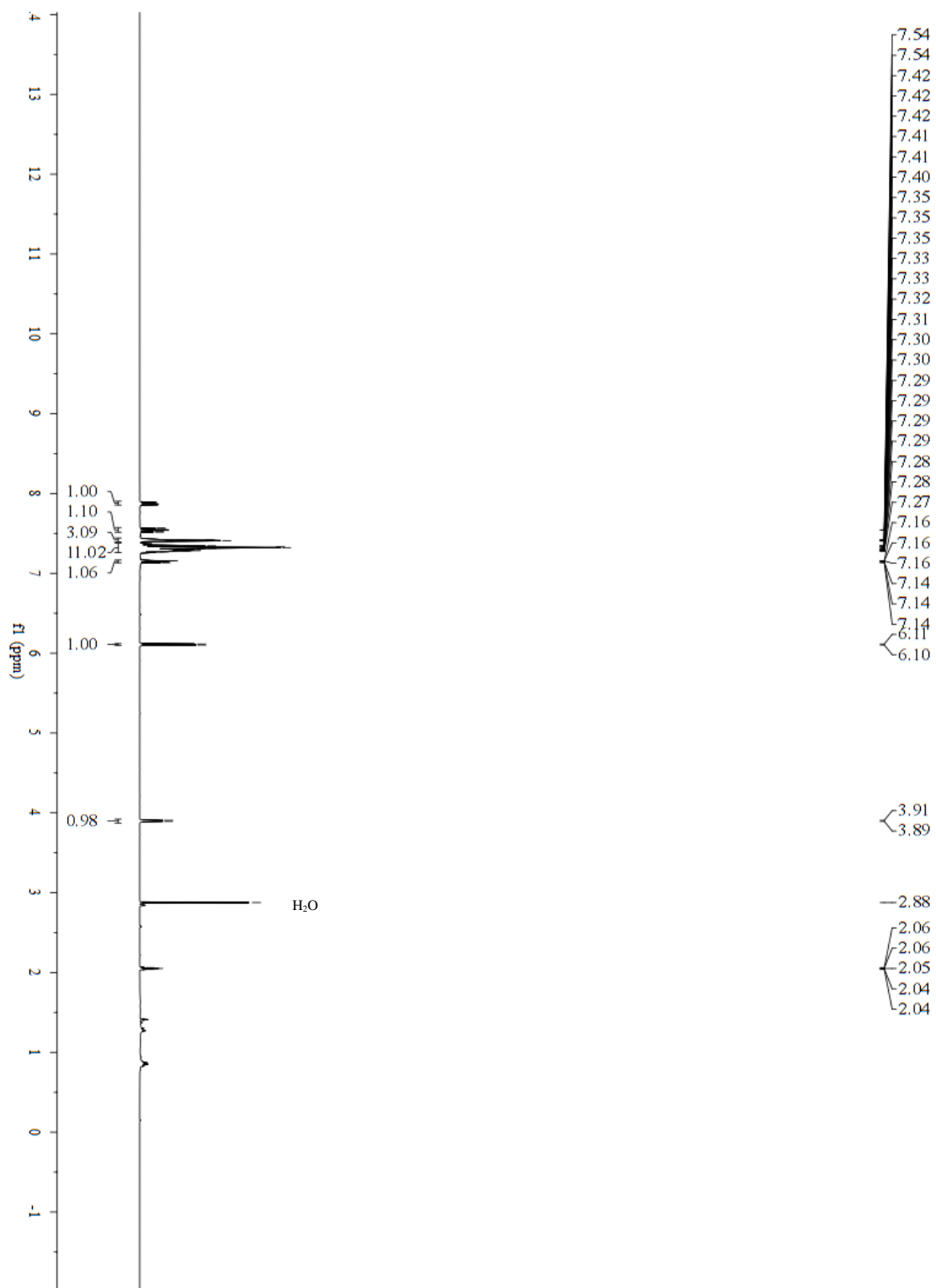
3b

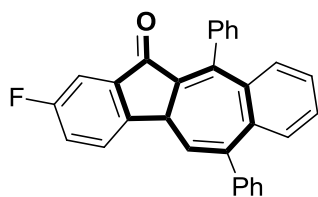
^{13}C NMR (100 MHz, CDCl_3)





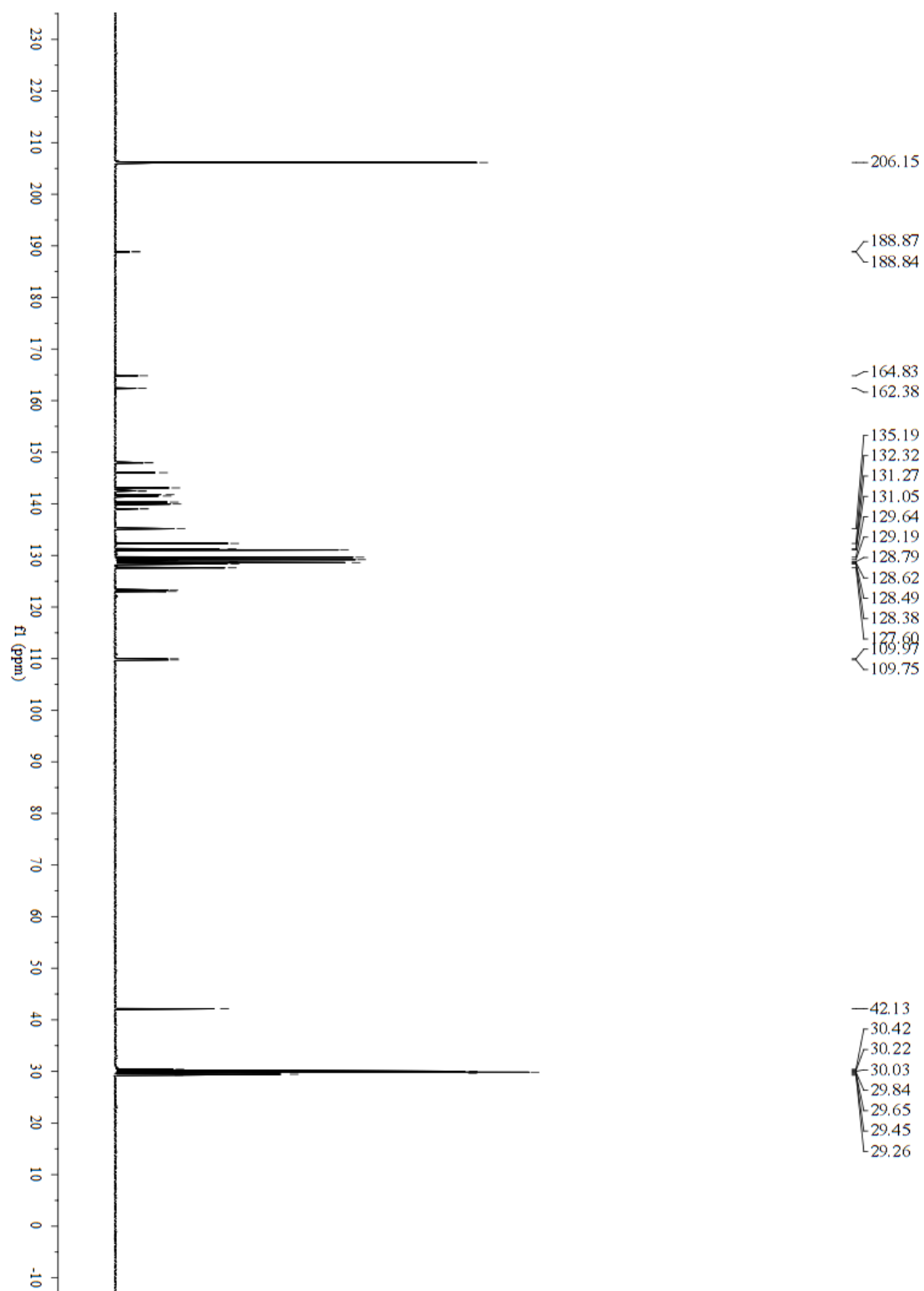
¹H NMR (400 MHz, acetone)

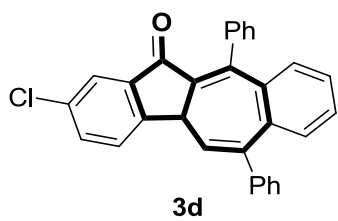




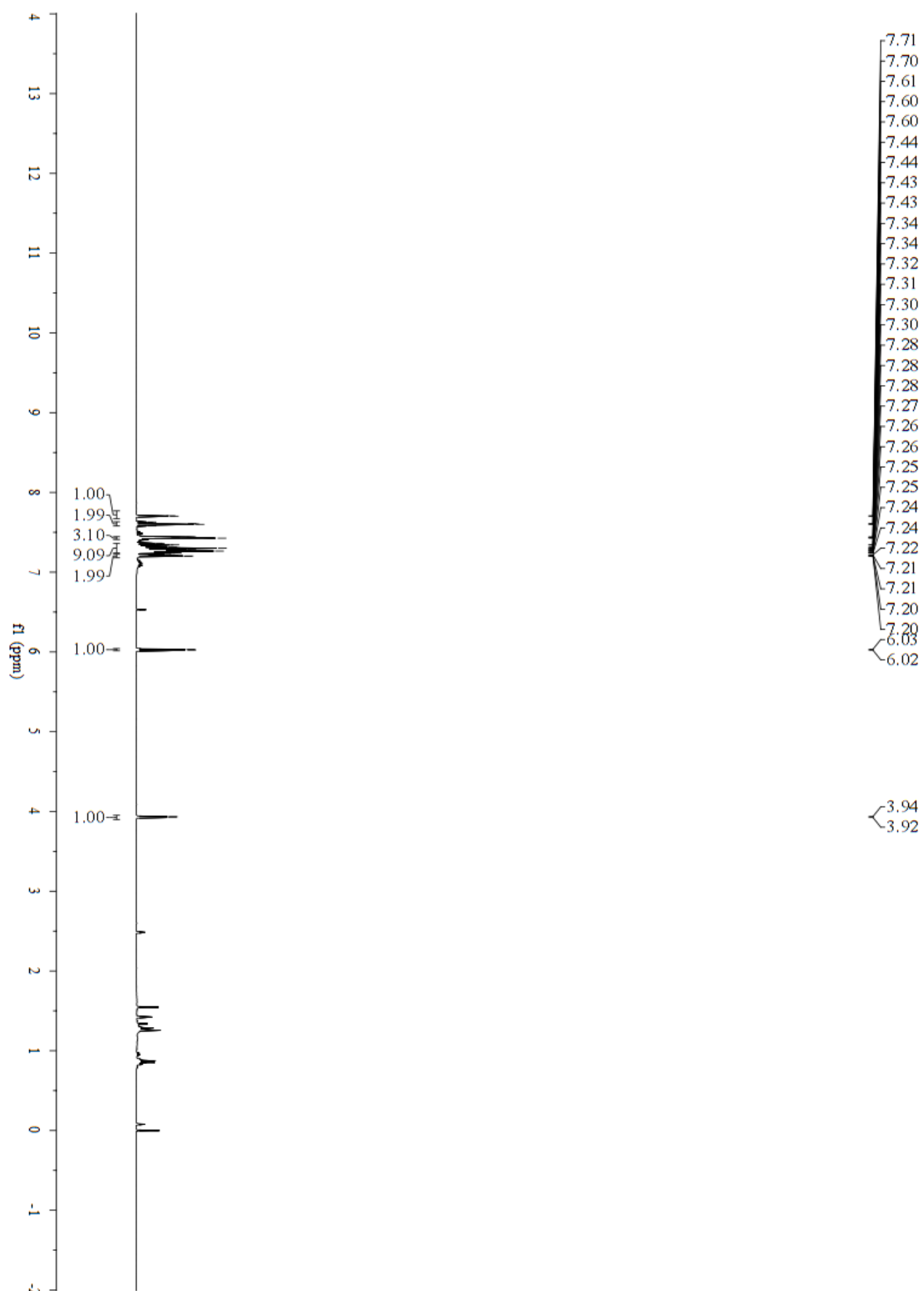
3c

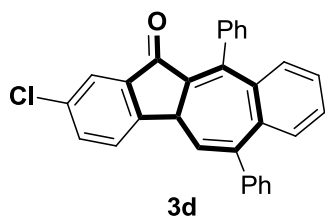
^{13}C NMR (100 MHz, acetone)



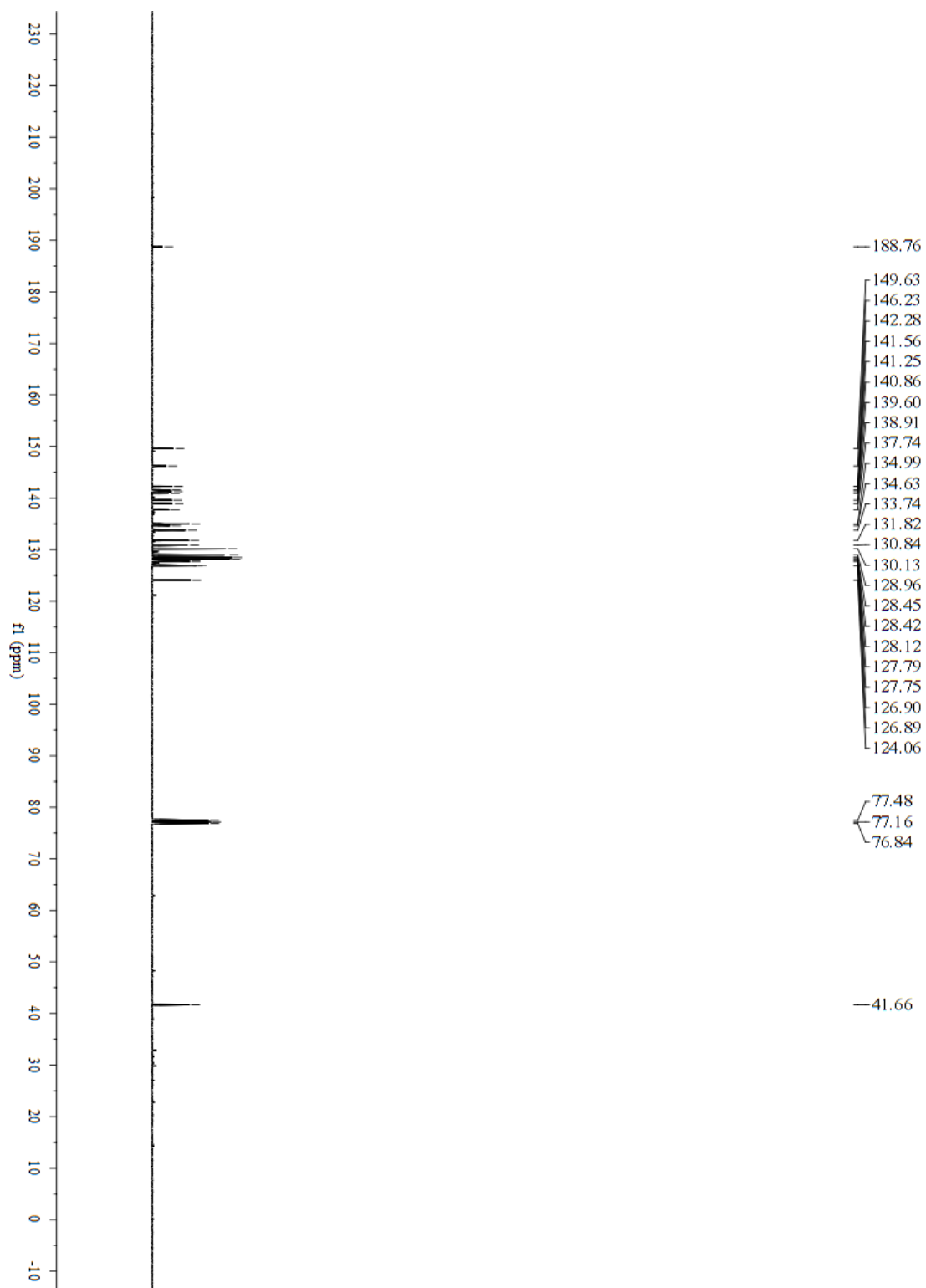


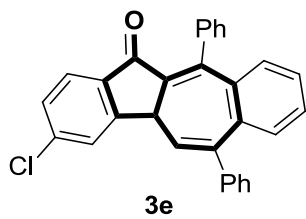
¹H NMR (400 MHz, CDCl₃)



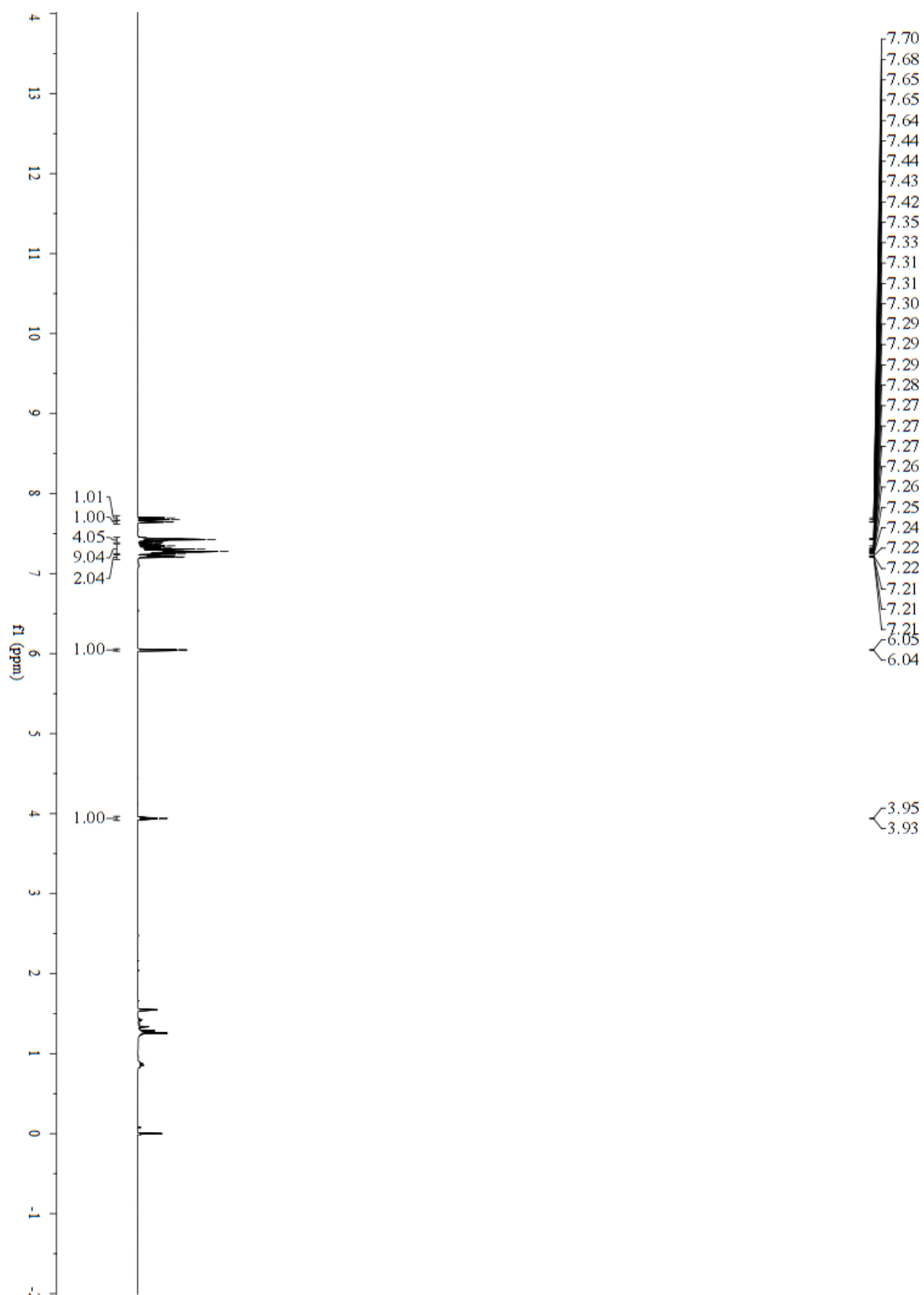


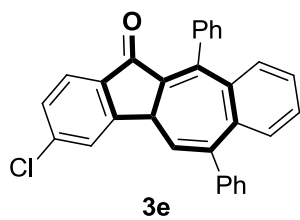
^{13}C NMR (100 MHz, CDCl_3)



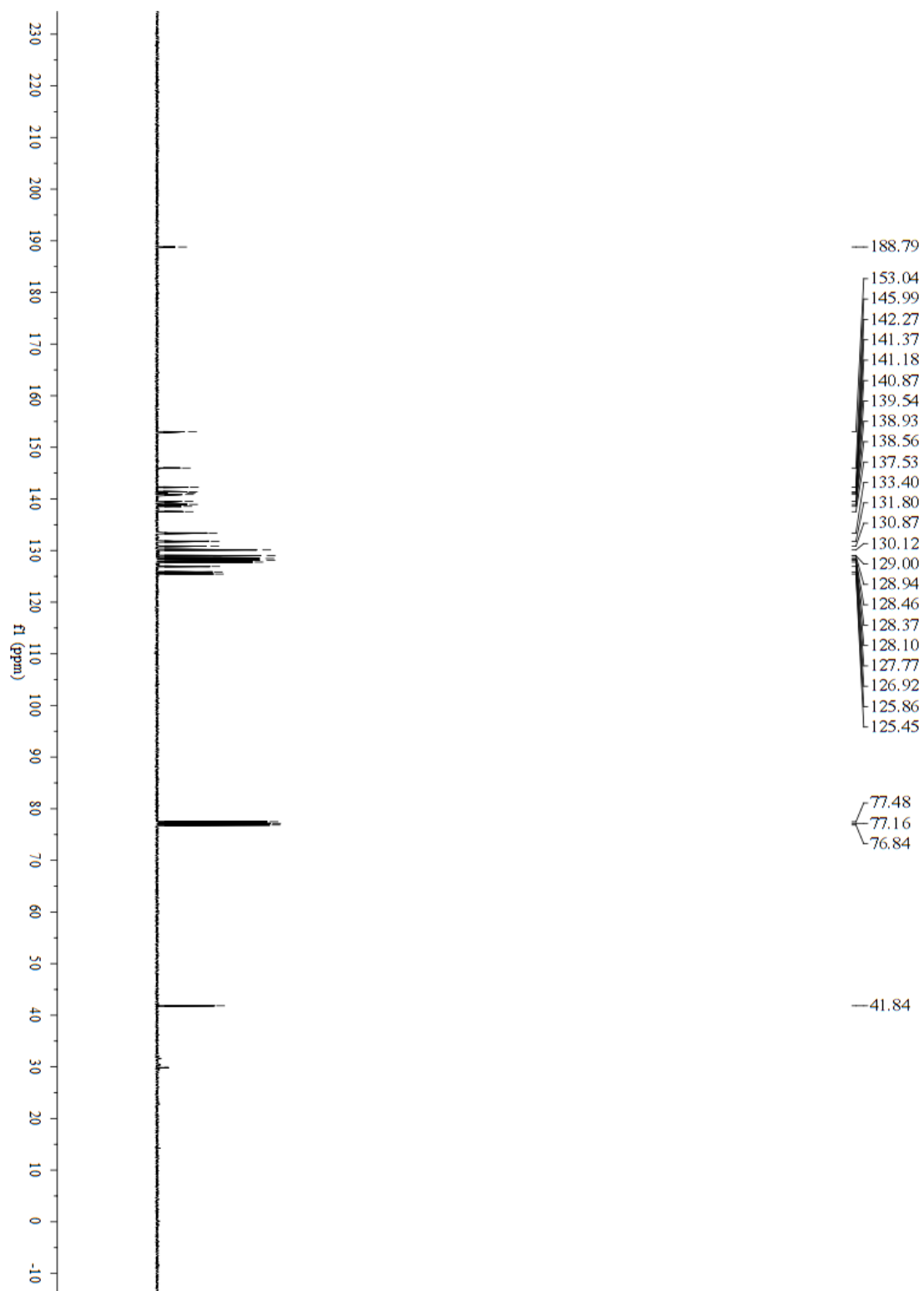


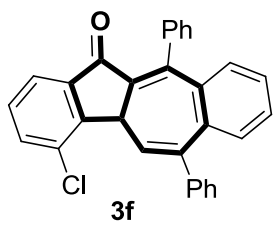
¹H NMR (400 MHz, CDCl₃)



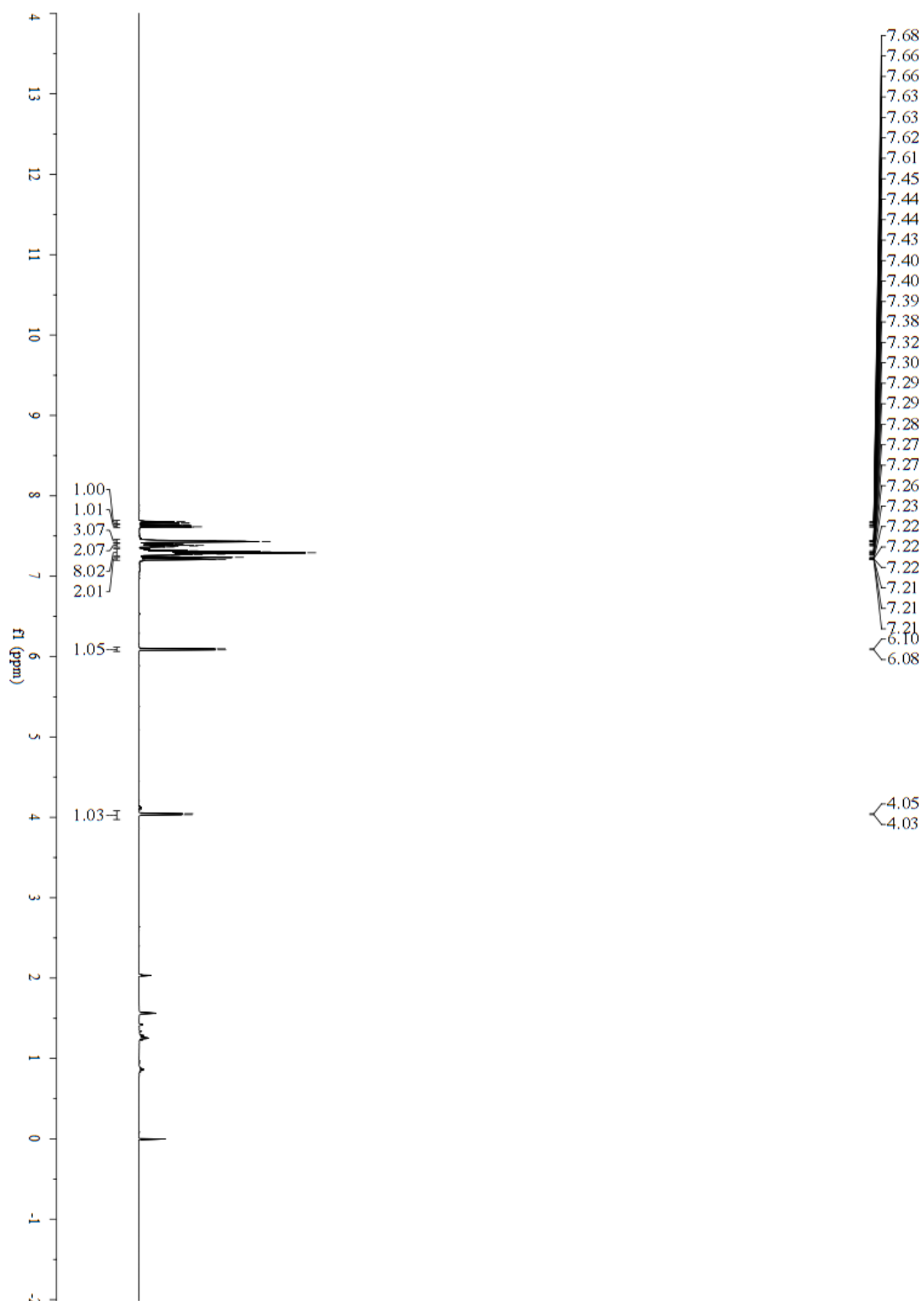


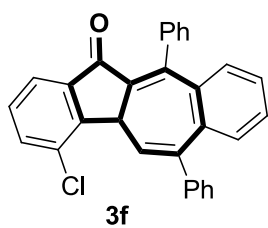
¹³C NMR (100 MHz, CDCl₃)



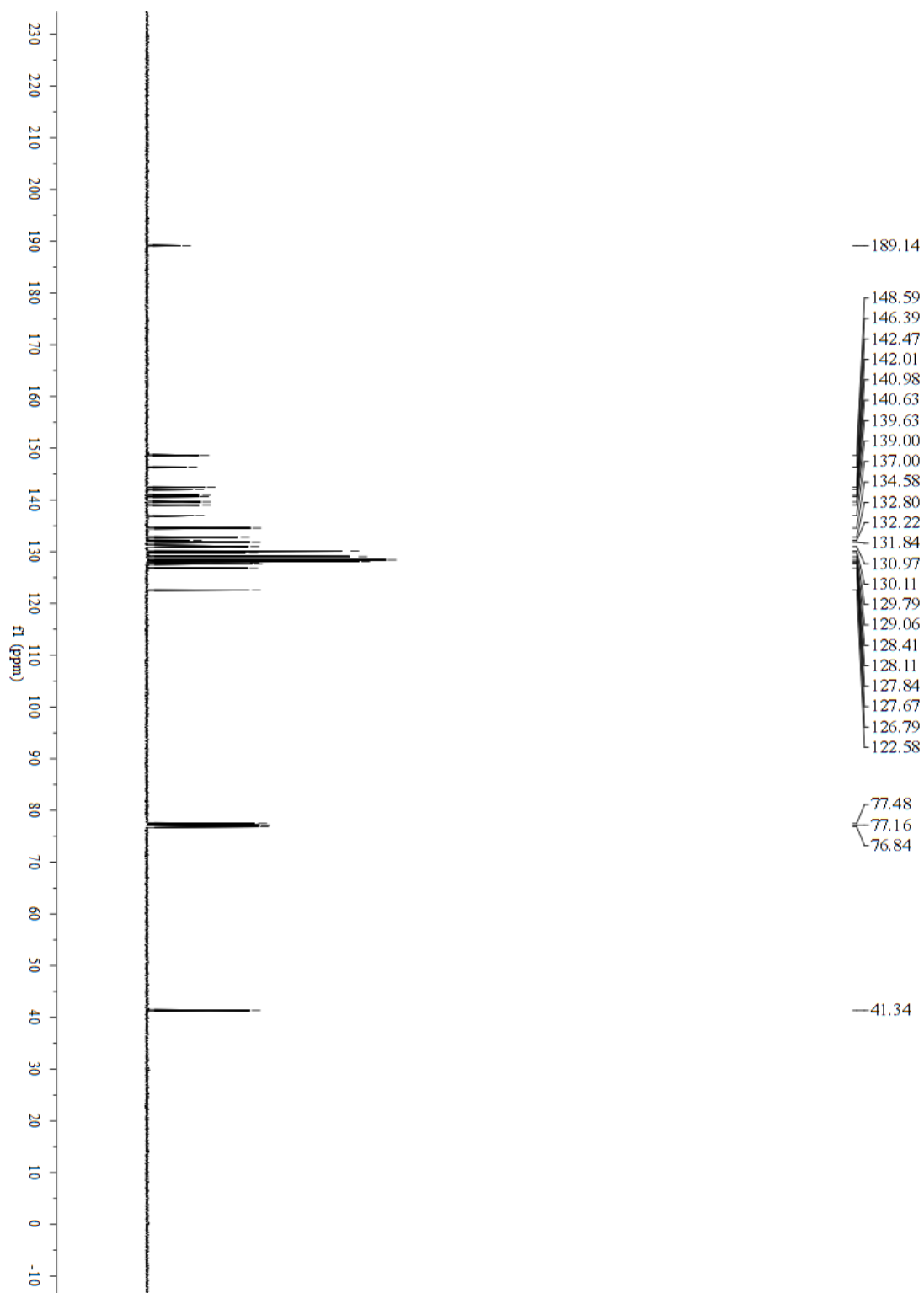


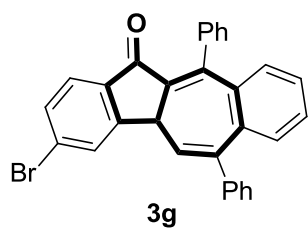
¹H NMR (400 MHz, CDCl₃)



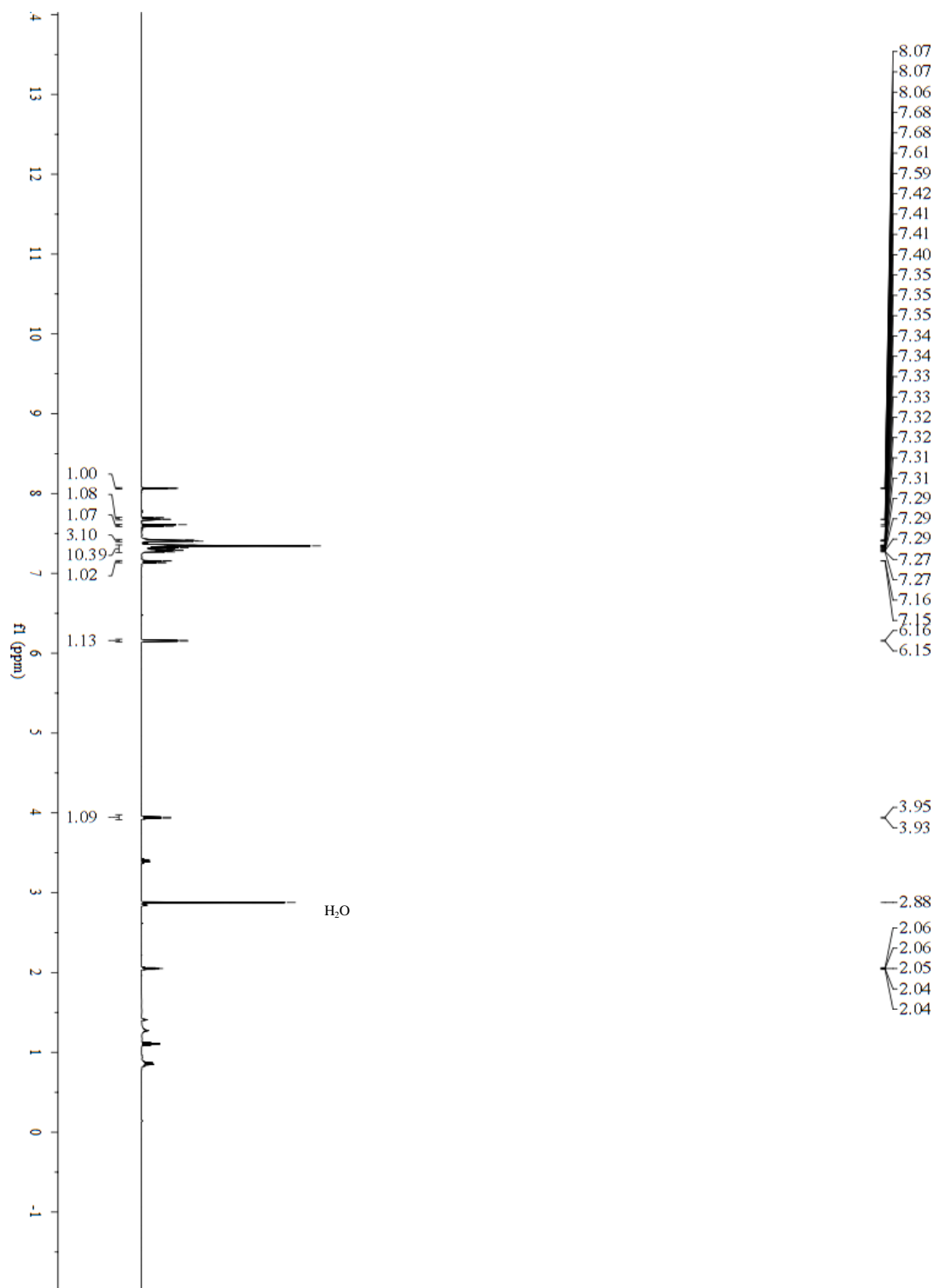


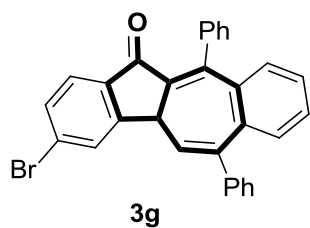
^{13}C NMR (100 MHz, CDCl_3)



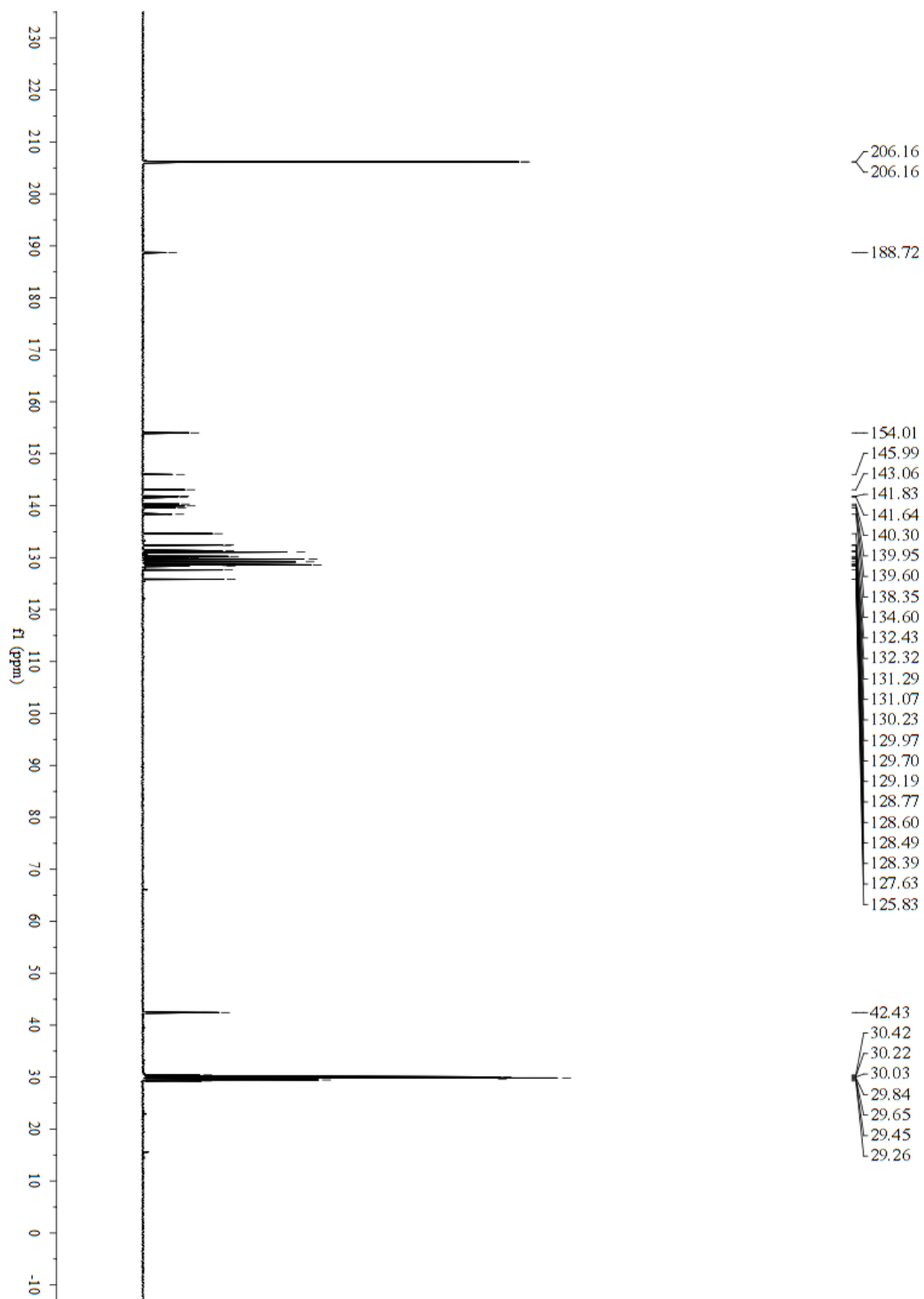


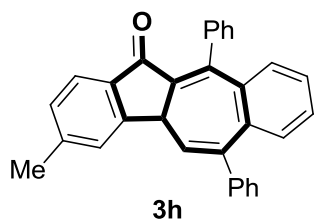
¹H NMR (400 MHz, acetone)



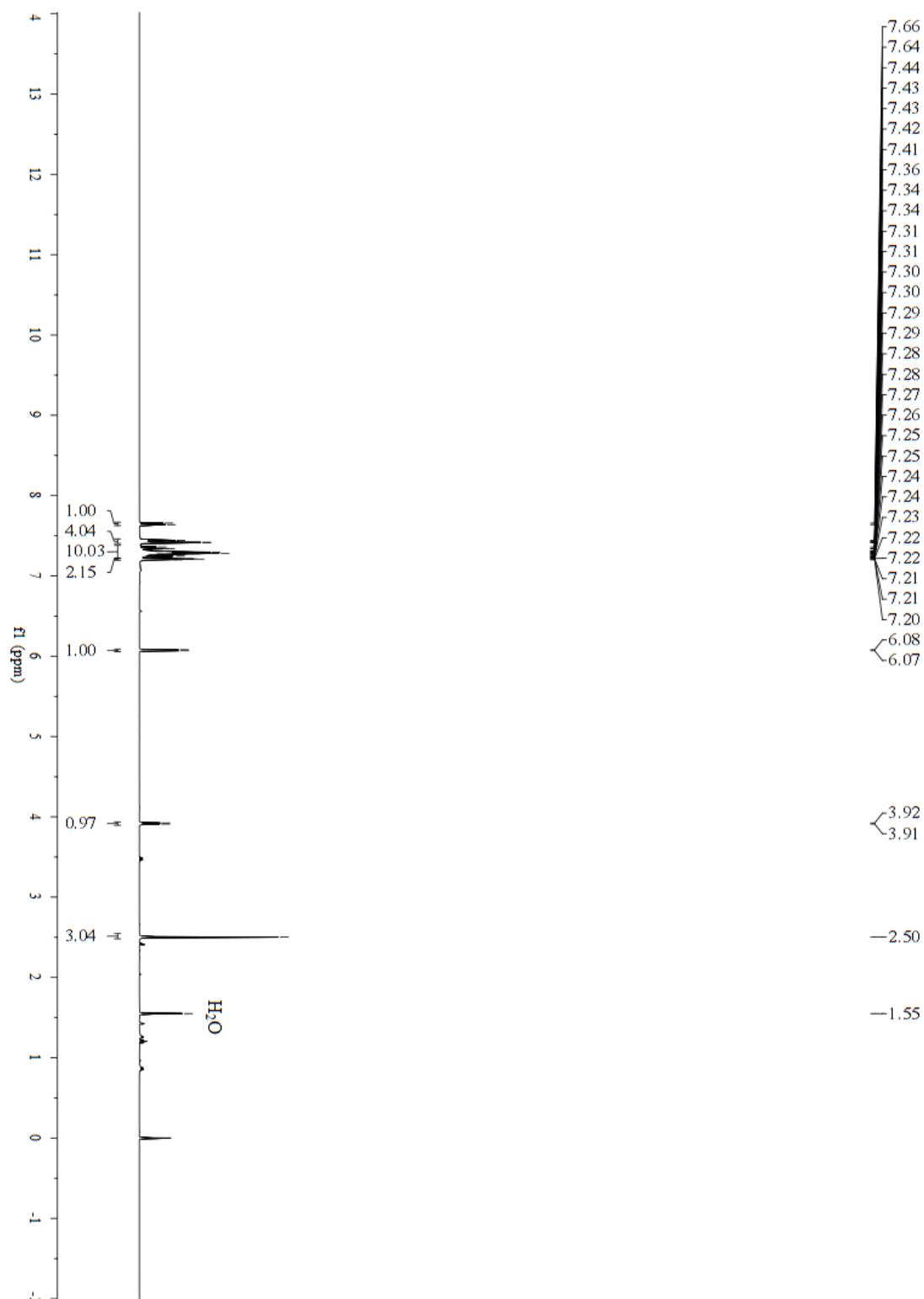


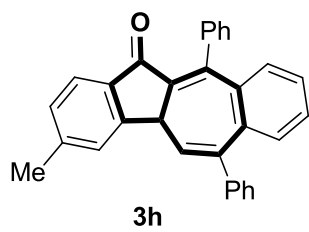
¹³C NMR (100 MHz, acetone)



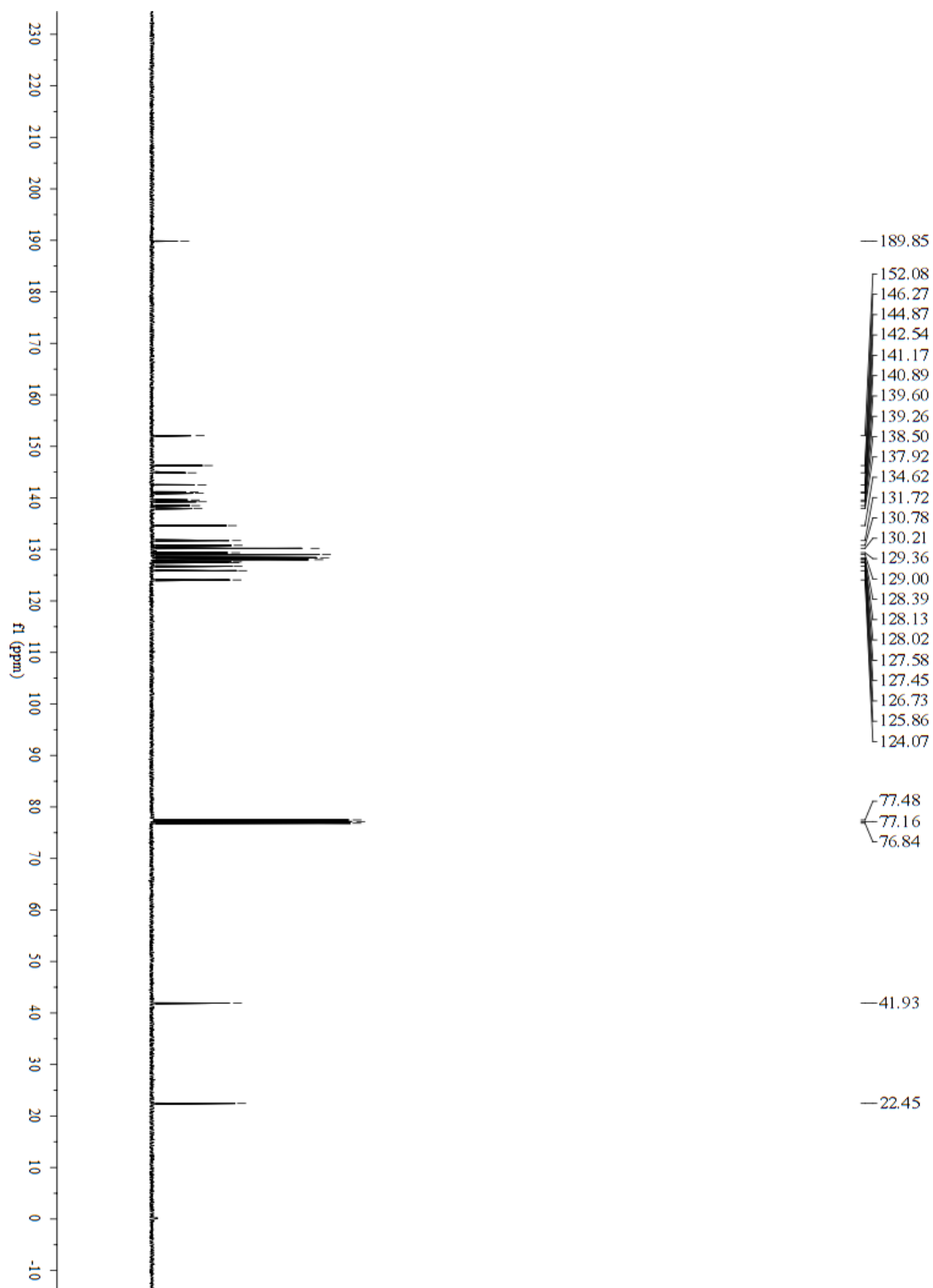


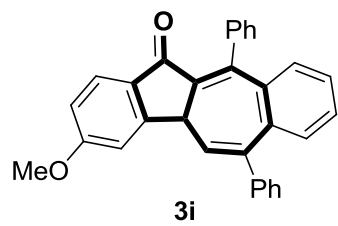
¹H NMR (400 MHz, CDCl₃)



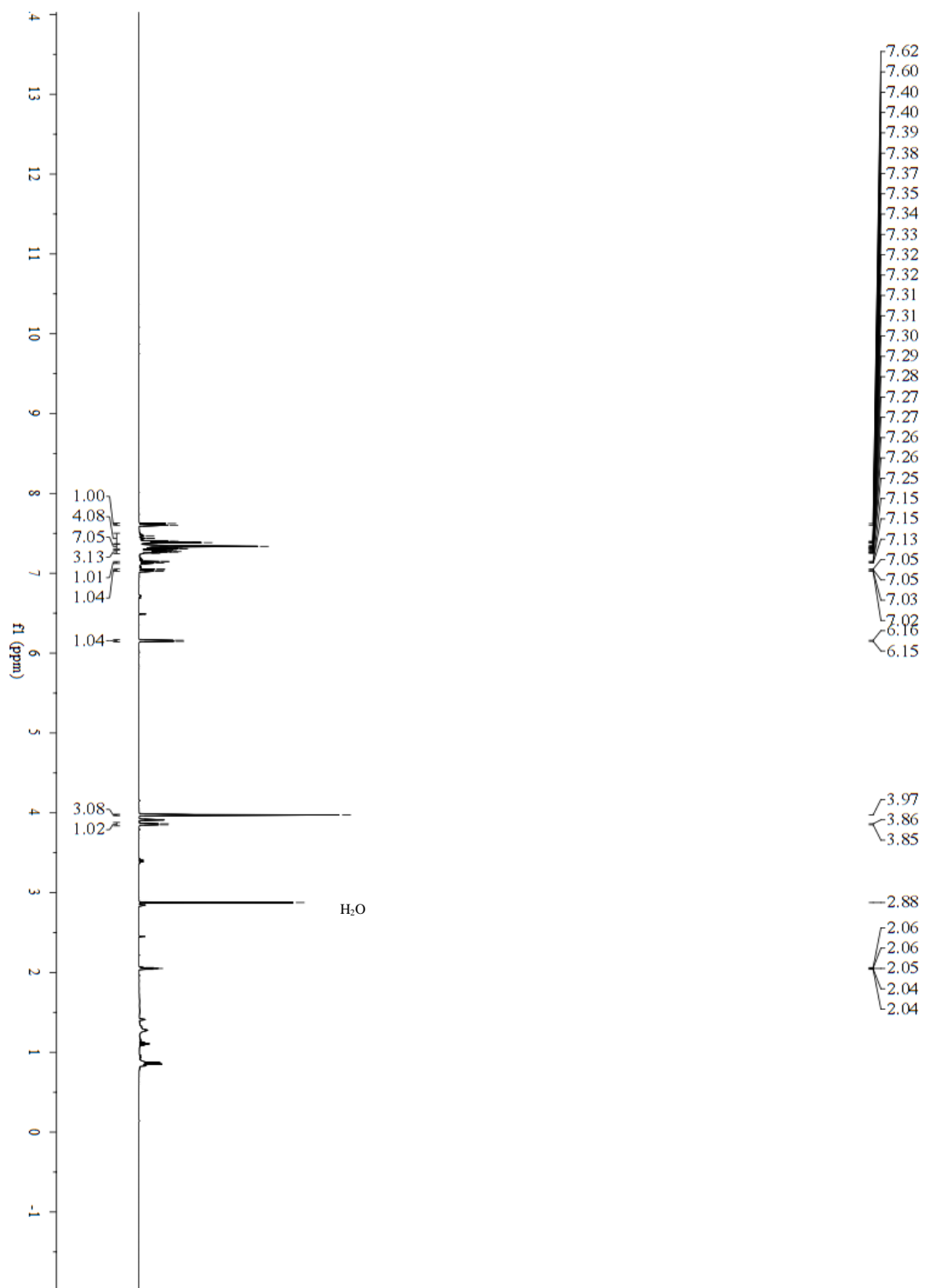


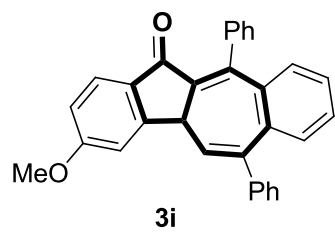
^{13}C NMR (100 MHz, CDCl_3)



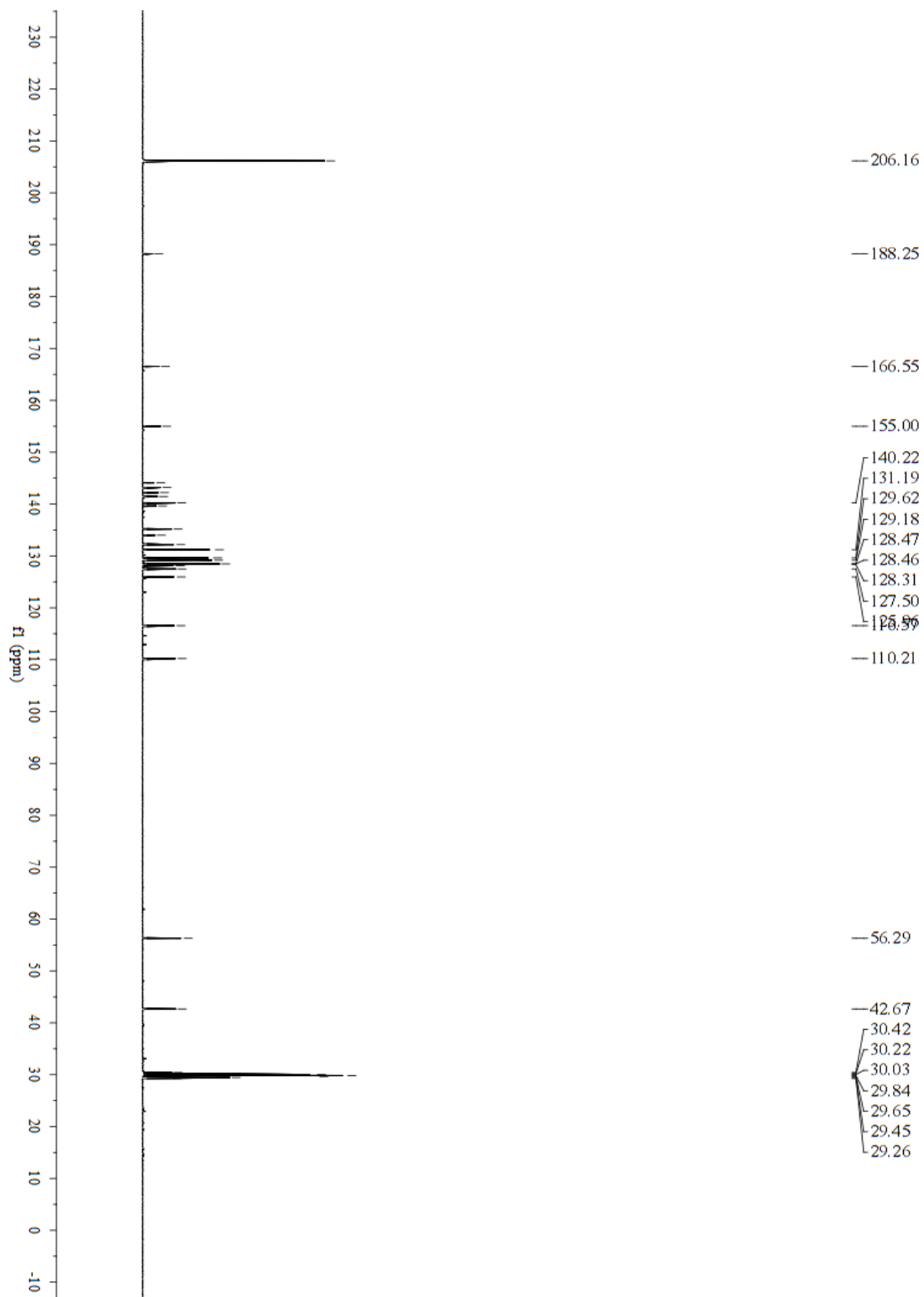


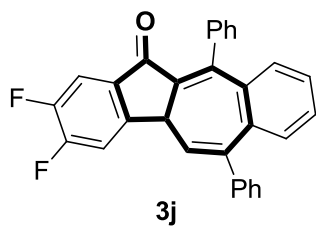
¹H NMR (400 MHz, acetone)



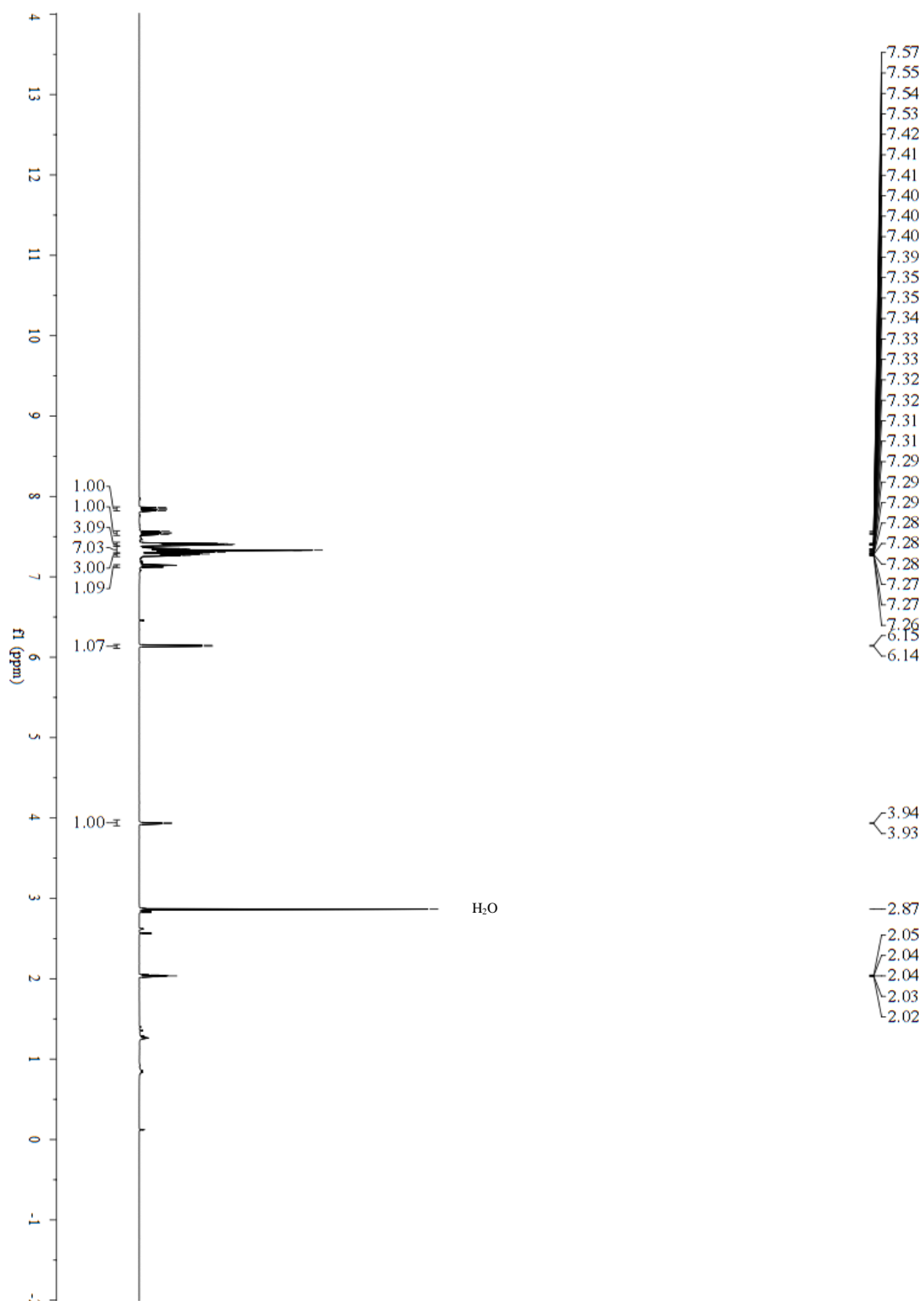


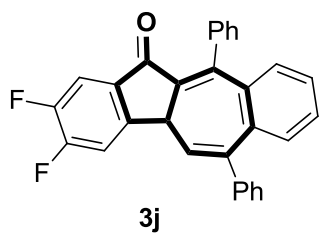
¹³C NMR (100 MHz, acetone)



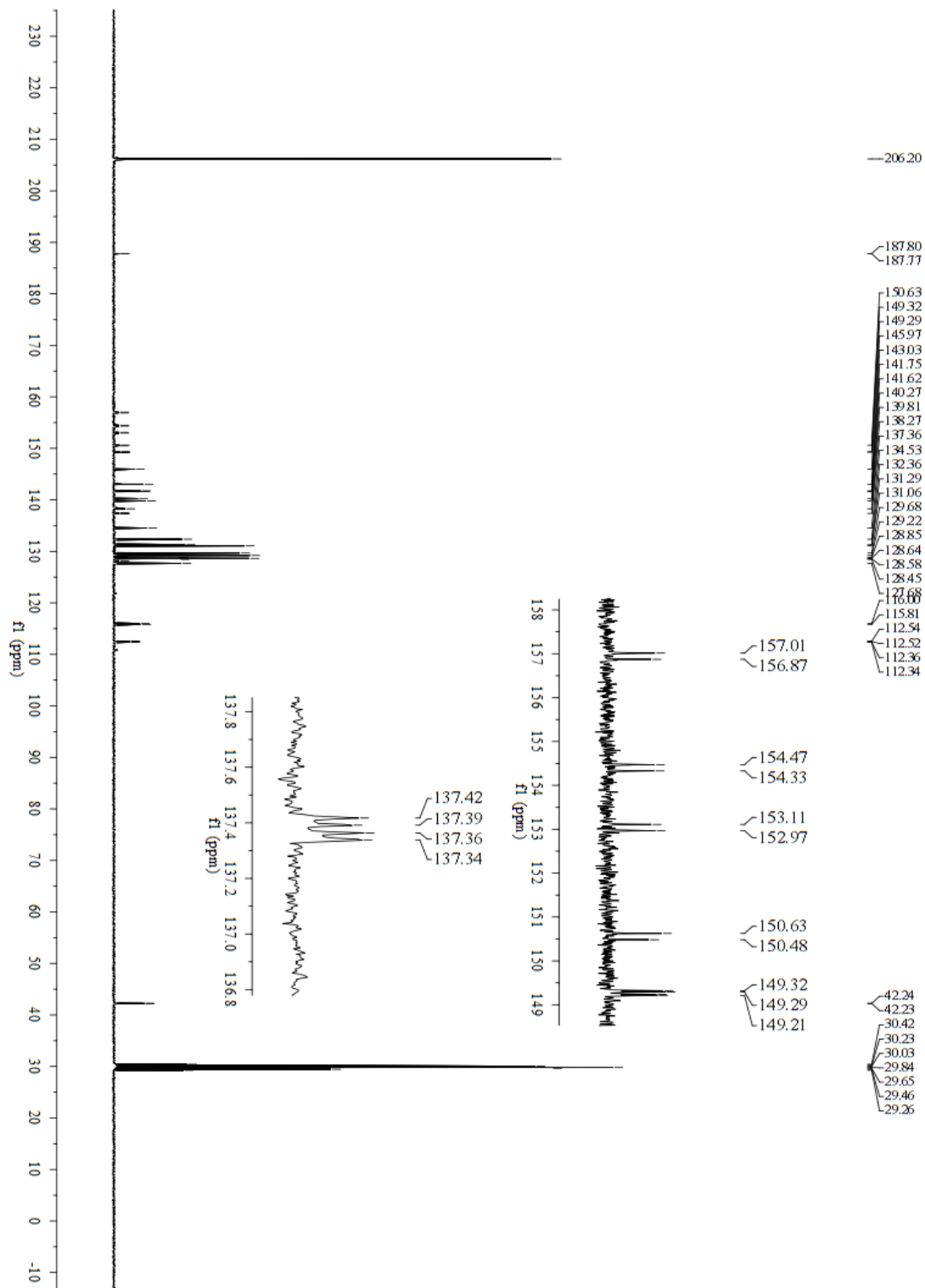


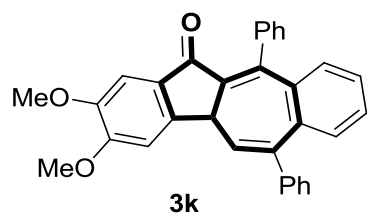
¹H NMR (400 MHz, acetone)



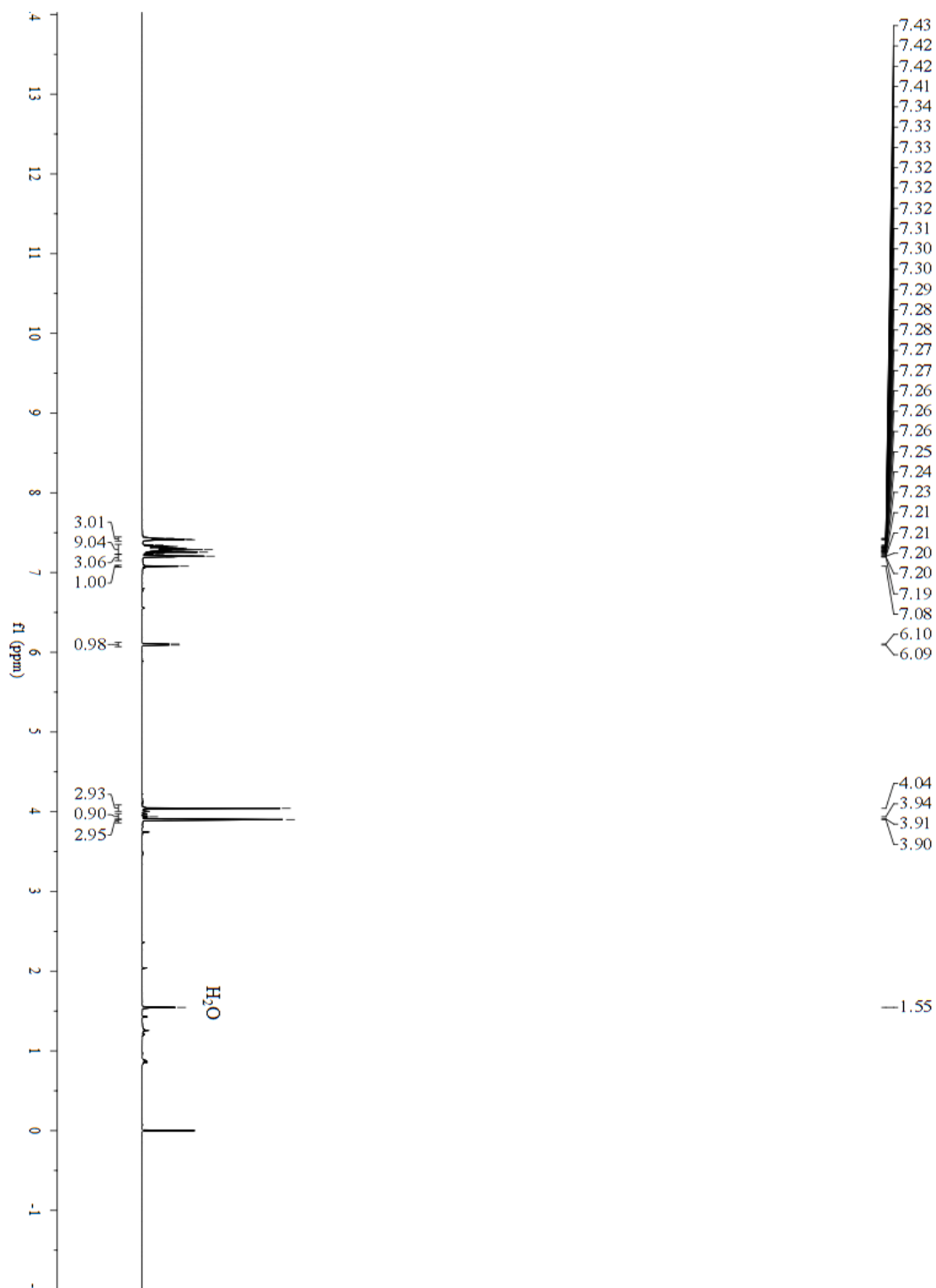


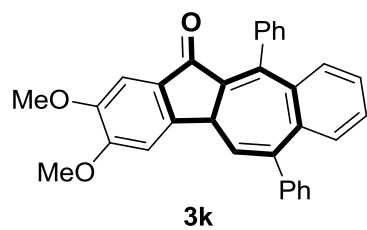
^{13}C NMR (100 MHz, acetone)



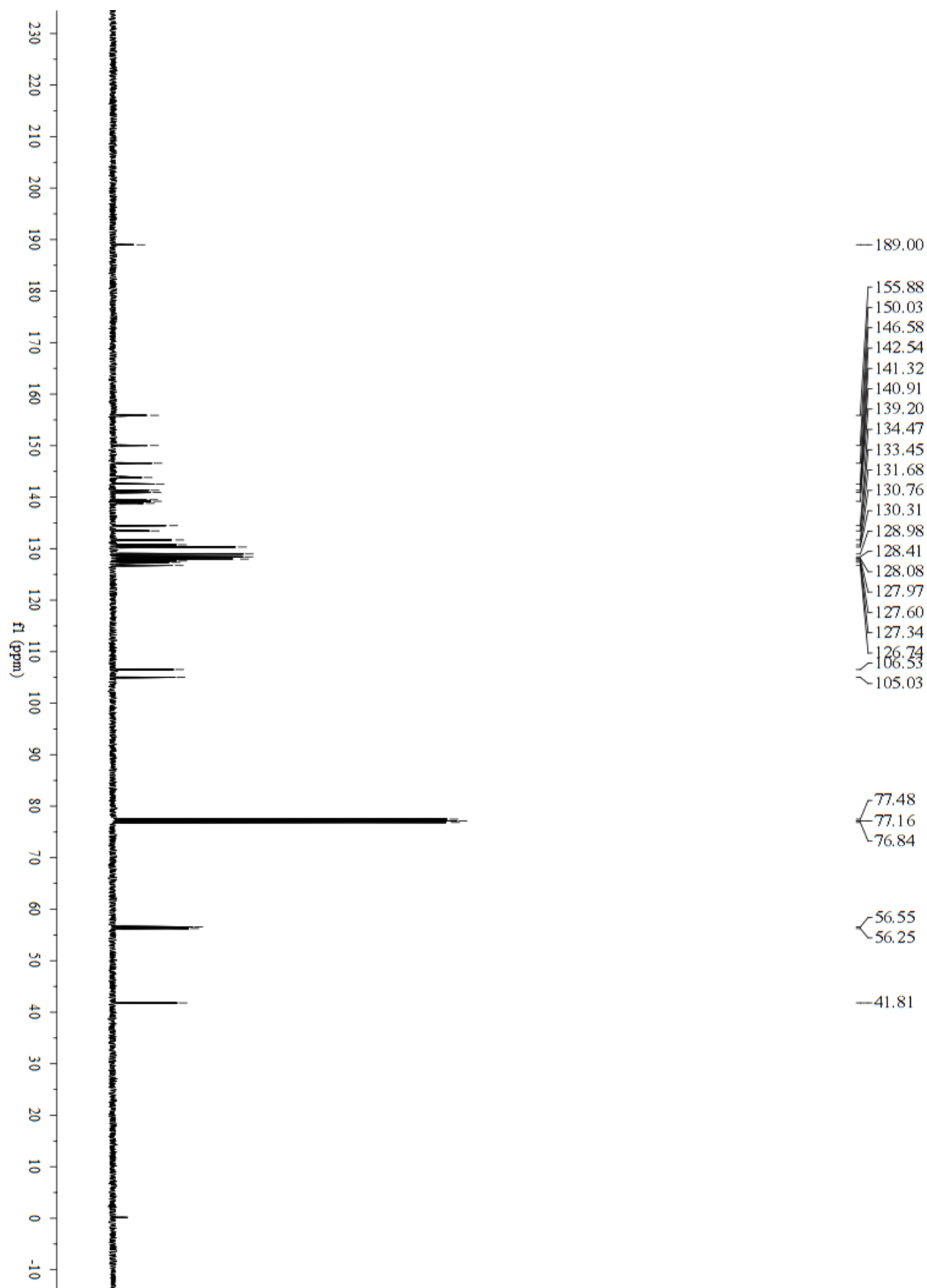


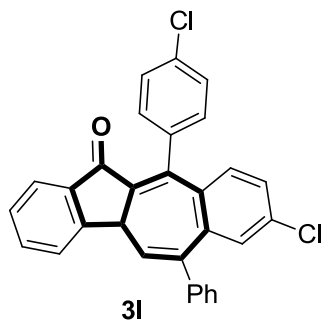
¹H NMR (400 MHz, CDCl₃)



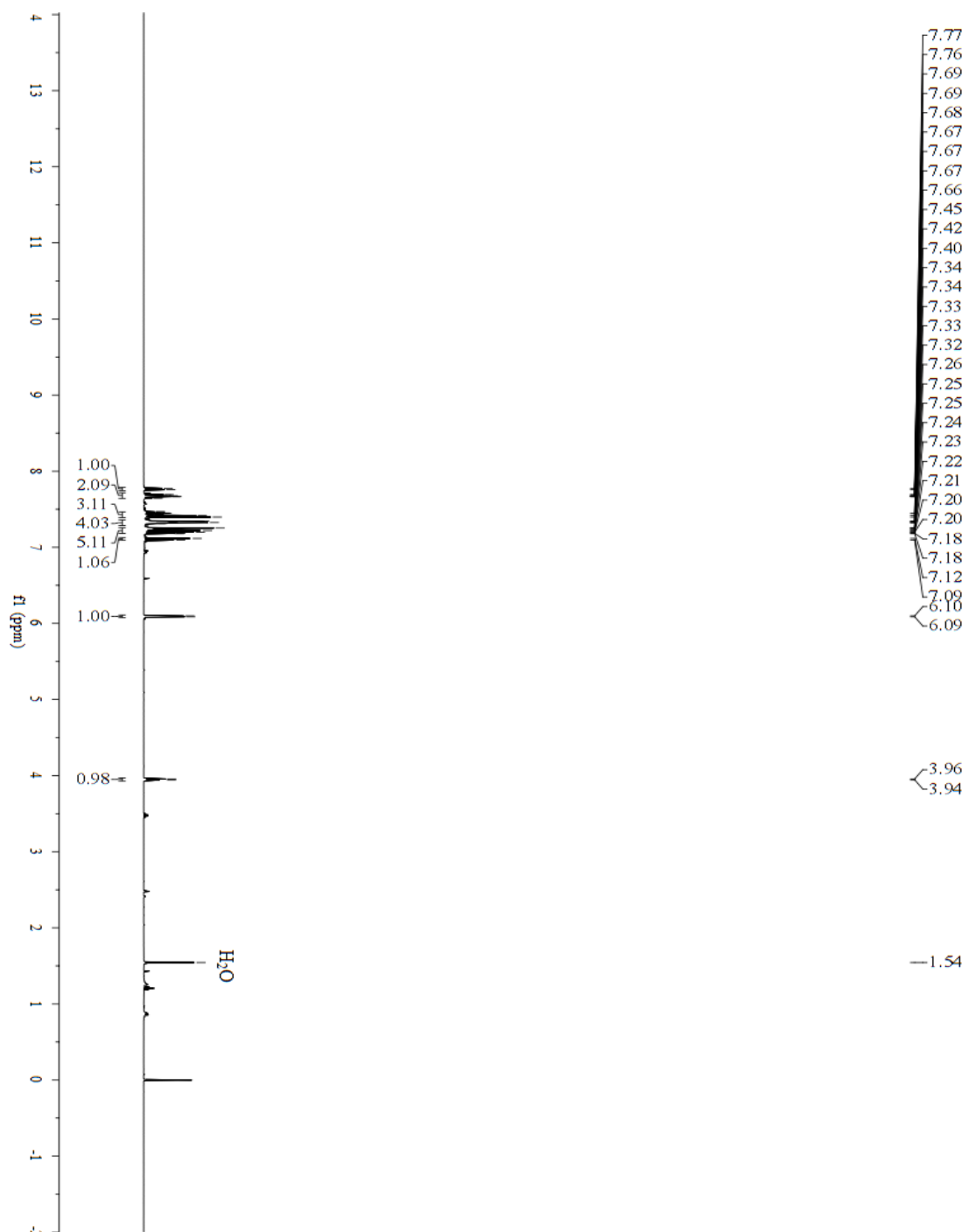


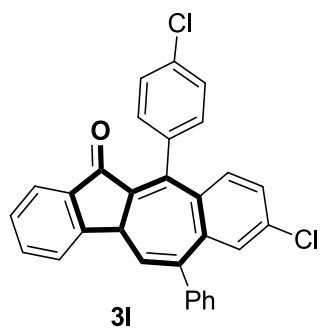
^{13}C NMR (100 MHz, CDCl_3)



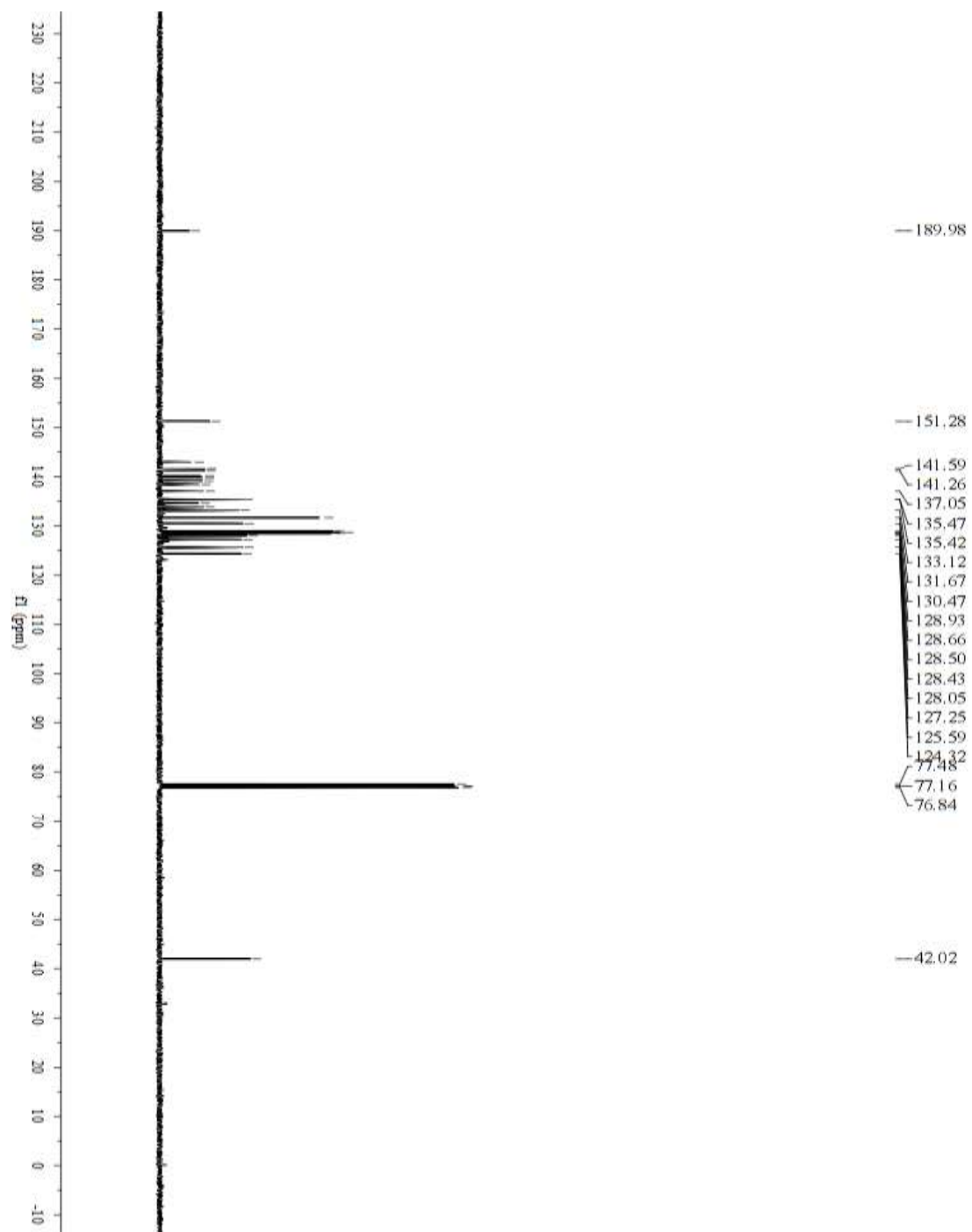


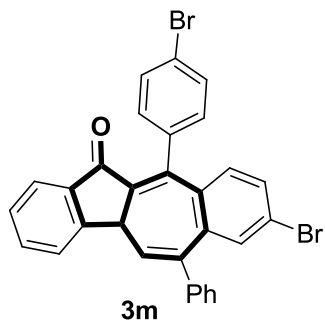
¹H NMR (400 MHz, CDCl₃)



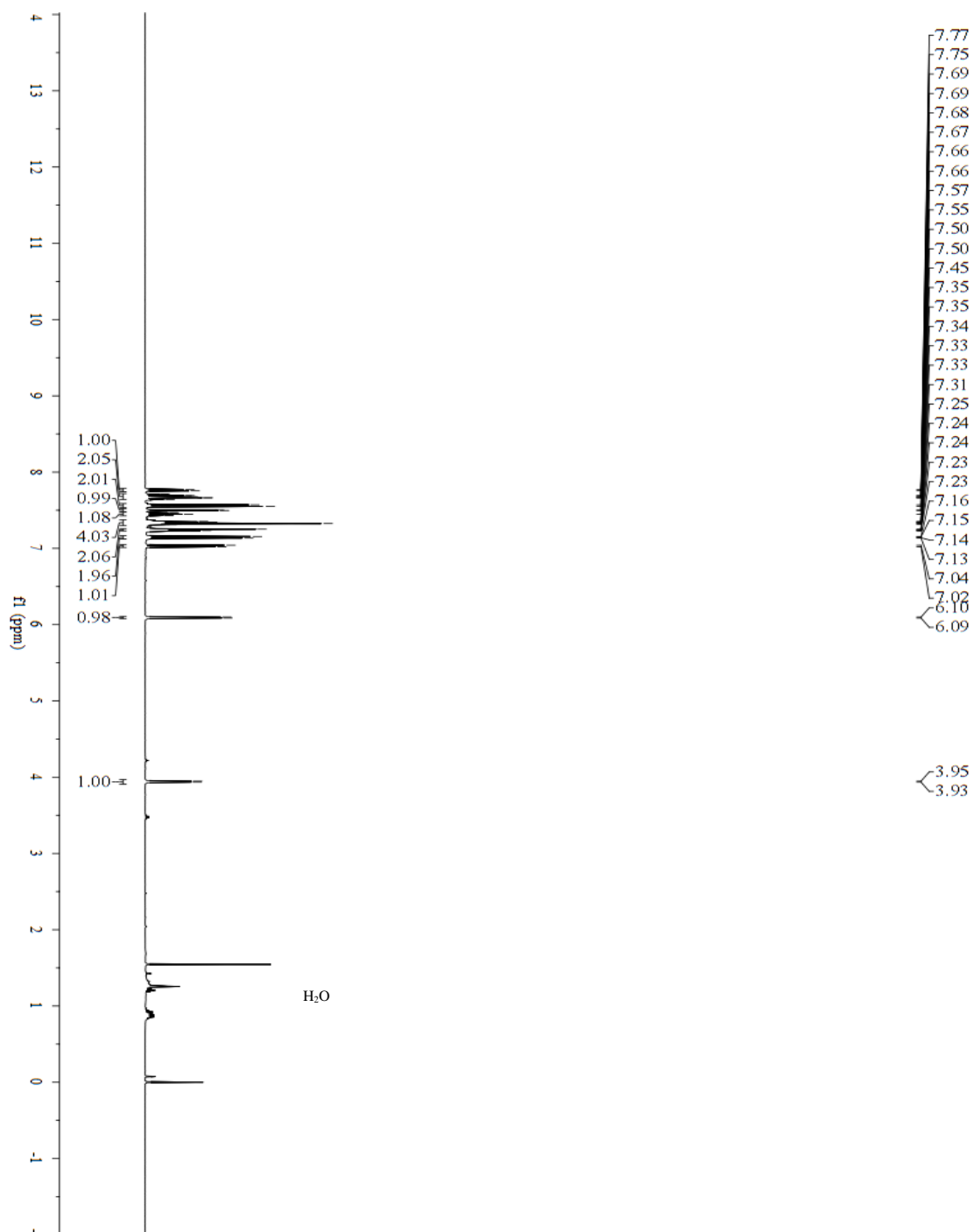


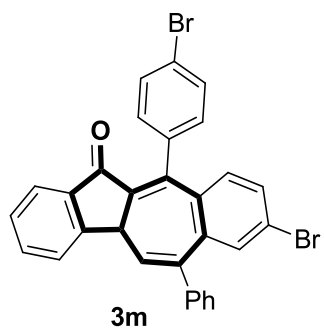
^{13}C NMR (100 MHz, CDCl_3)



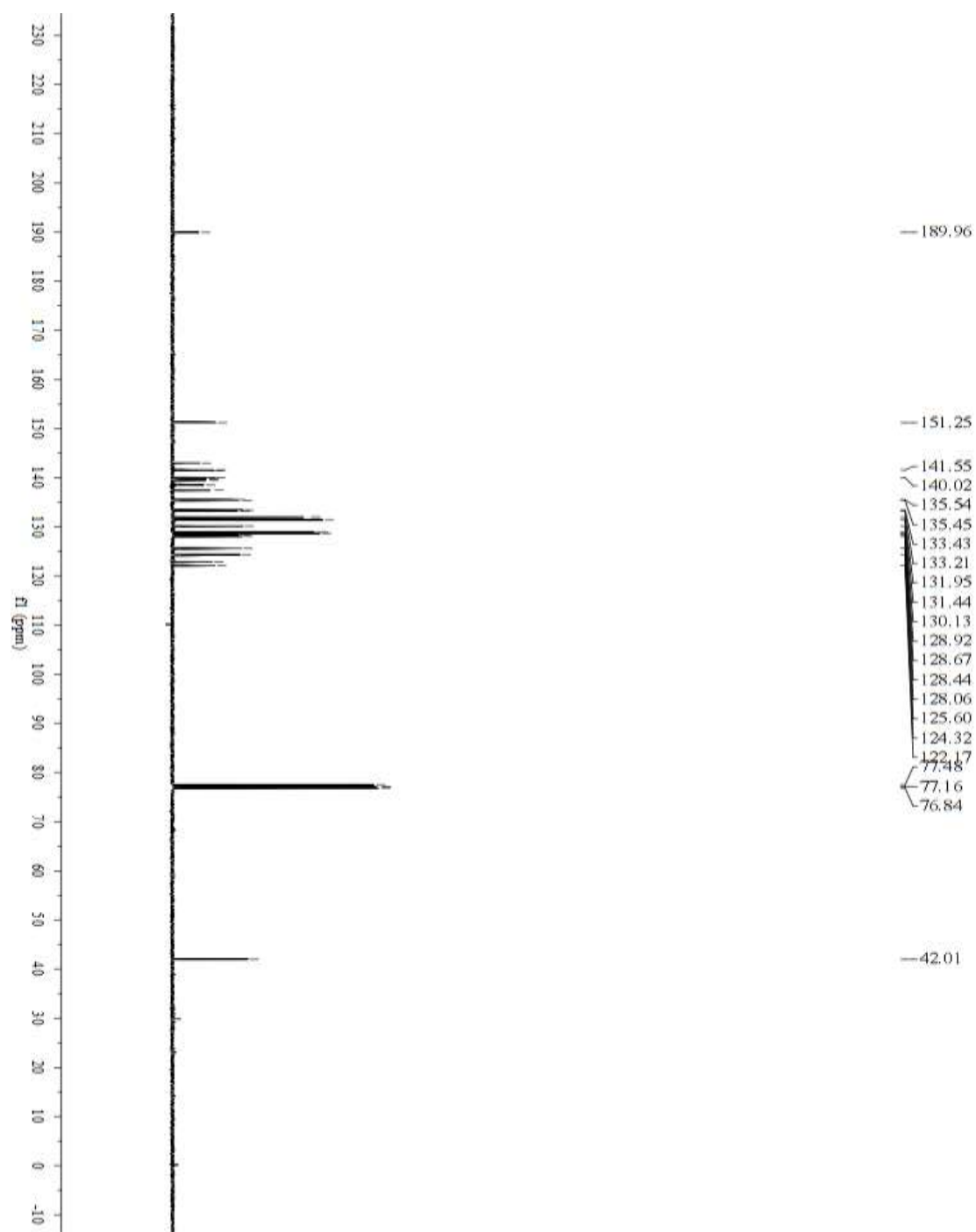


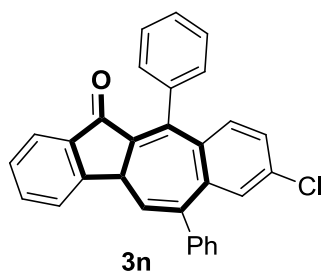
$^1\text{H NMR}$ (400 MHz, CDCl_3)



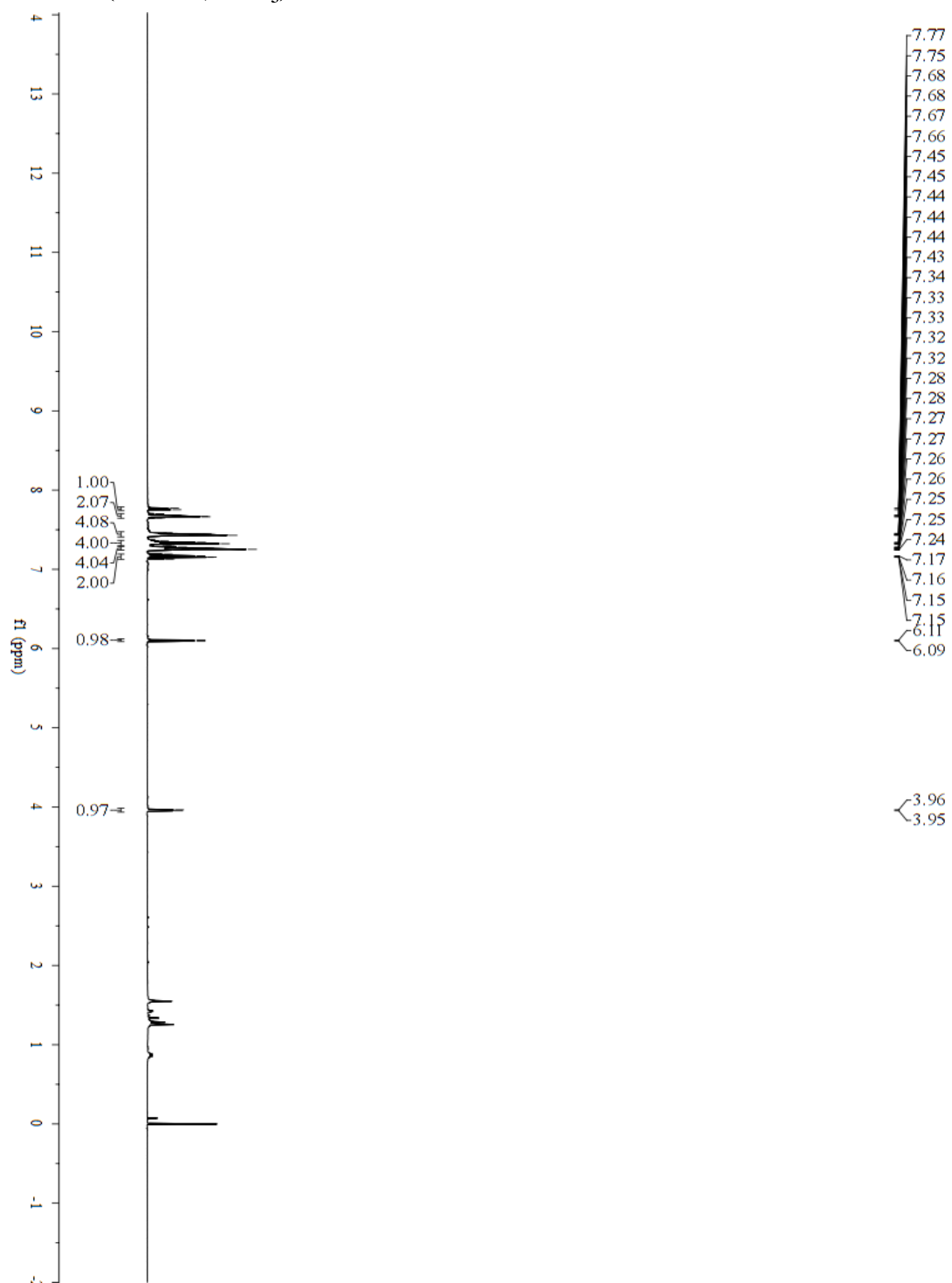


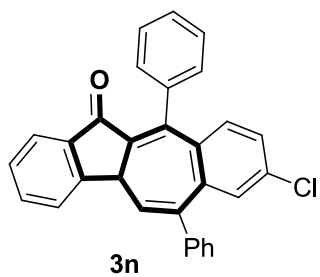
^{13}C NMR (100 MHz, CDCl_3)



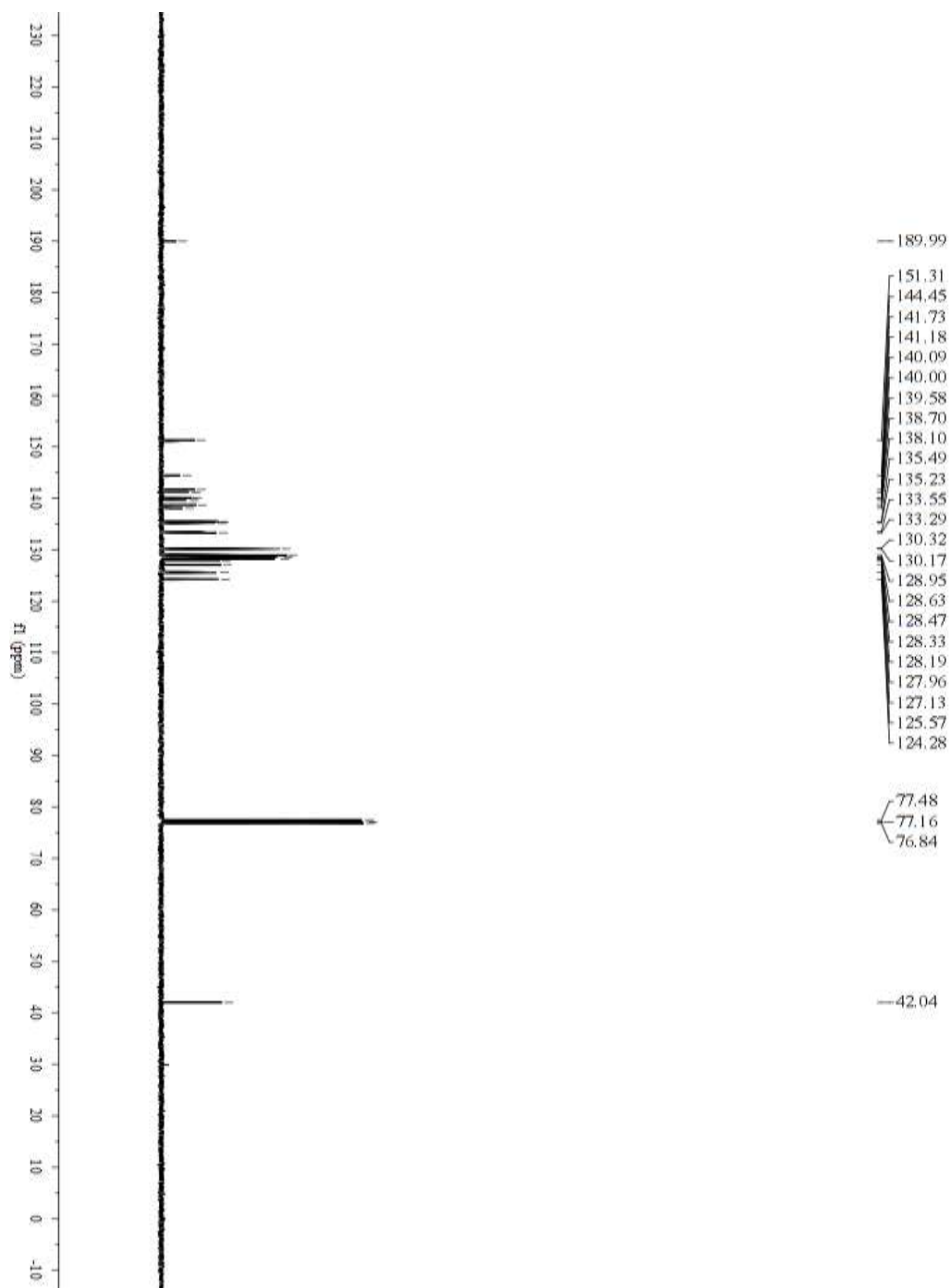


¹H NMR (400 MHz, CDCl₃)

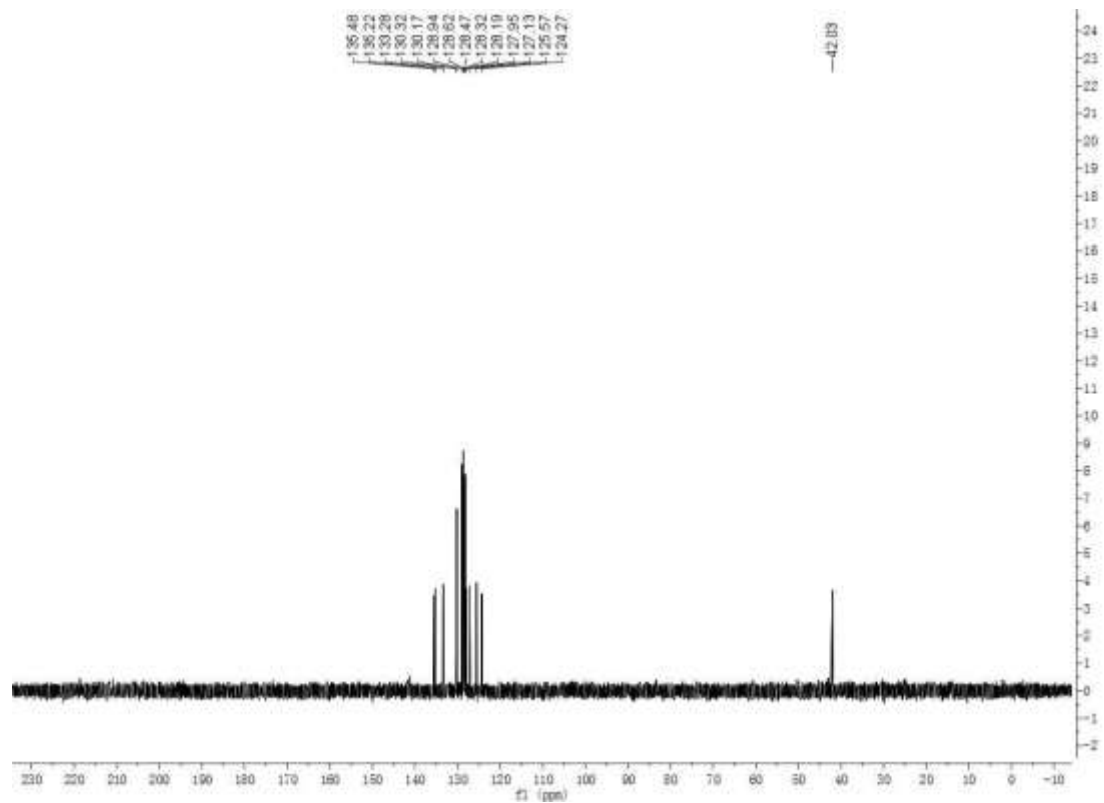




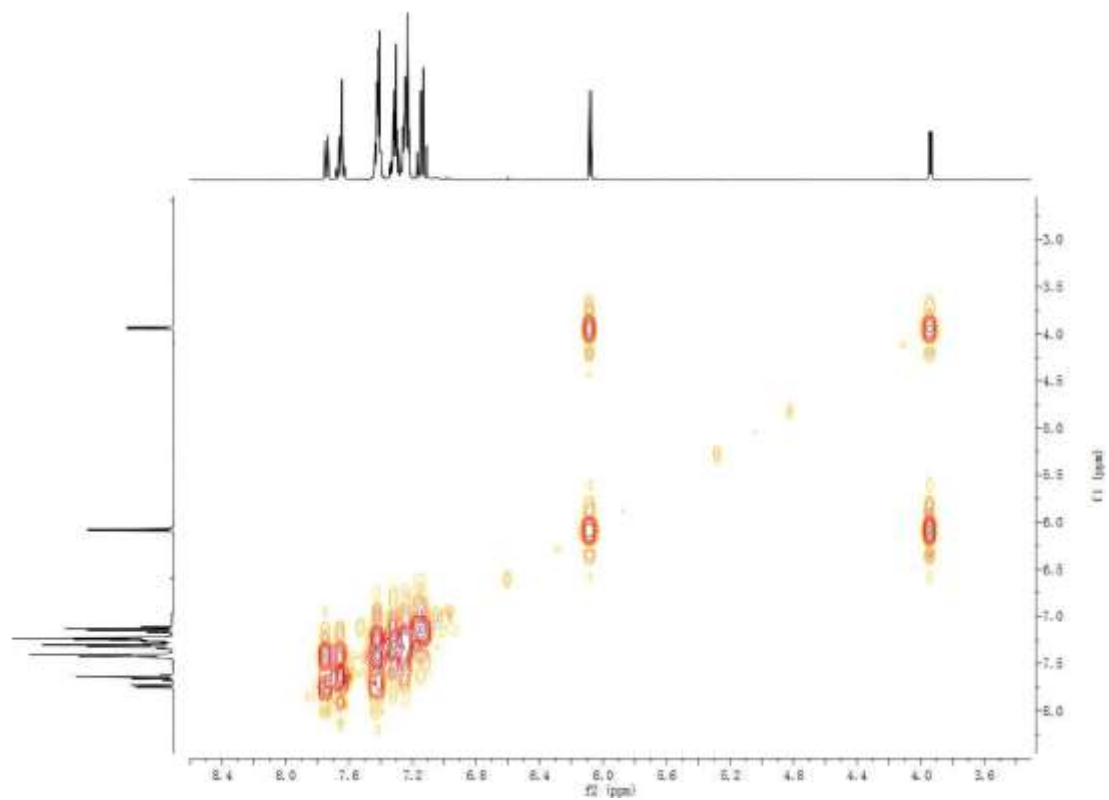
^{13}C NMR (100 MHz, CDCl_3)



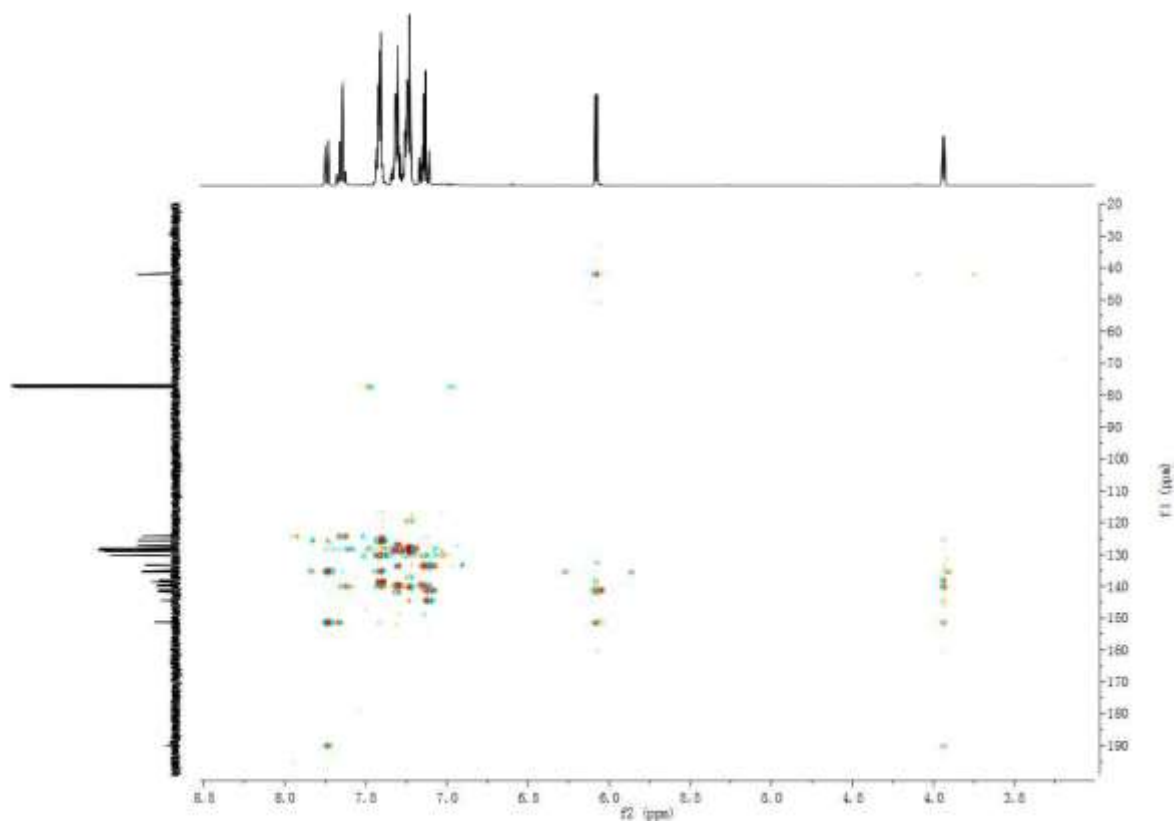
3n-DEPT



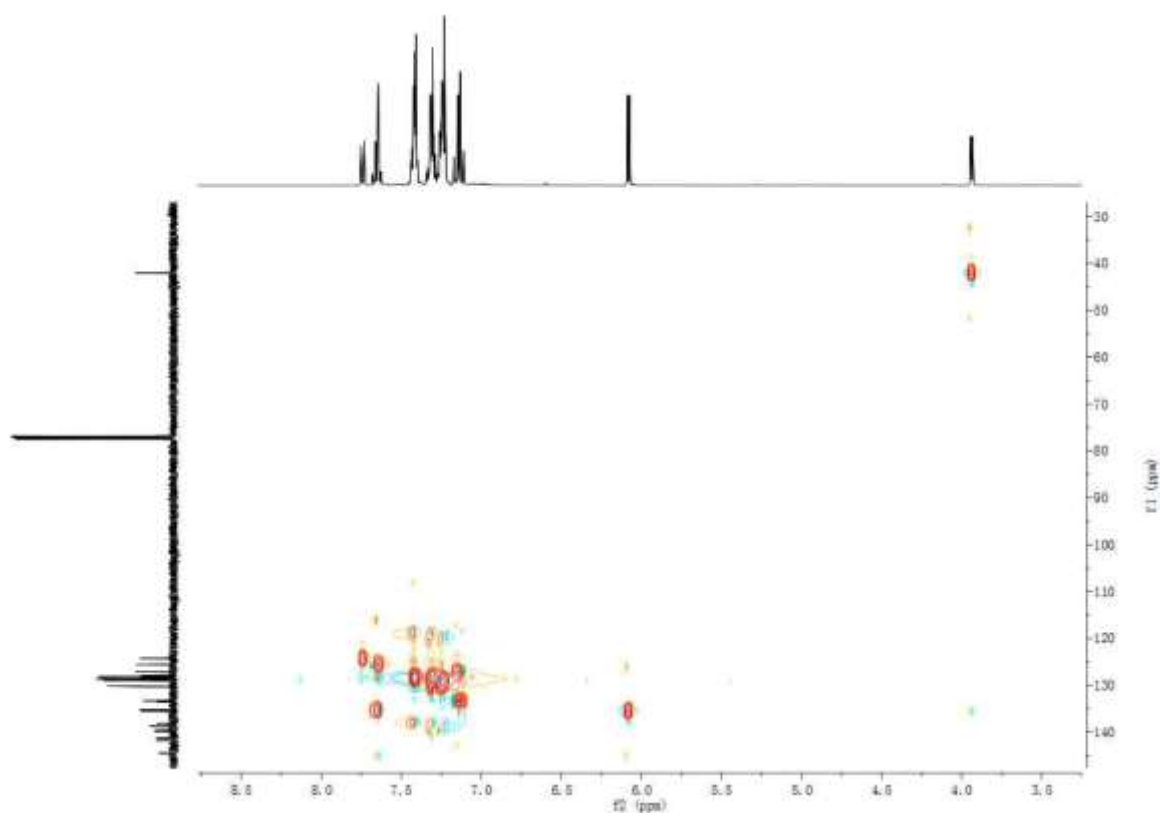
3n- ¹H-¹H COSY

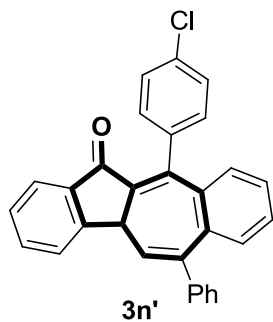


3n- HMBC

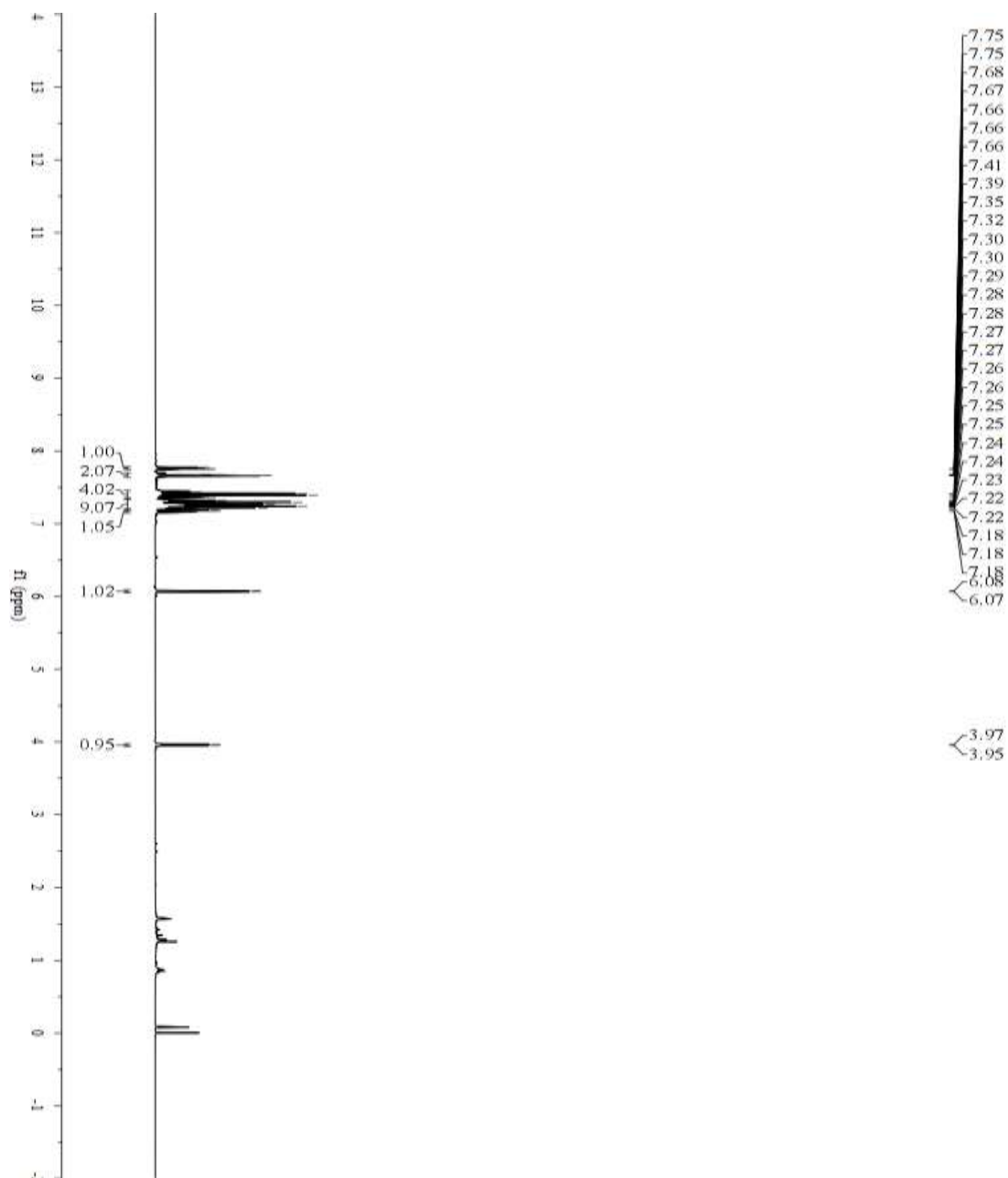


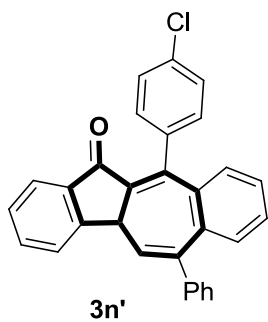
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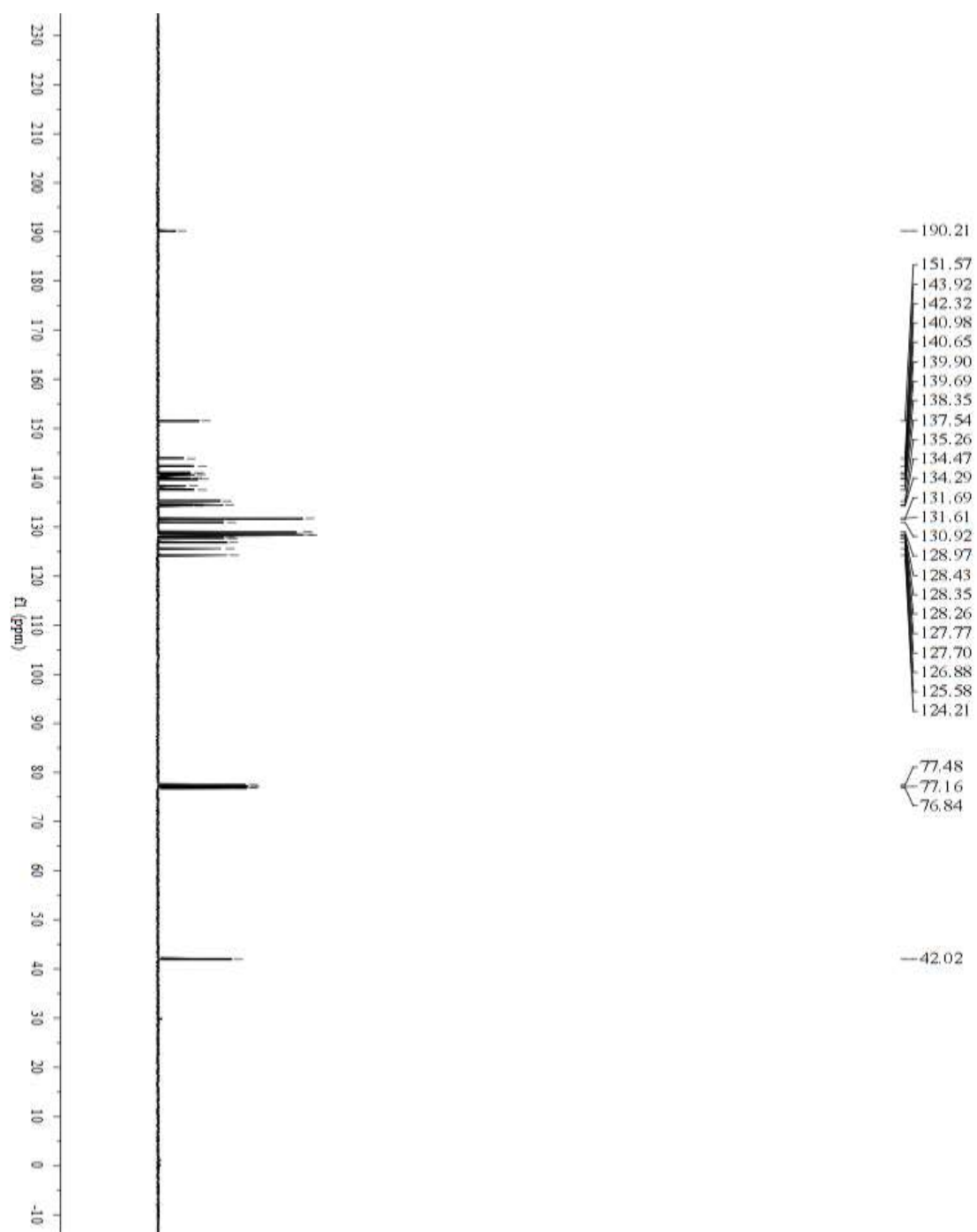


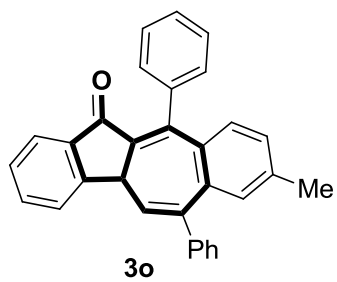
$^1\text{H NMR}$ (400 MHz, CDCl_3)



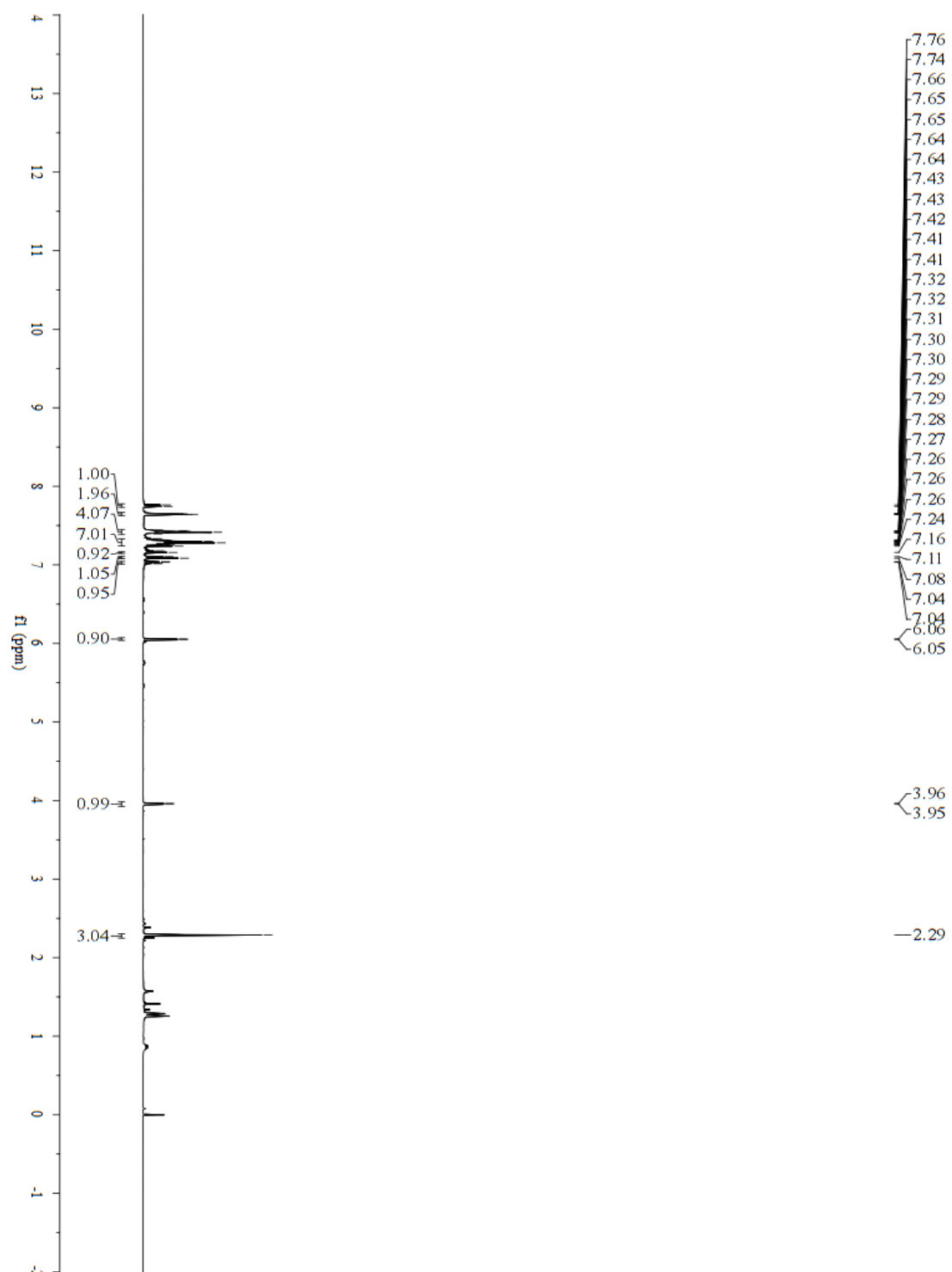


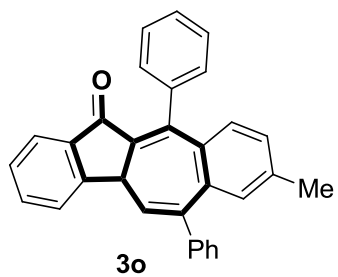
^{13}C NMR (100 MHz, CDCl_3)



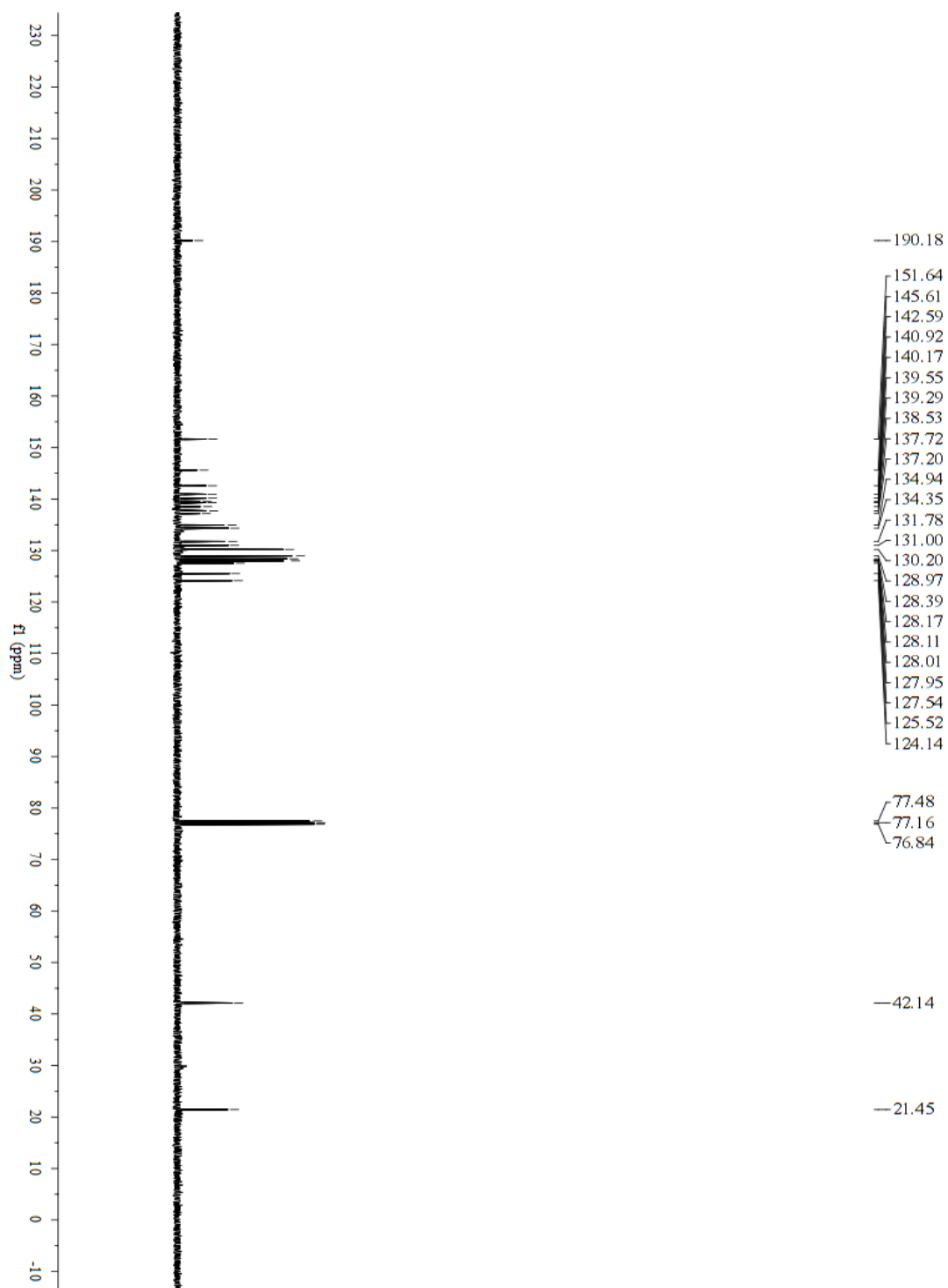


¹H NMR (400 MHz, CDCl₃)

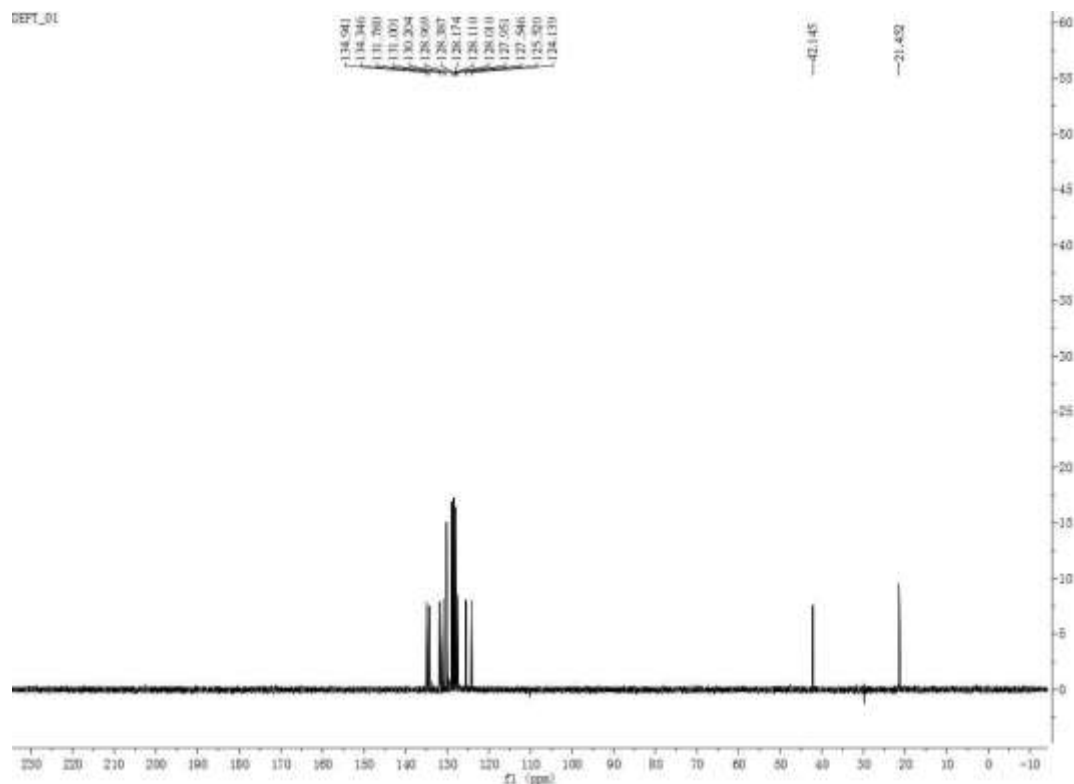




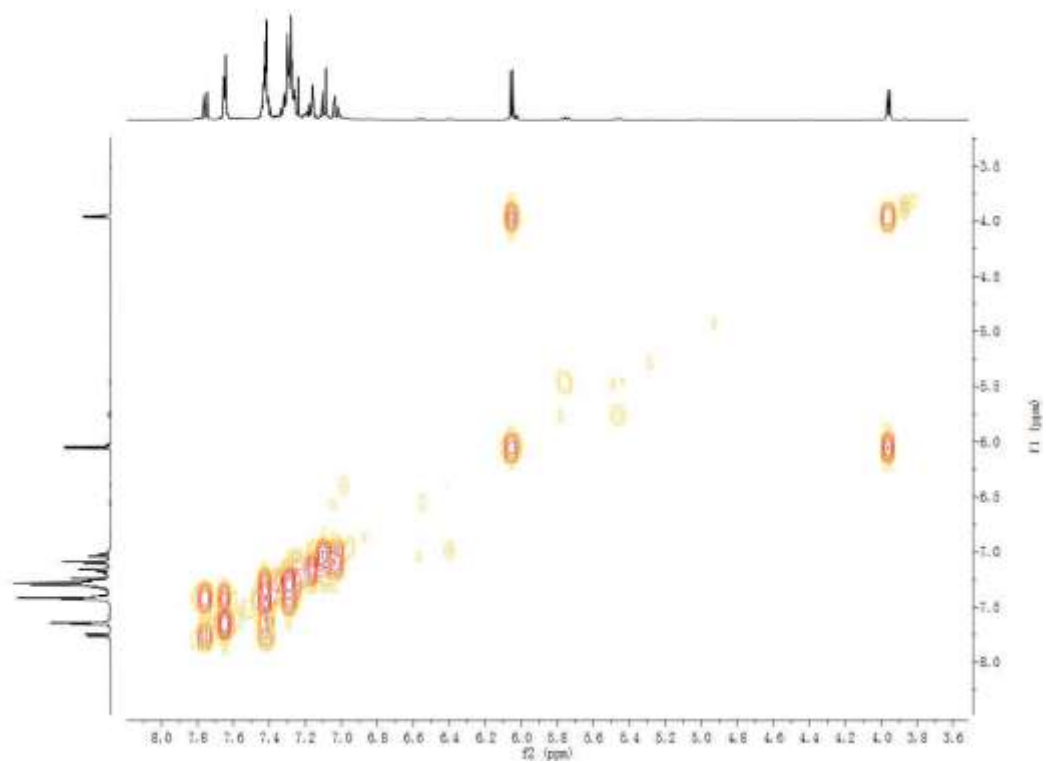
^{13}C NMR (100 MHz, CDCl_3)



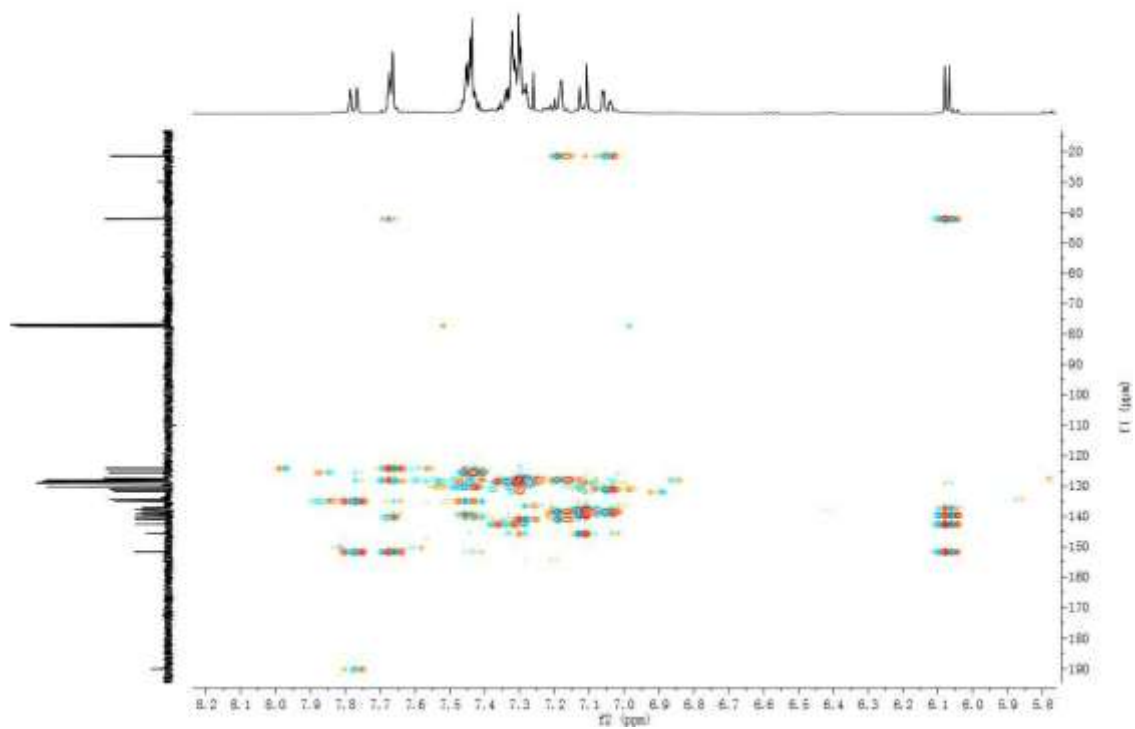
3o-DEPT



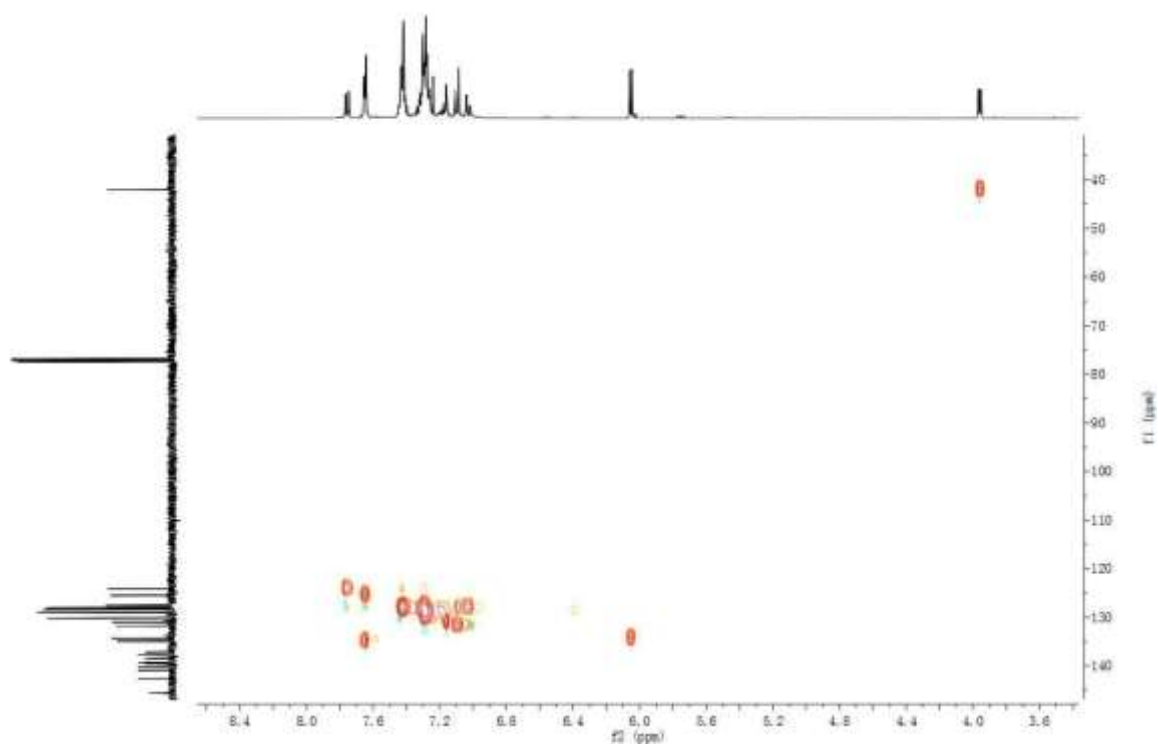
3o- ¹H-¹H COSY

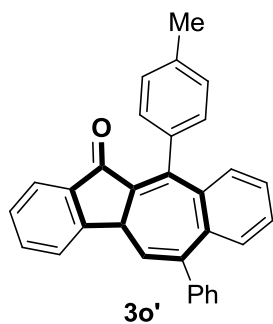


3o- HMBC

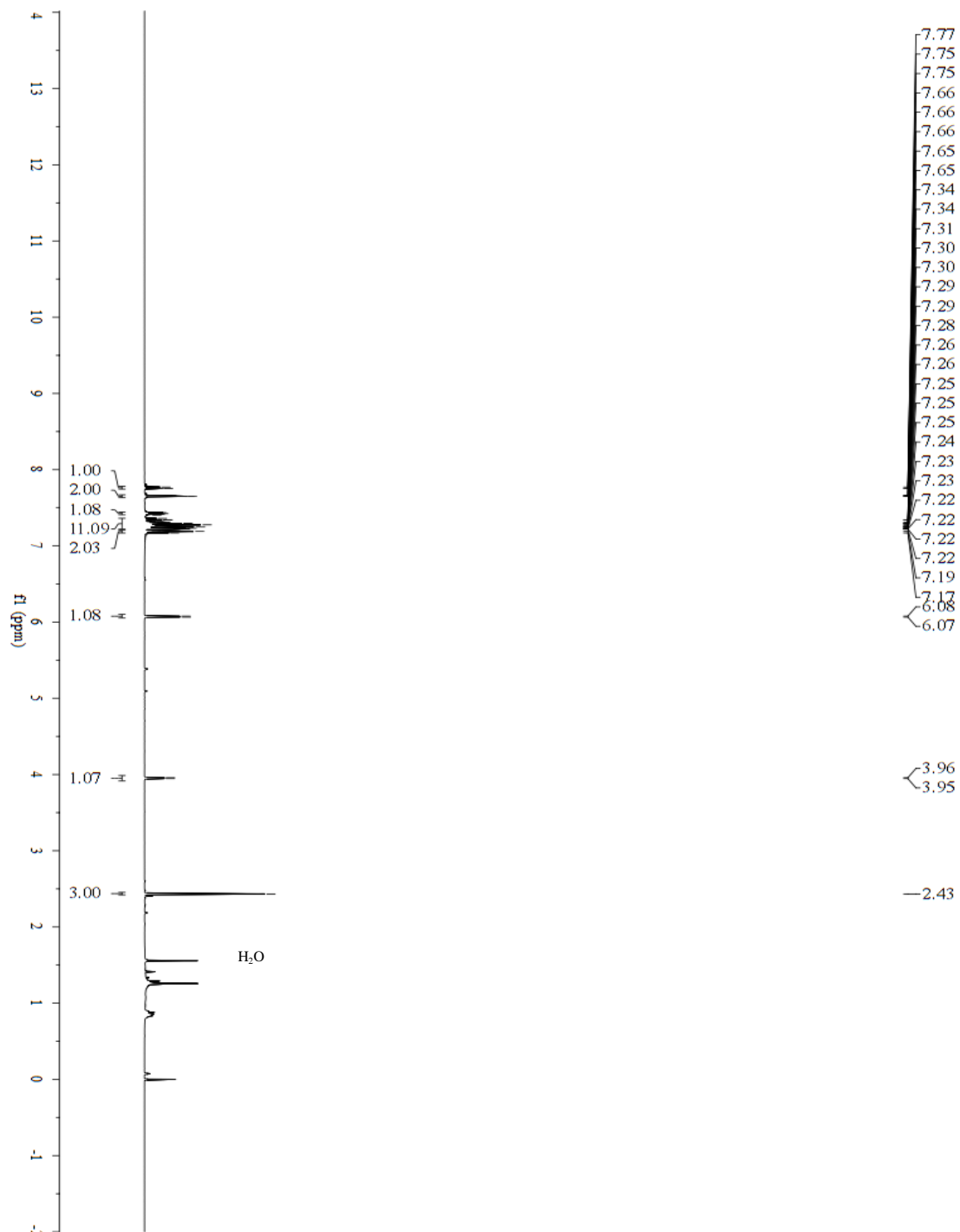


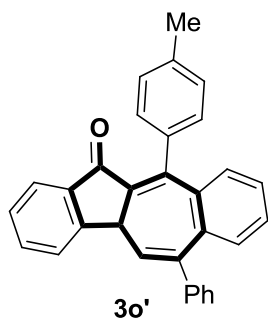
3o- HSQC



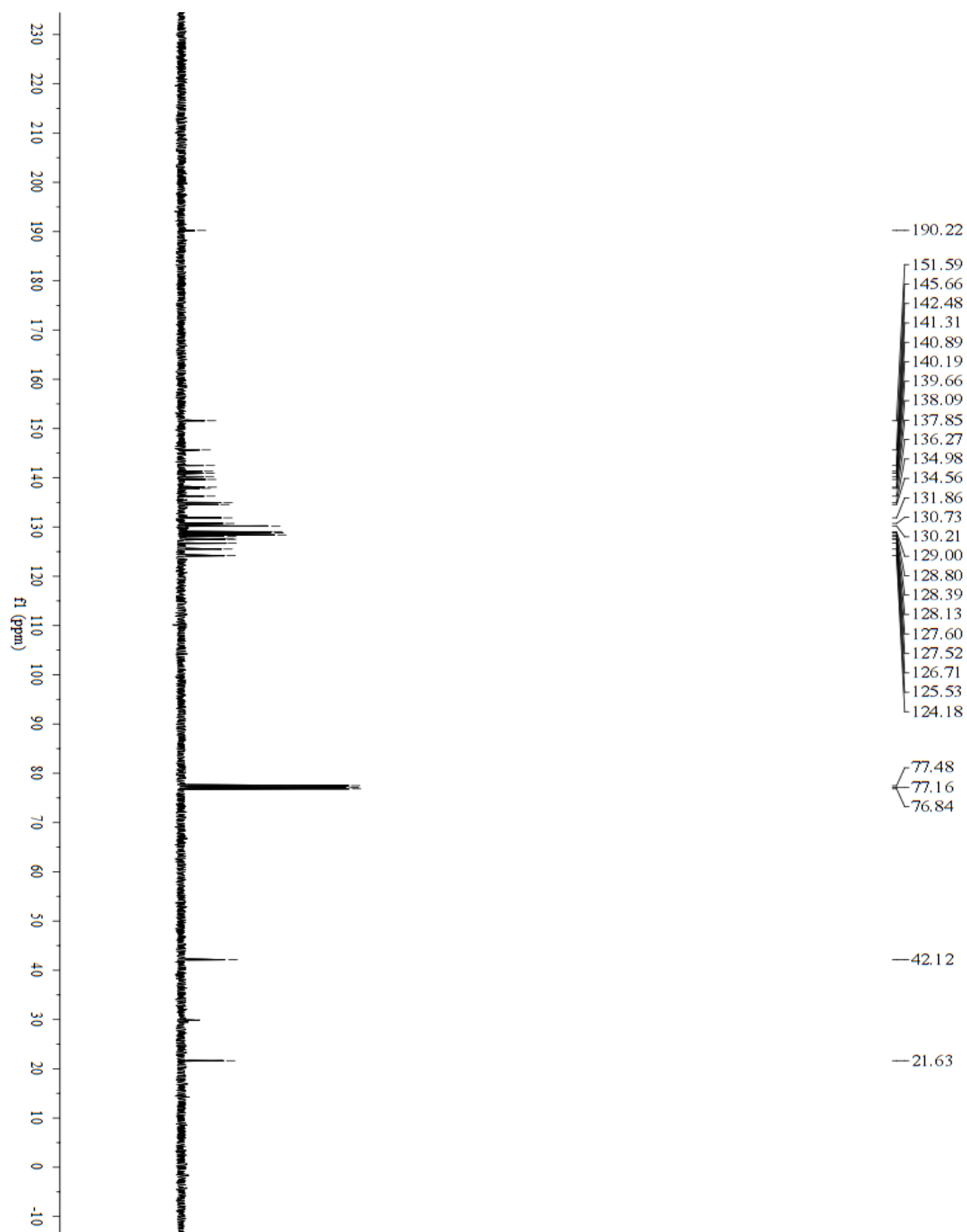


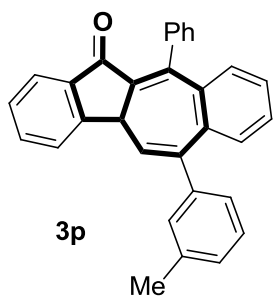
$^1\text{H NMR}$ (400 MHz, CDCl_3)



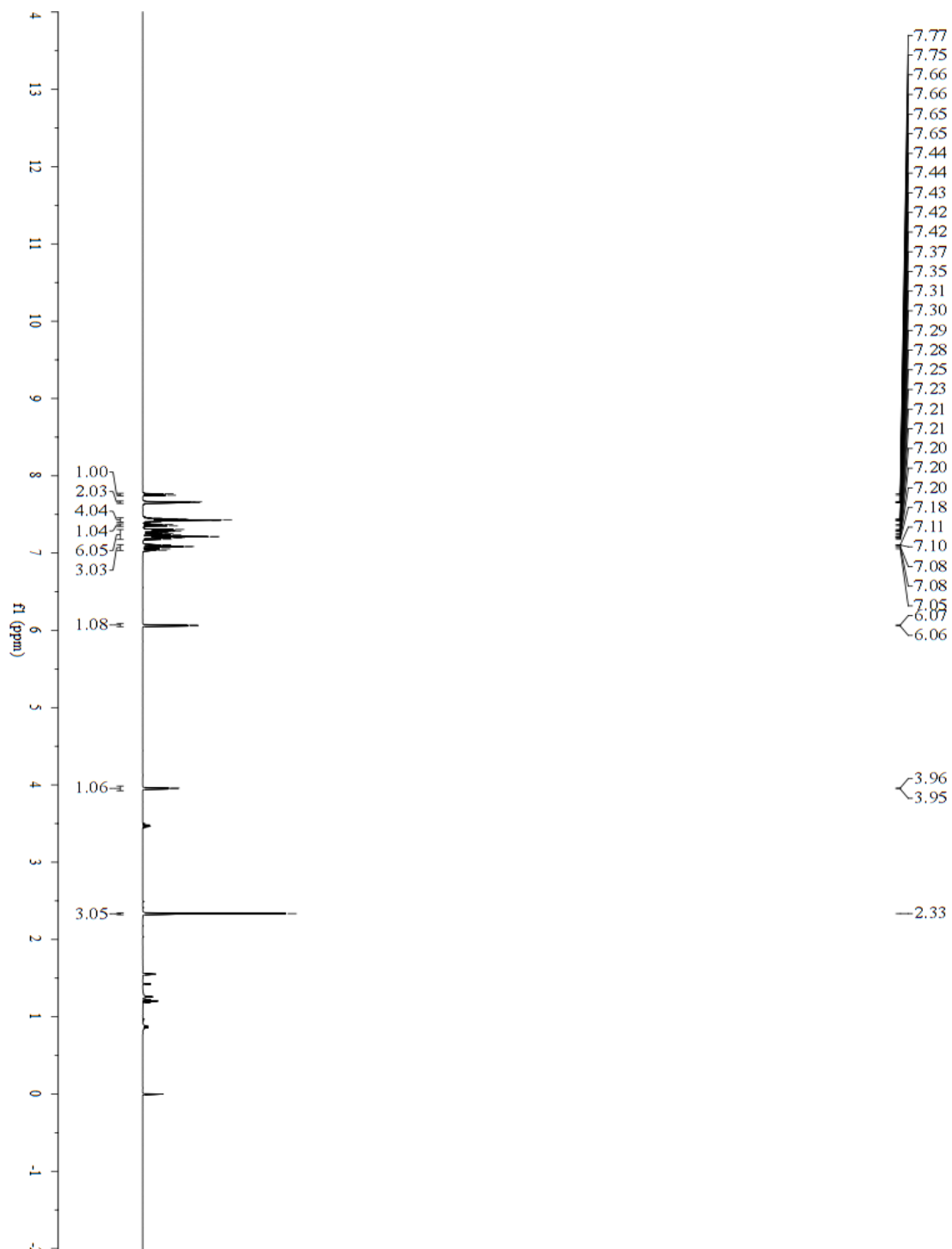


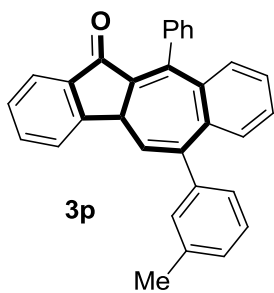
^{13}C NMR (100 MHz, CDCl_3)



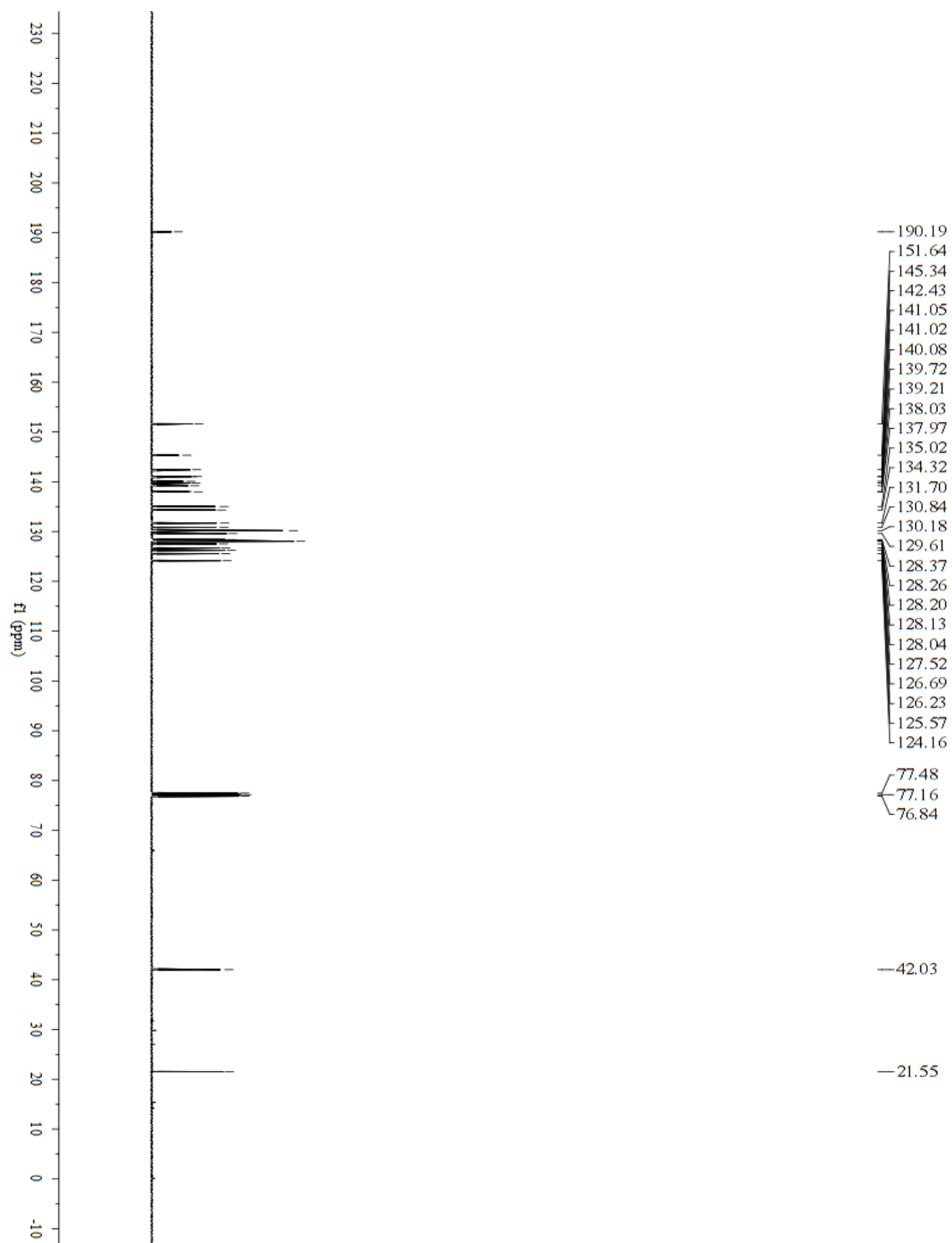


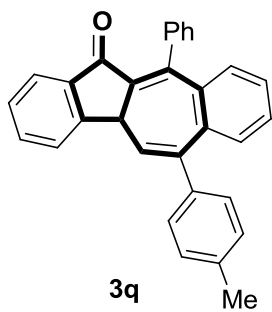
$^1\text{H NMR}$ (400 MHz, CDCl_3)



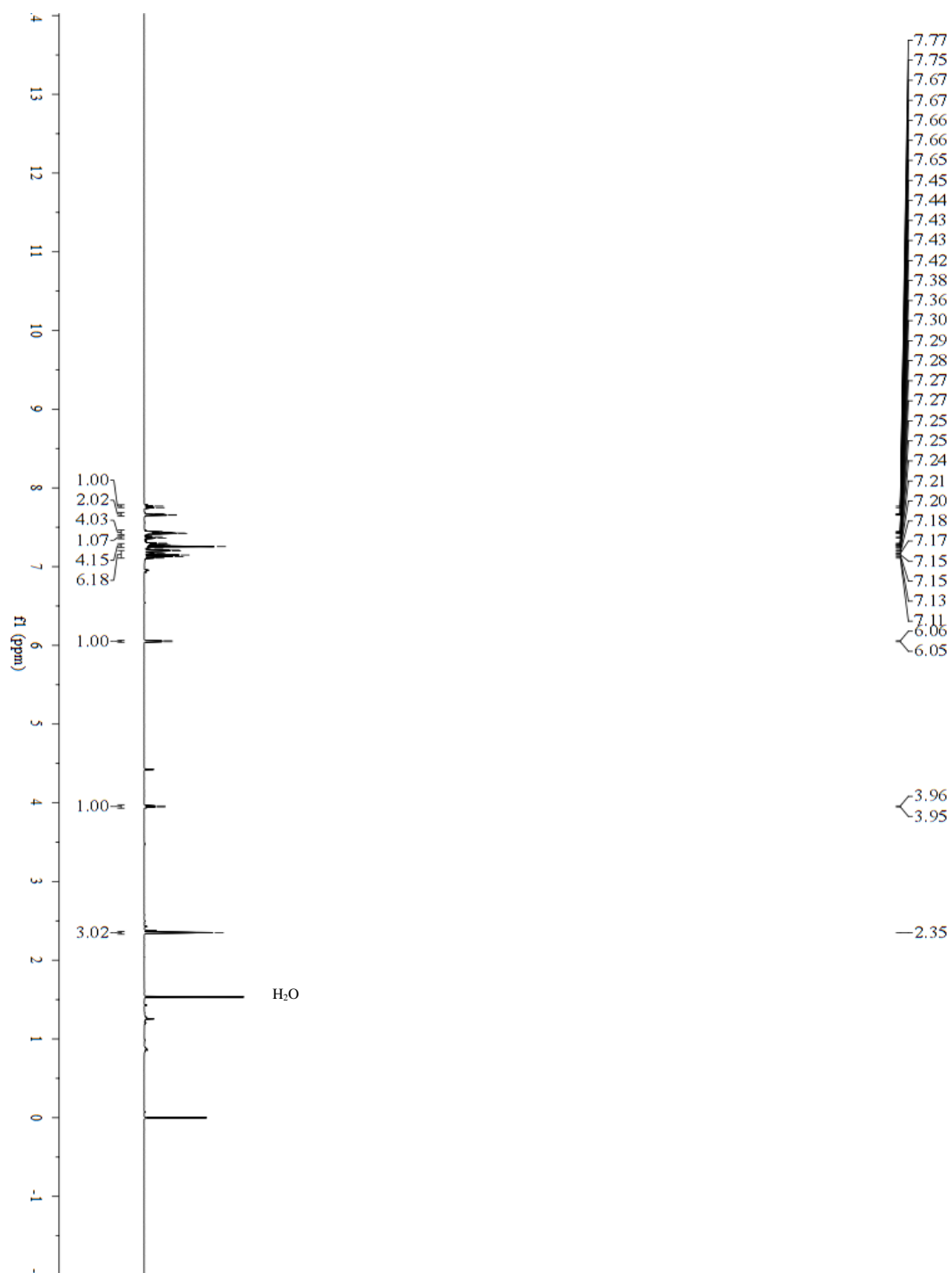


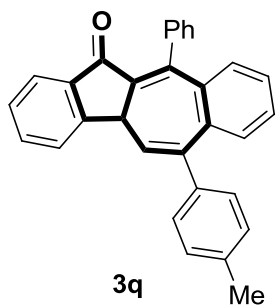
^{13}C NMR (100 MHz, CDCl_3)



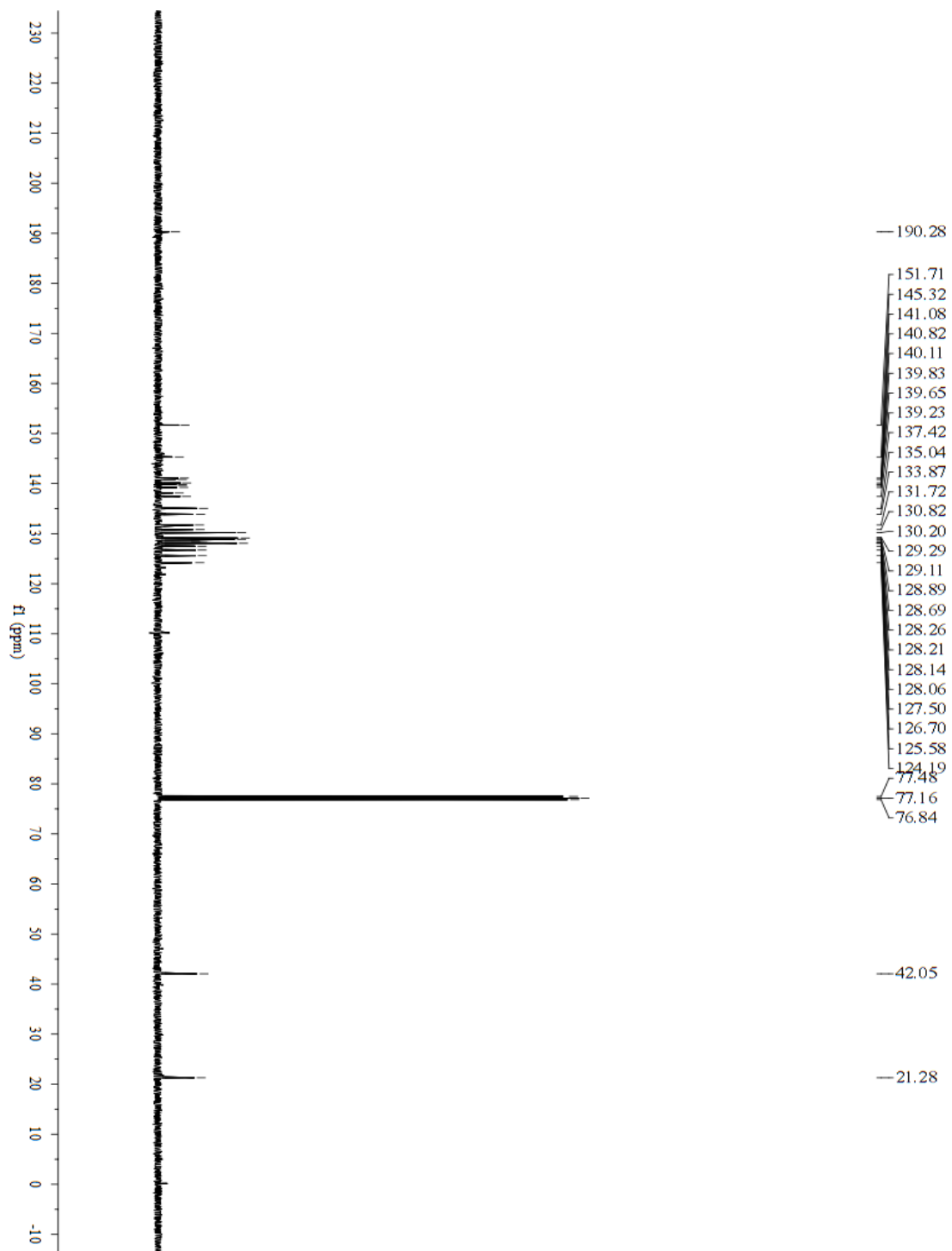


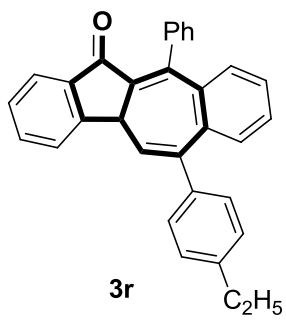
¹H NMR (400 MHz, CDCl₃)



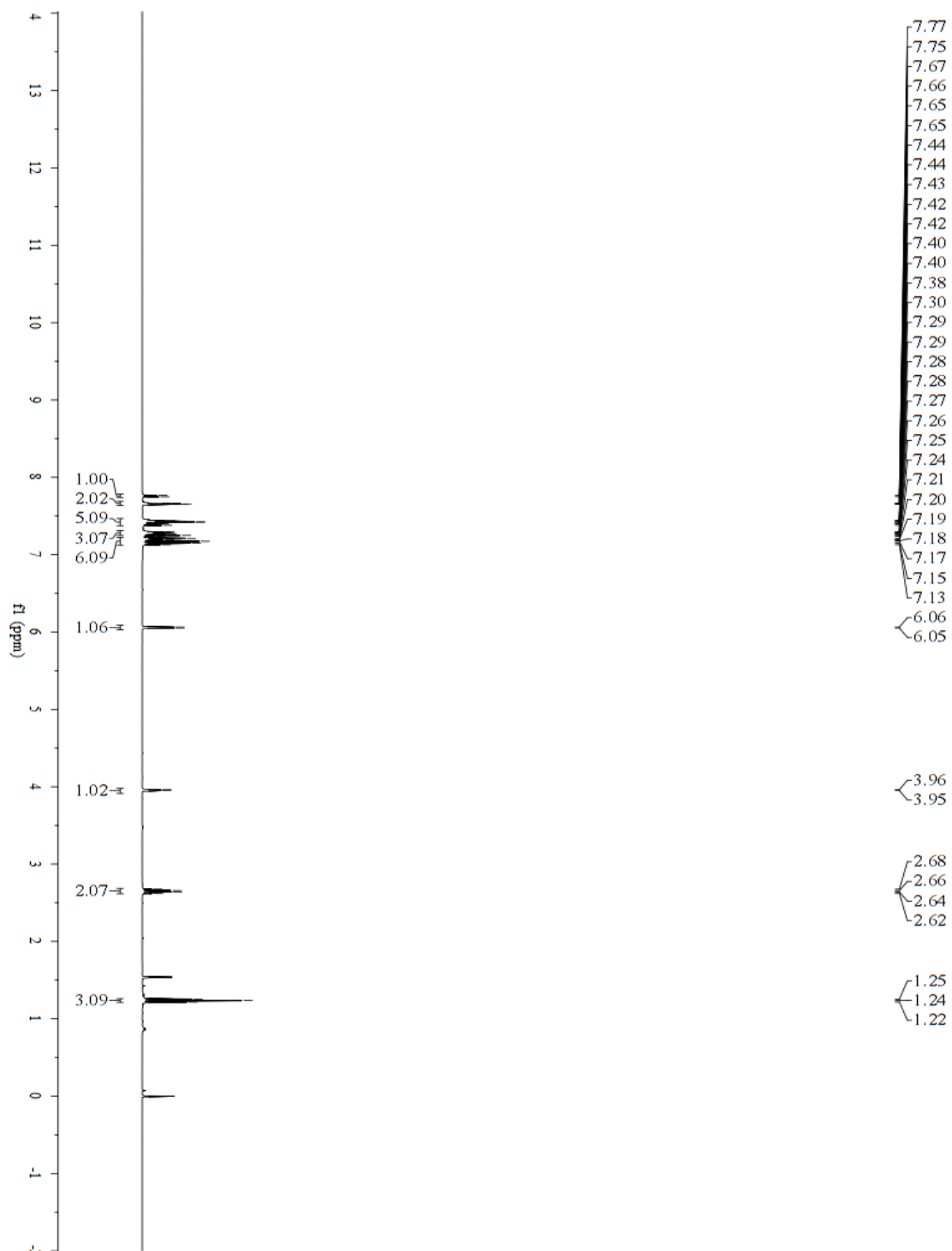


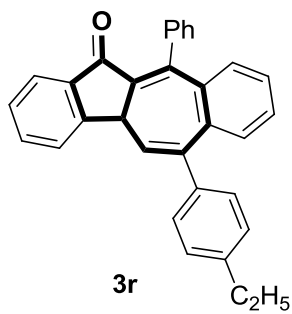
^{13}C NMR (100 MHz, CDCl_3)



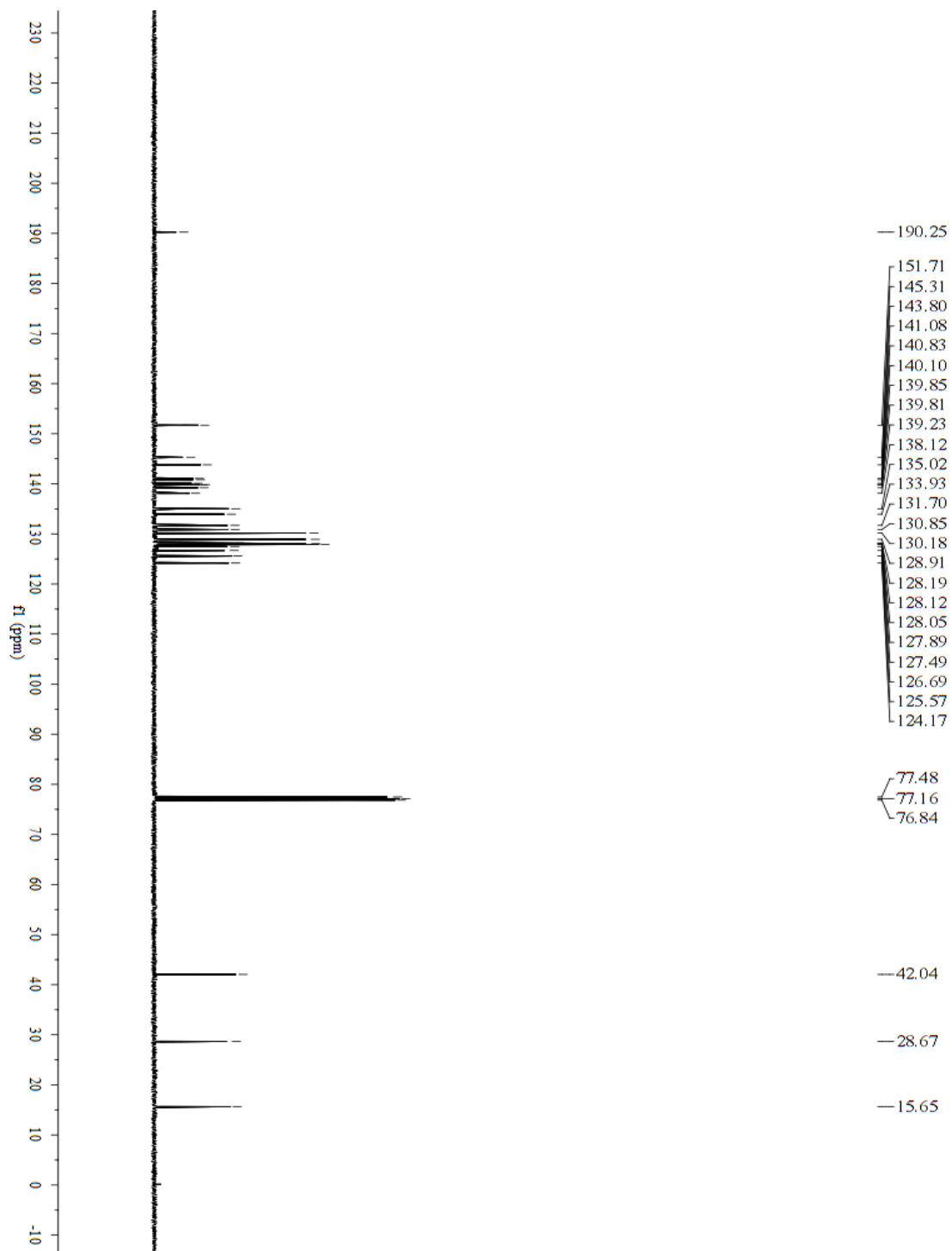


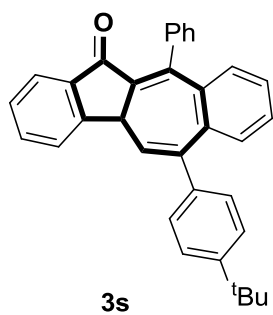
$^1\text{H NMR}$ (400 MHz, CDCl_3)



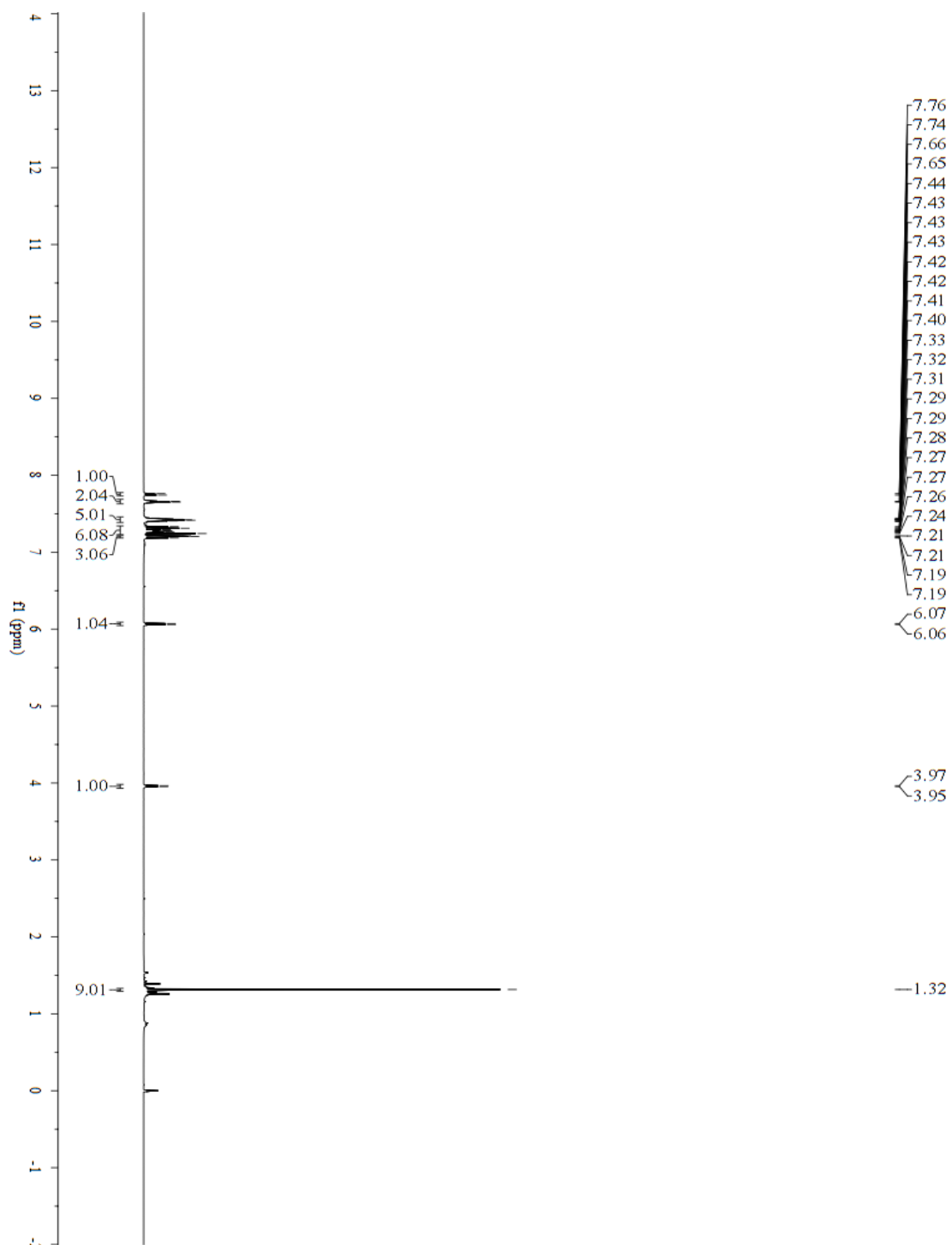


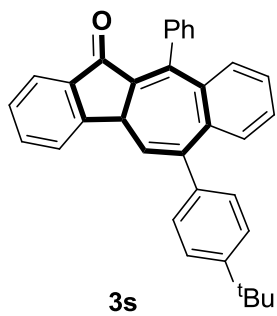
^{13}C NMR (100 MHz, CDCl_3)



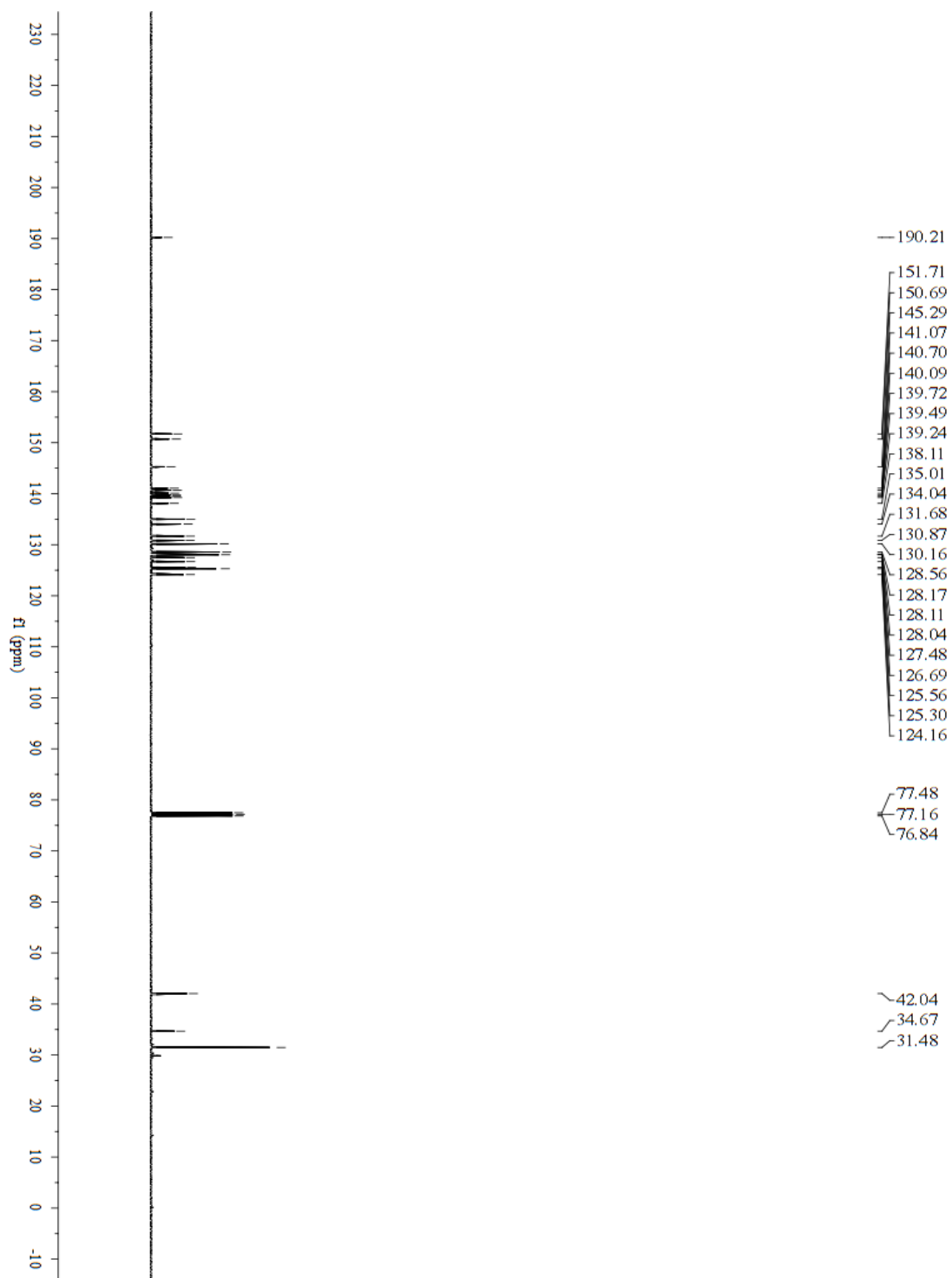


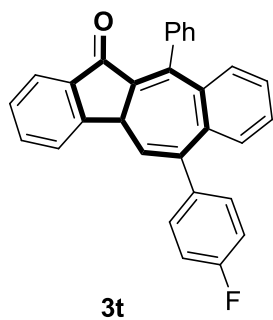
¹H NMR (400 MHz, CDCl₃)



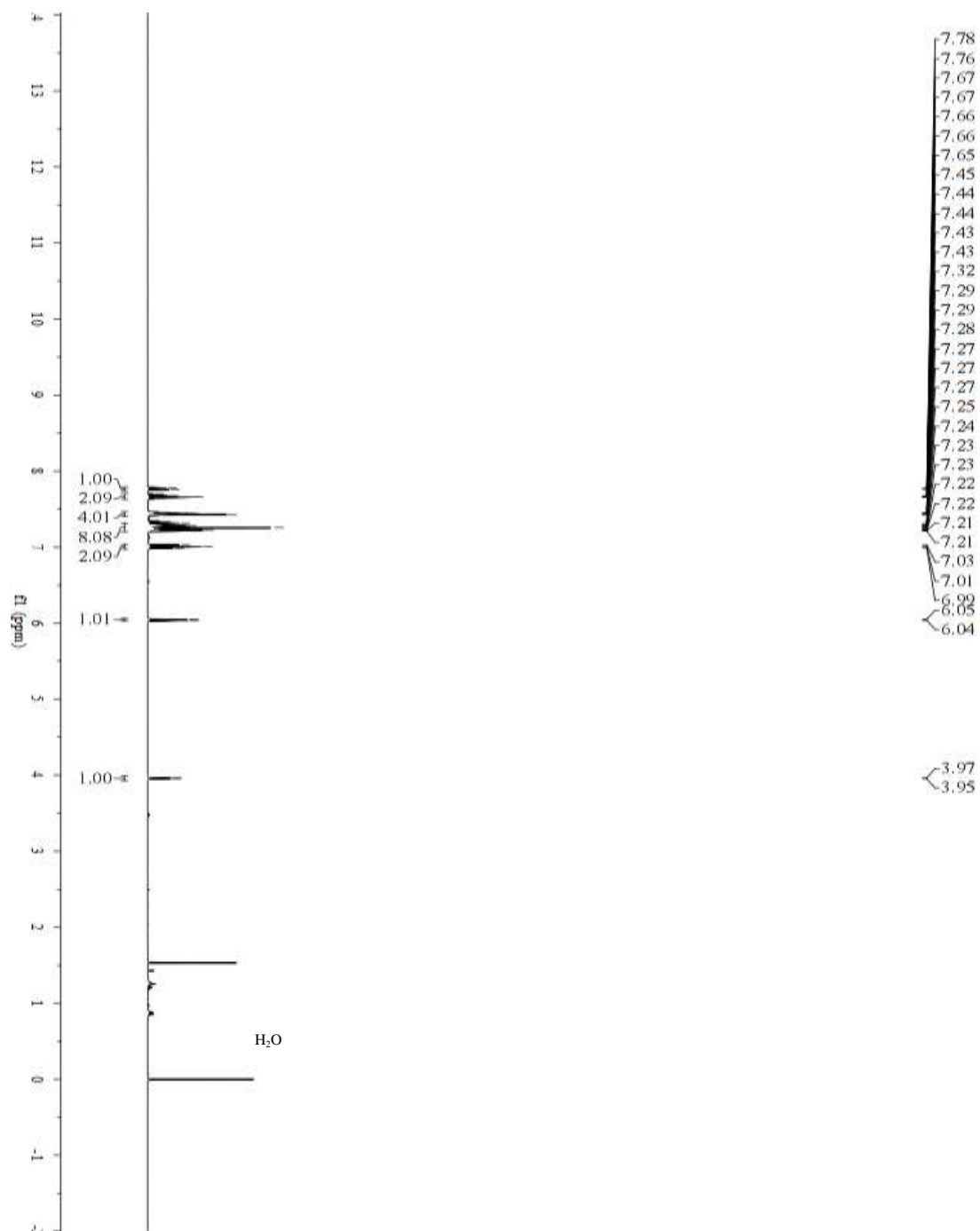


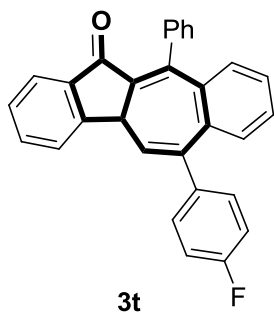
^{13}C NMR (100 MHz, CDCl_3)



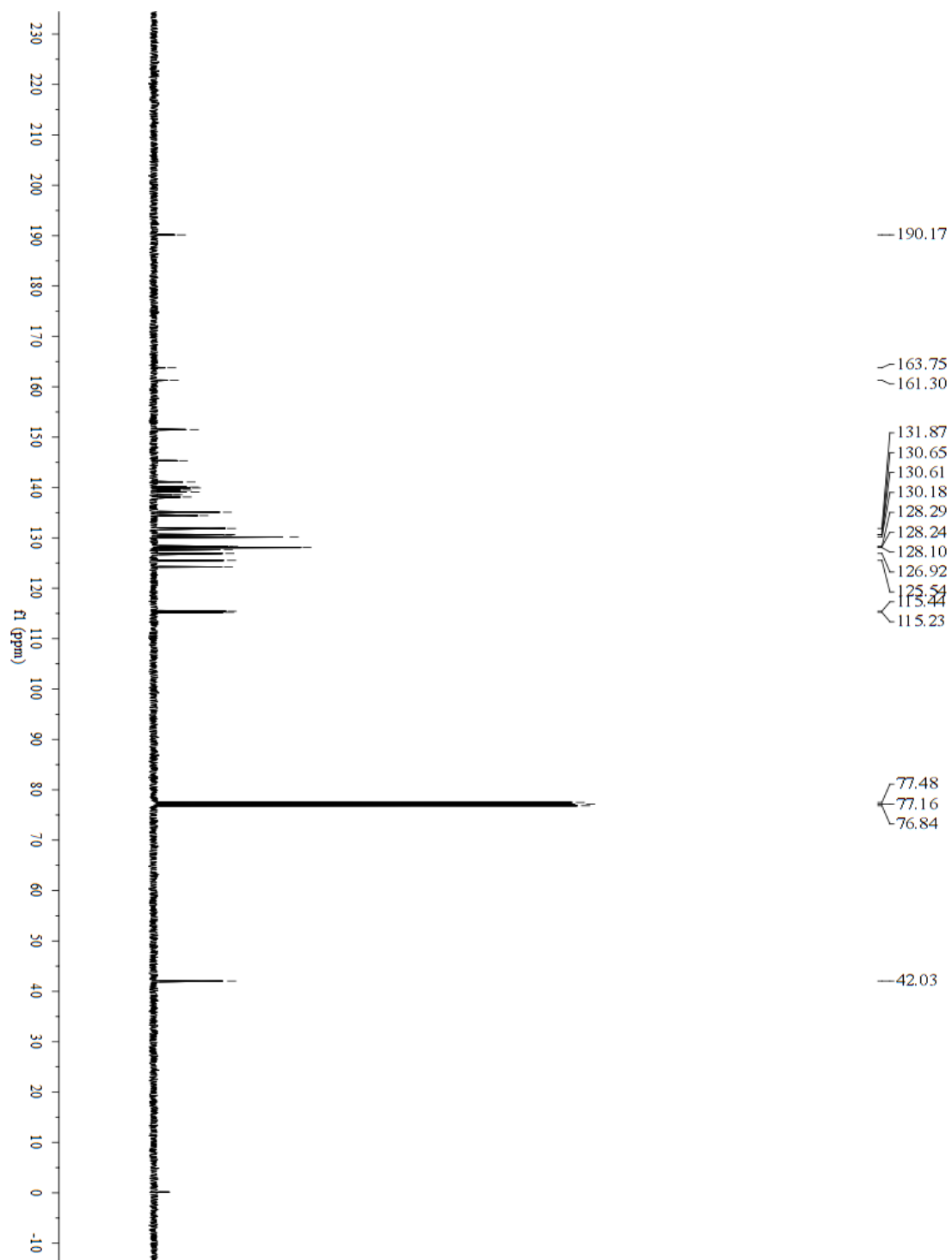


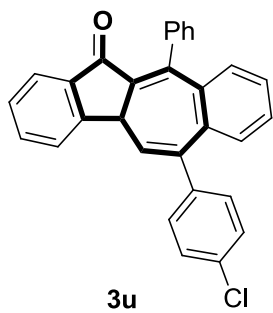
¹H NMR (400 MHz, CDCl₃)



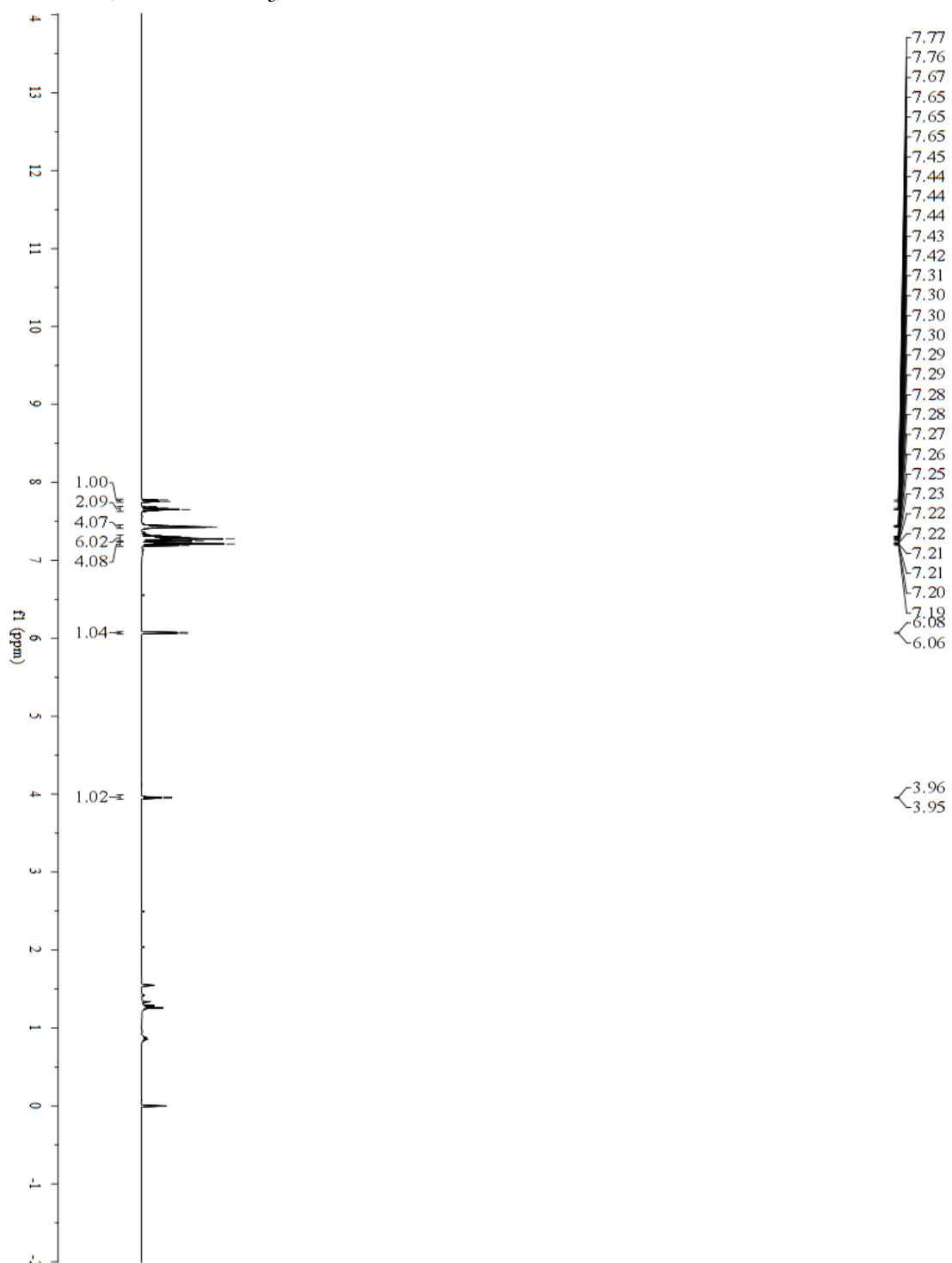


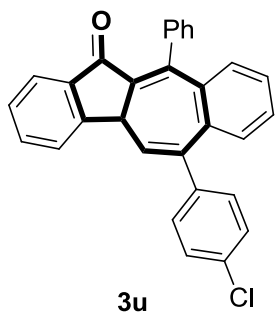
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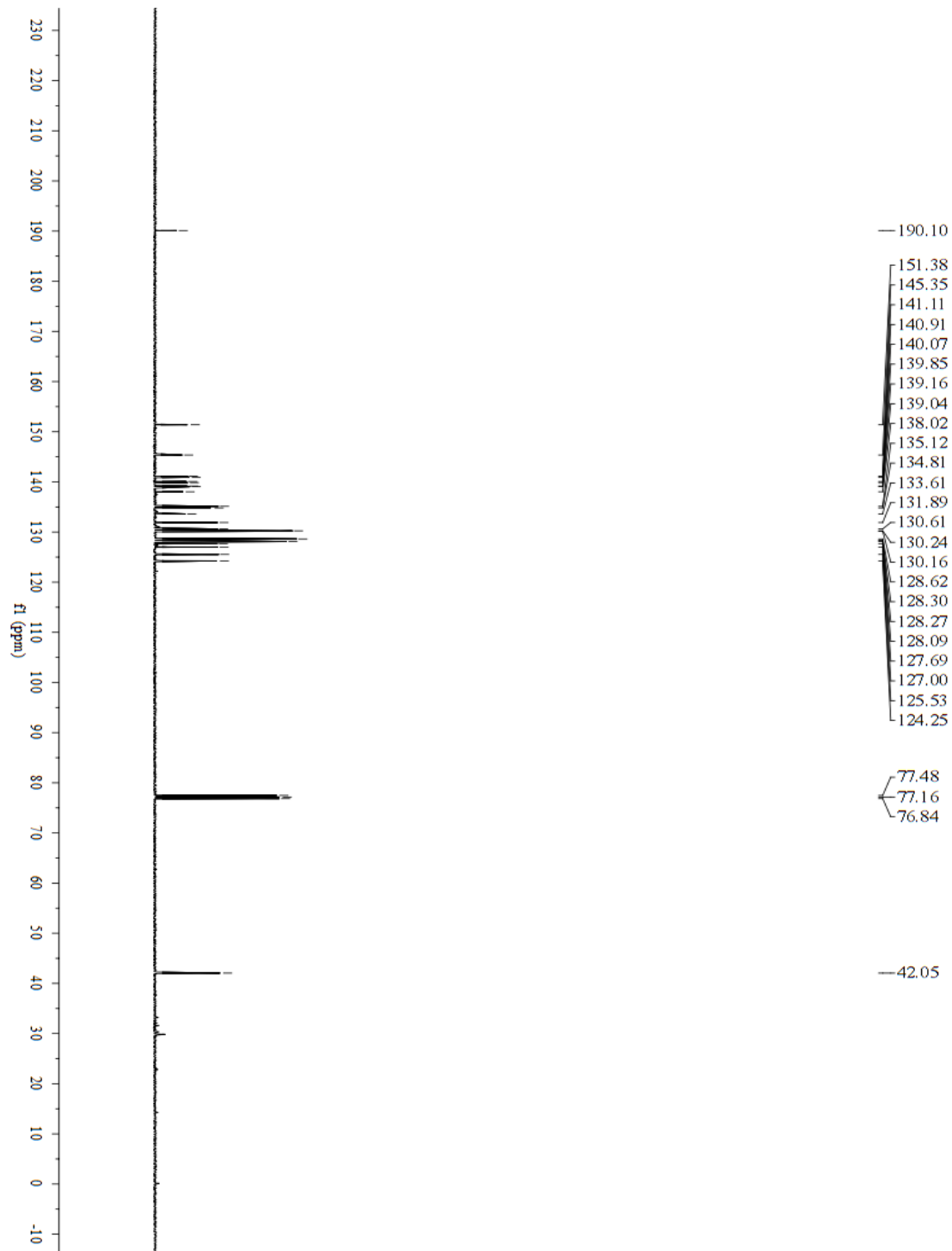


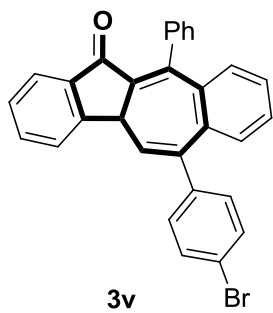
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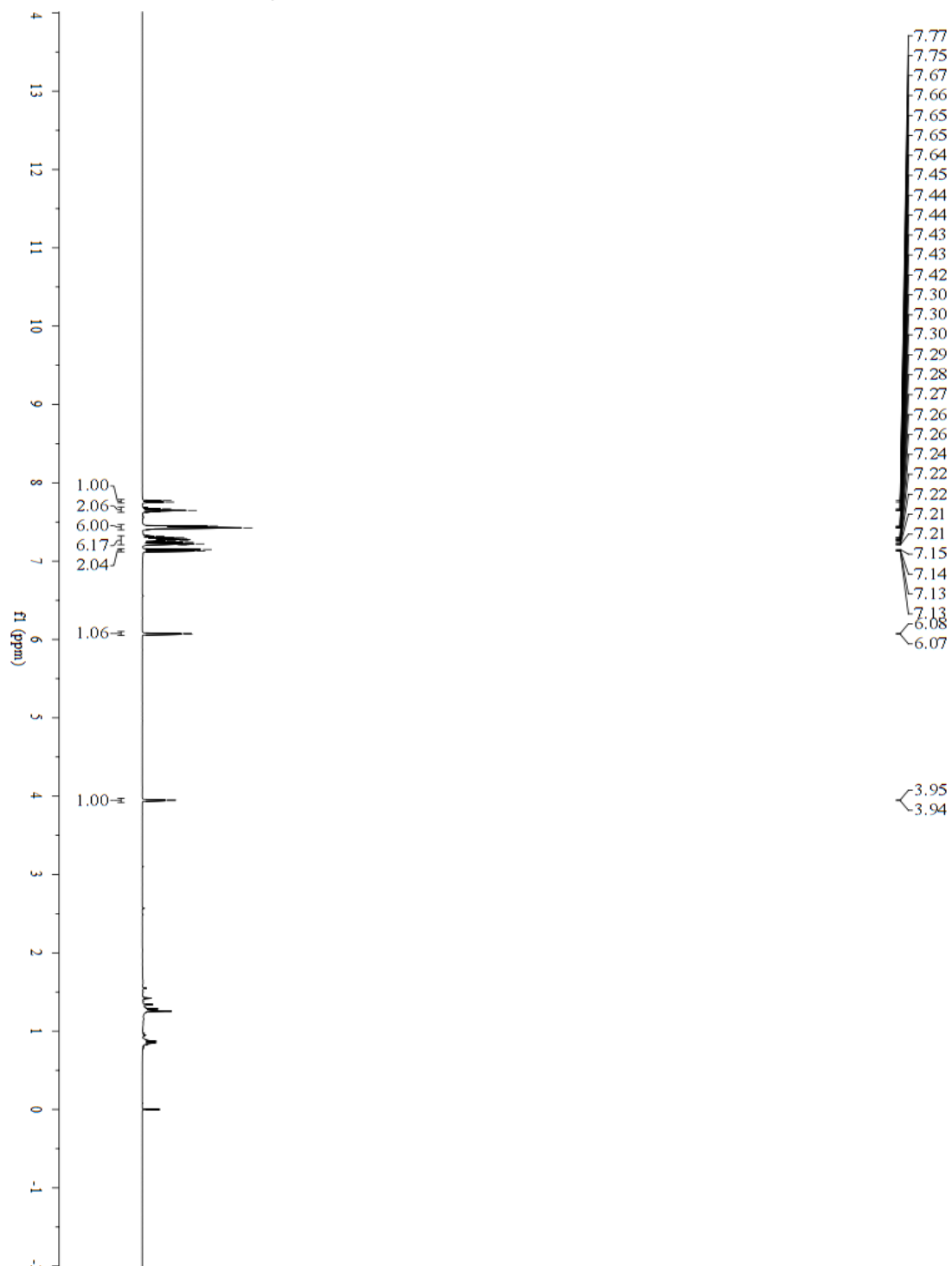


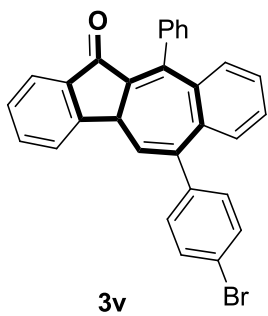
¹³C NMR (100 MHz, CDCl₃)



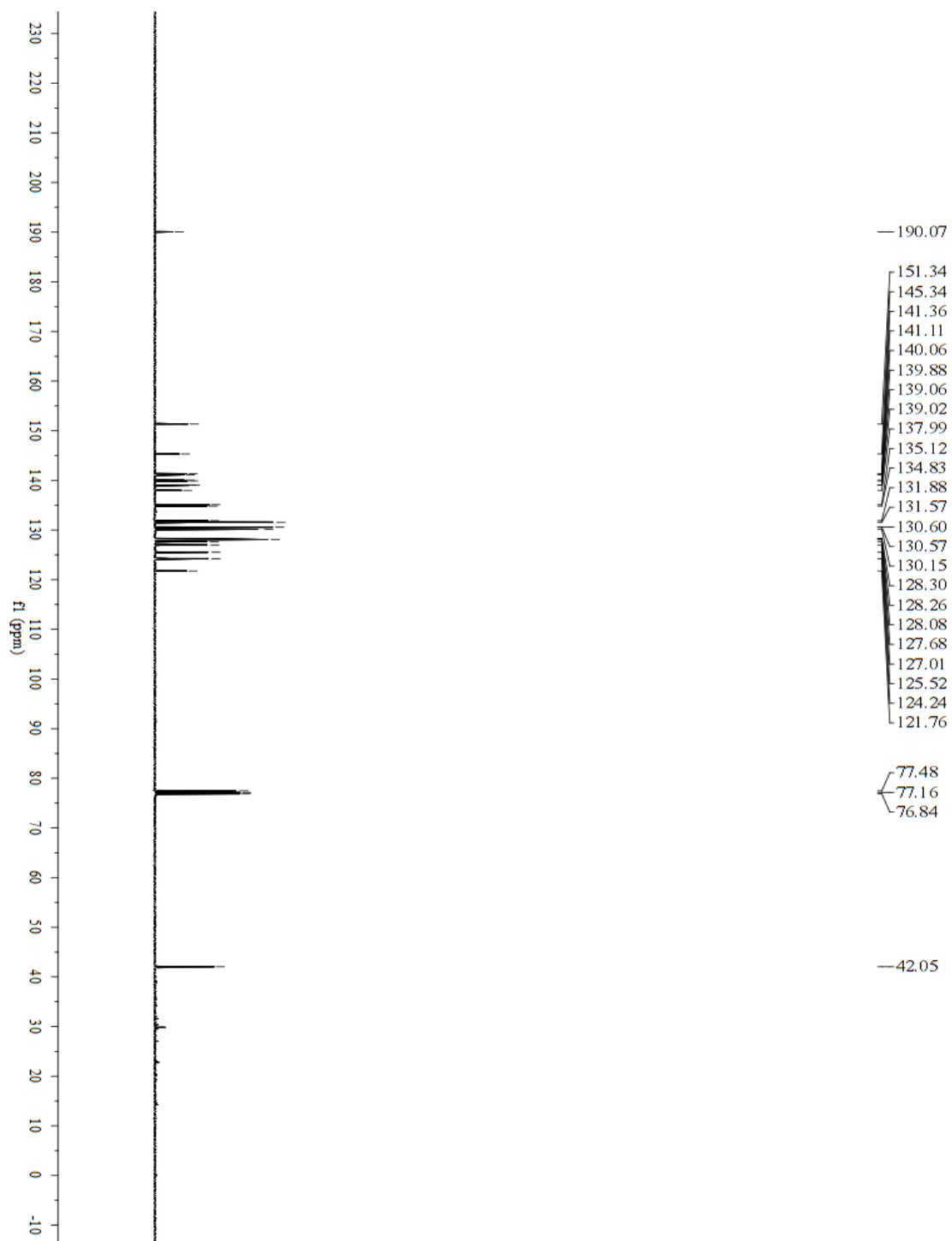


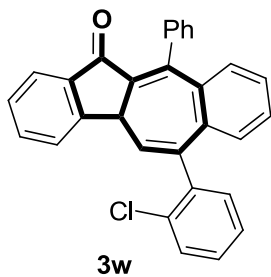
¹H NMR (400 MHz, CDCl₃)



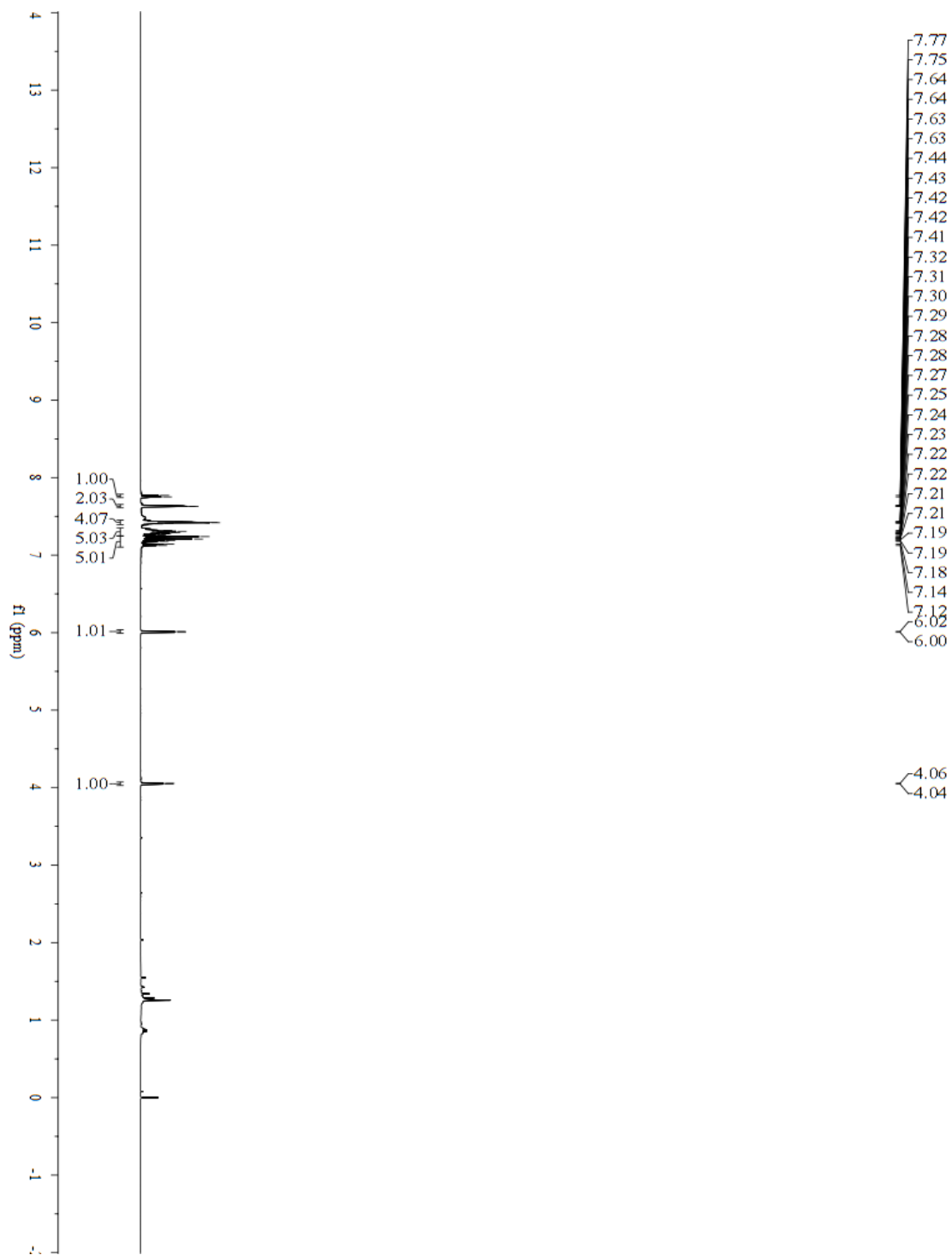


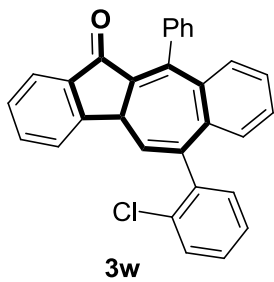
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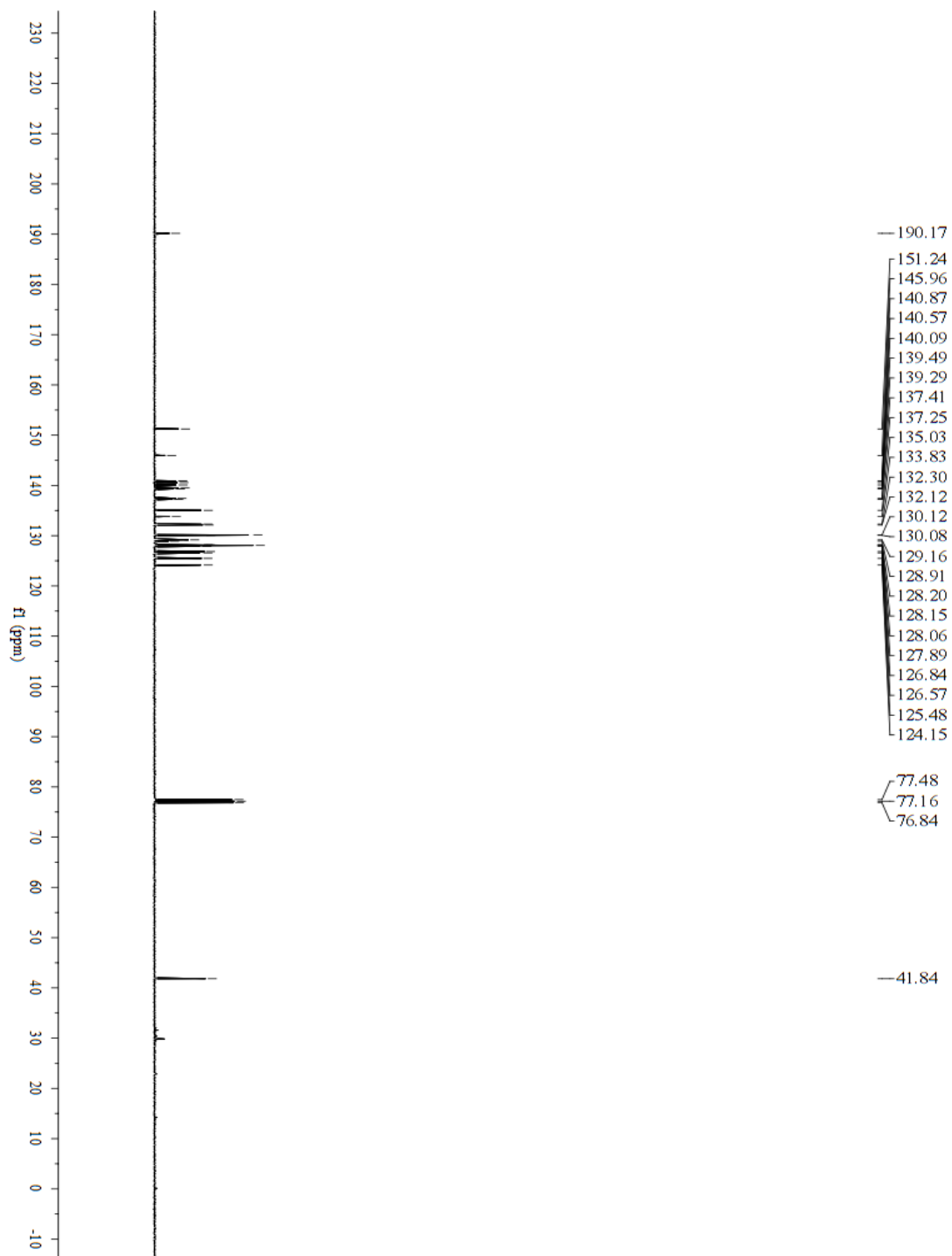


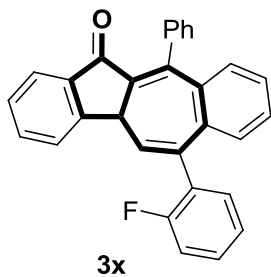
$^1\text{H NMR}$ (400 MHz, CDCl_3)



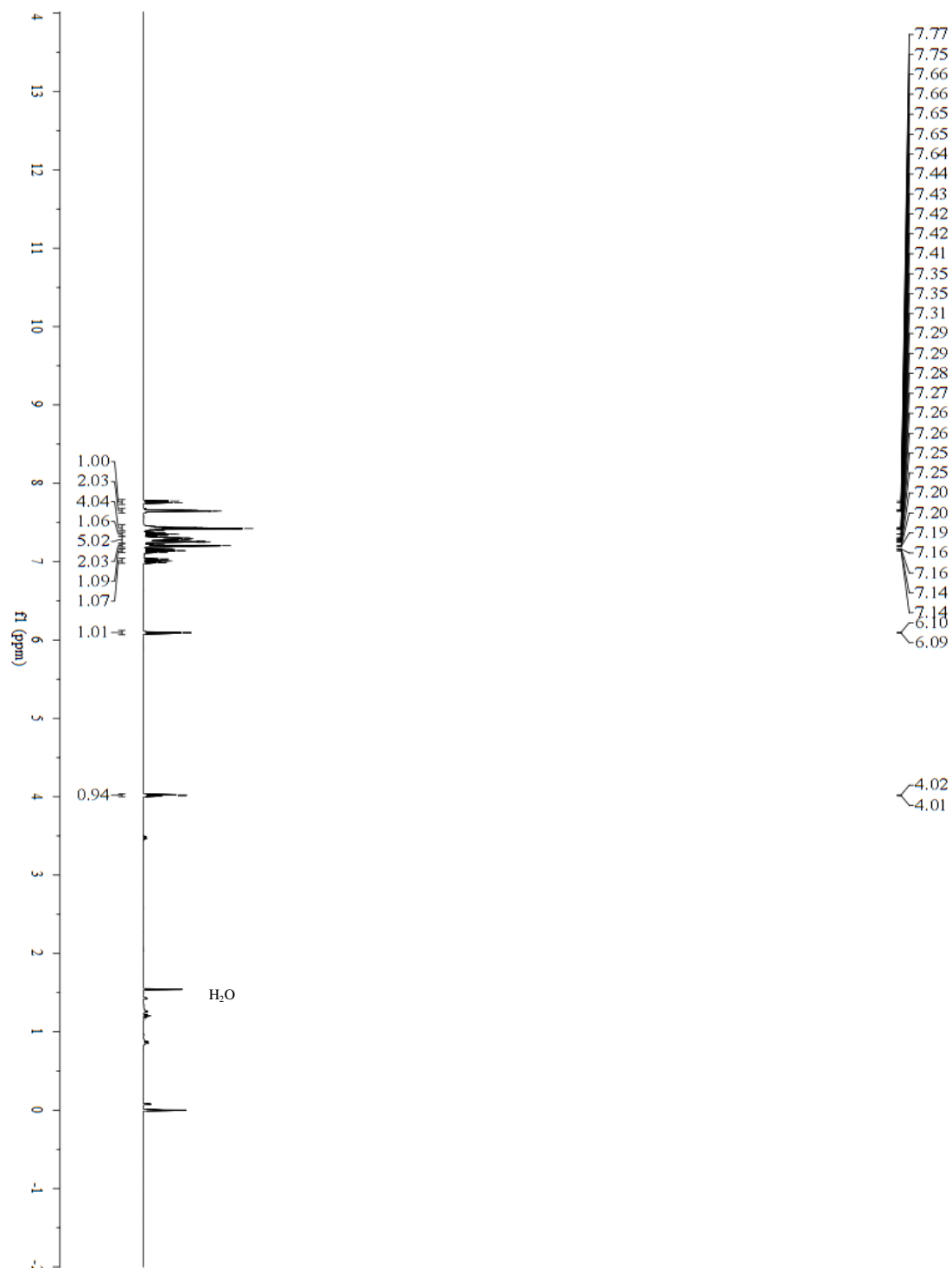


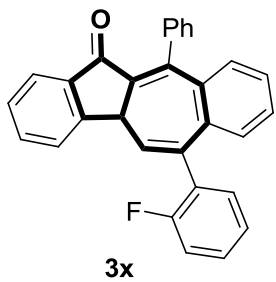
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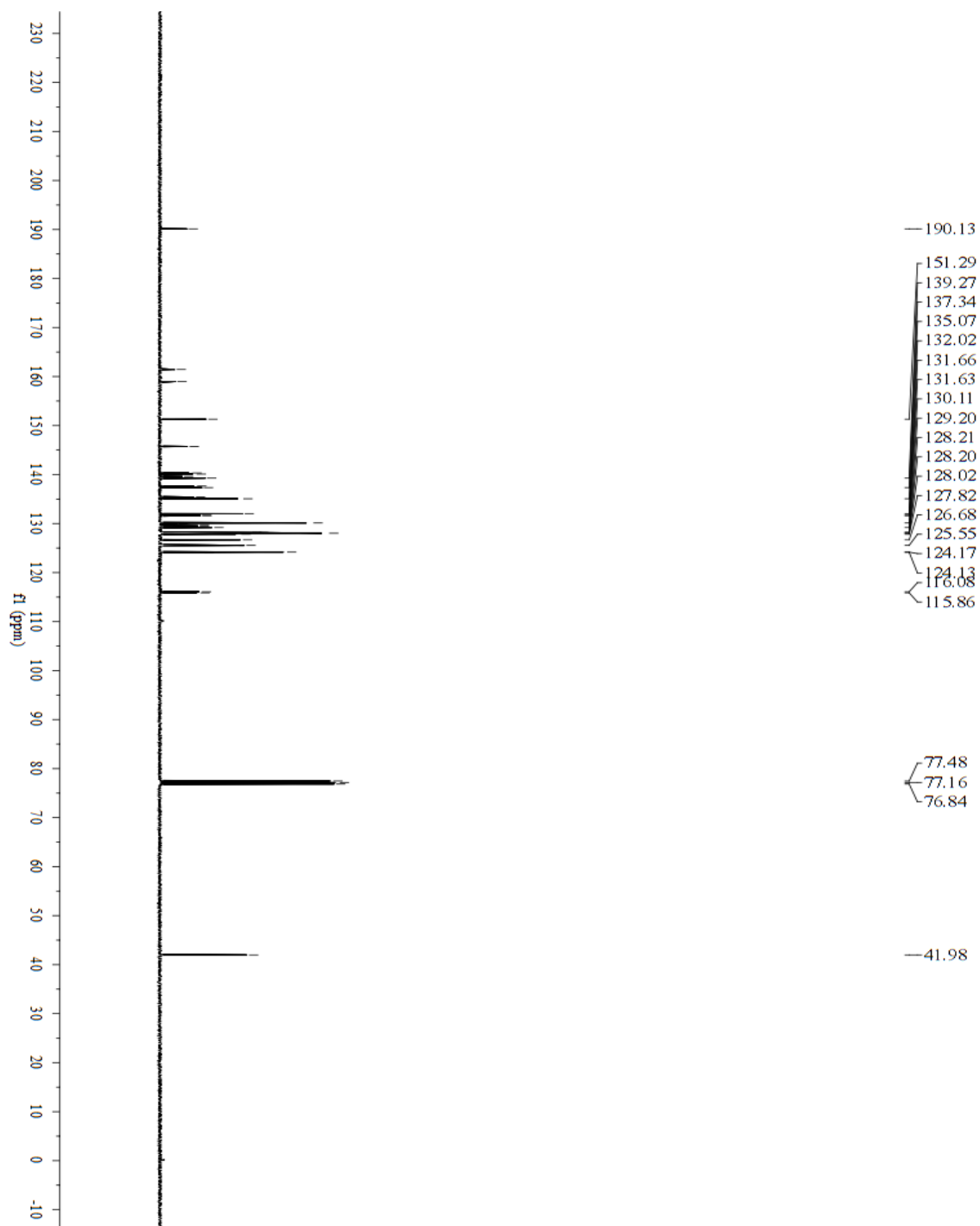
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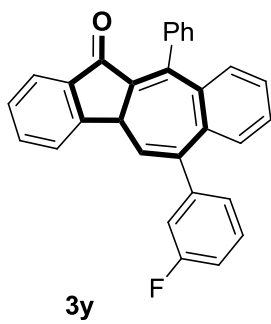




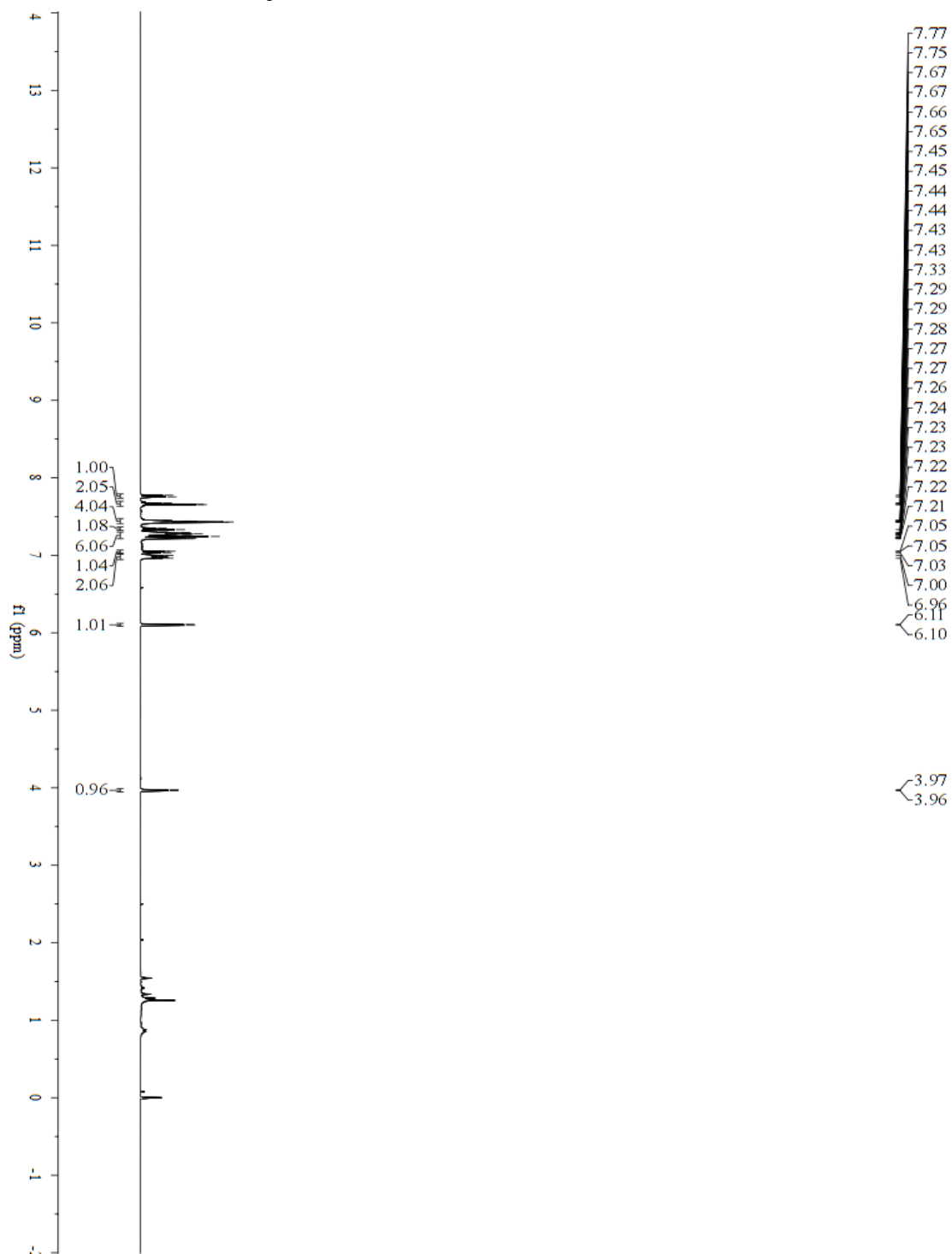
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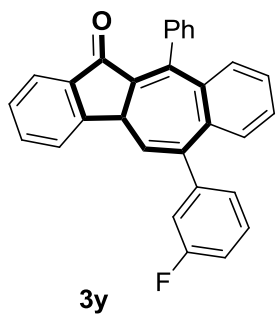
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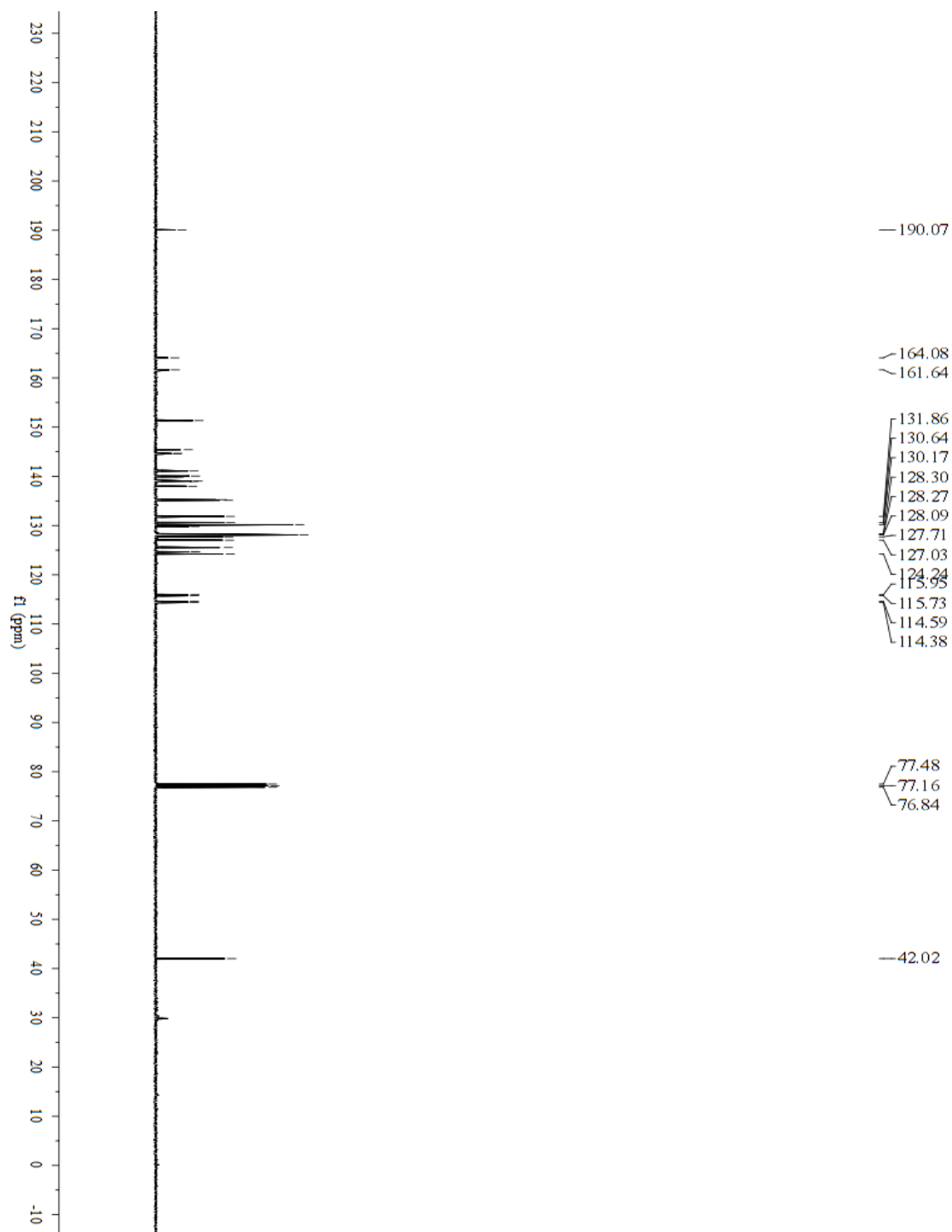


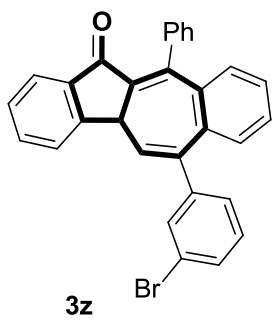
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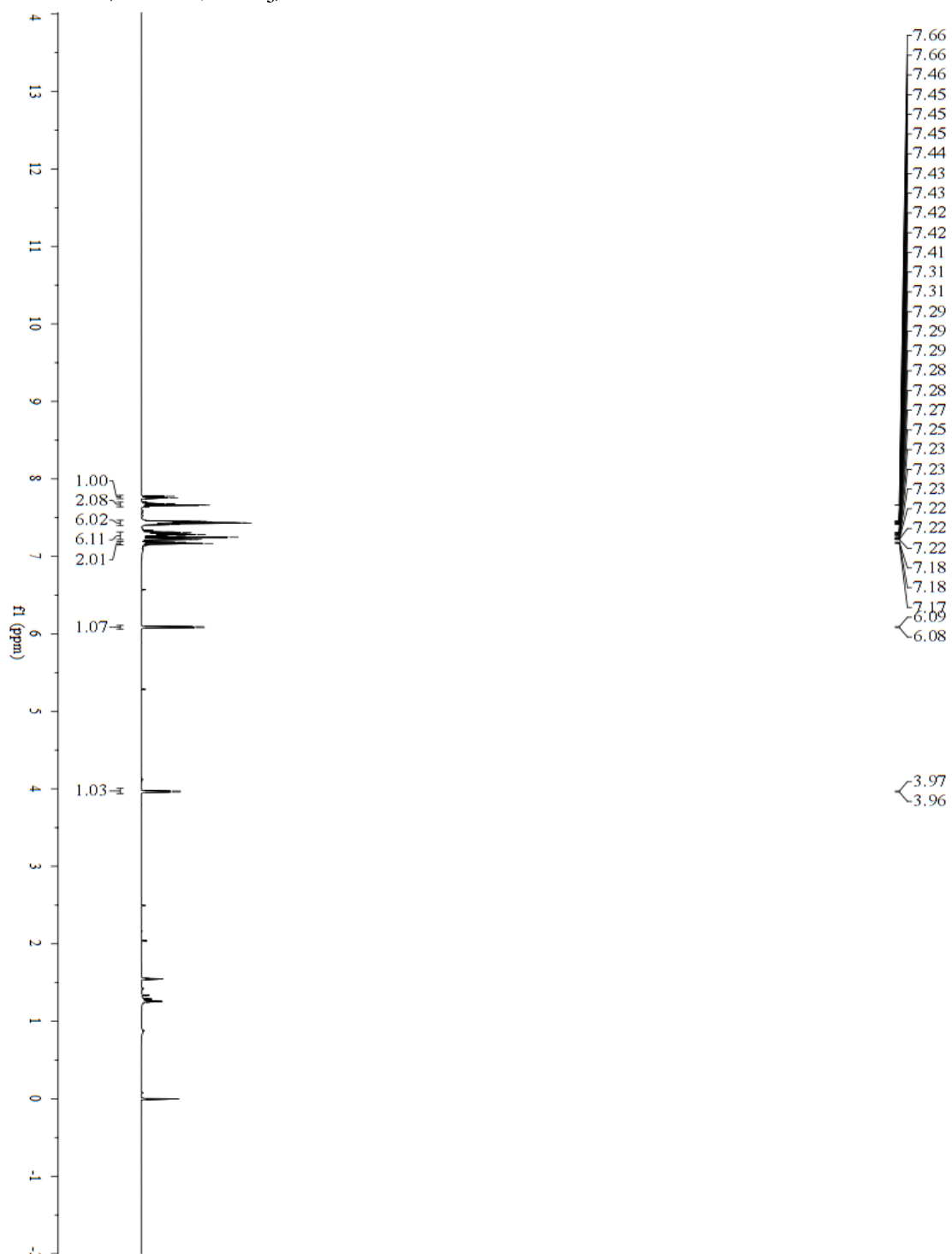


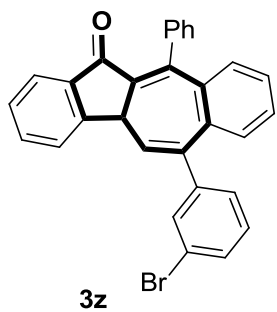
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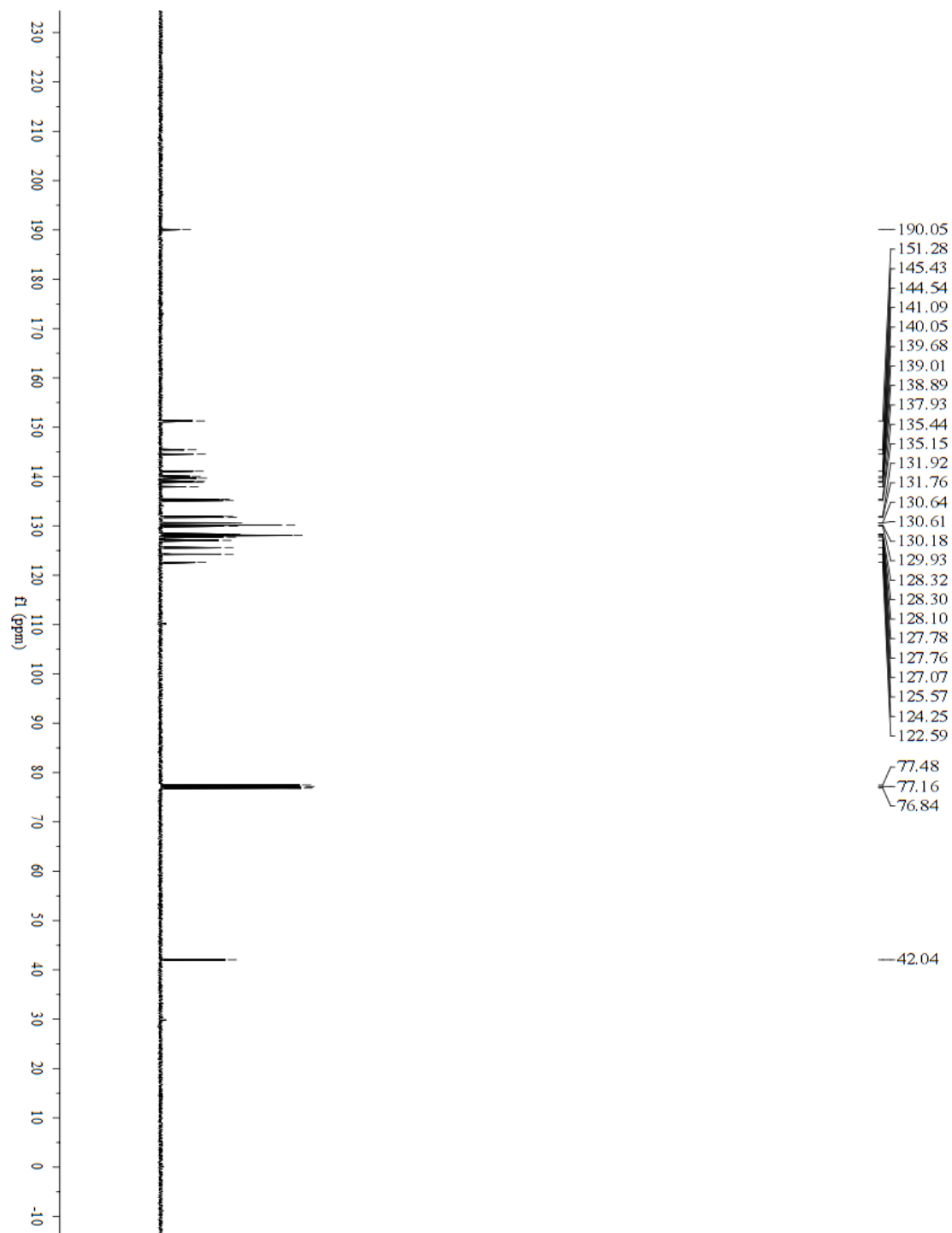


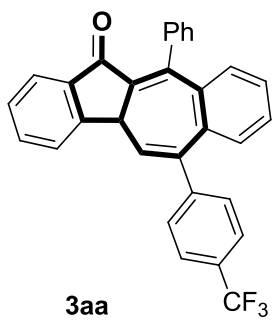
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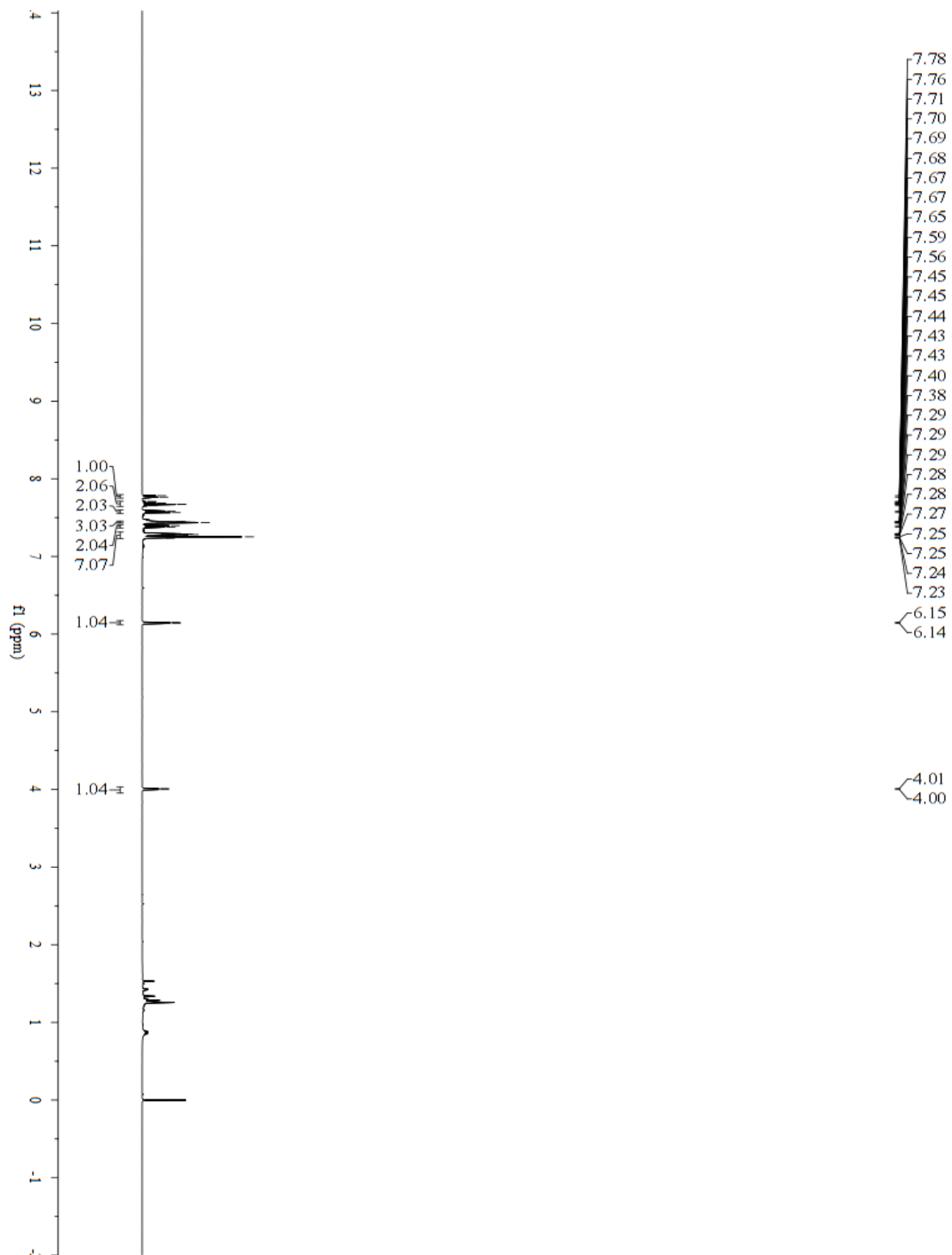


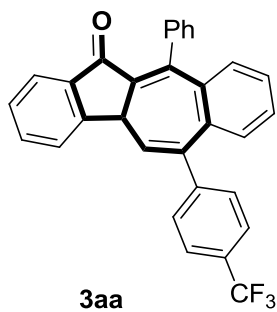
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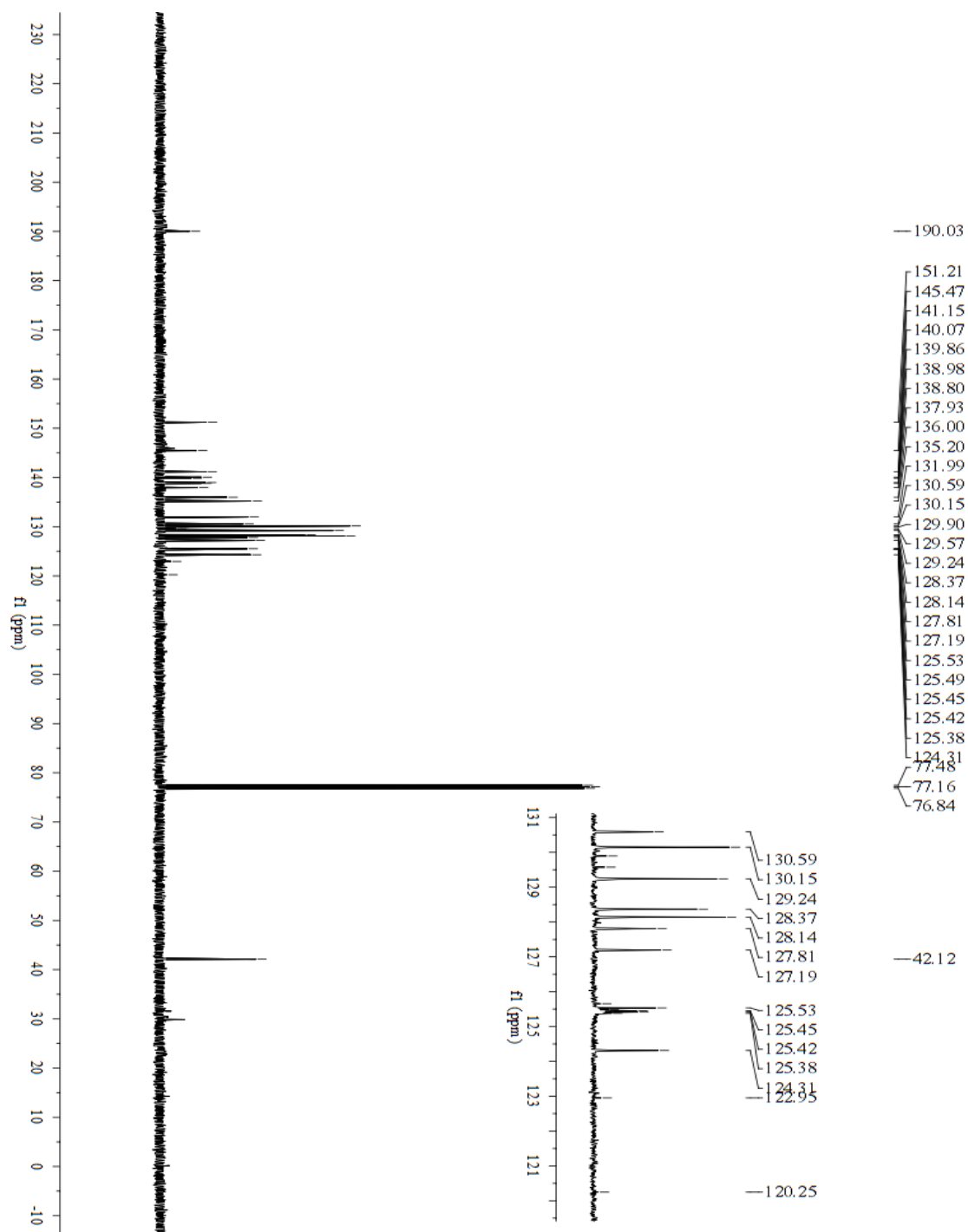


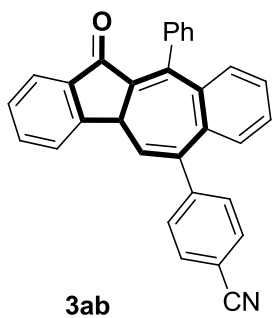
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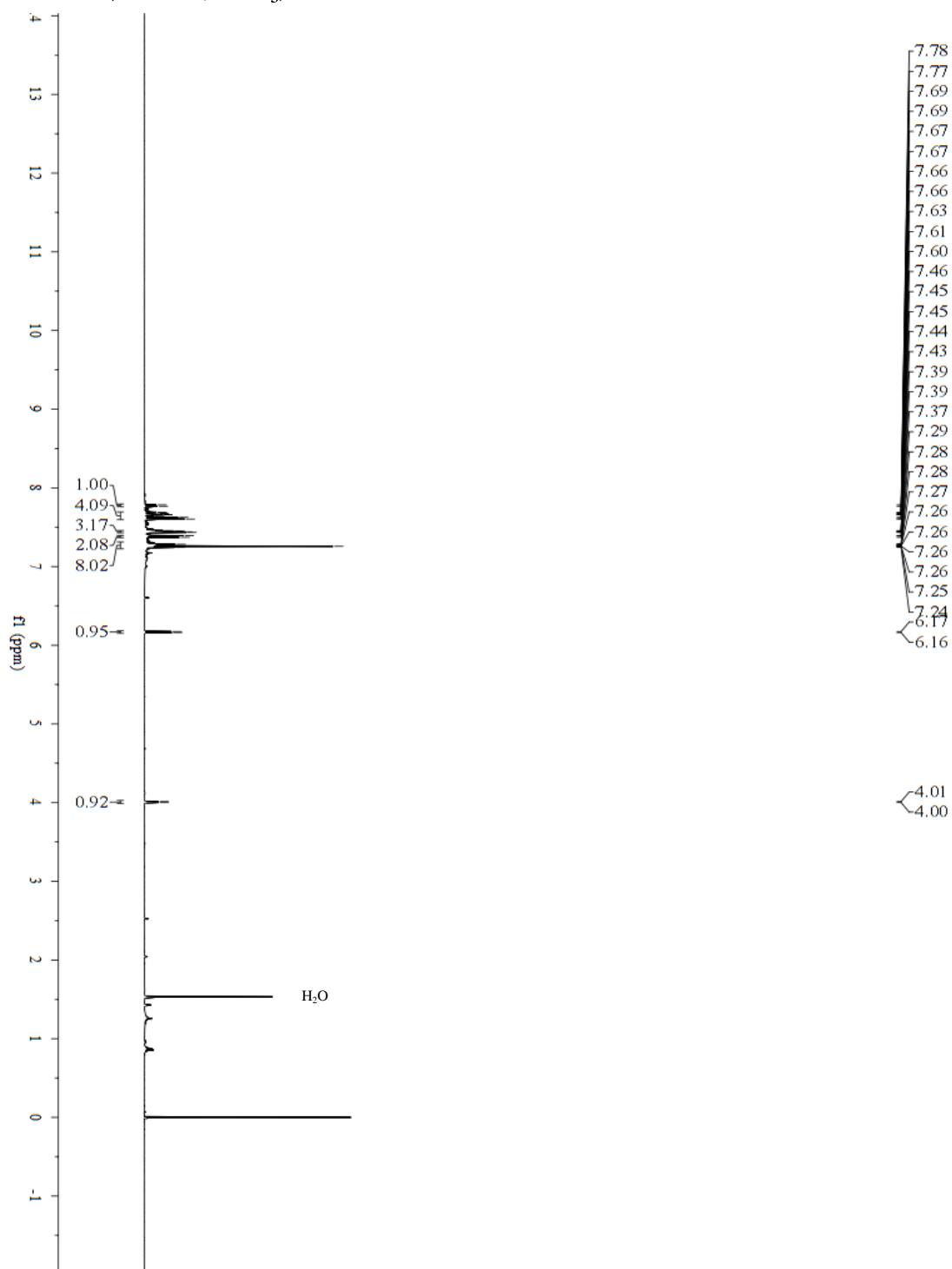


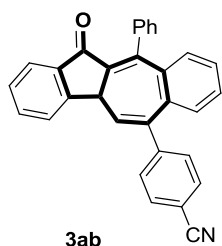
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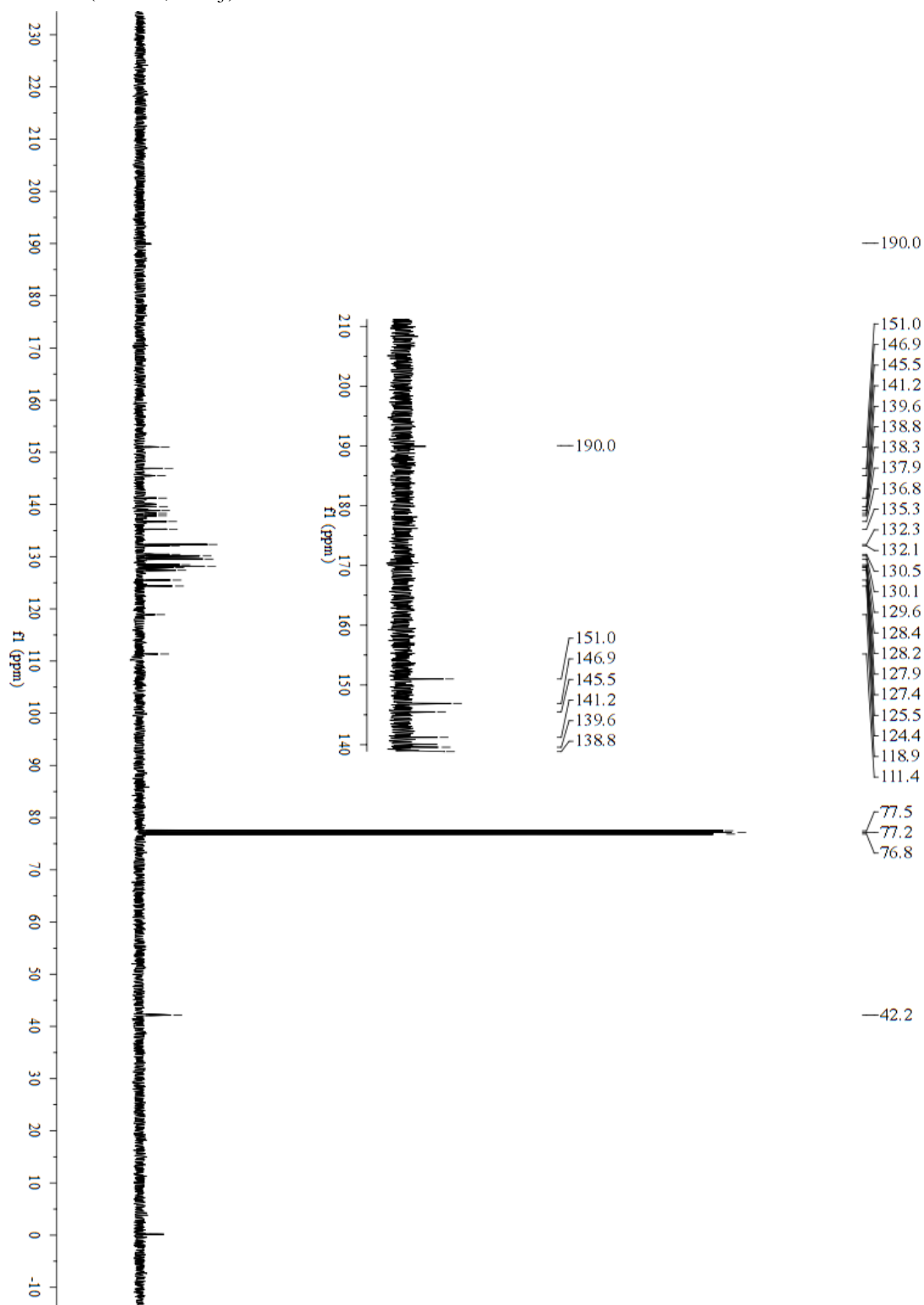


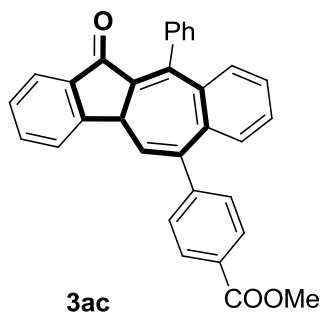
$^1\text{H NMR}$ (400 MHz, CDCl_3)



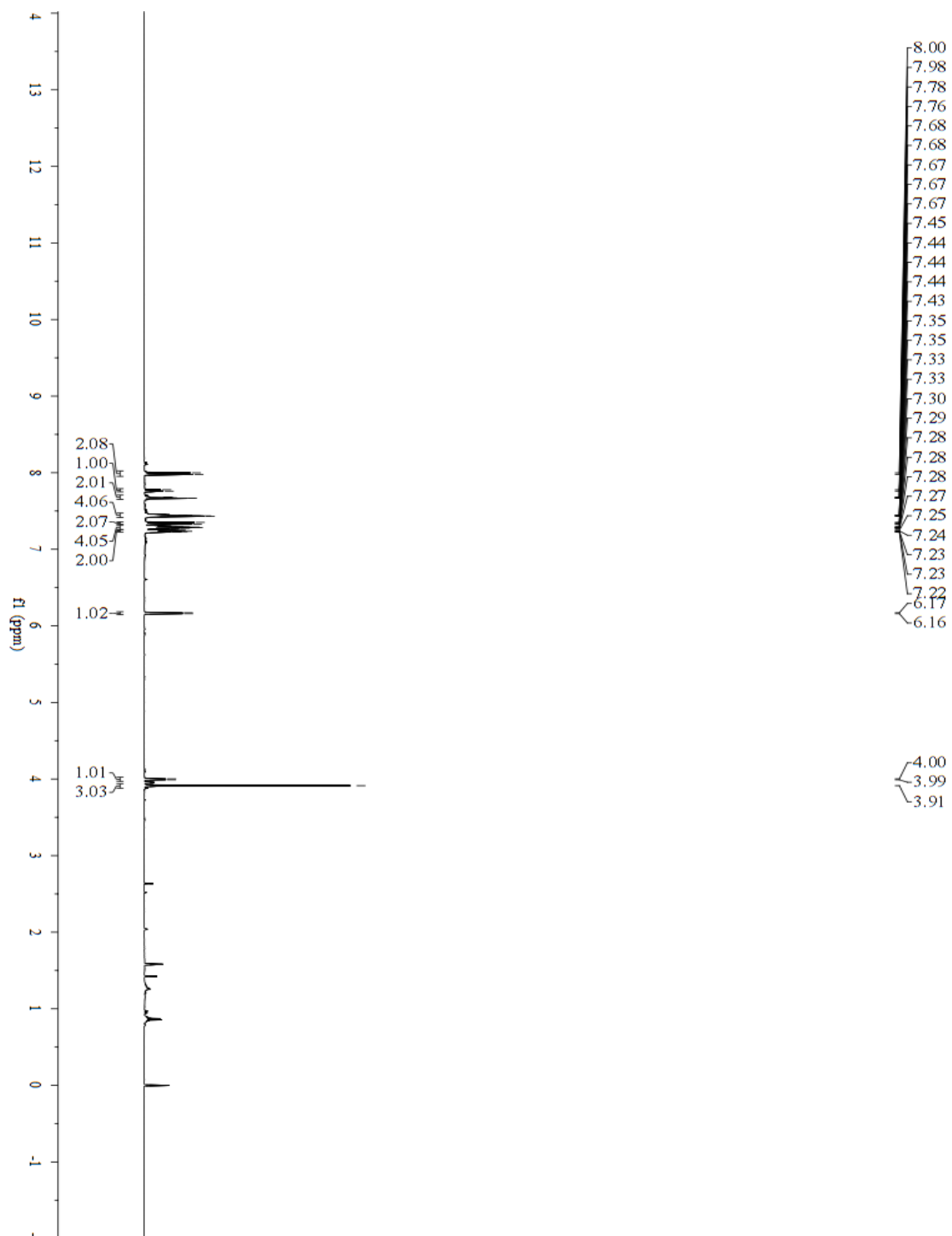


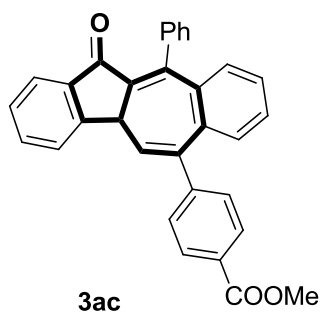
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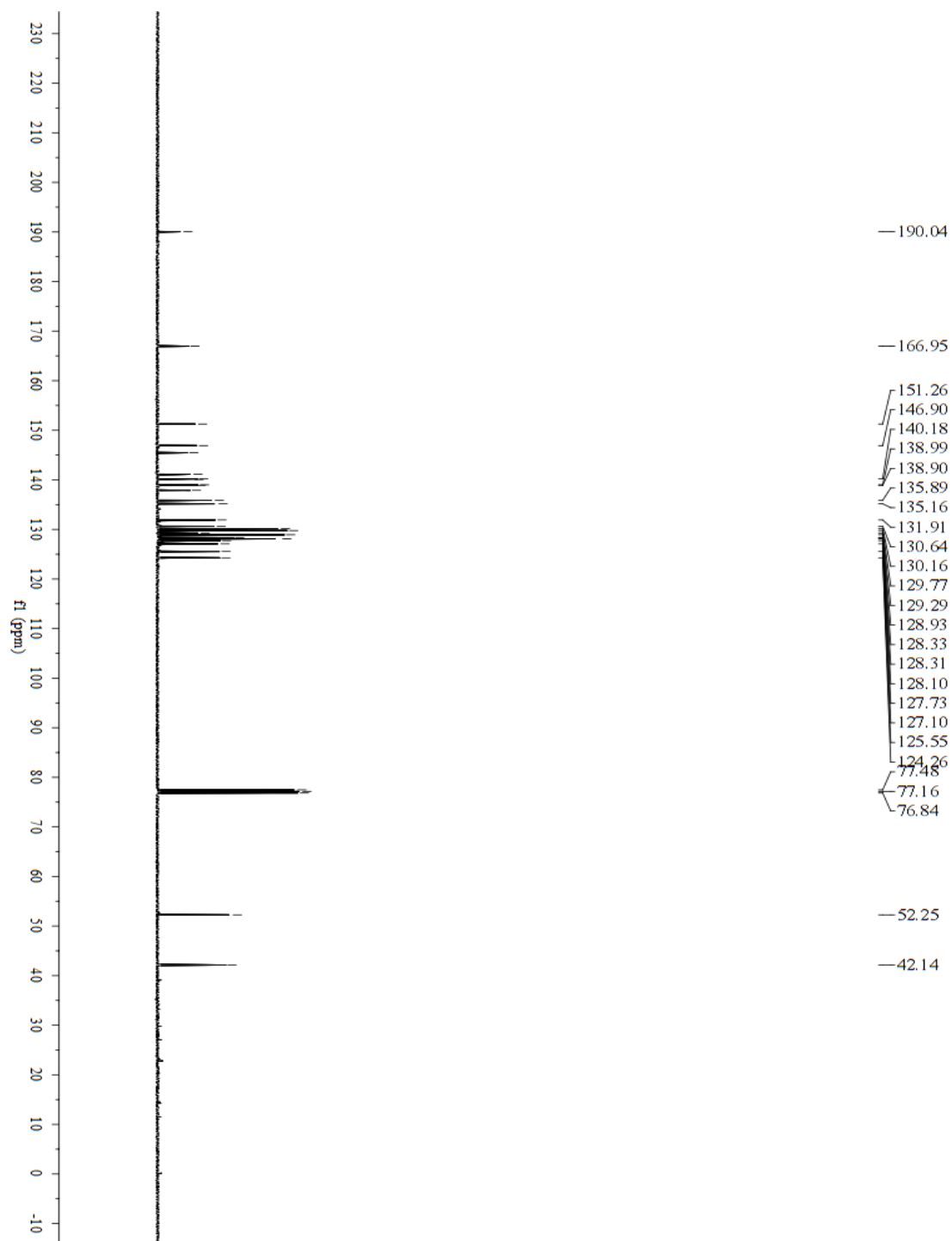


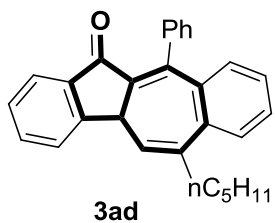
$^1\text{H NMR}$ (400 MHz, CDCl_3)





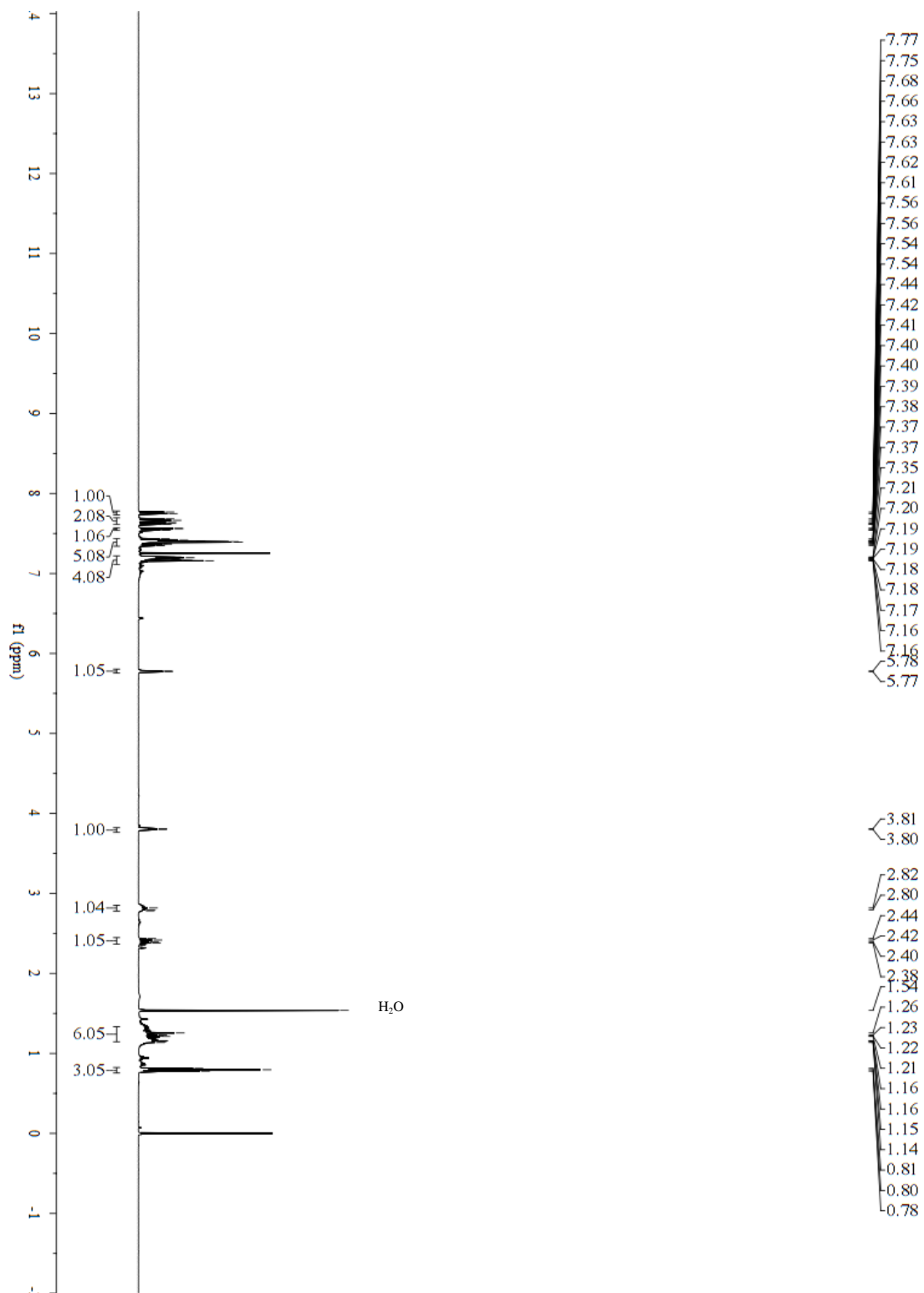
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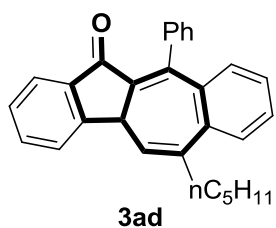




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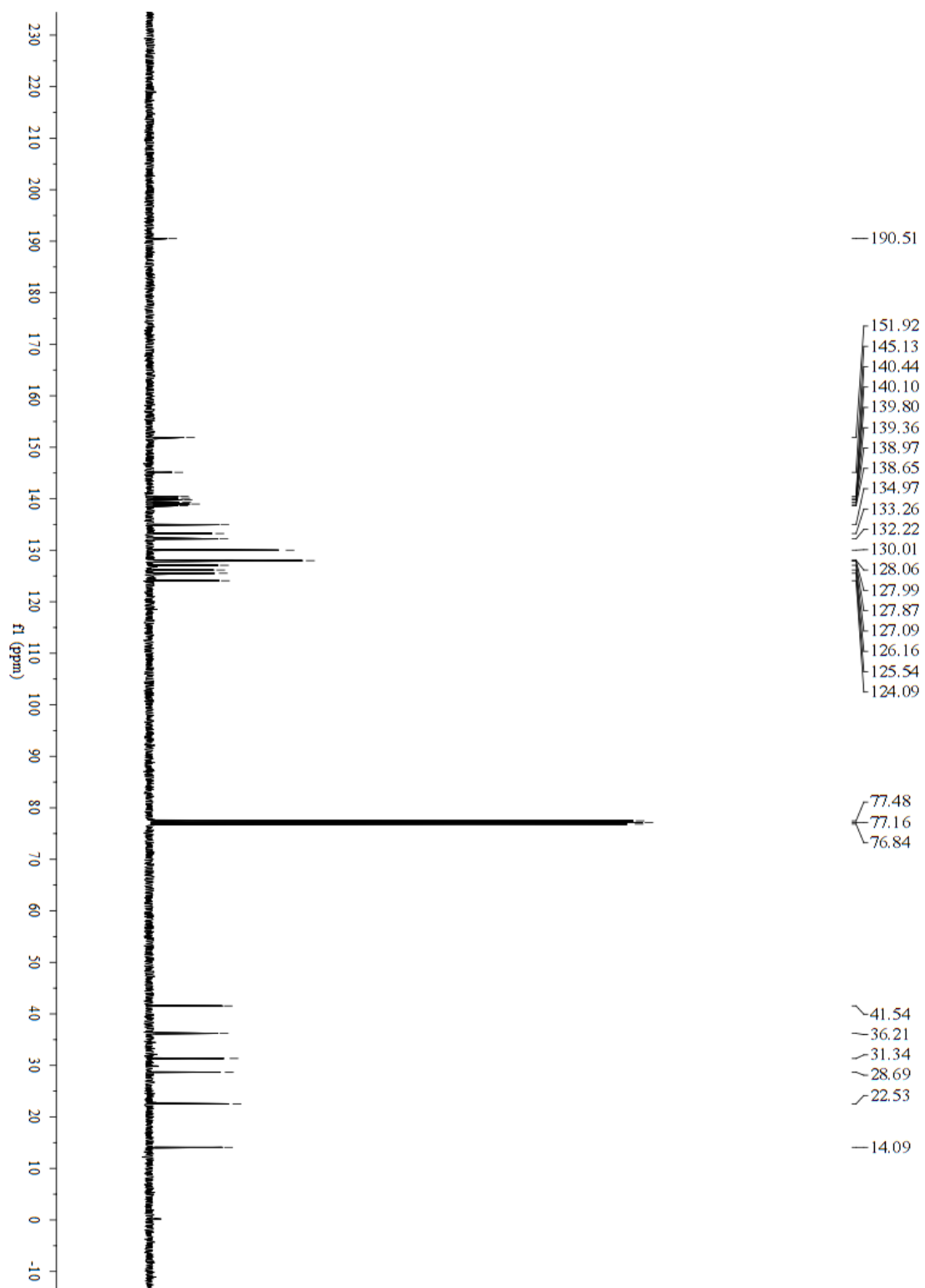
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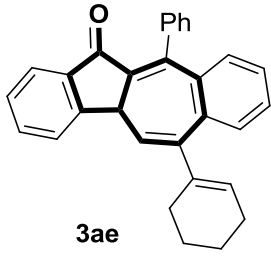




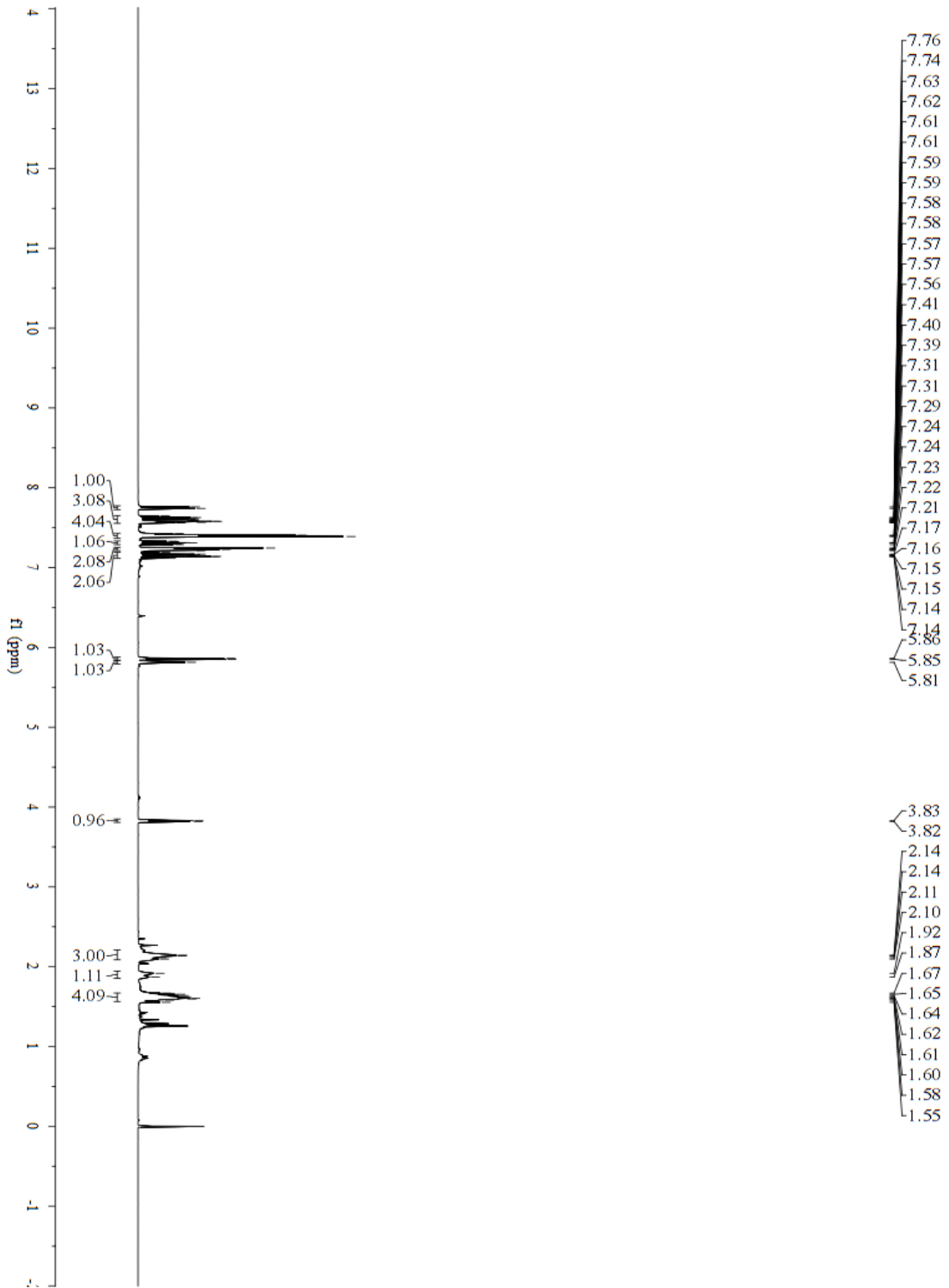
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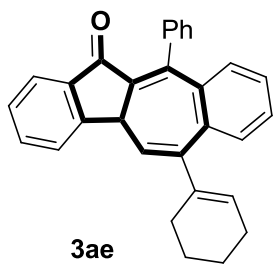
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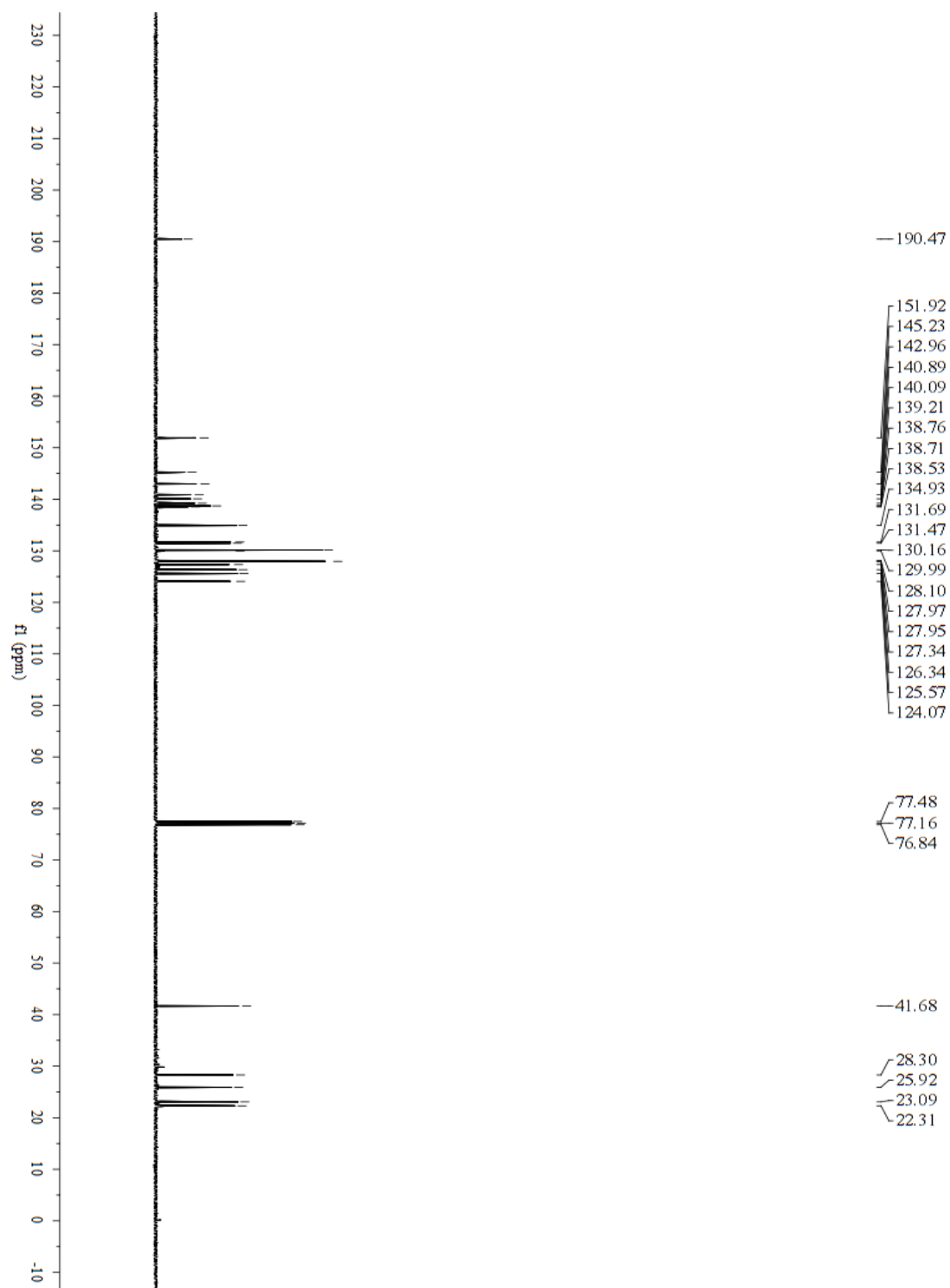


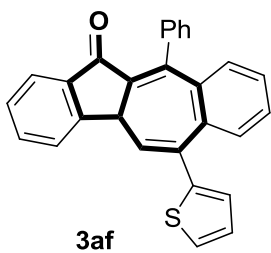
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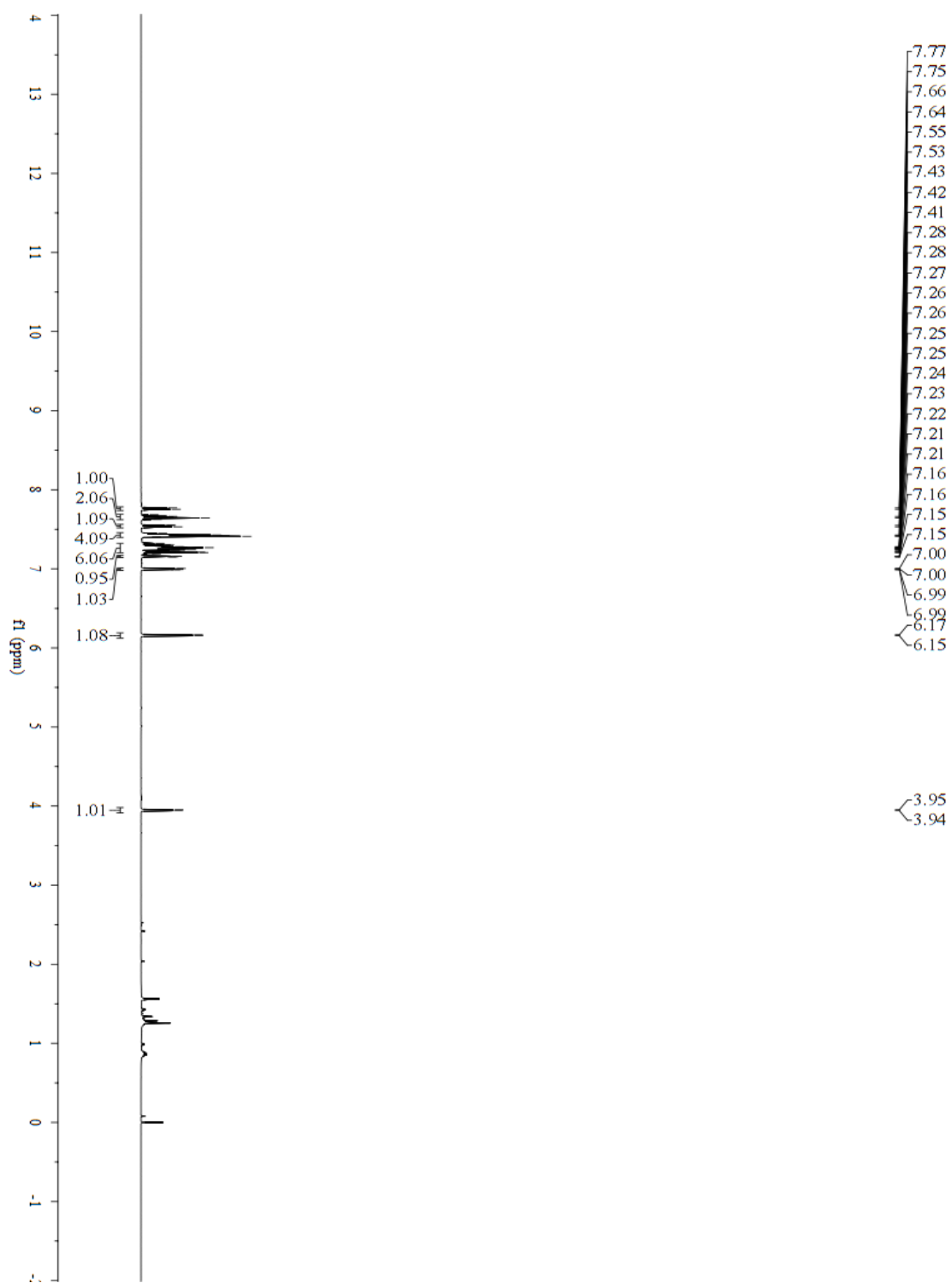


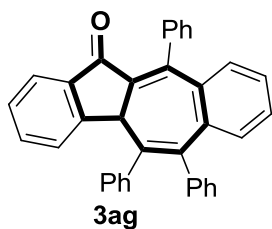
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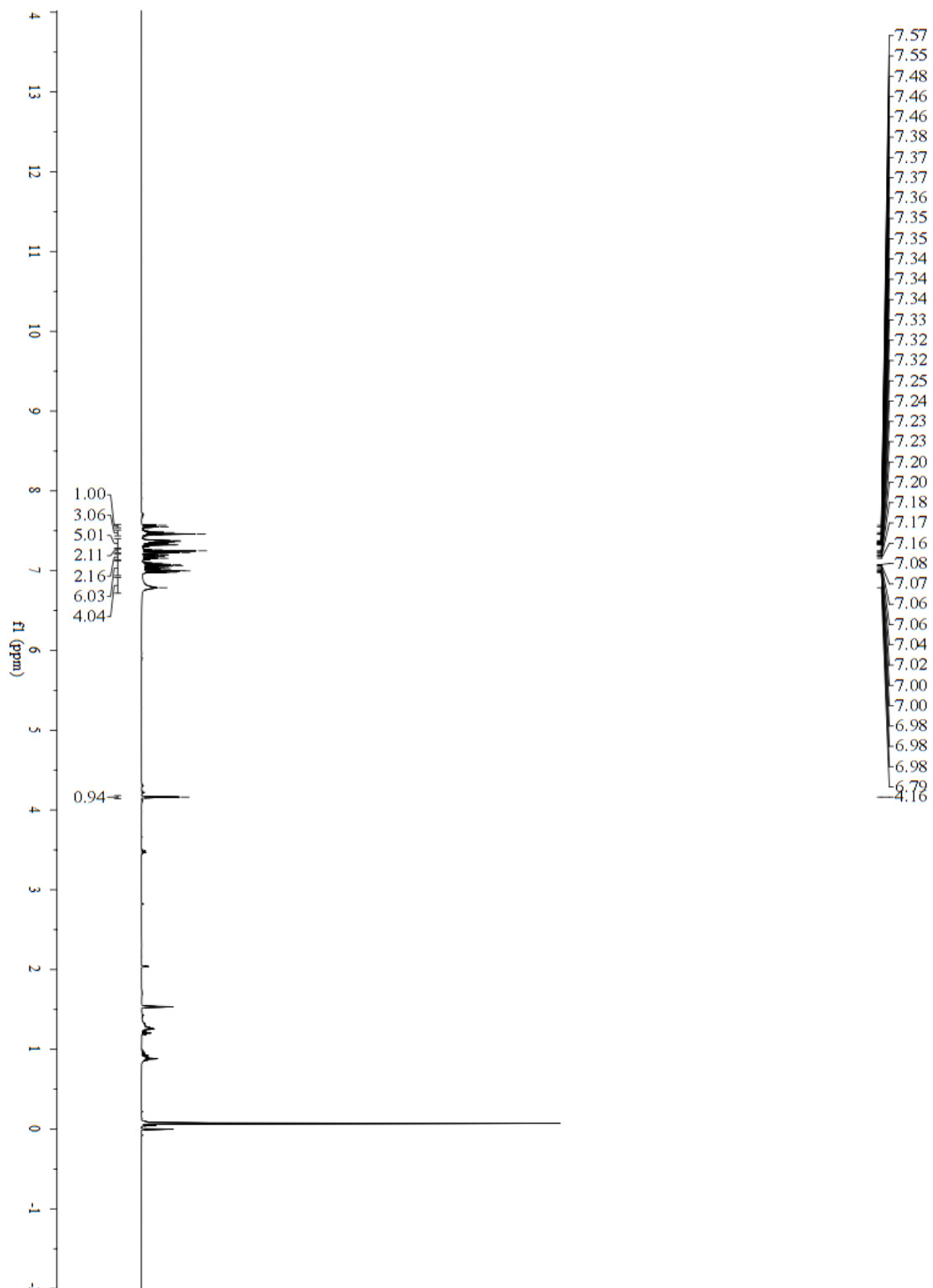


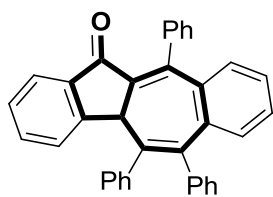
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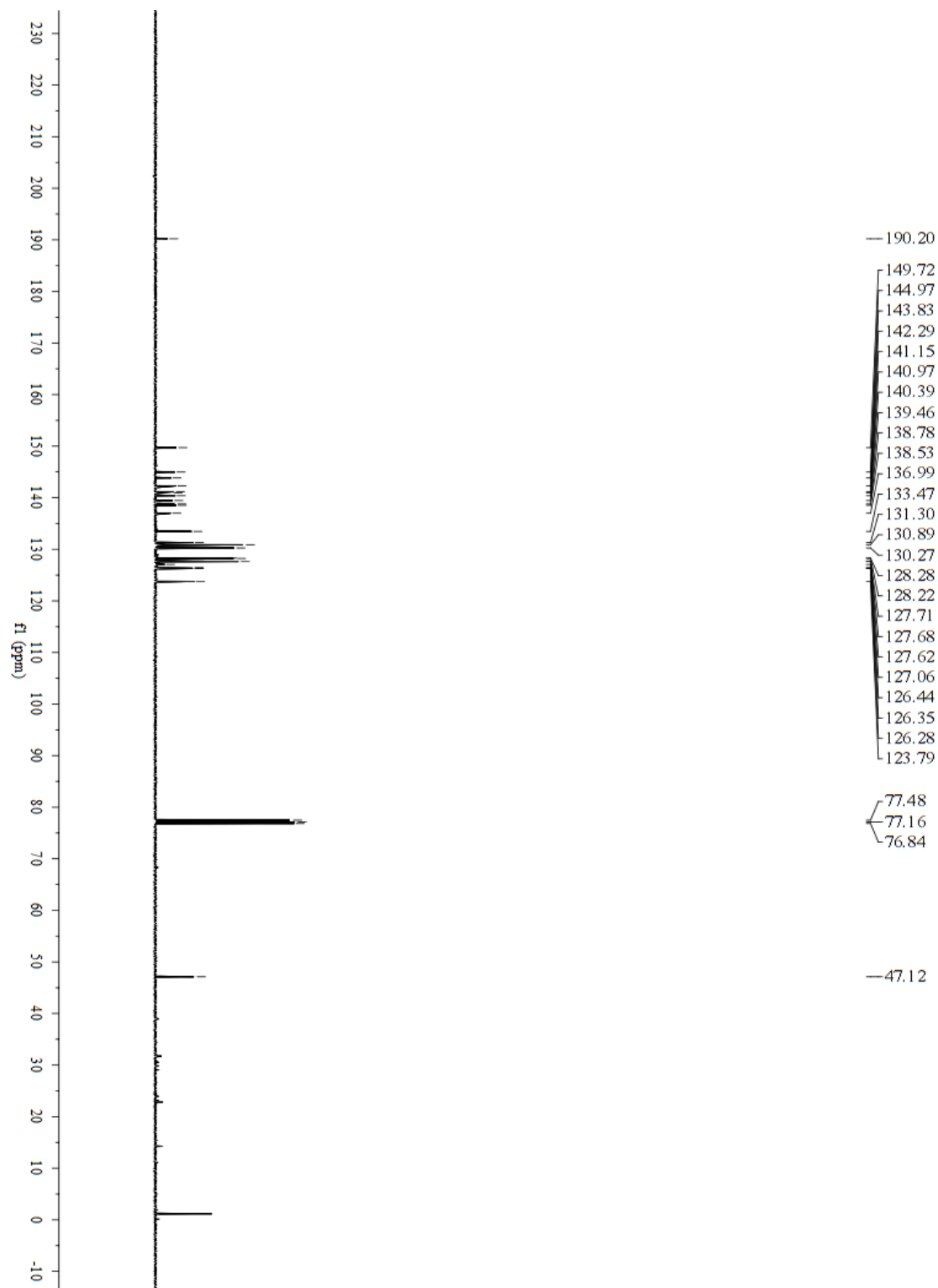
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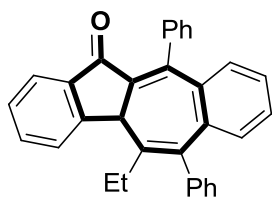




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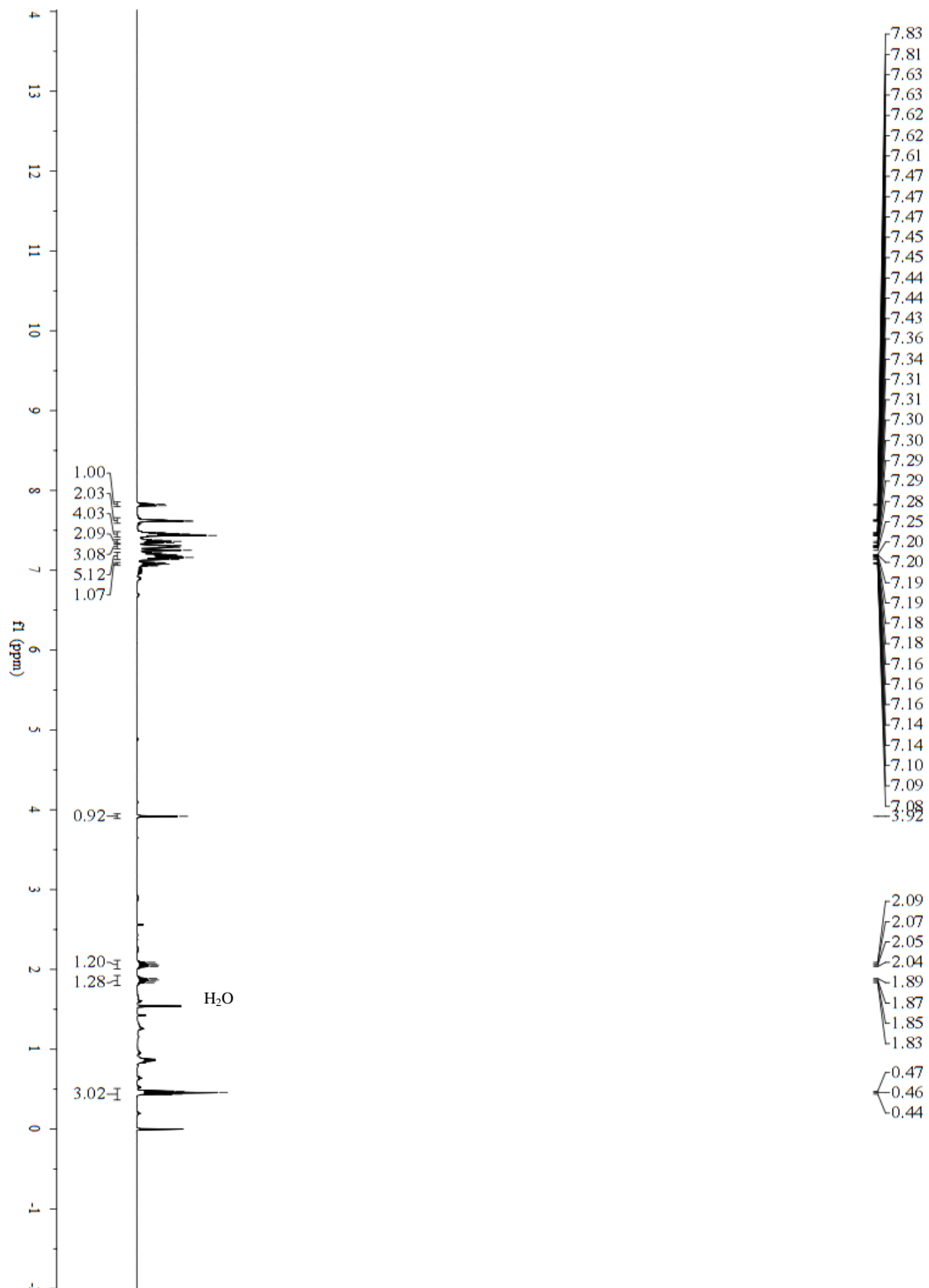
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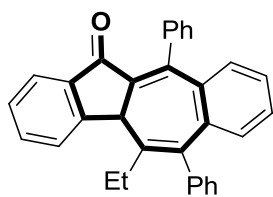




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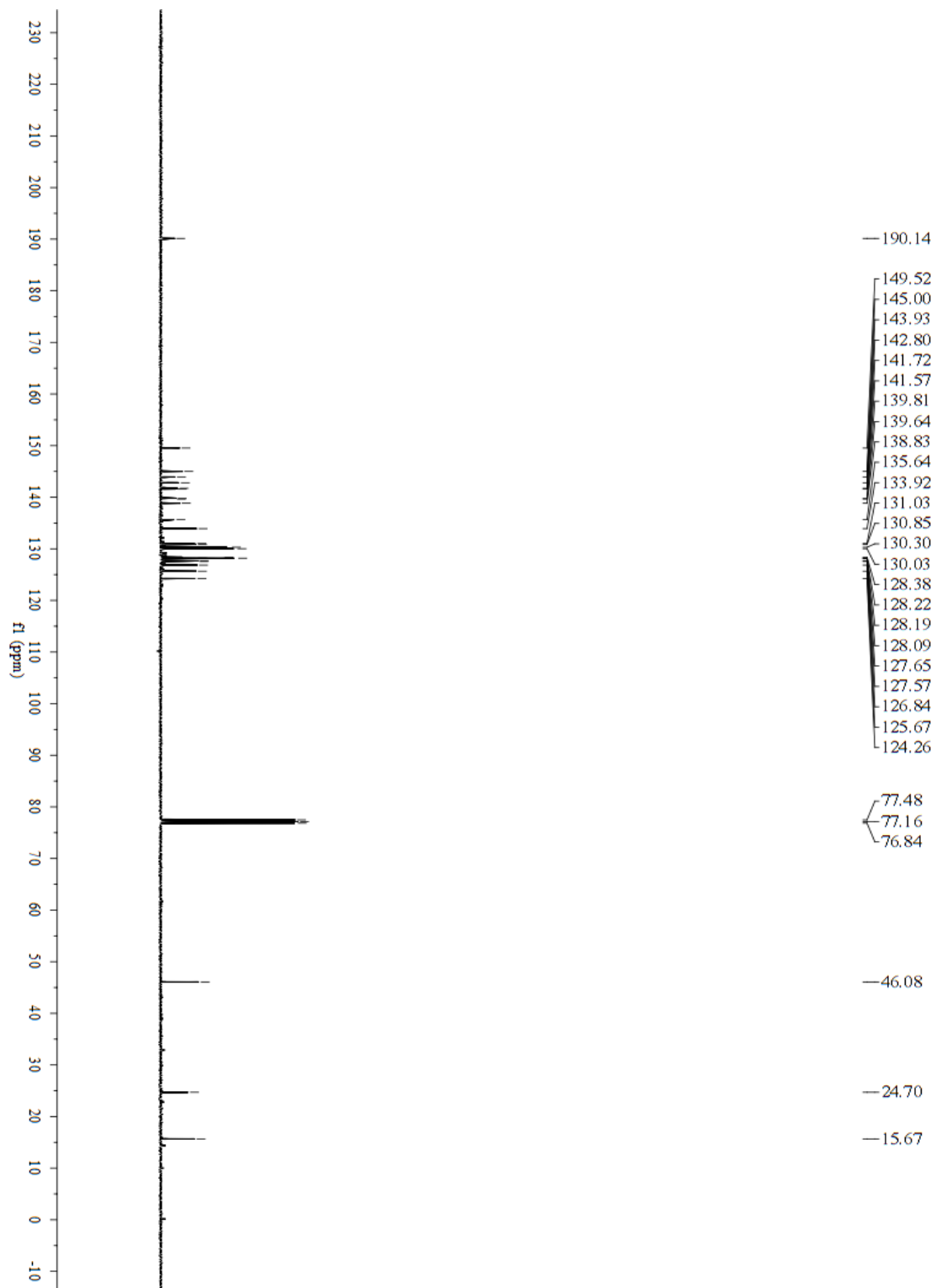
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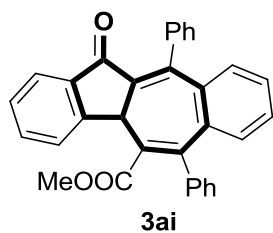




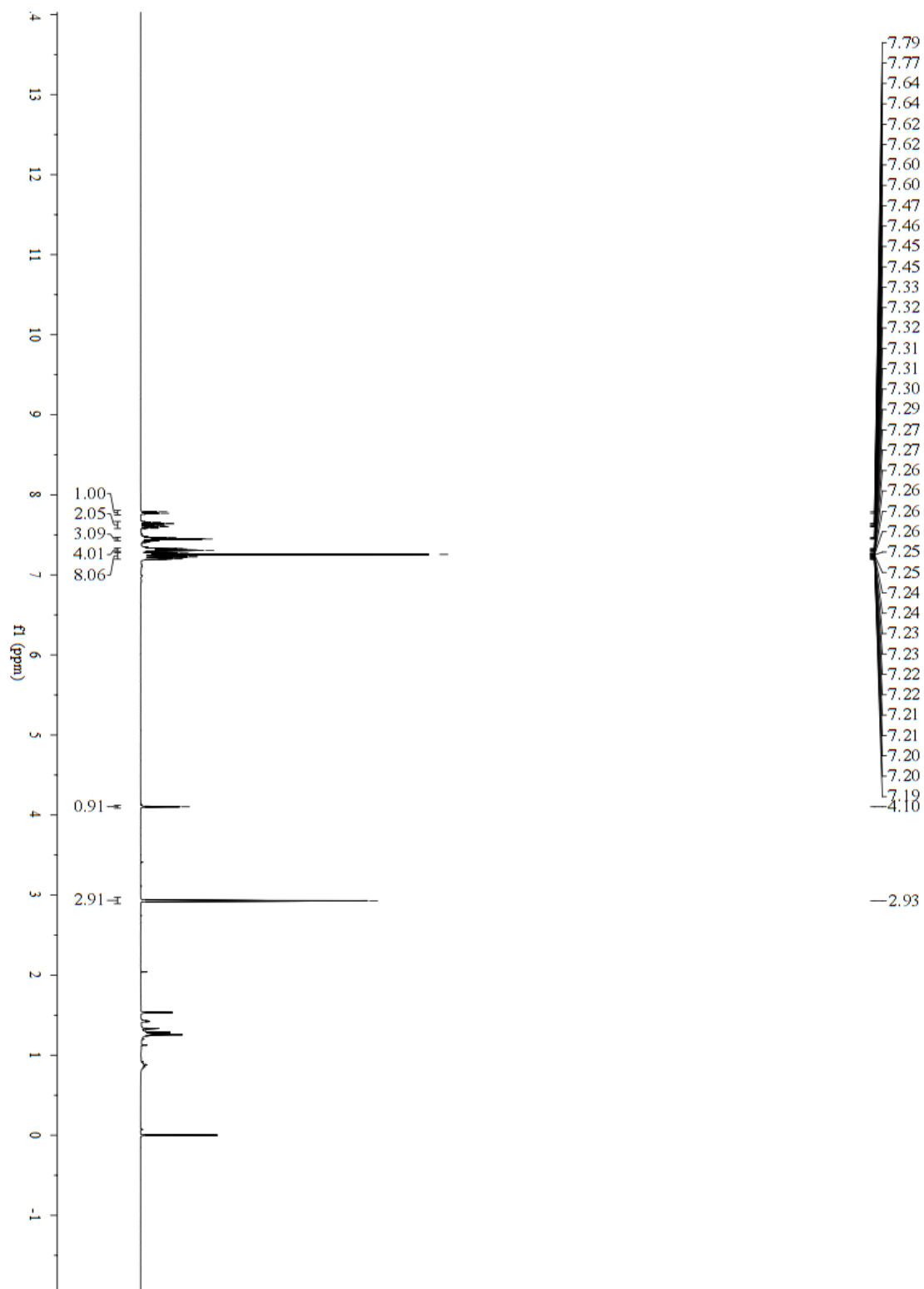
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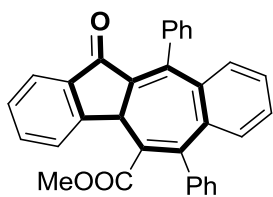
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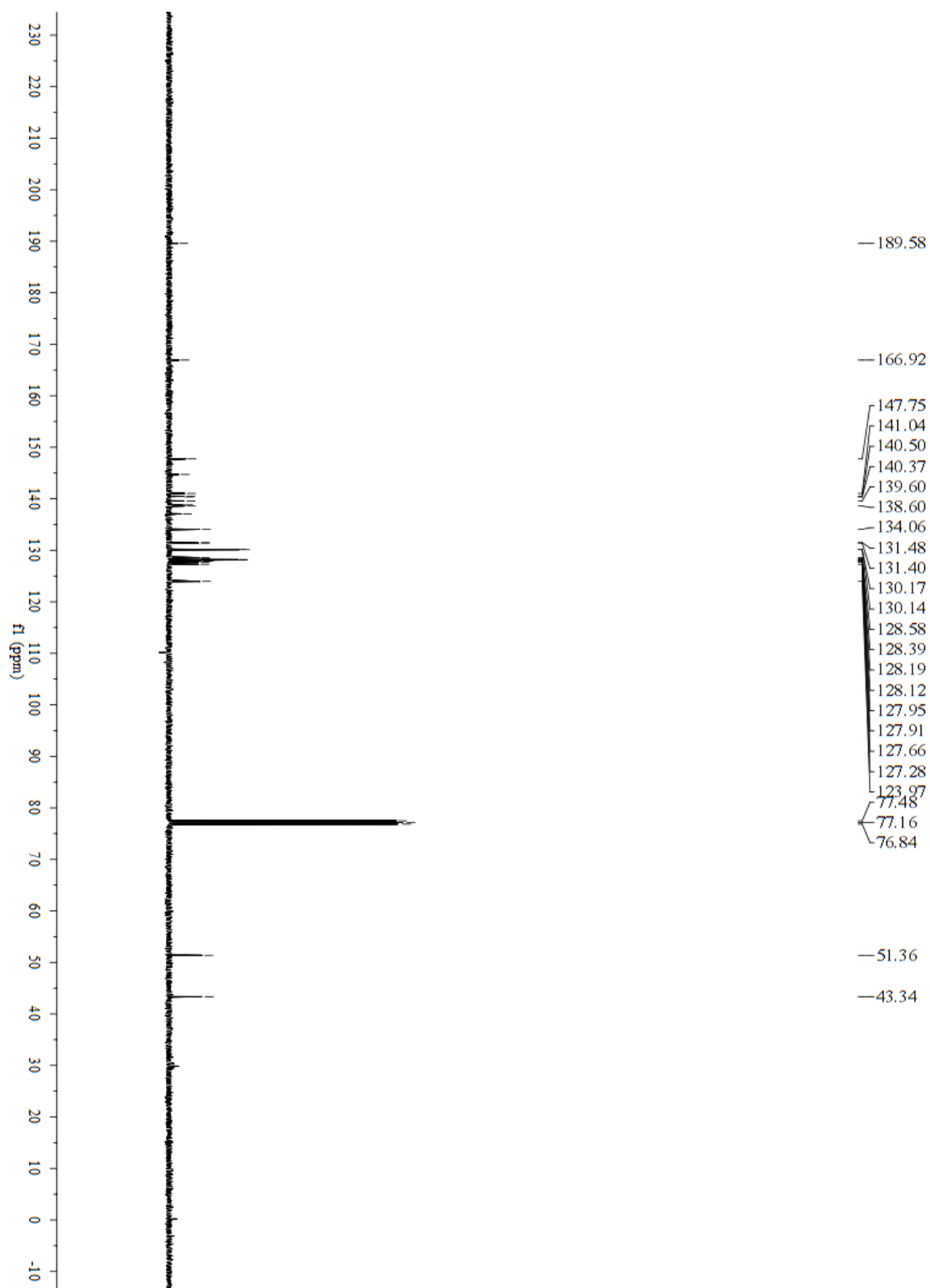
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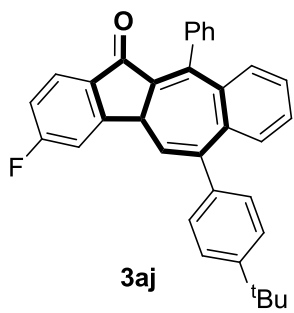




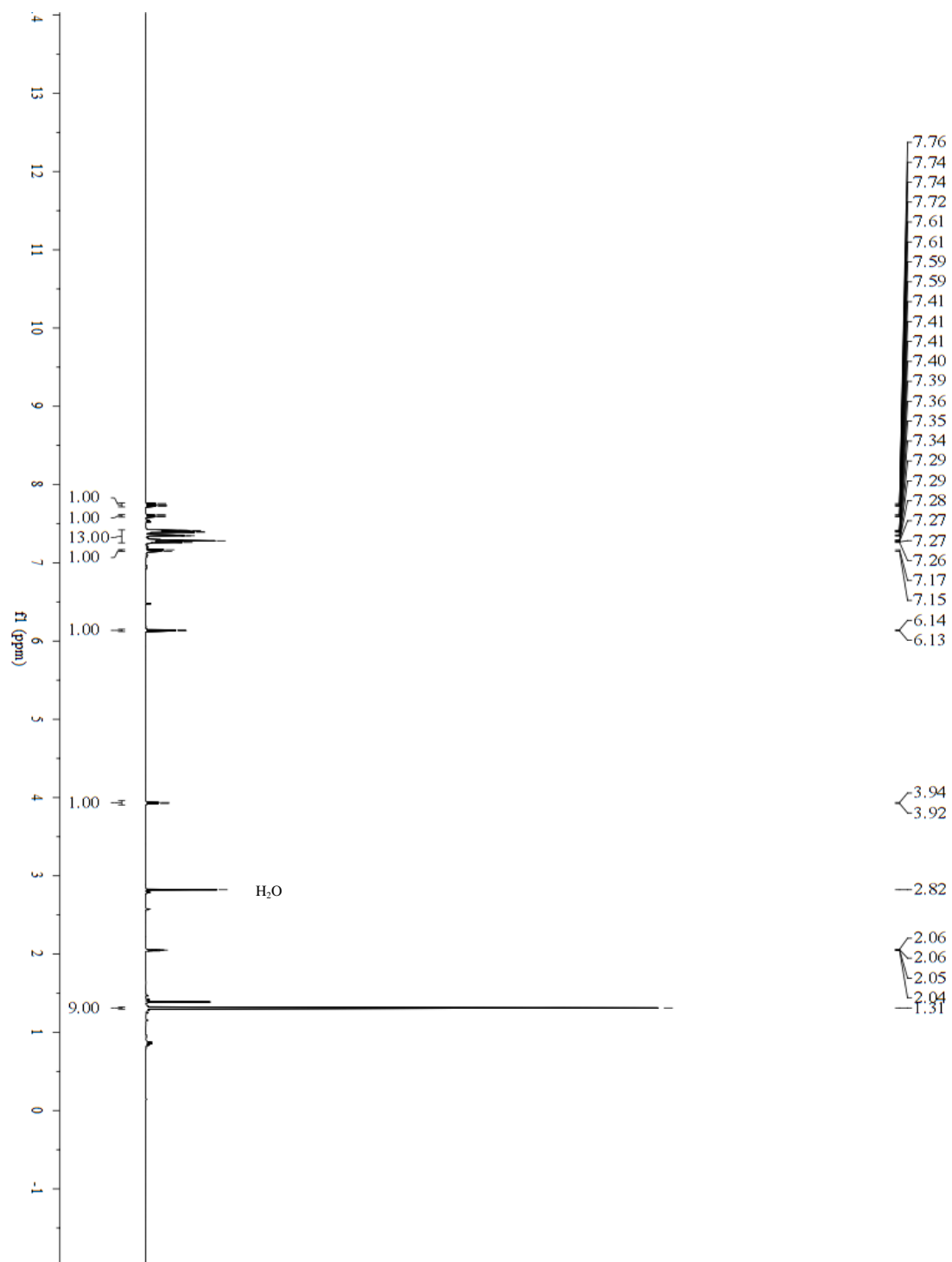
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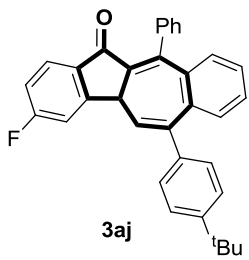
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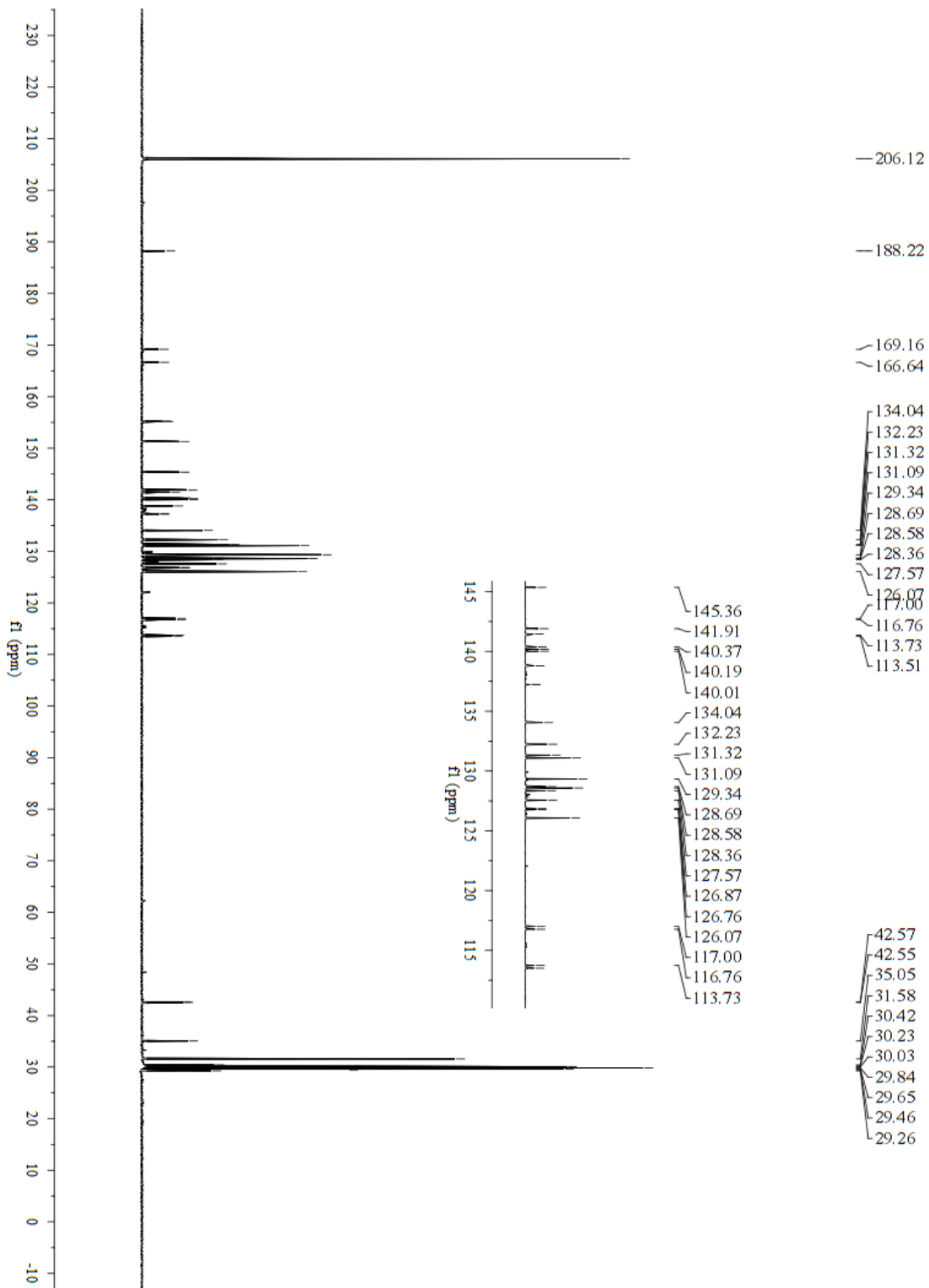


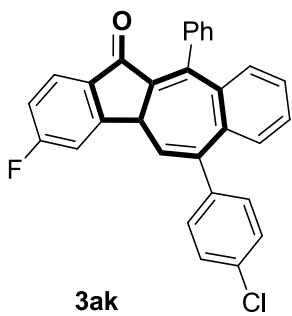
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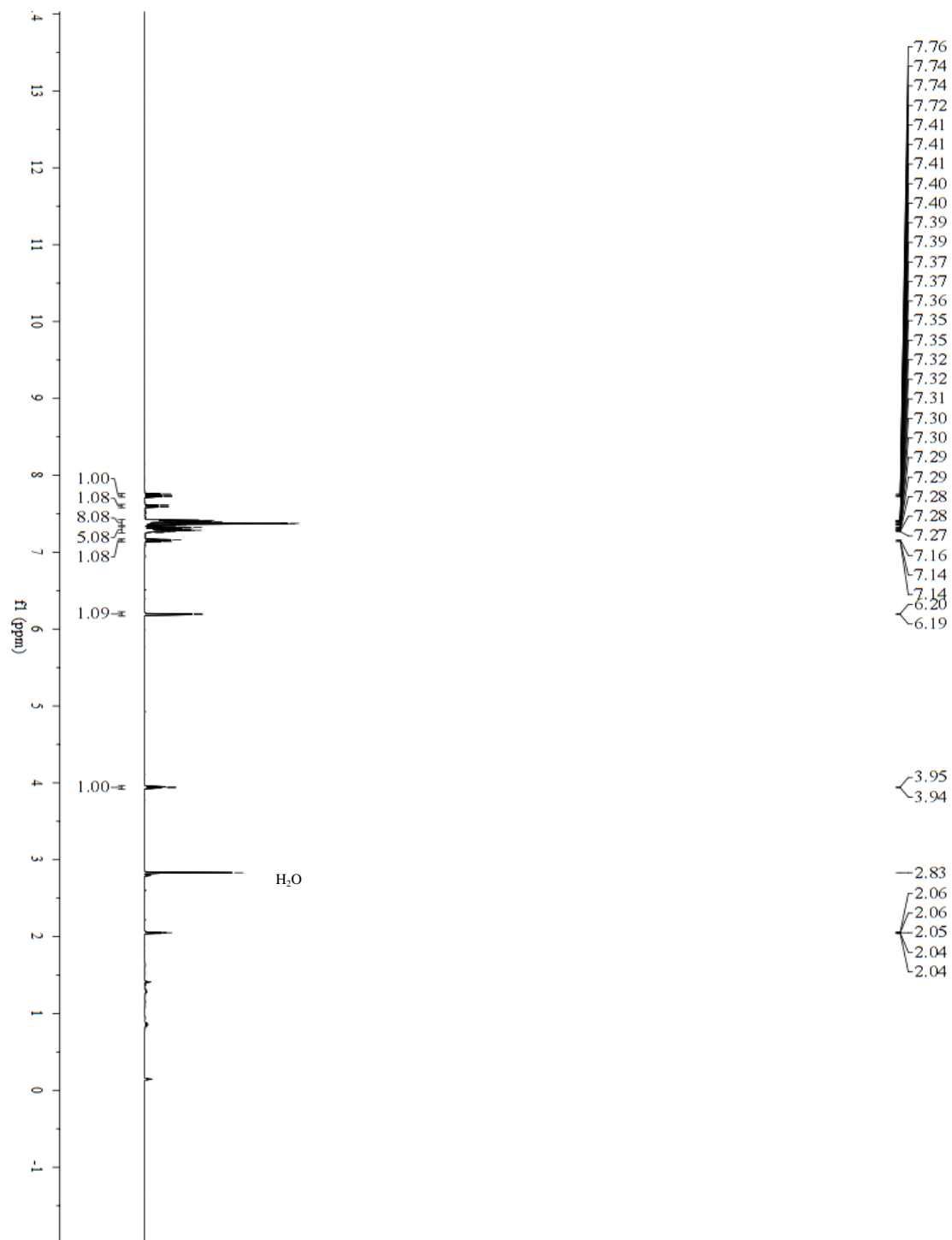


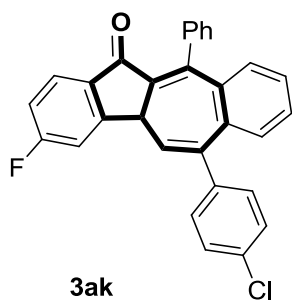
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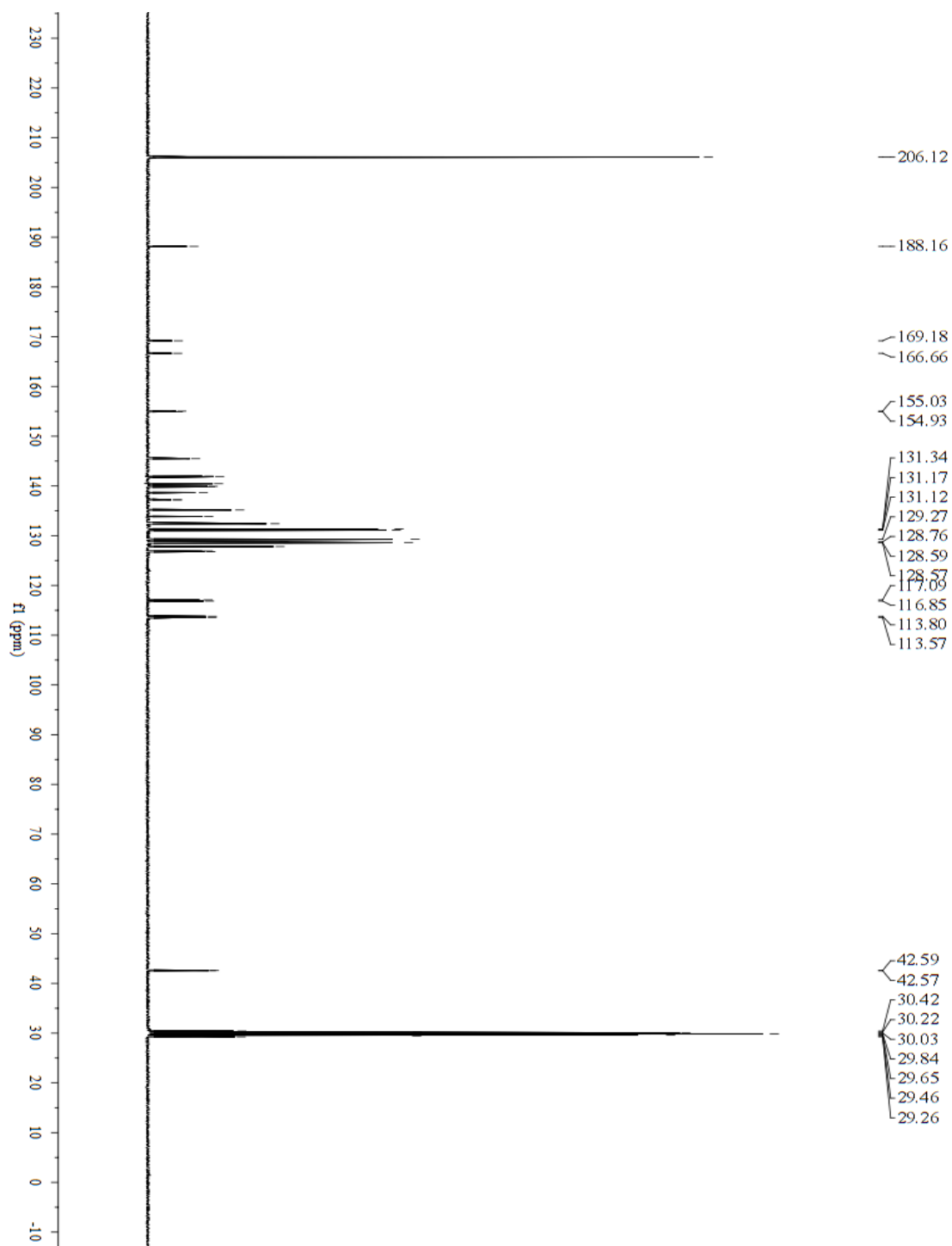


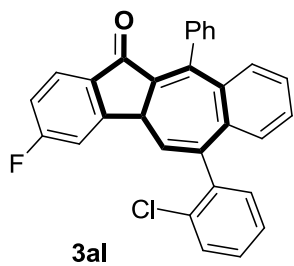
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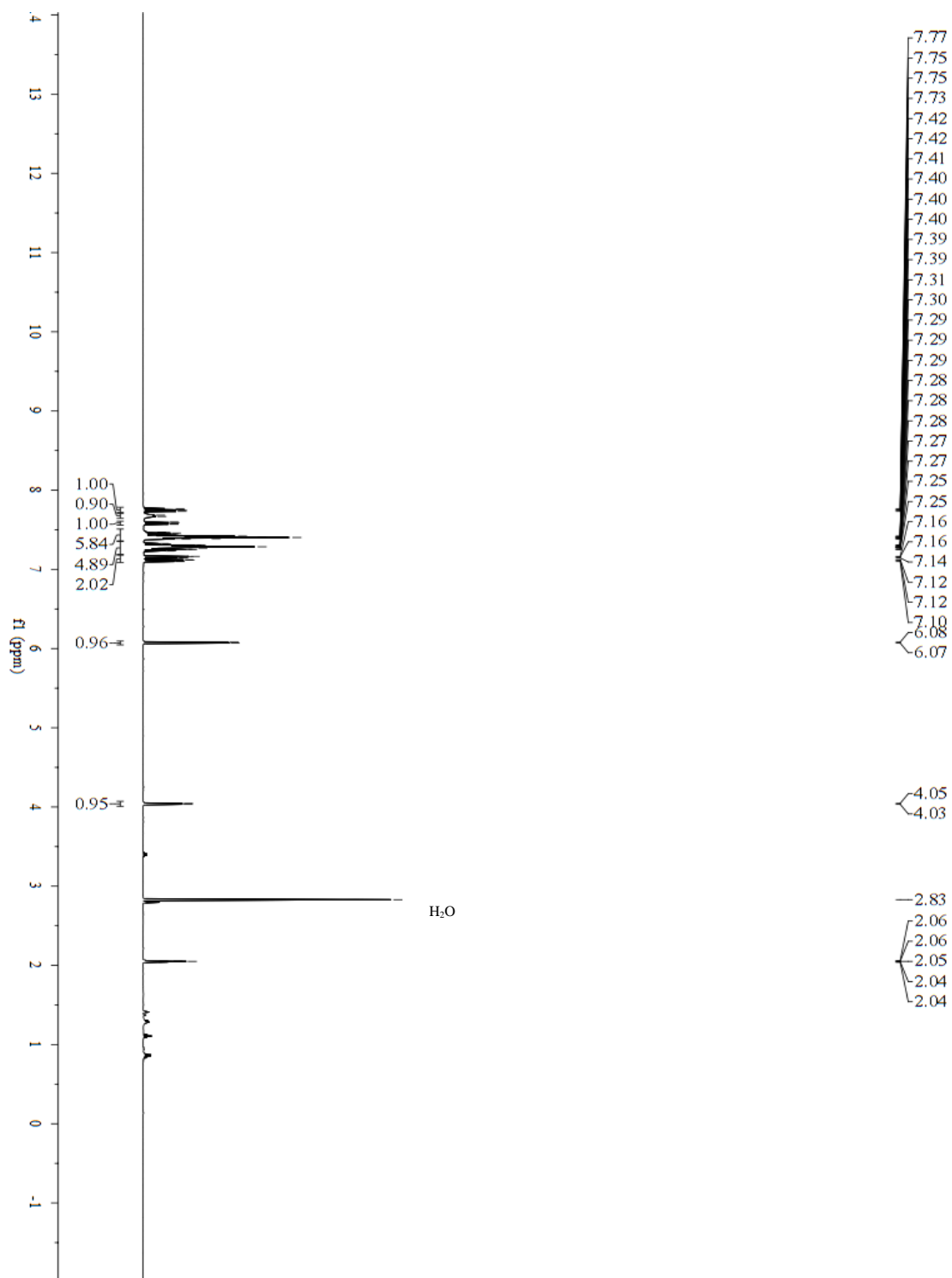


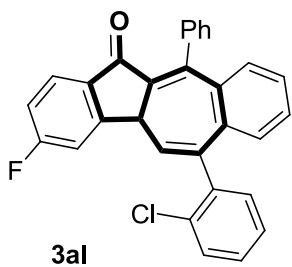
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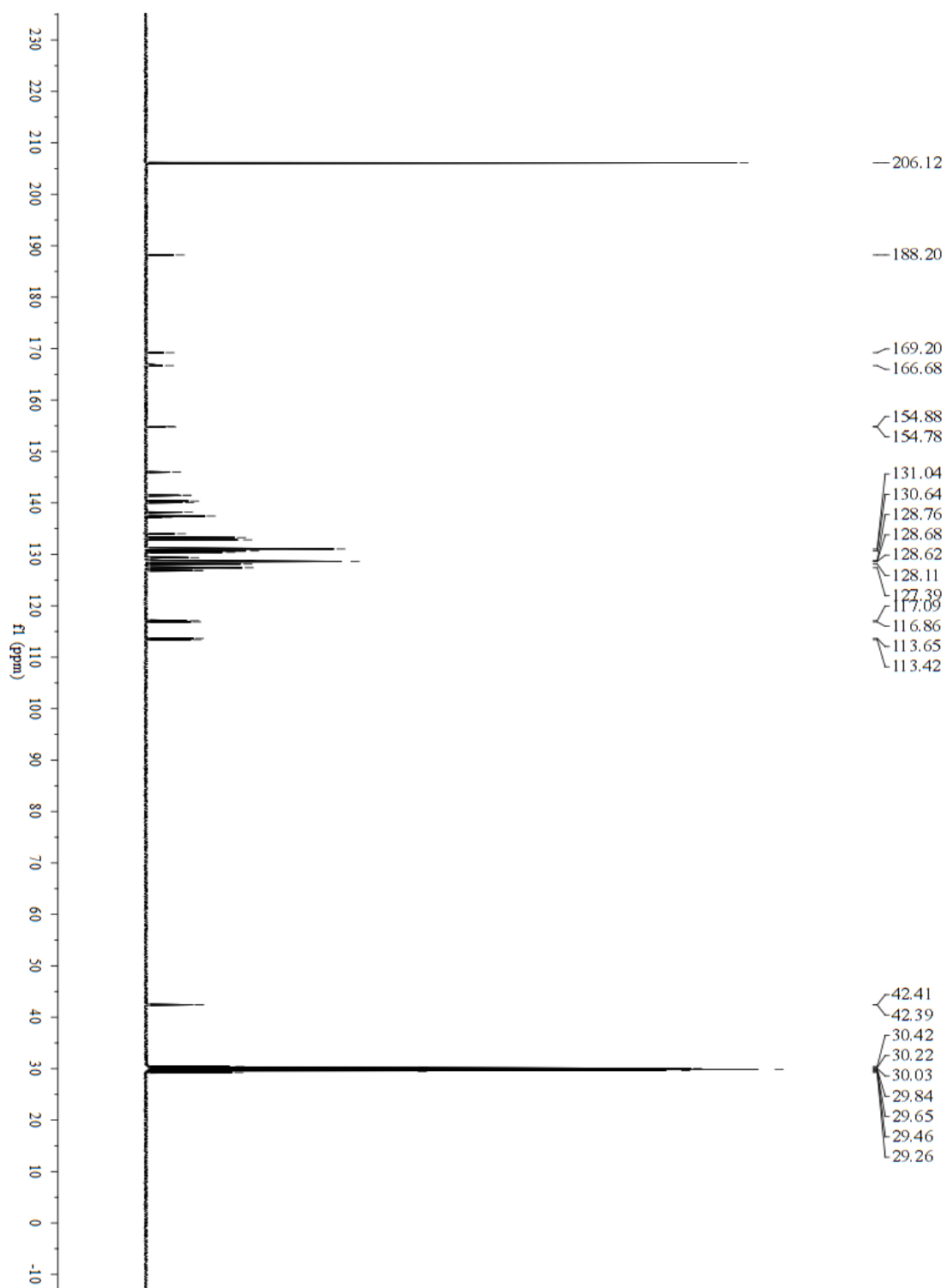


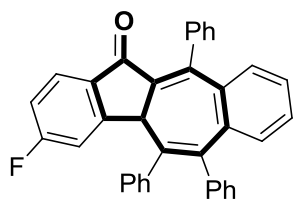
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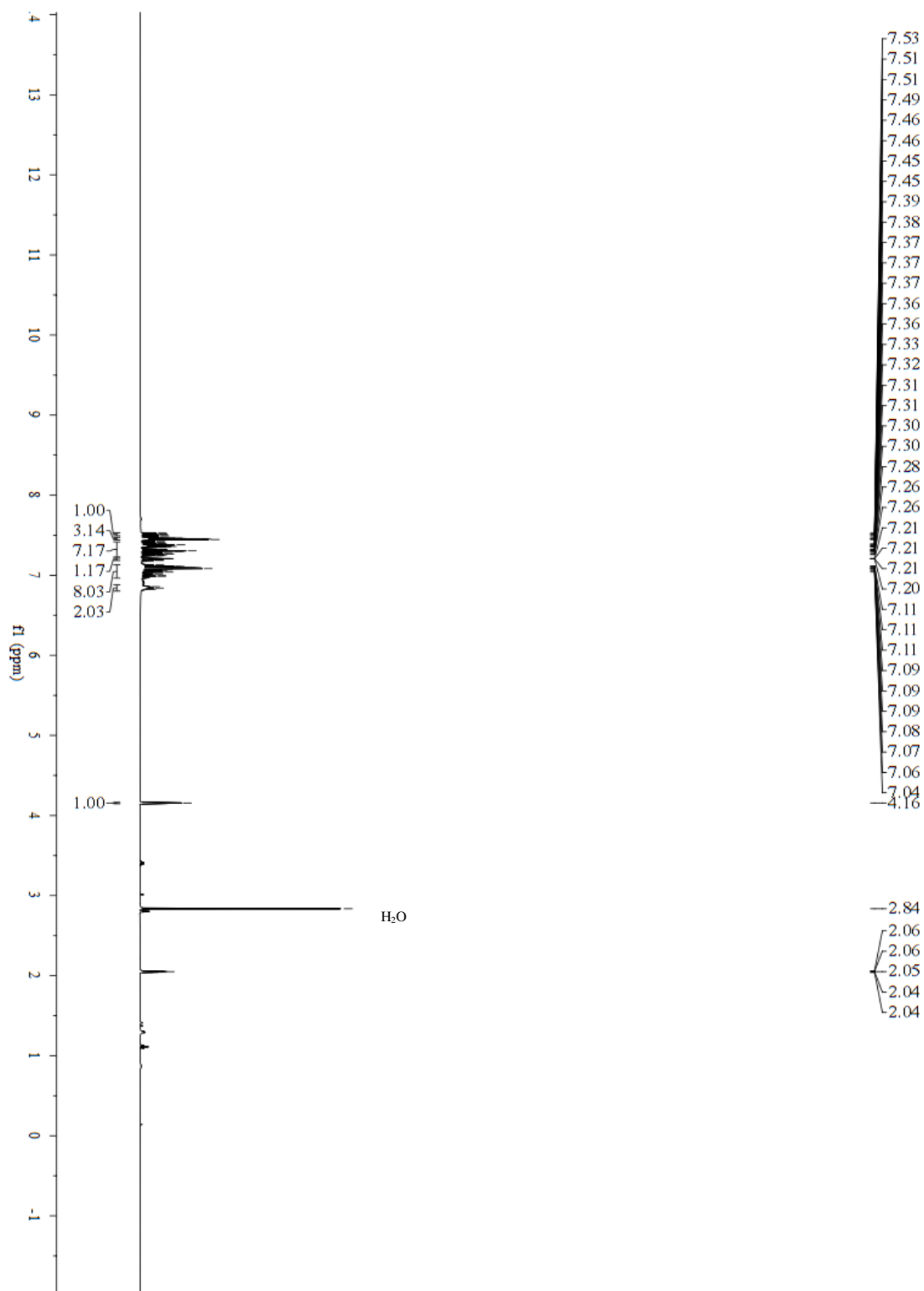
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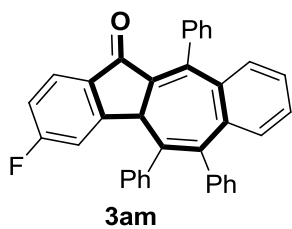




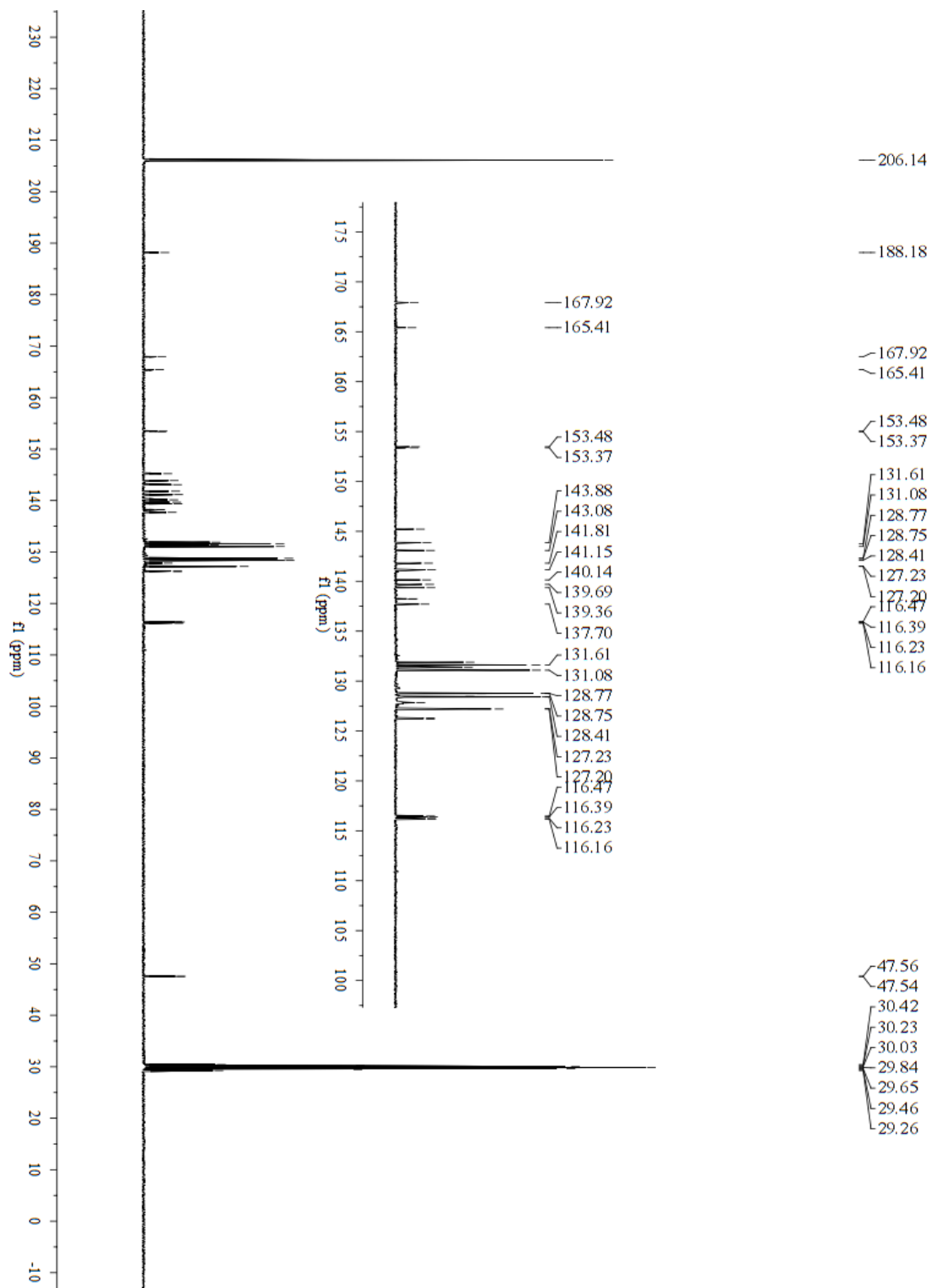
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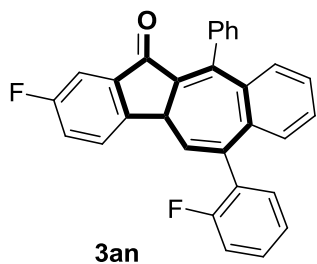
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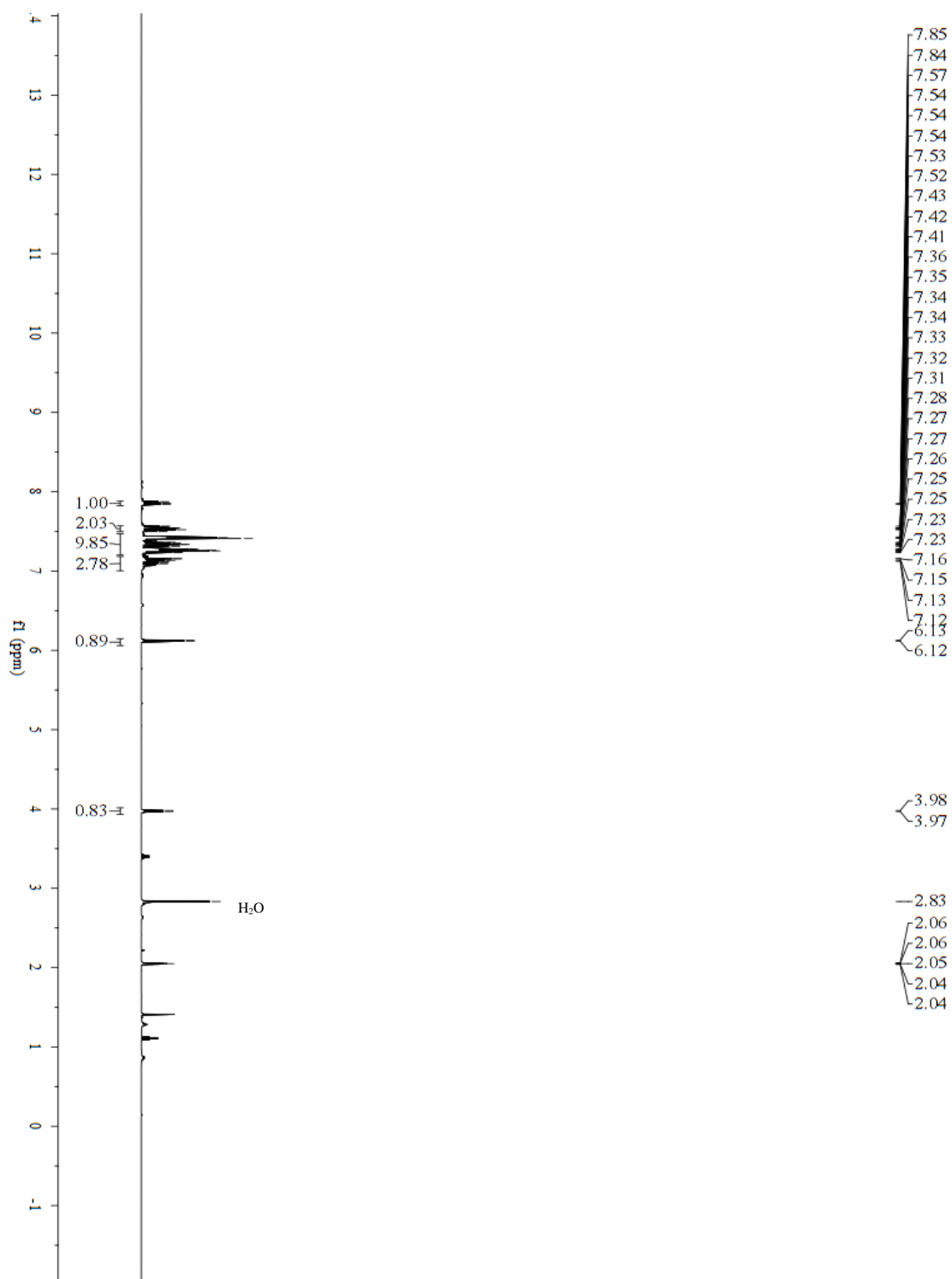


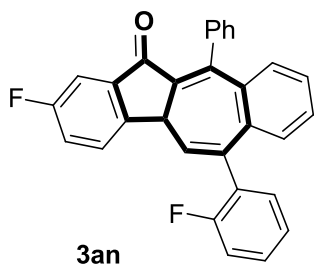
¹³C NMR (100 MHz, acetone)



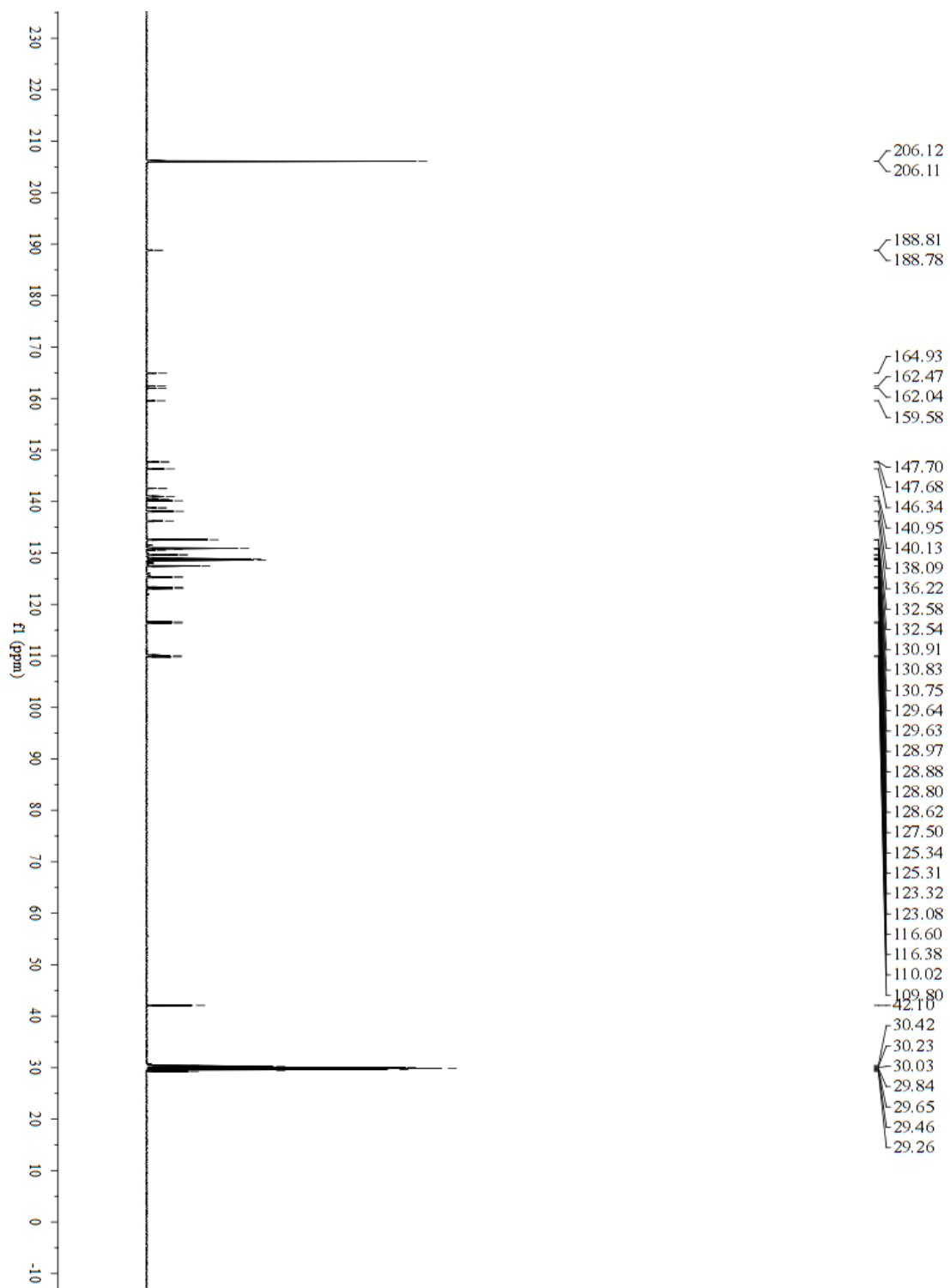


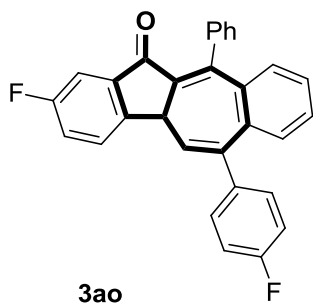
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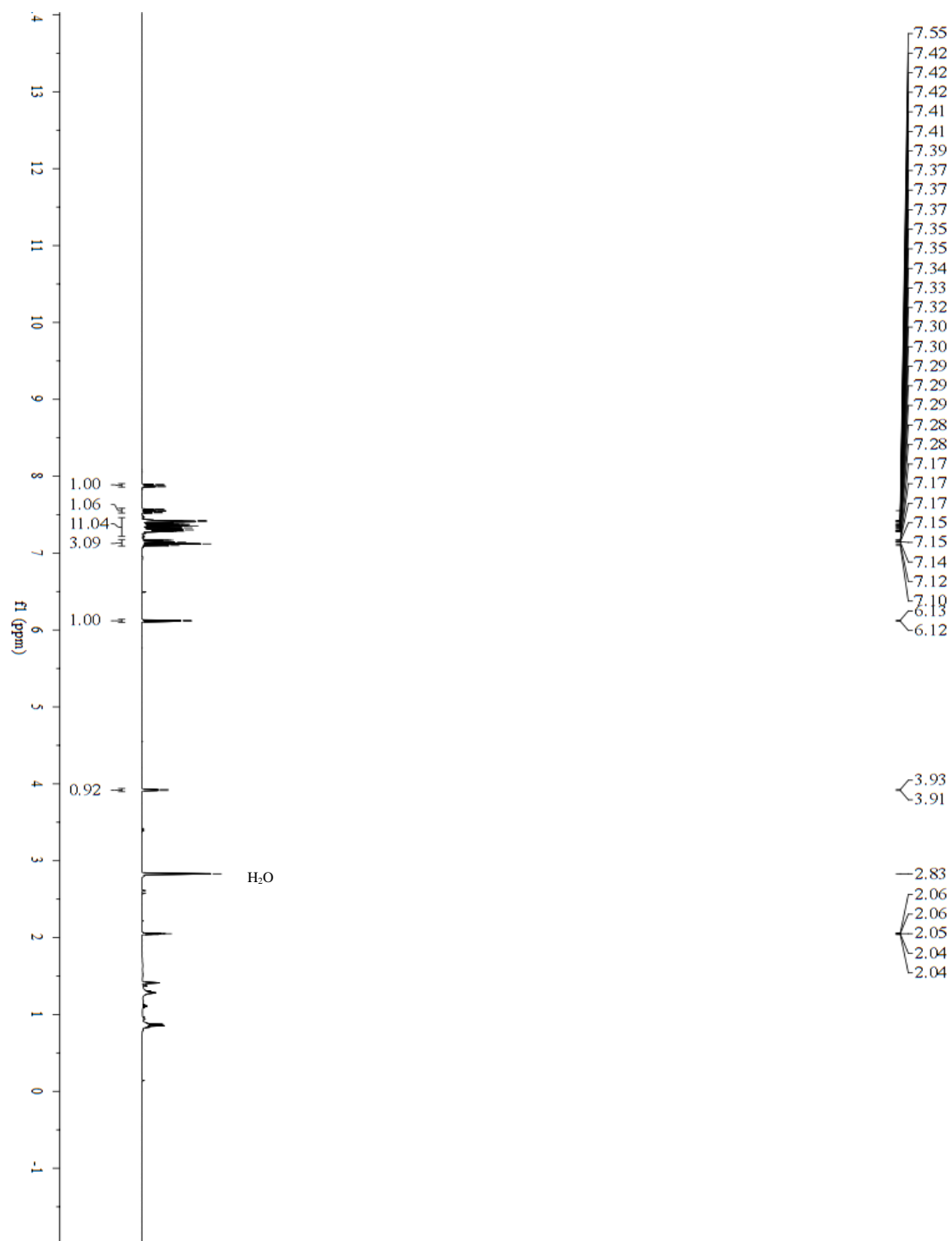


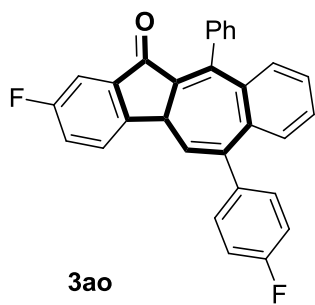
^{13}C NMR (100 MHz, acetone)



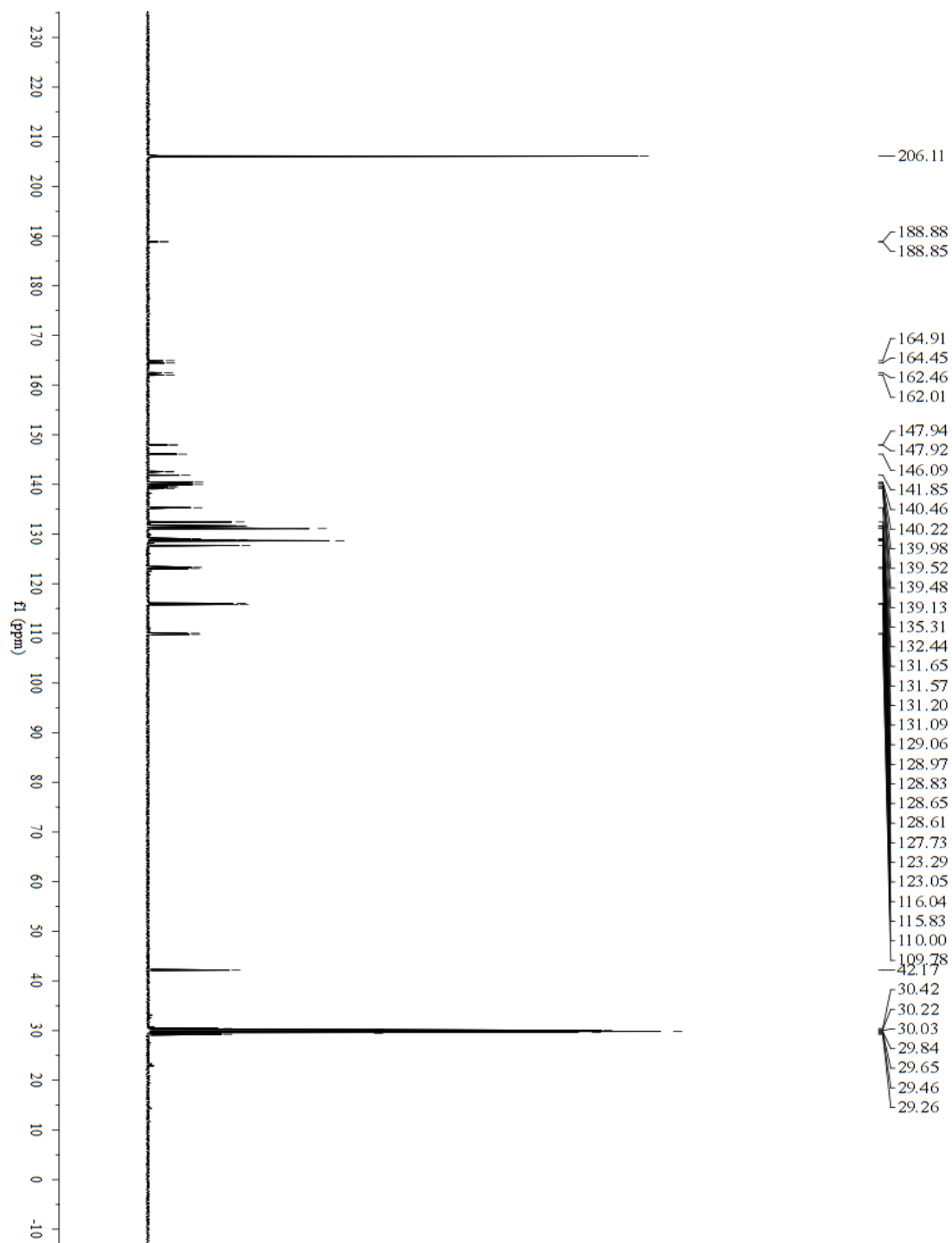


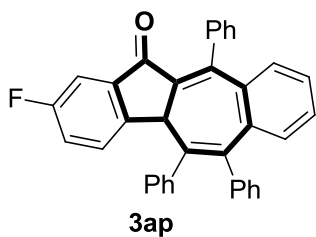
$^1\text{H NMR}$ (400 MHz, acetone)



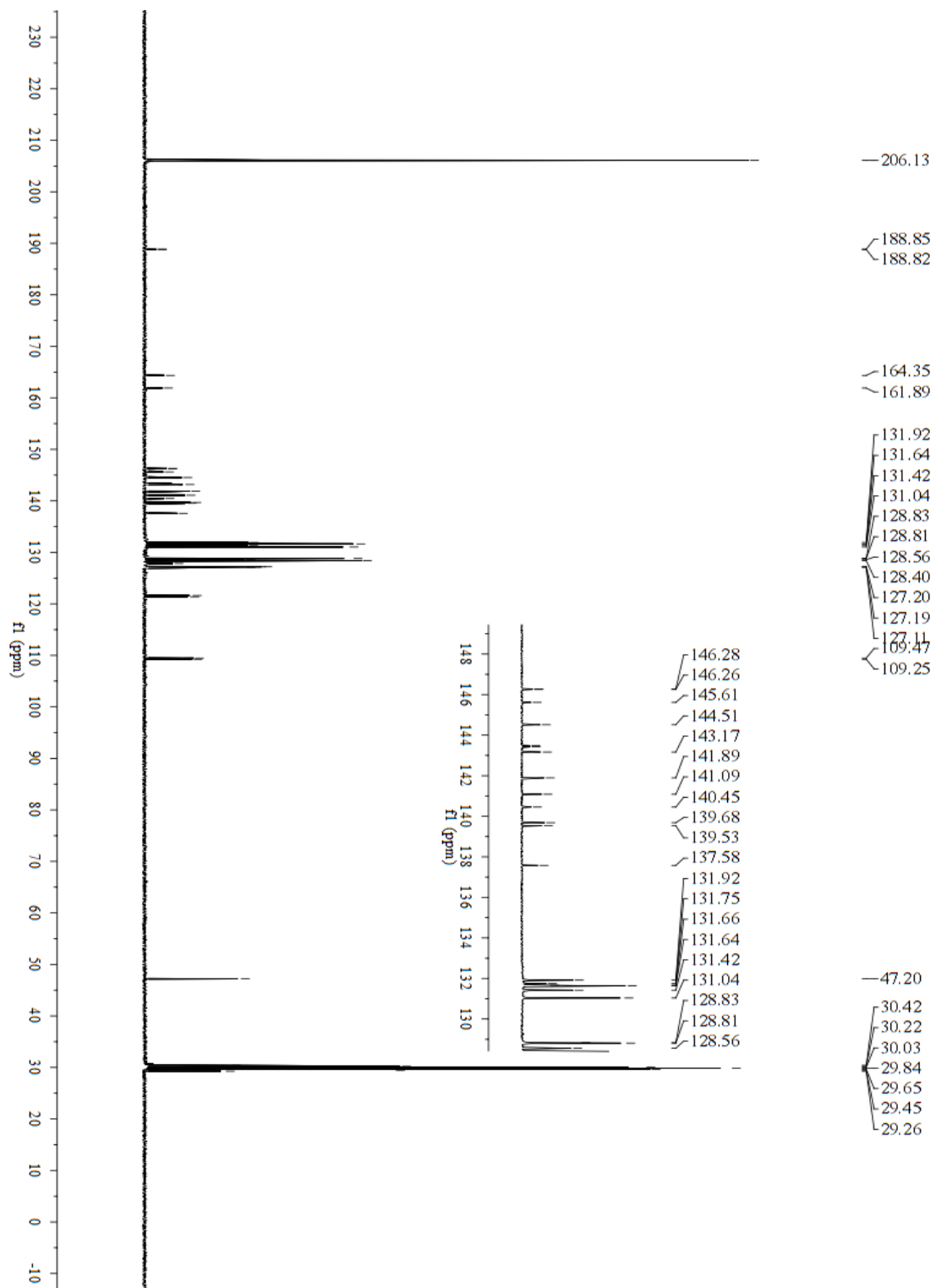


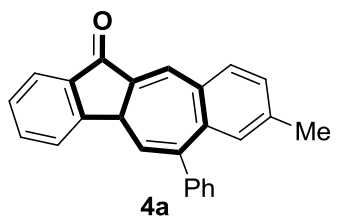
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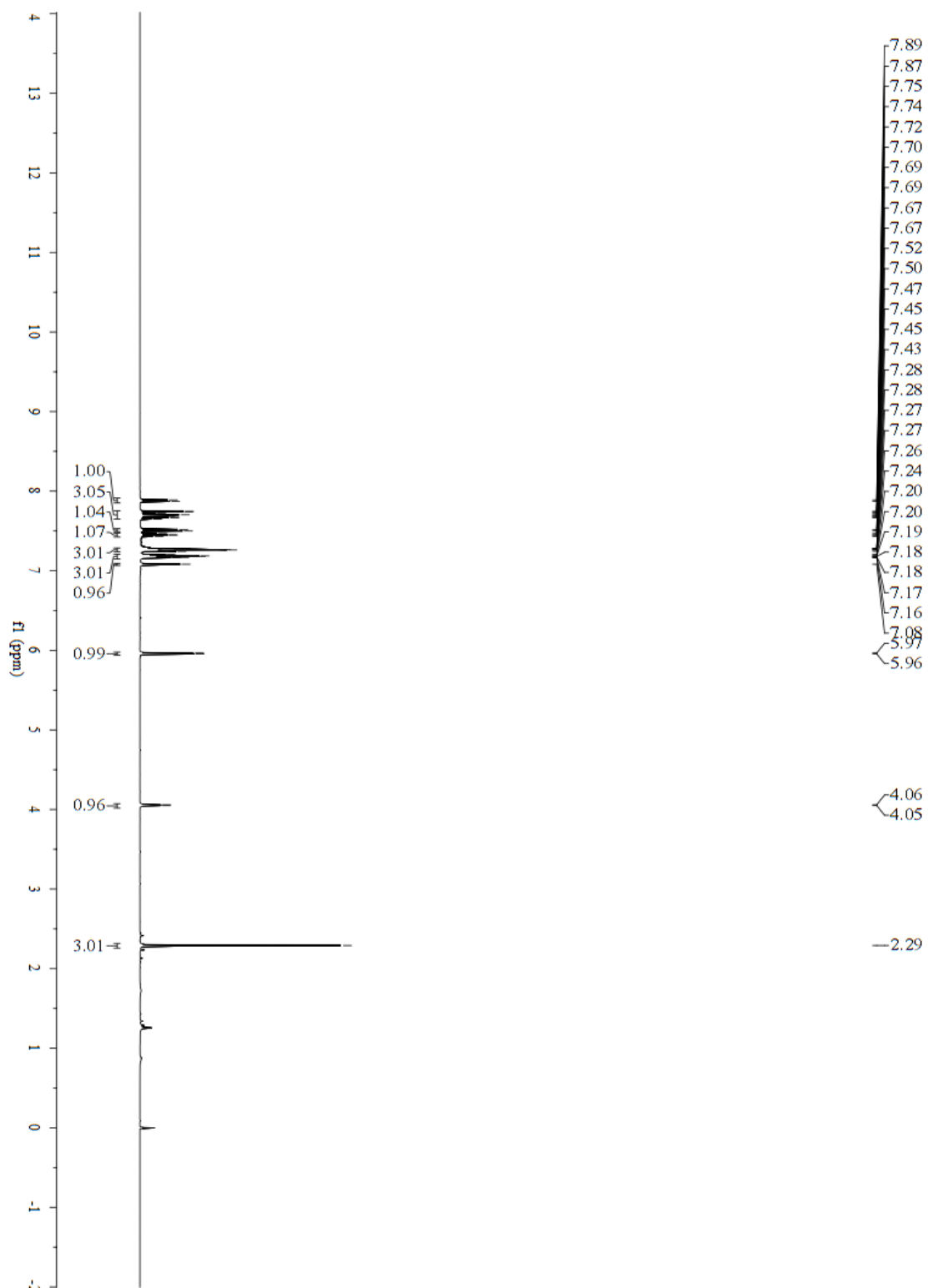


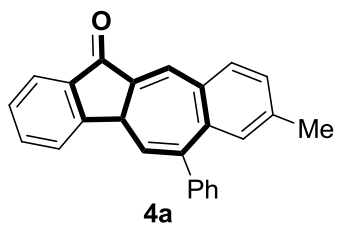
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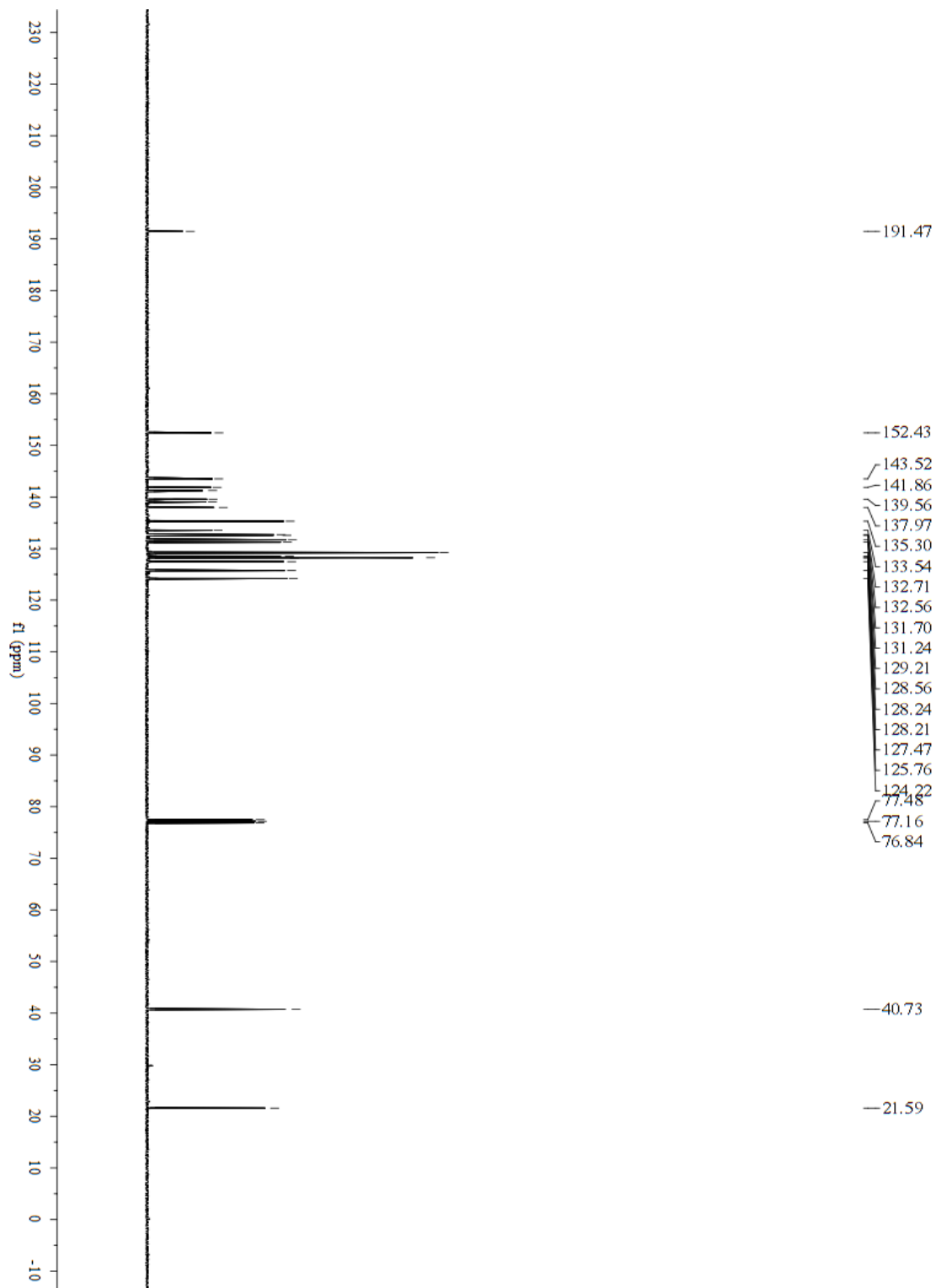


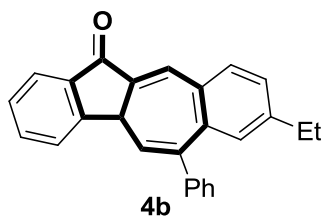
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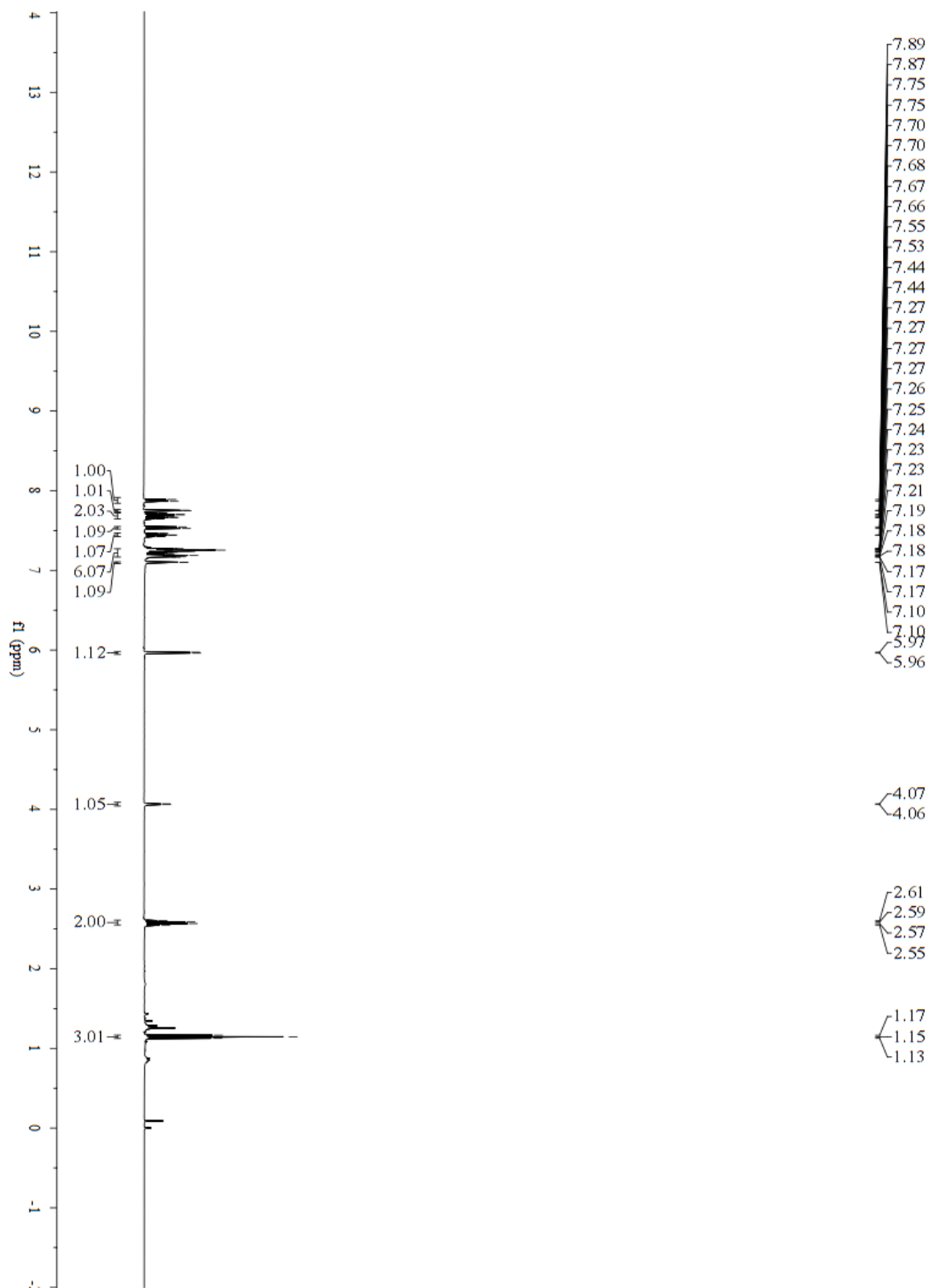


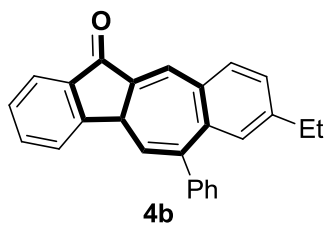
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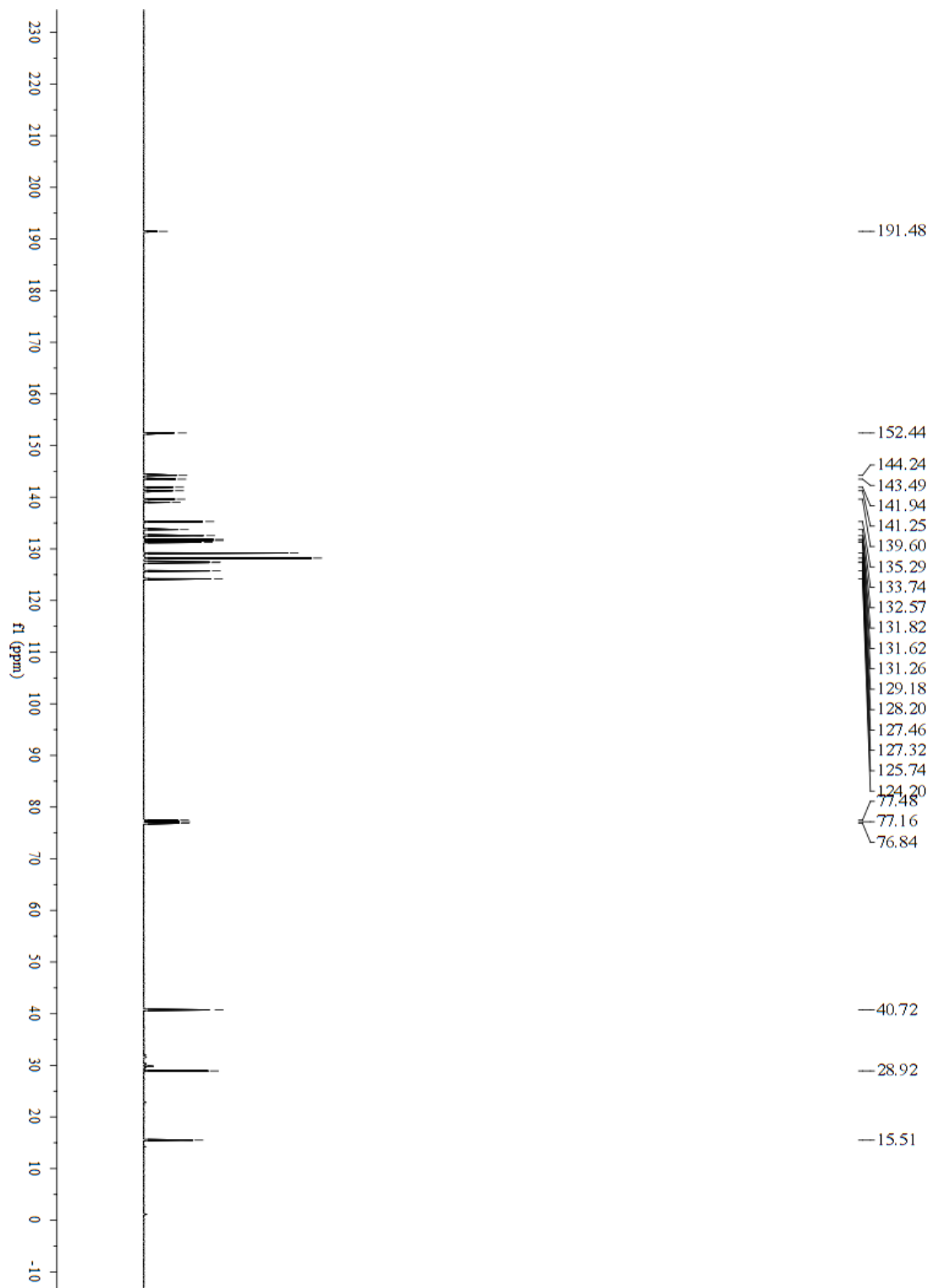


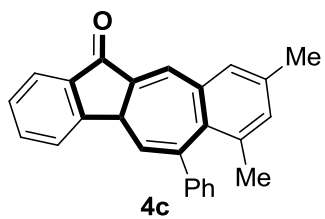
$^1\text{H NMR}$ (400 MHz, CDCl_3)



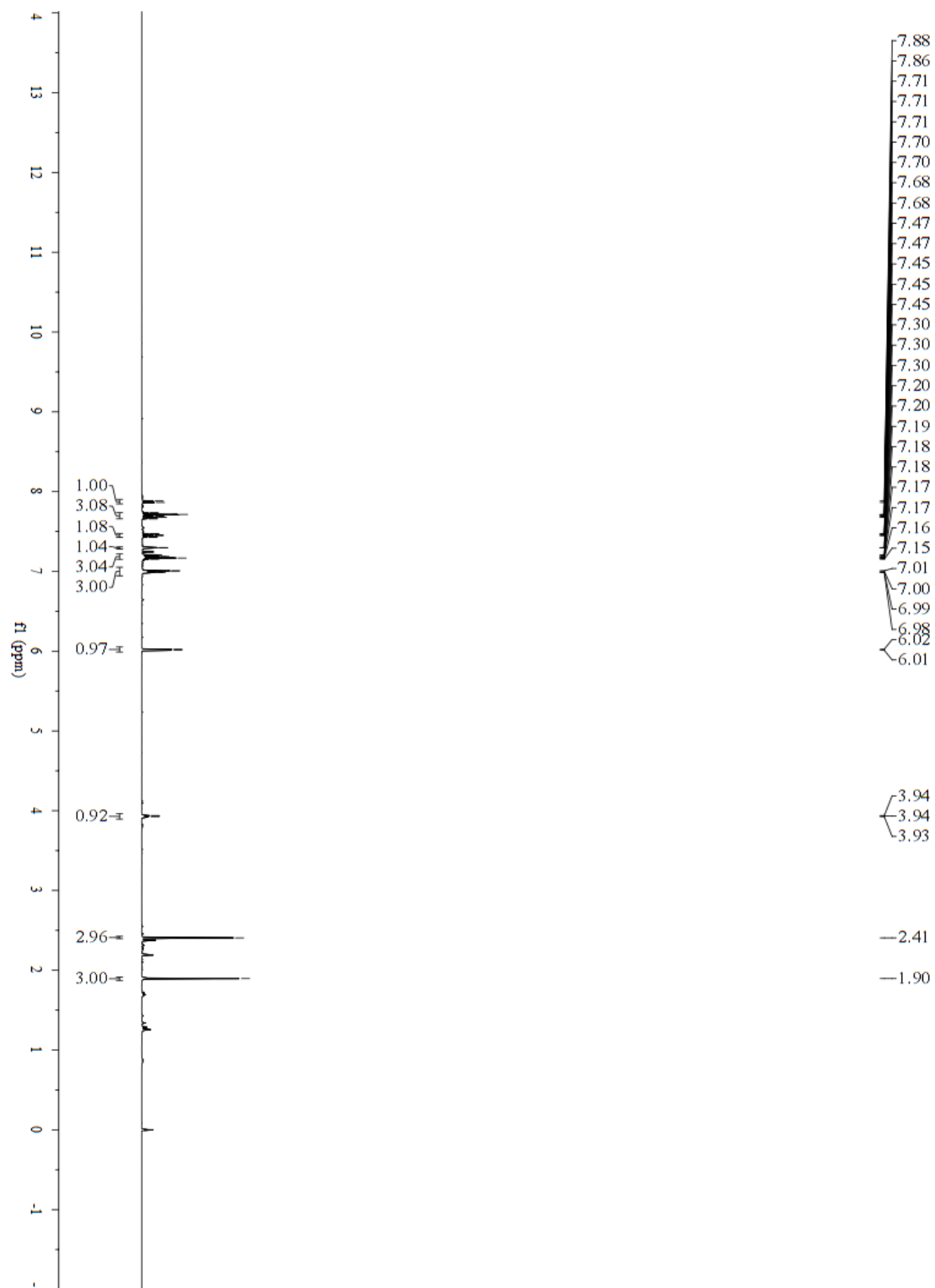


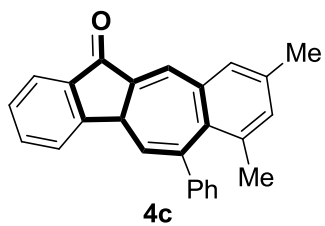
¹³C NMR (100 MHz, CDCl₃)



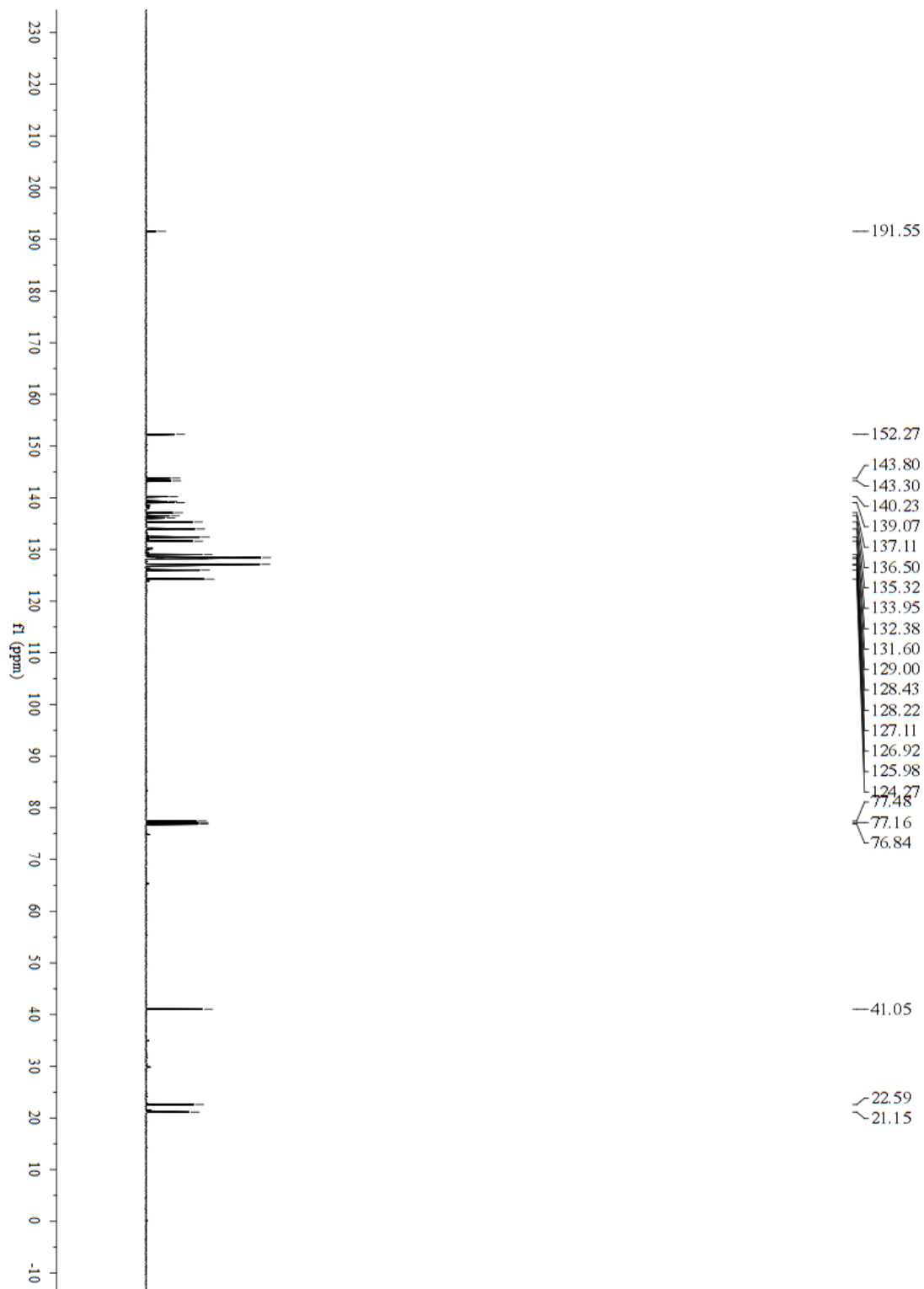


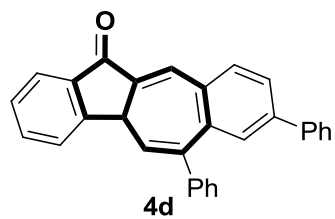
$^1\text{H NMR}$ (400 MHz, CDCl_3)



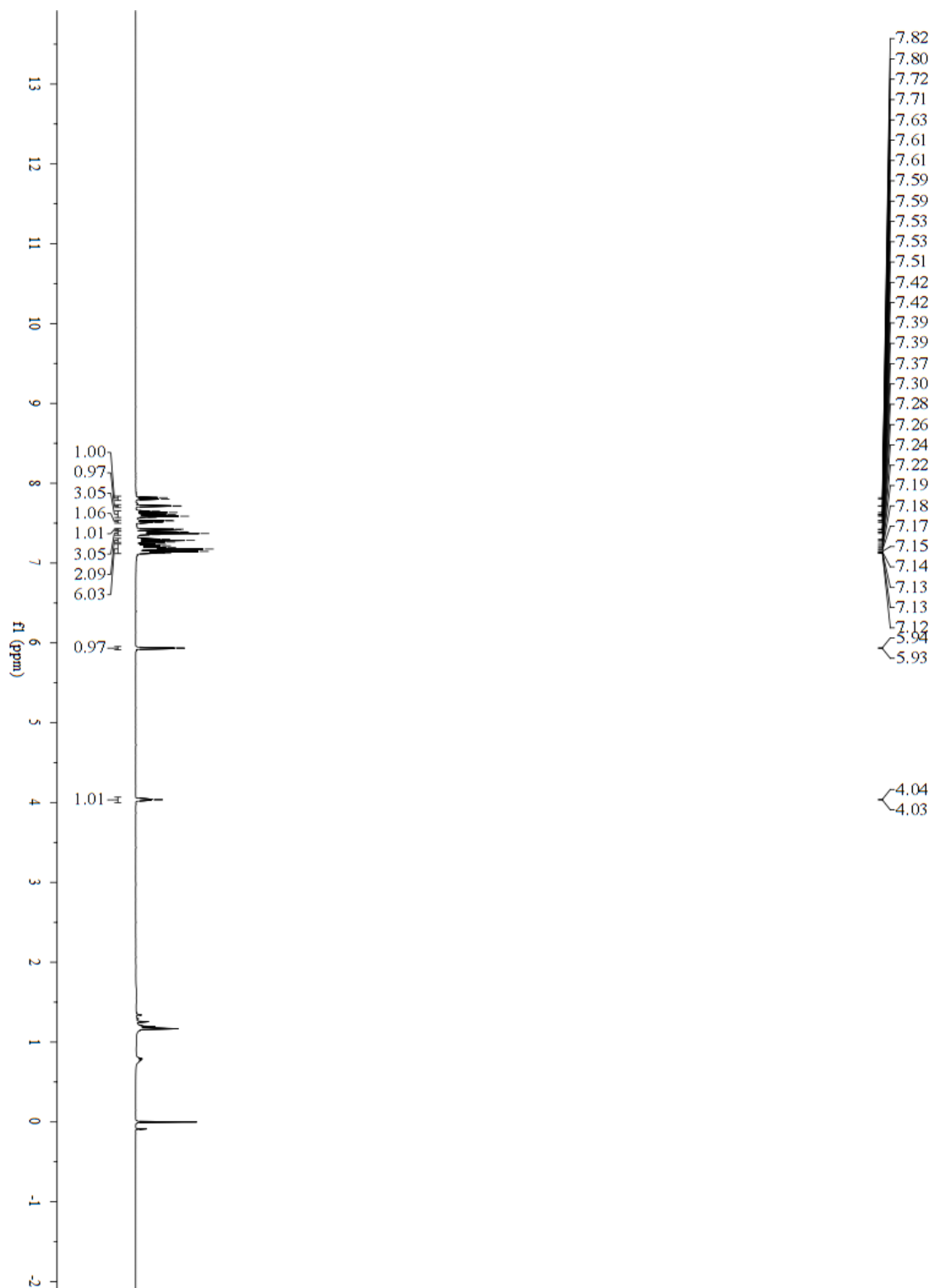


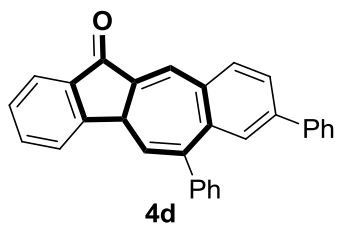
^{13}C NMR (100 MHz, CDCl_3)



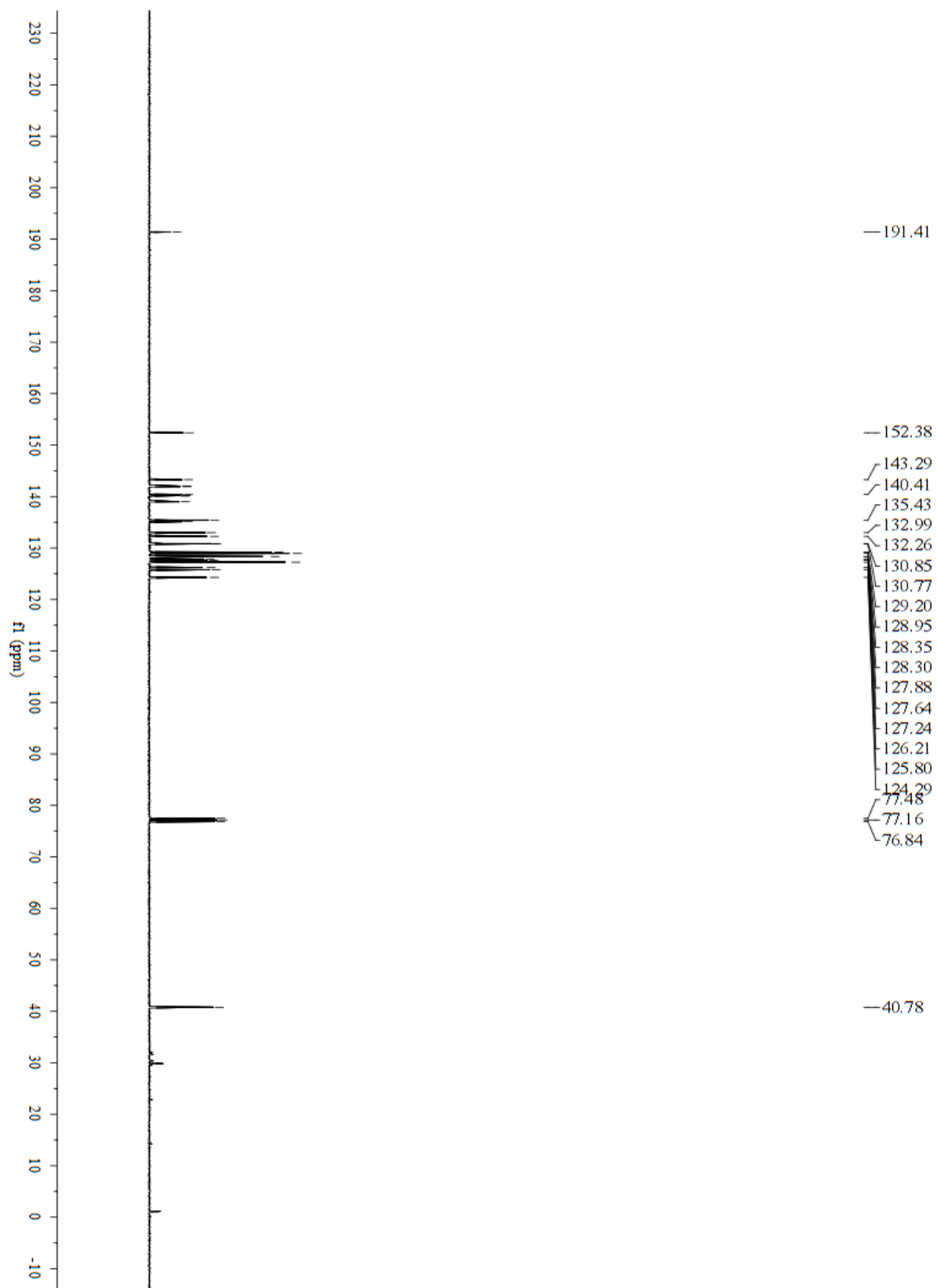


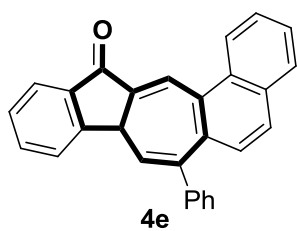
$^1\text{H NMR}$ (400 MHz, CDCl_3)



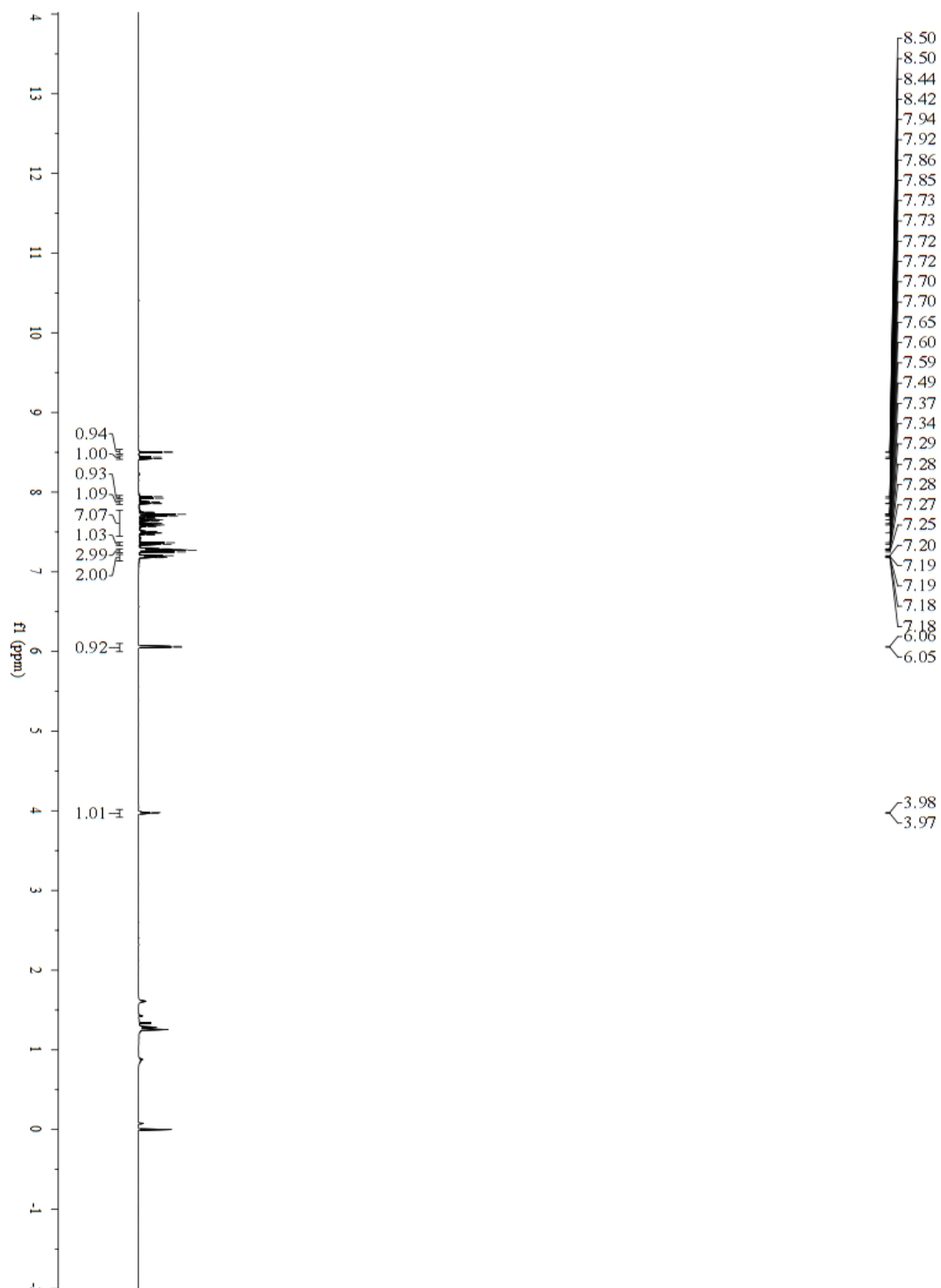


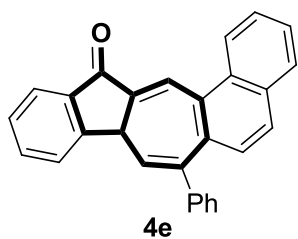
¹³C NMR (100 MHz, CDCl₃)



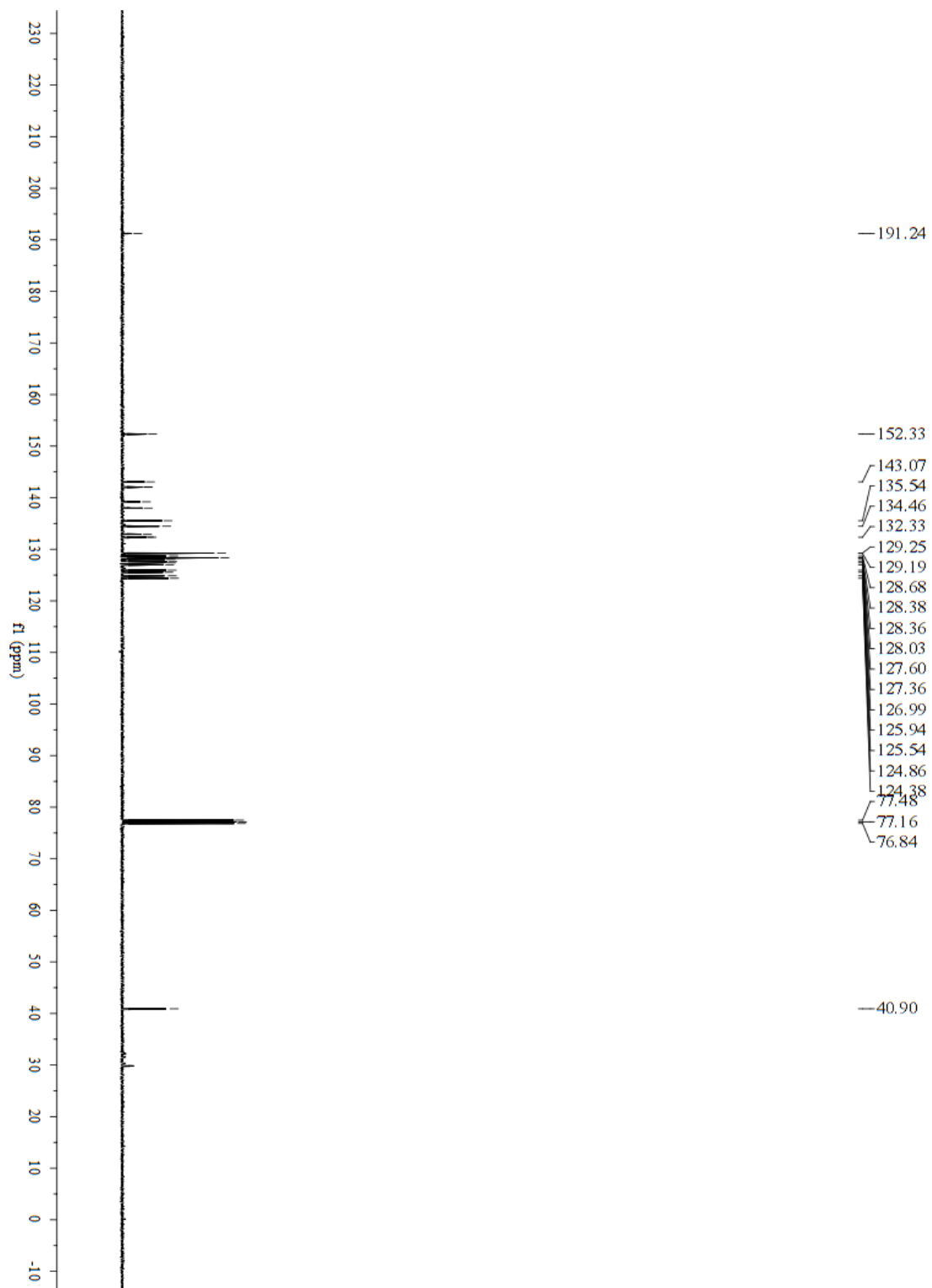


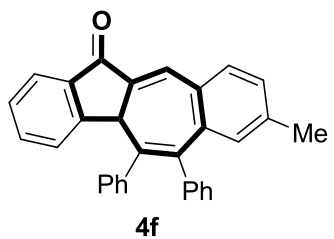
¹H NMR (400 MHz, CDCl₃)



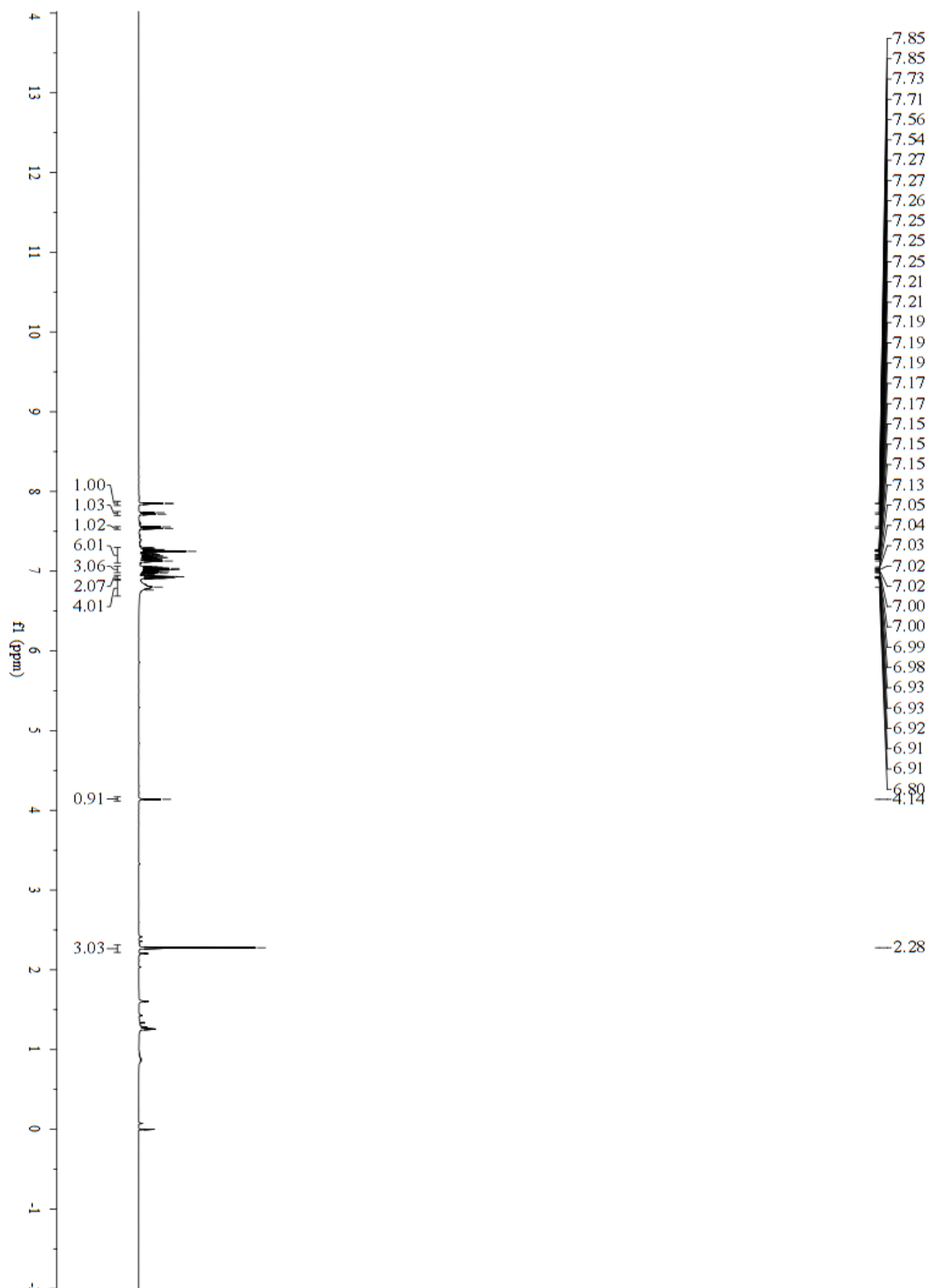


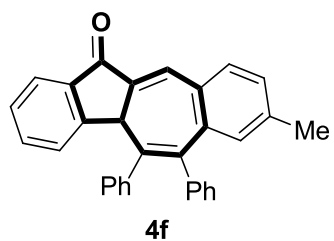
^{13}C NMR (100 MHz, CDCl_3)



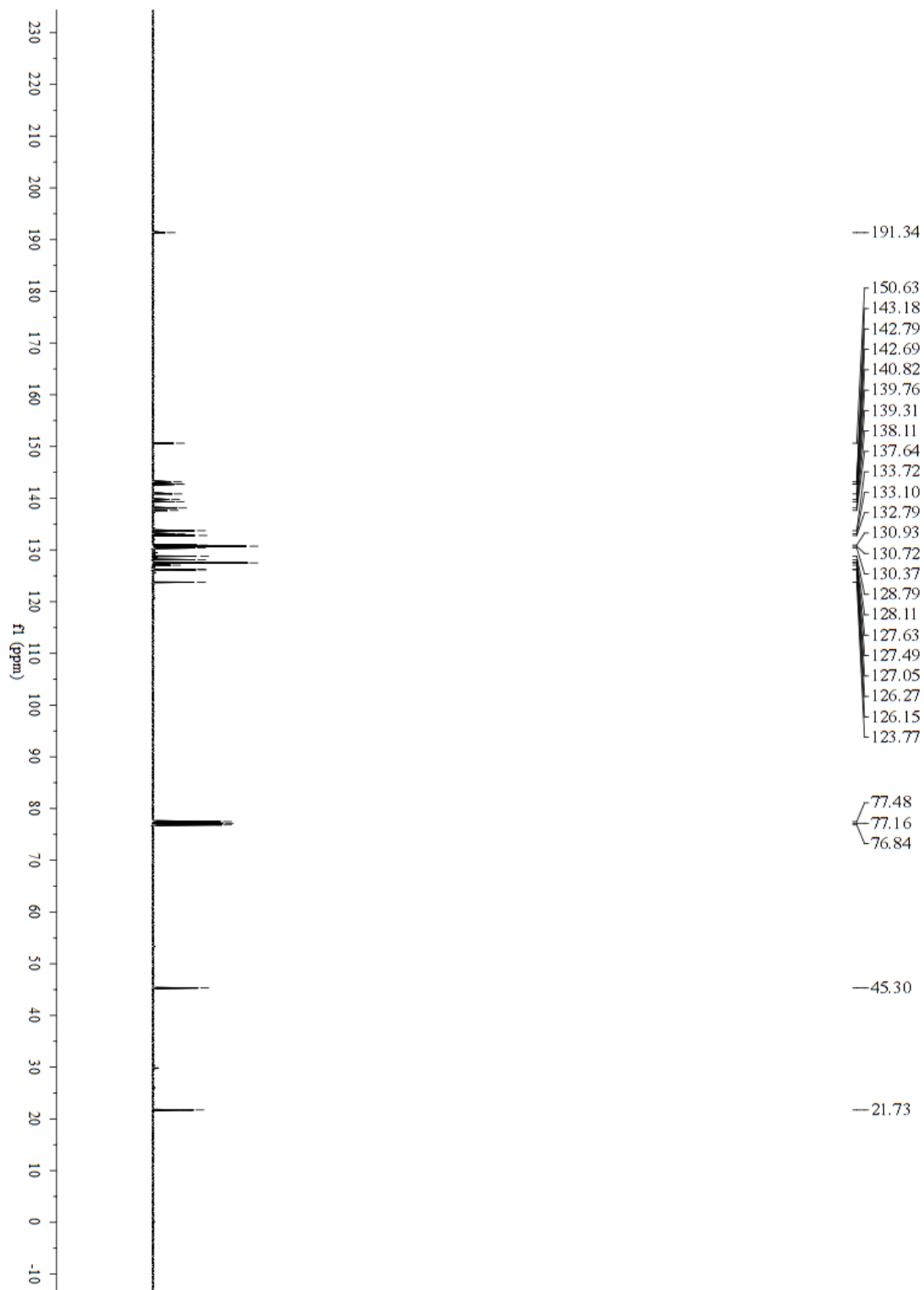


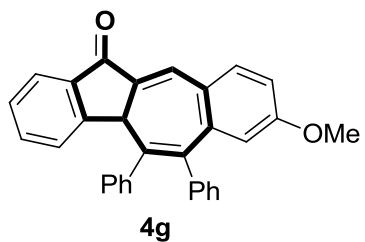
¹H NMR (400 MHz, CDCl₃)



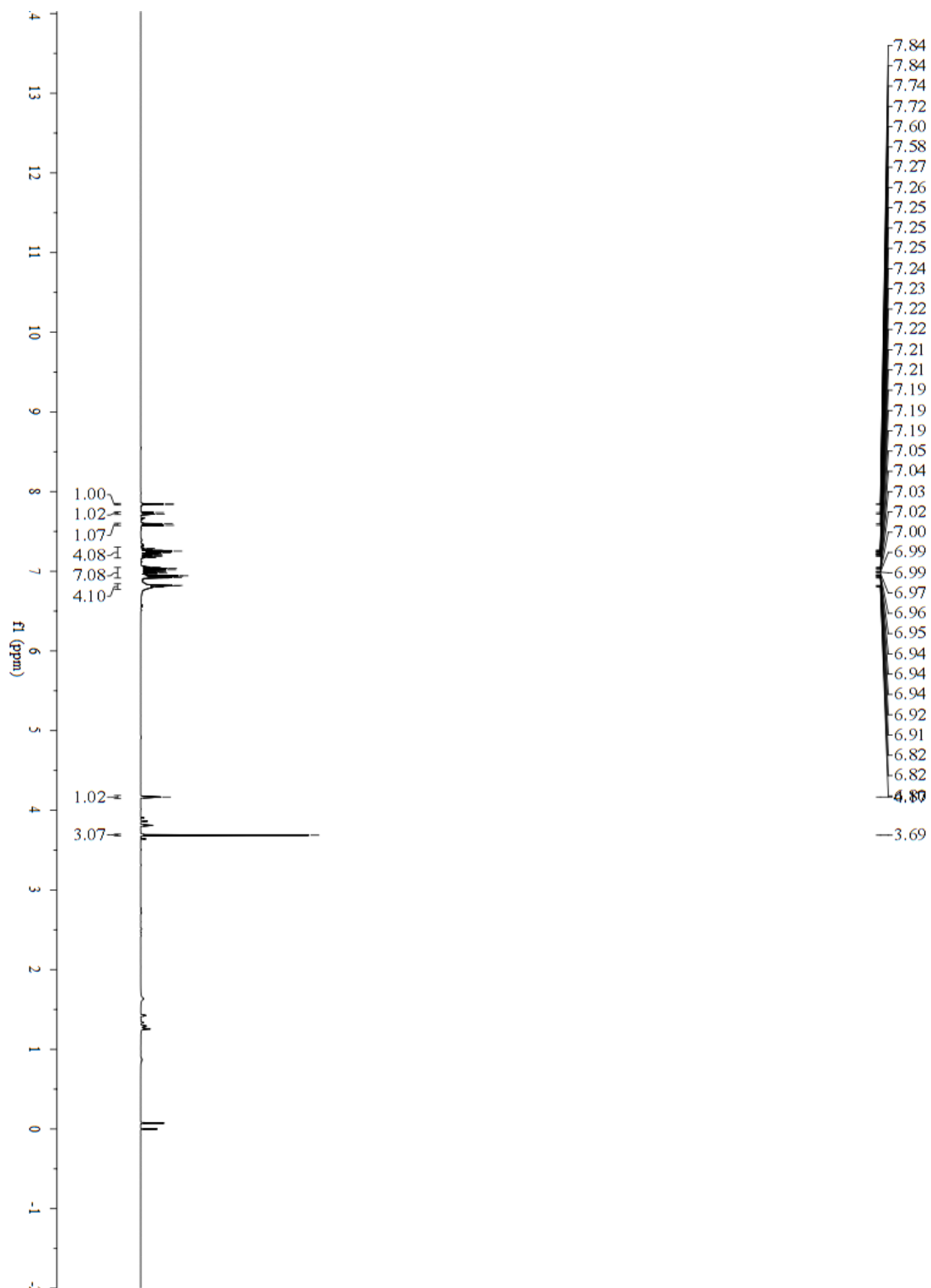


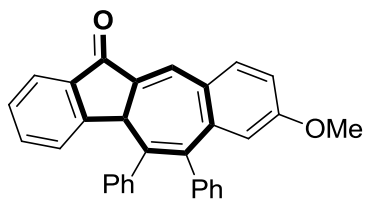
¹³C NMR (100 MHz, CDCl₃)





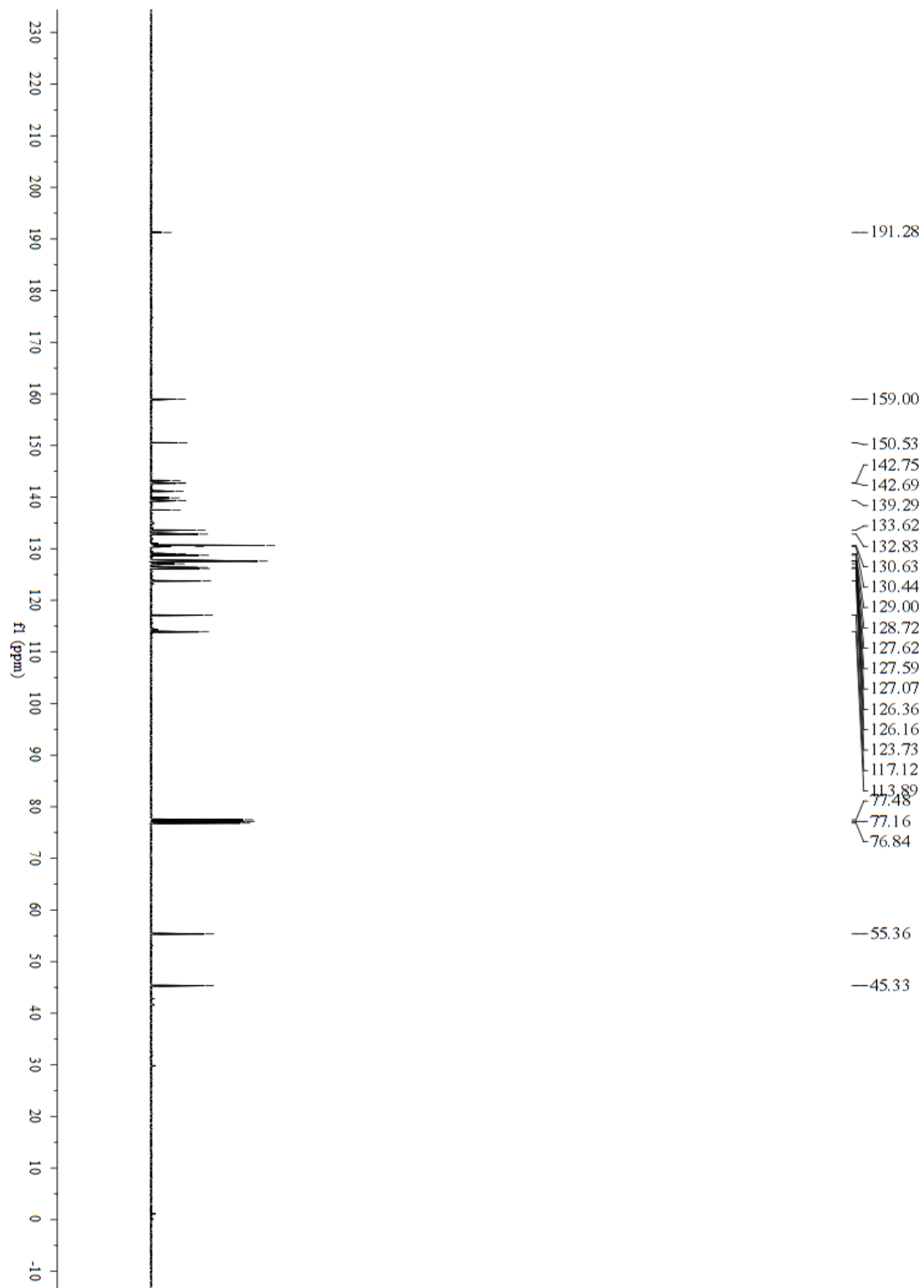
$^1\text{H NMR}$ (400 MHz, CDCl_3)

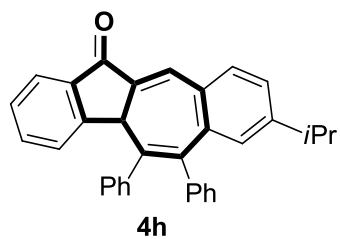




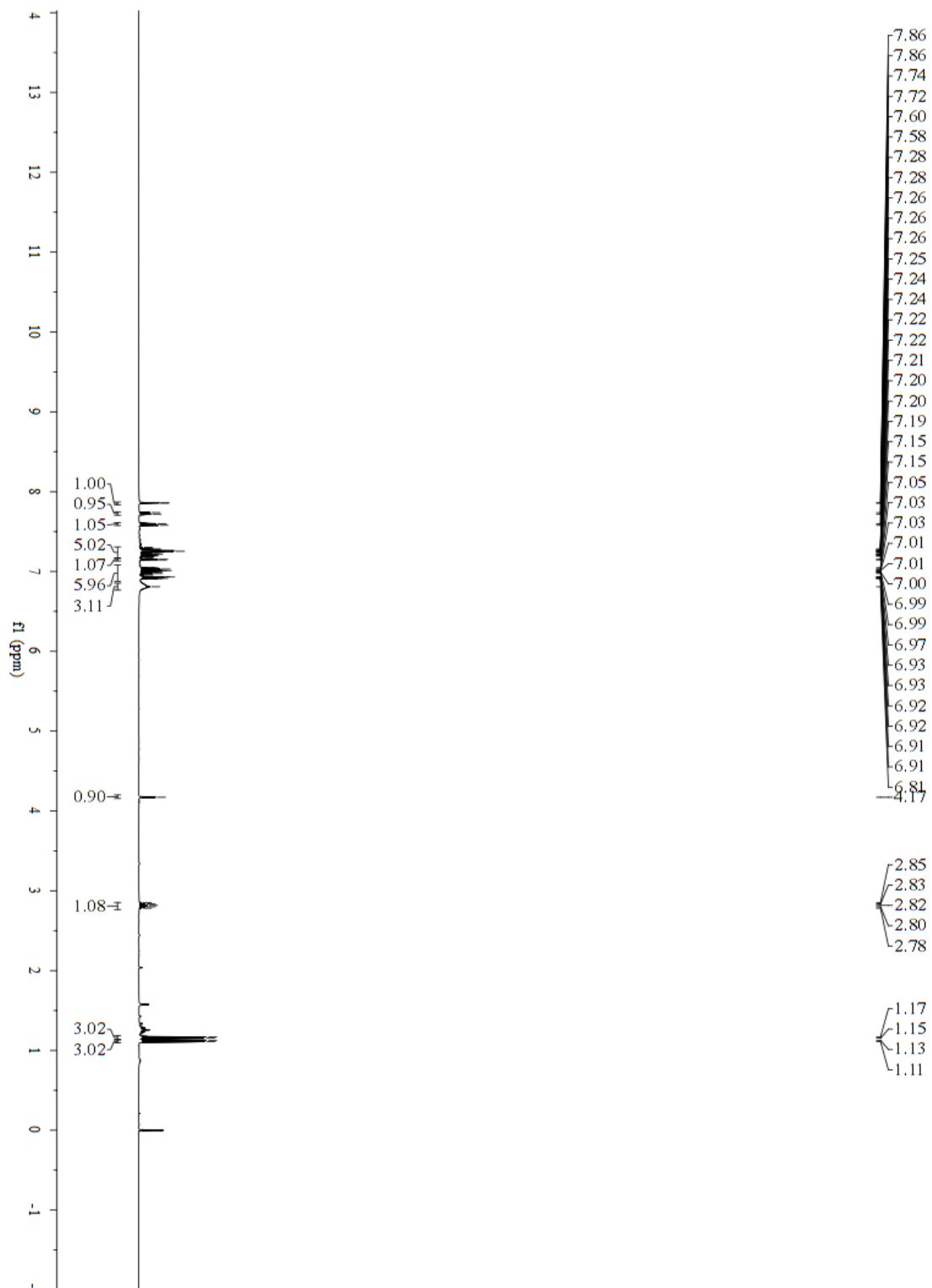
4g

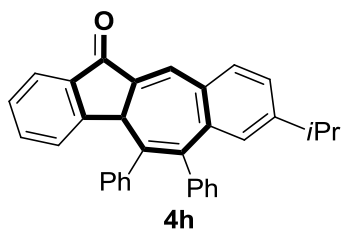
^{13}C NMR (100 MHz, CDCl_3)



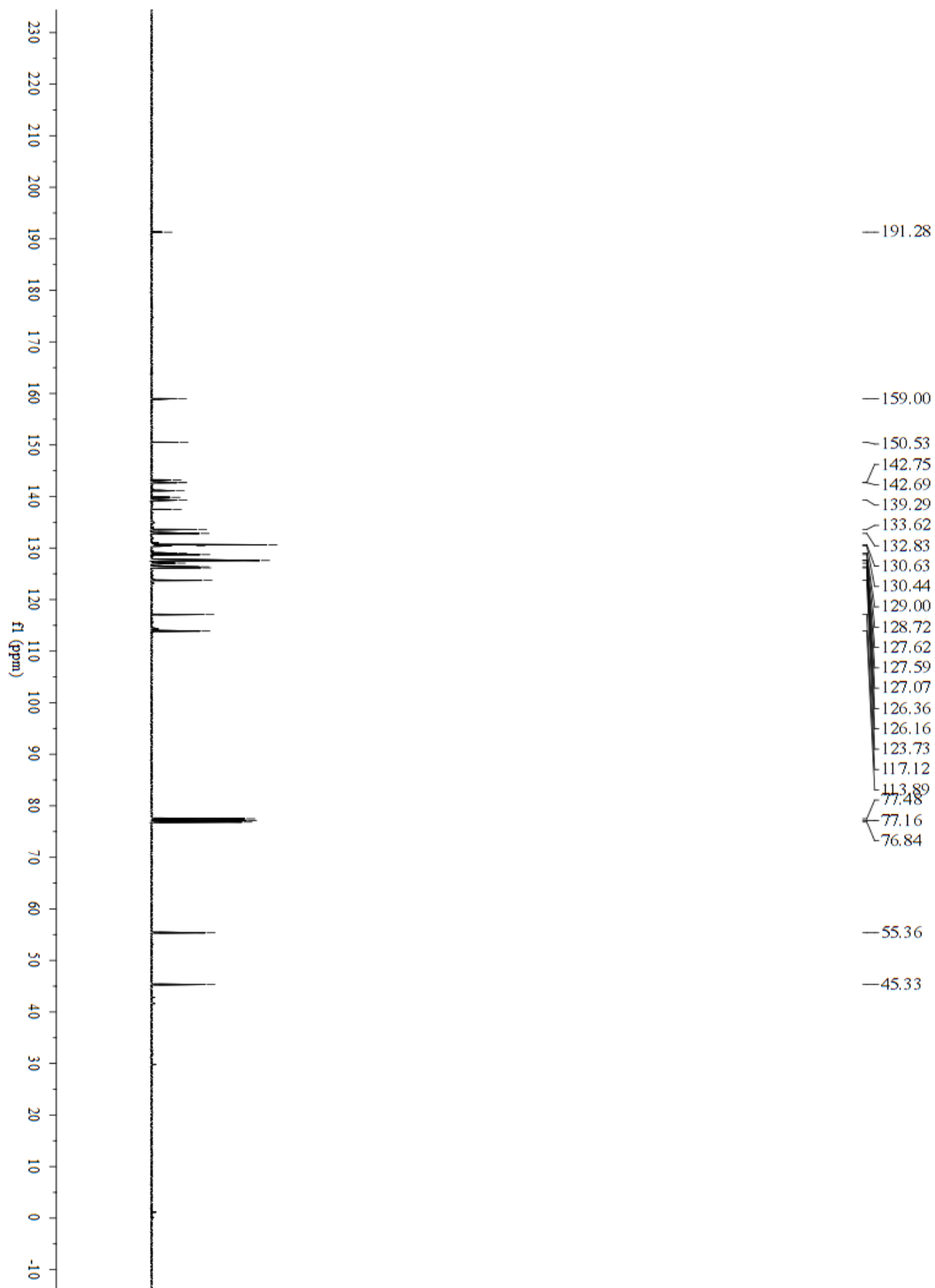


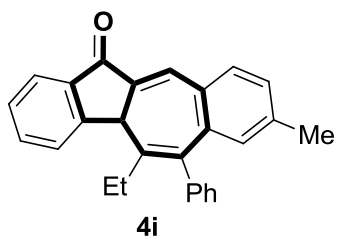
¹H NMR (400 MHz, CDCl₃)



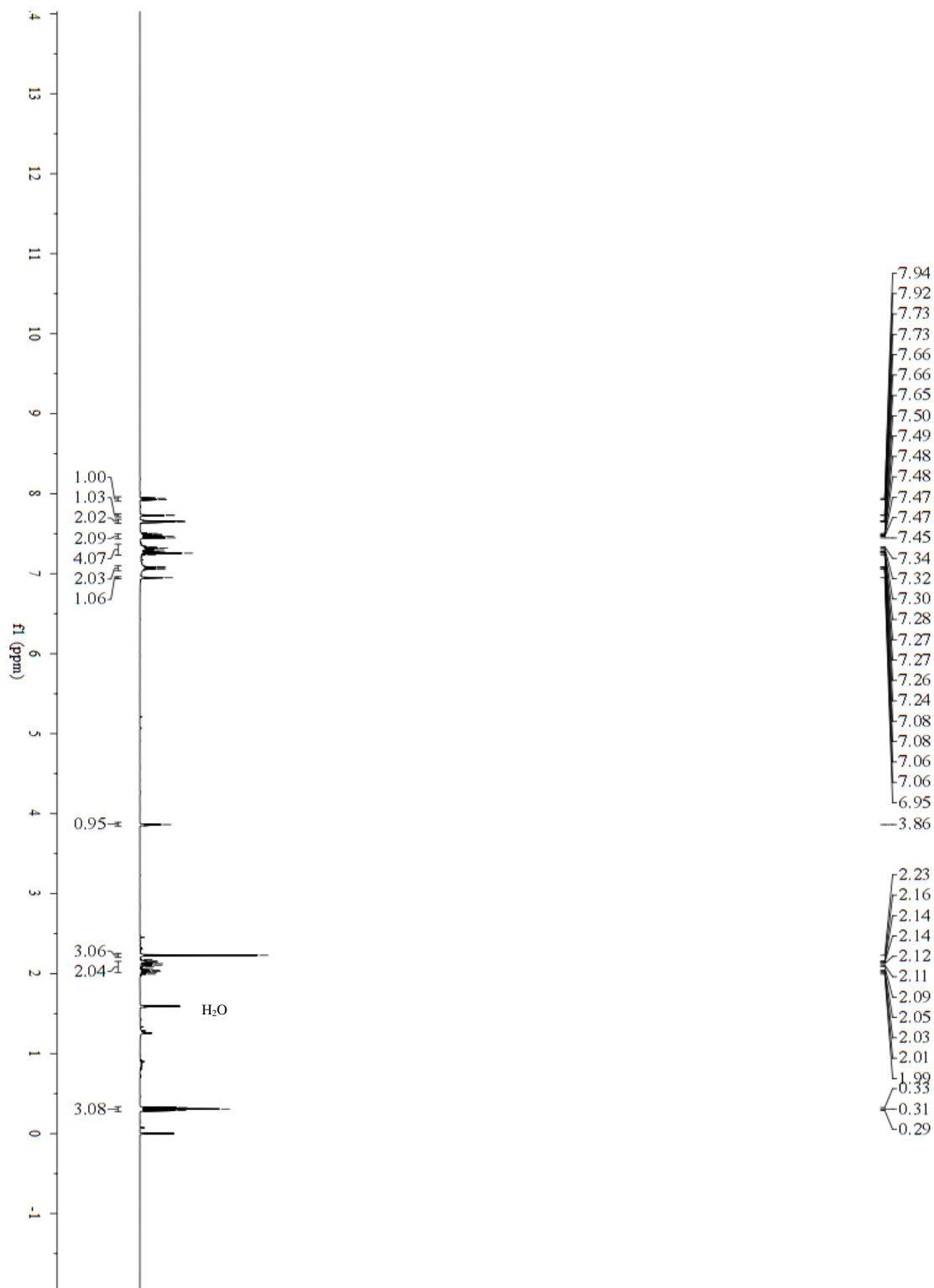


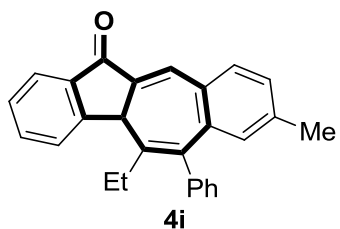
¹³C NMR (100 MHz, CDCl₃)



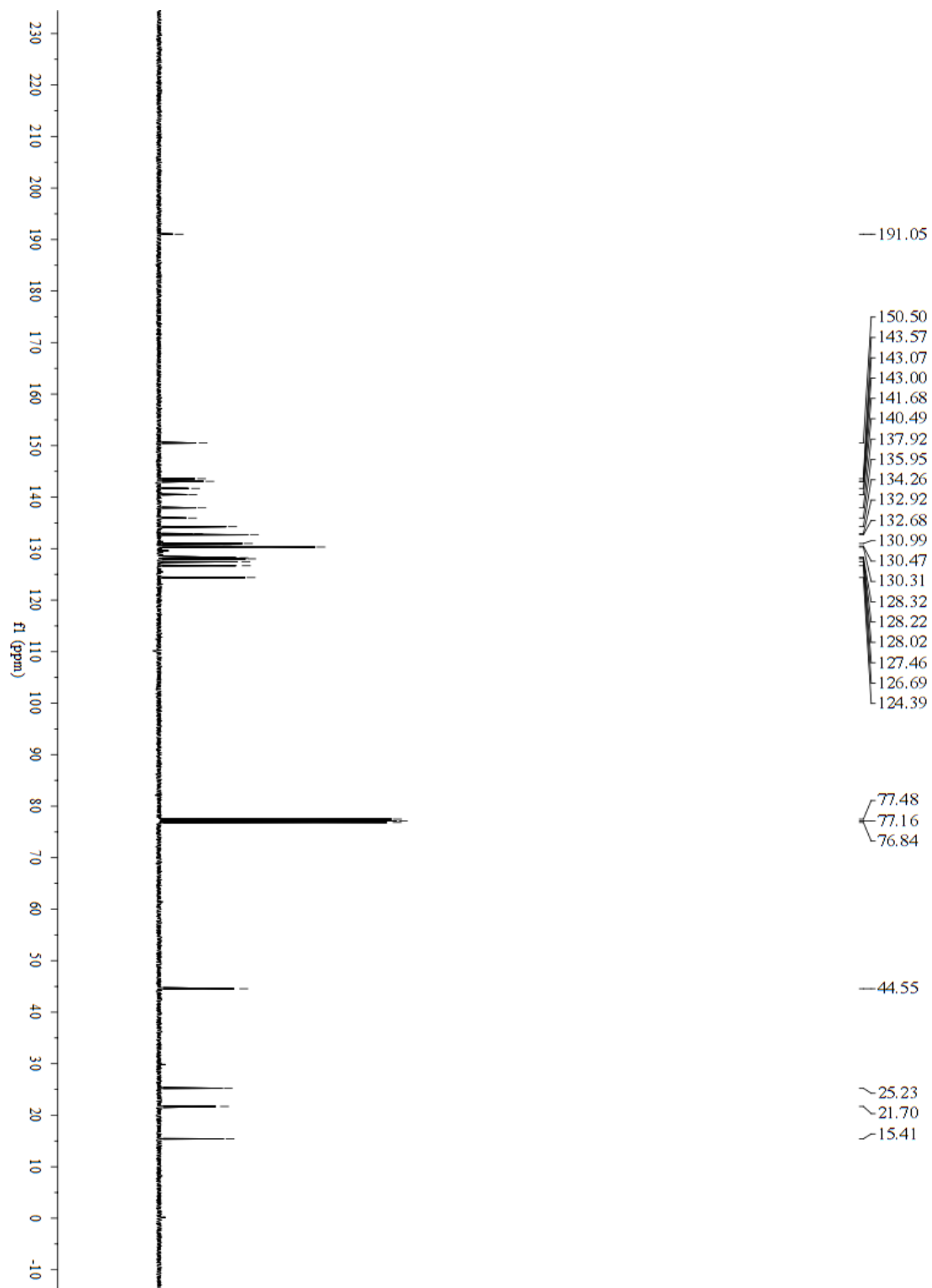


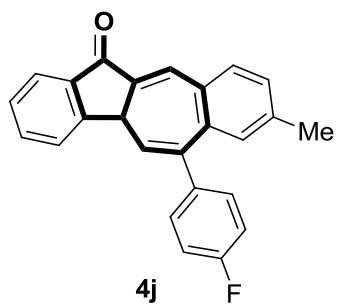
¹H NMR (400 MHz, CDCl₃)



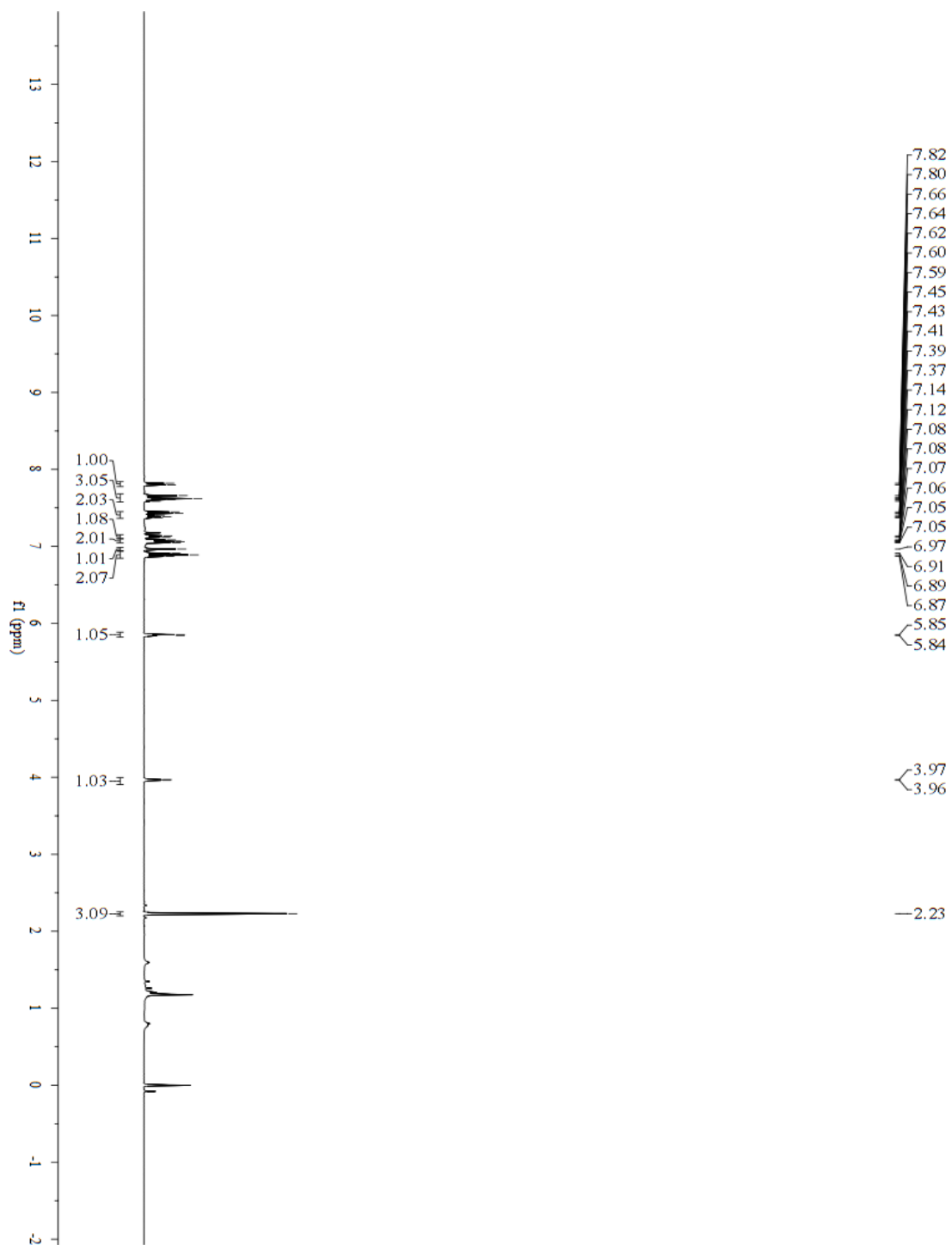


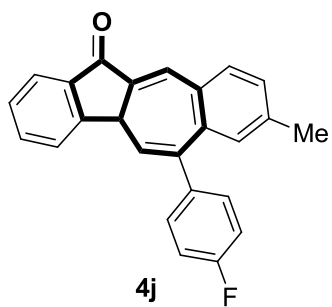
¹³C NMR (100 MHz, CDCl₃)



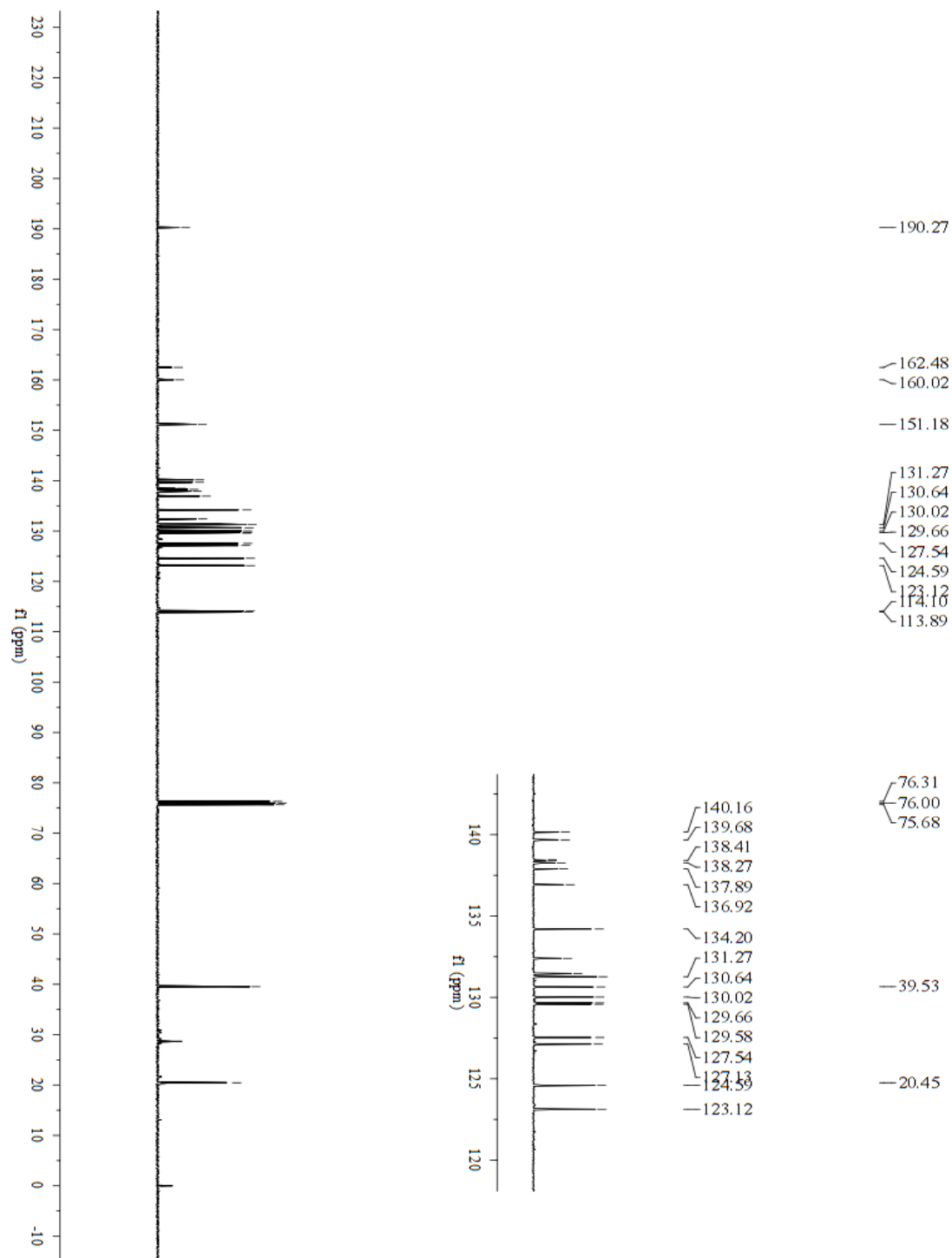


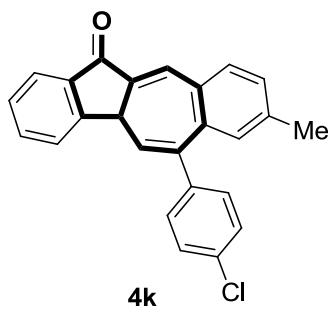
$^1\text{H NMR}$ (400 MHz, CDCl_3)



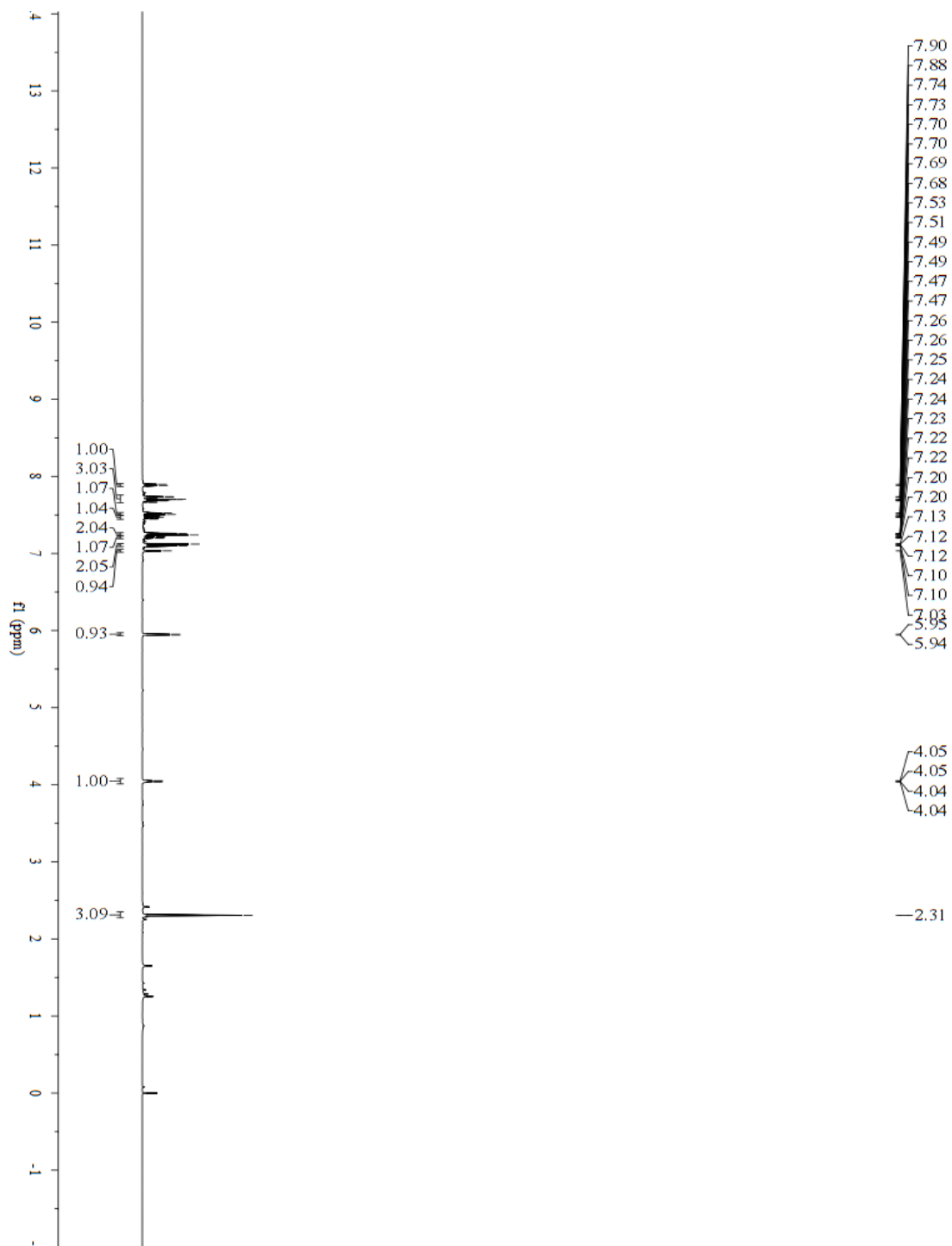


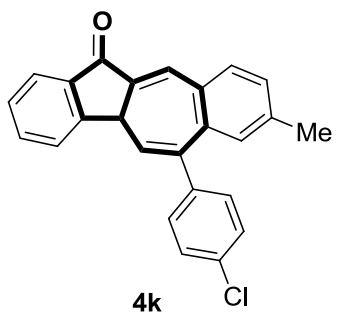
^{13}C NMR (100 MHz, CDCl_3)



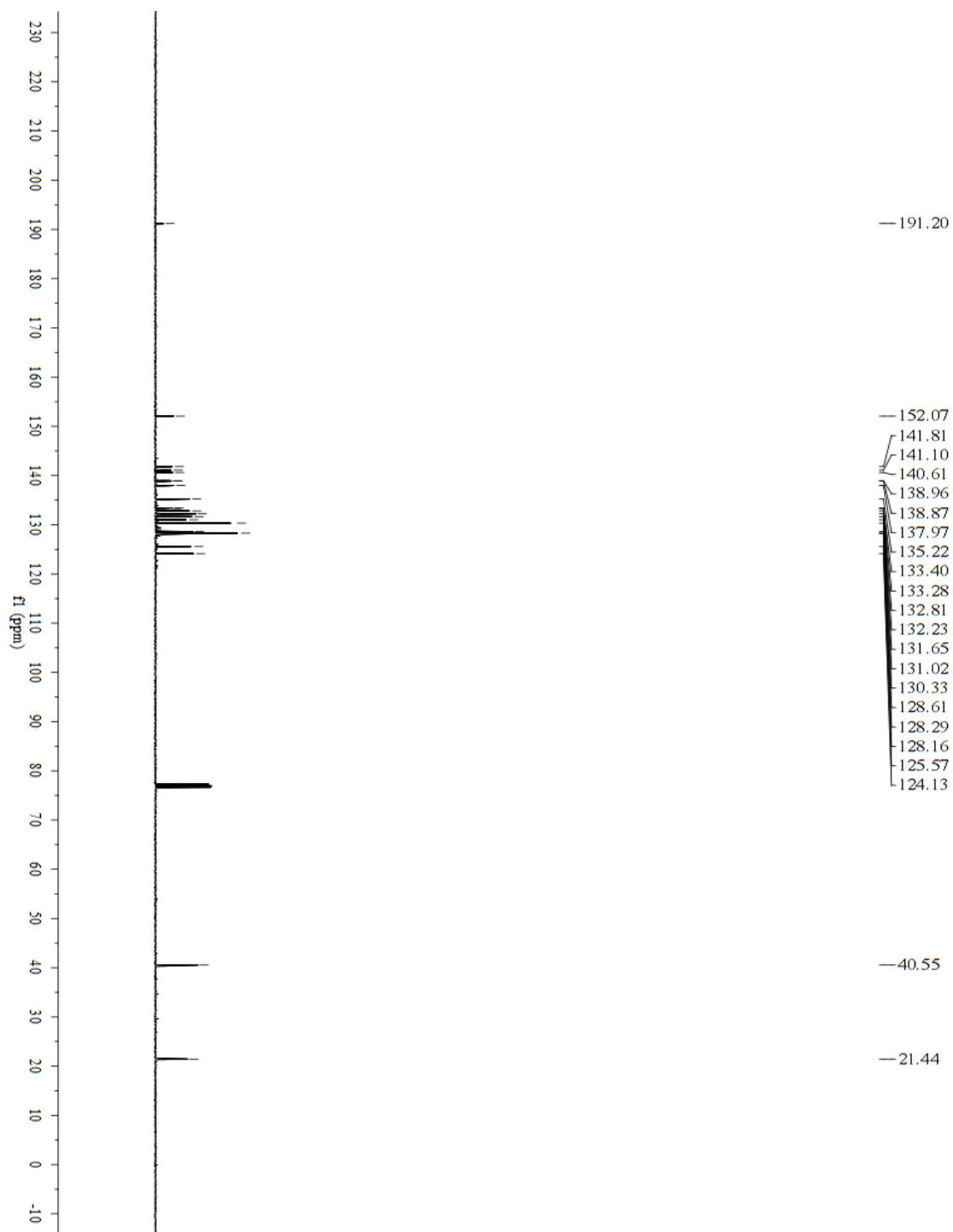


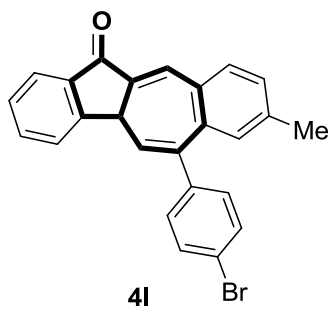
¹H NMR (400 MHz, CDCl₃)



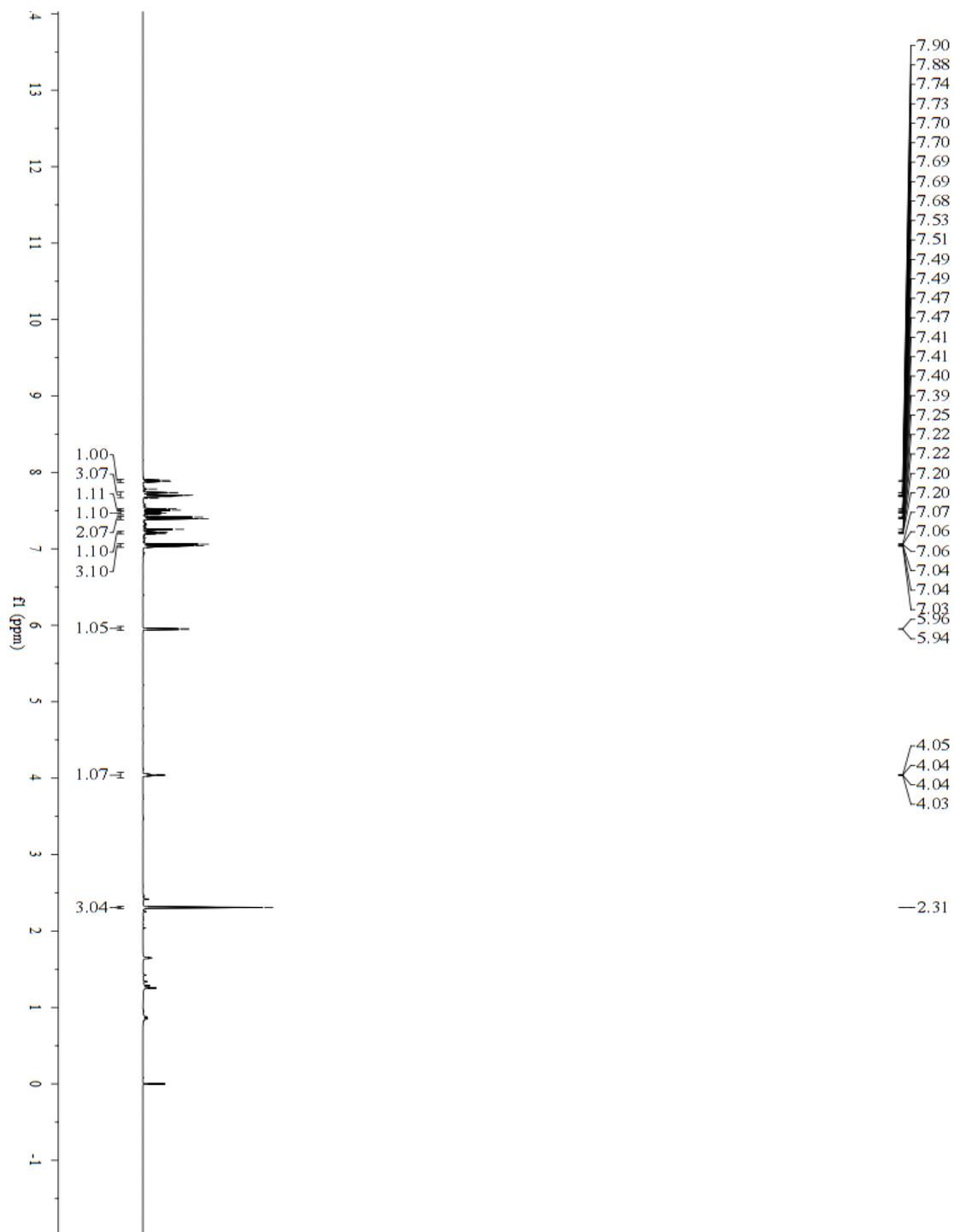


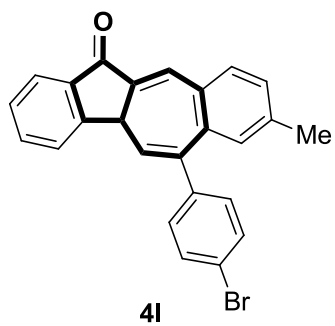
¹³C NMR (100 MHz, CDCl₃)



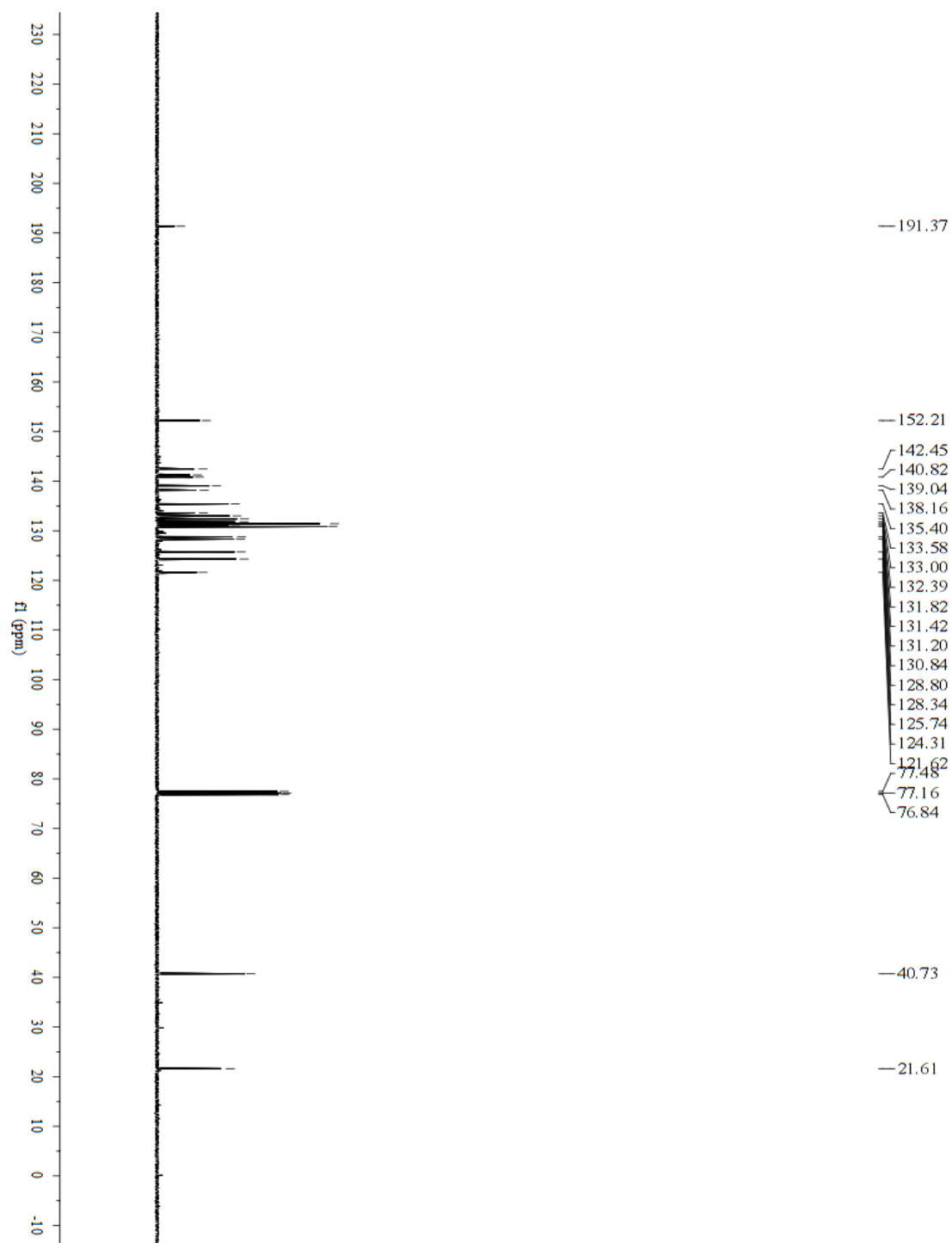


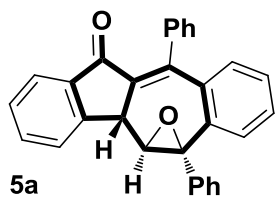
¹H NMR (400 MHz, CDCl₃)



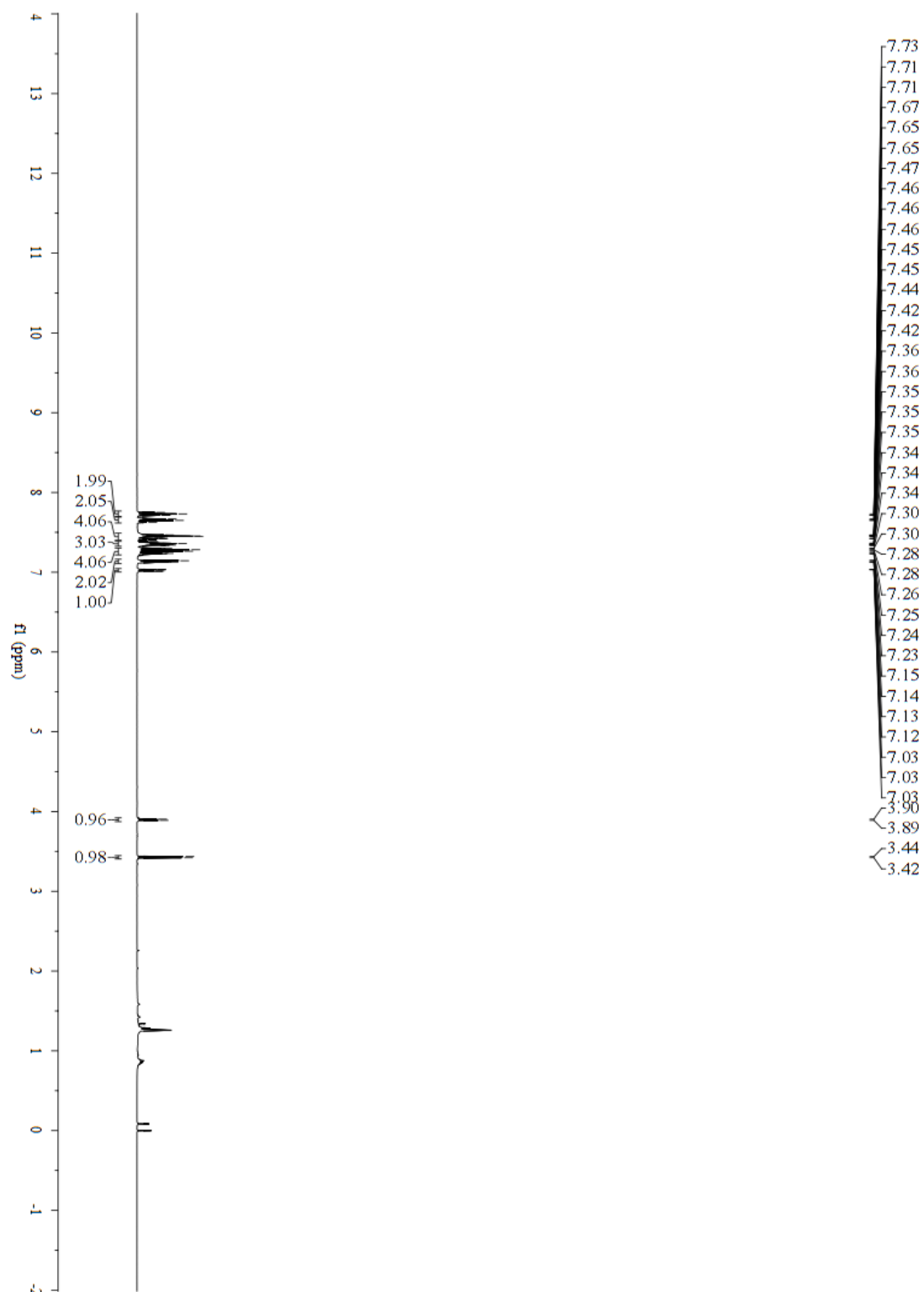


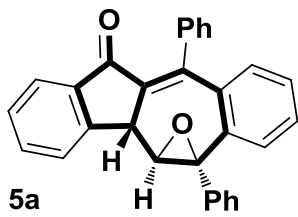
¹³C NMR (100 MHz, CDCl₃)



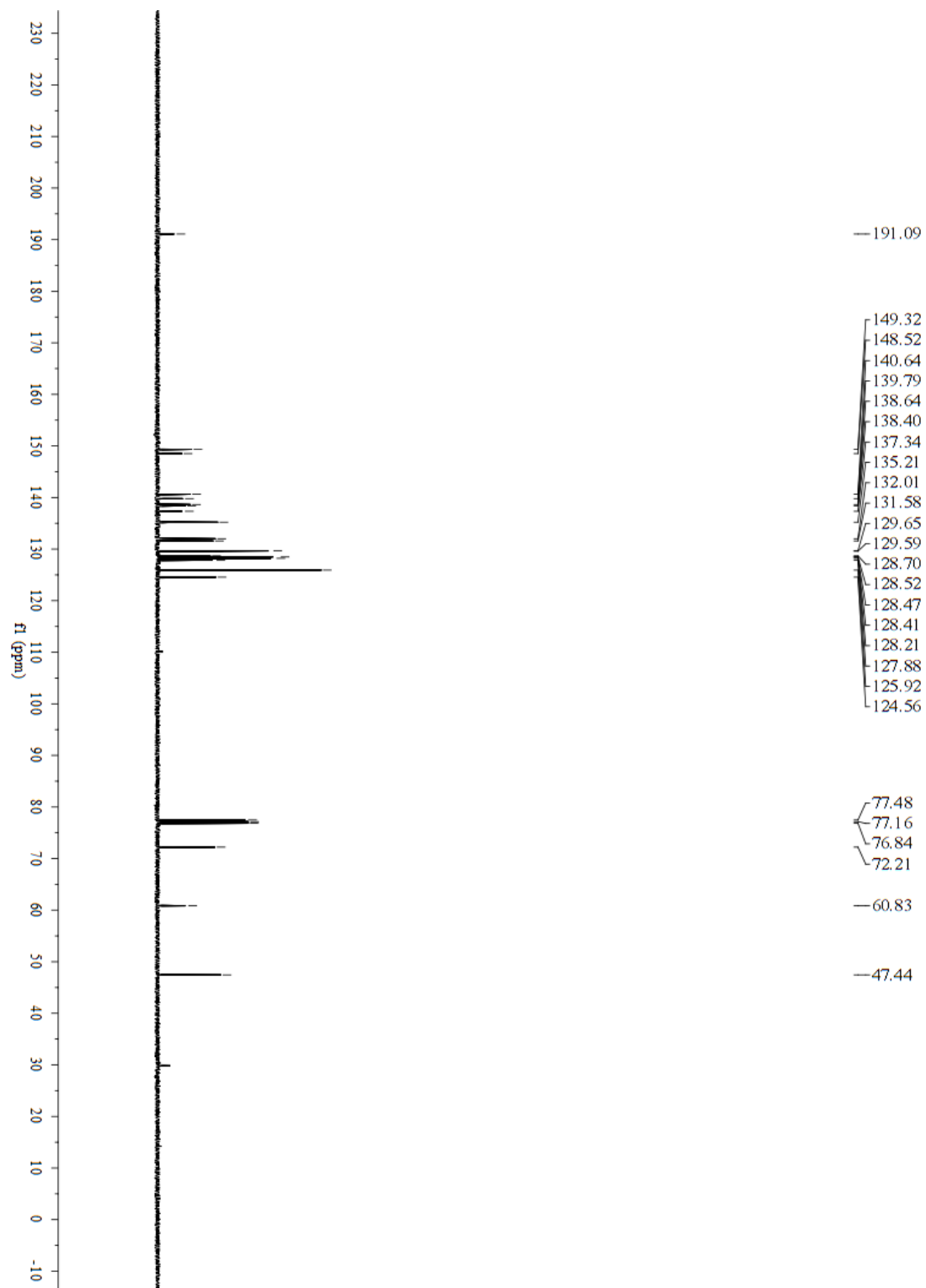


¹H NMR (400 MHz, CDCl₃)

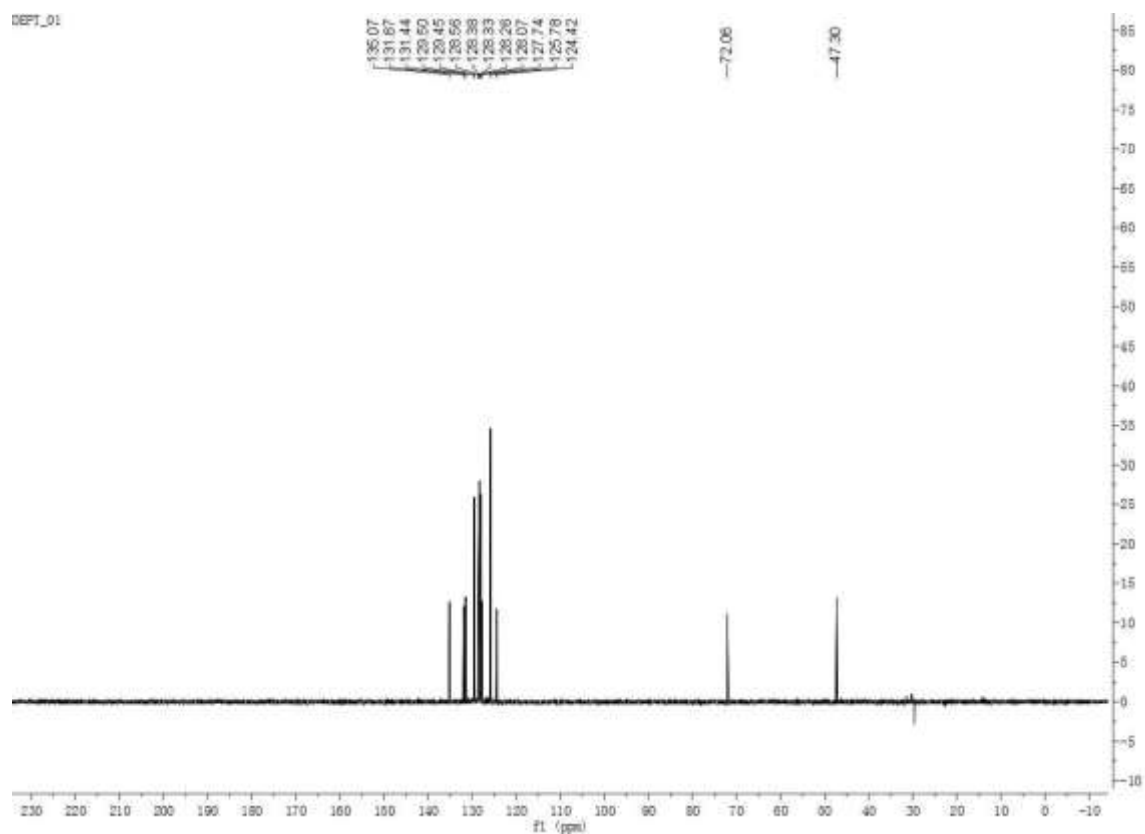




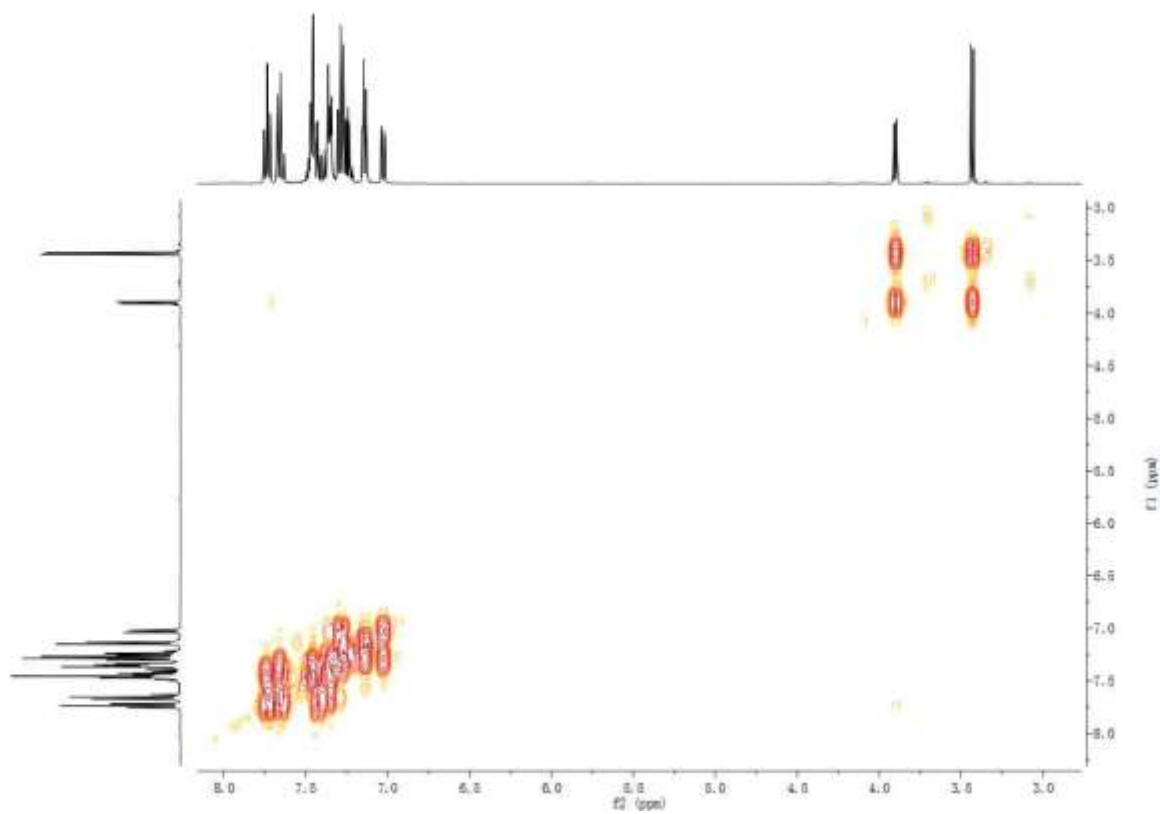
^{13}C NMR (100 MHz, CDCl_3)



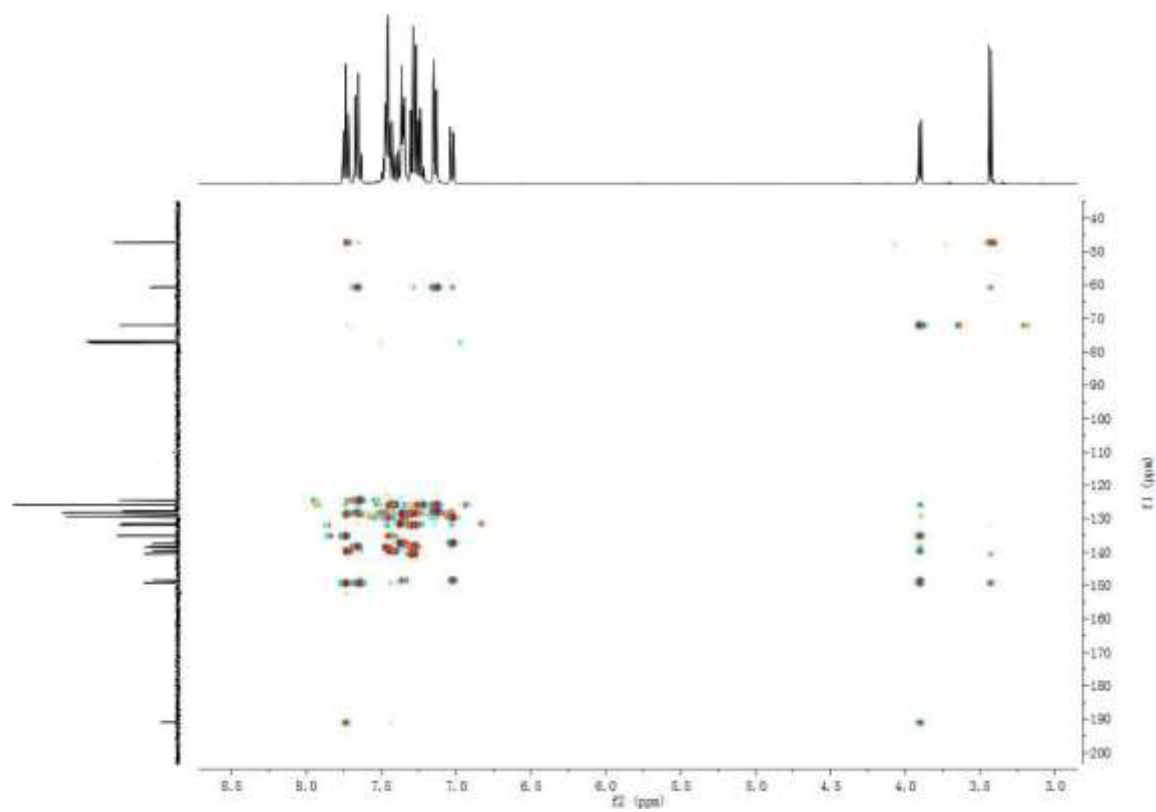
5a-DEPT



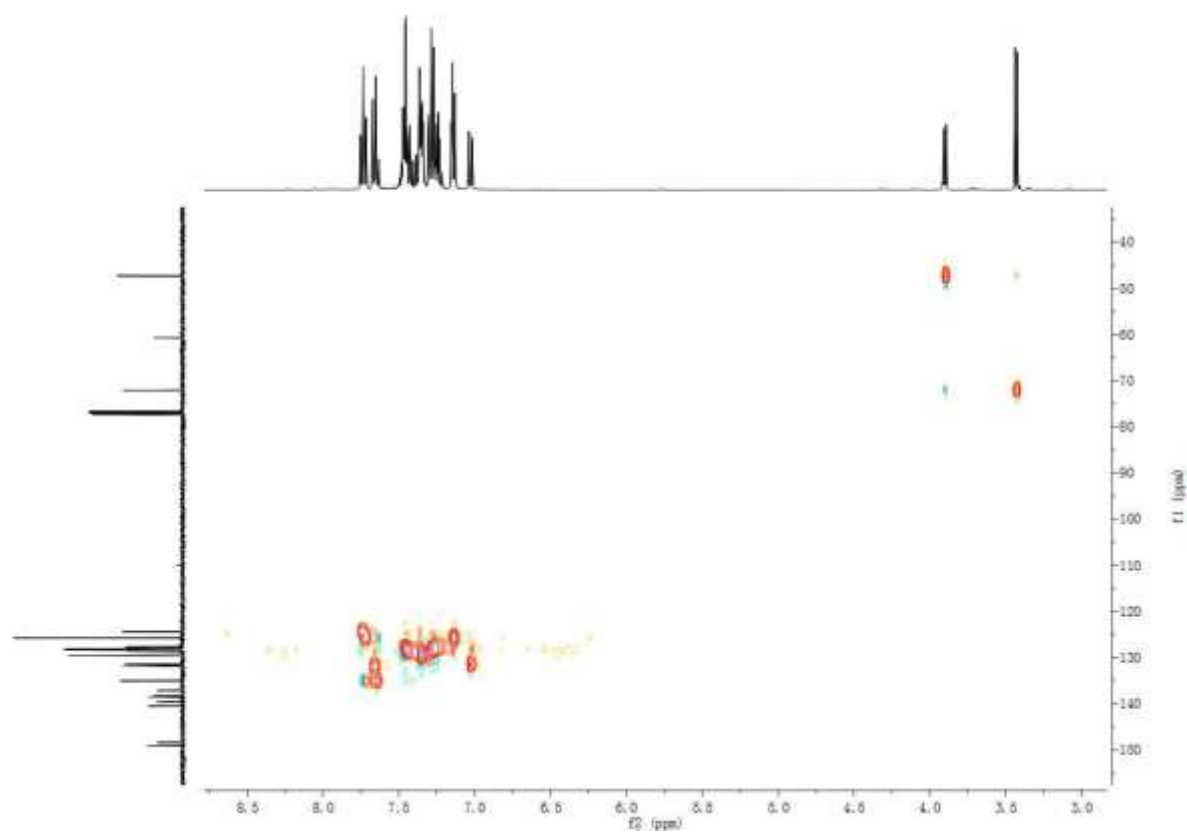
5a- ^1H - ^1H COSY

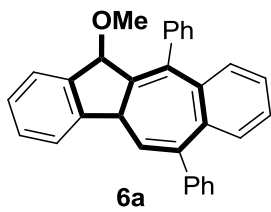


5a- HMBC

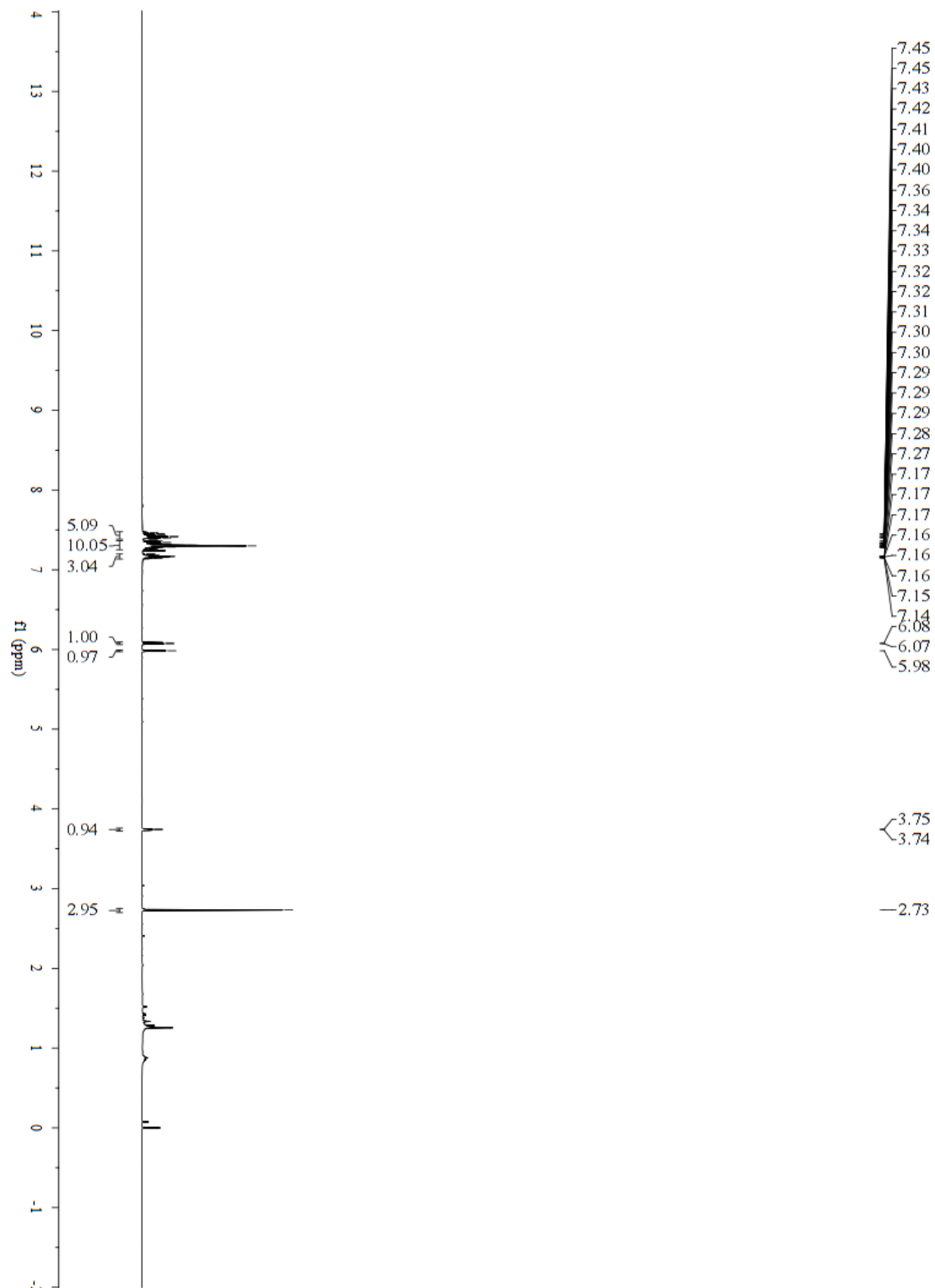


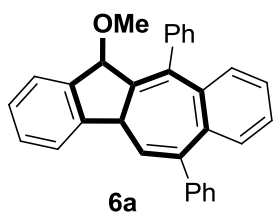
5a- HSQC



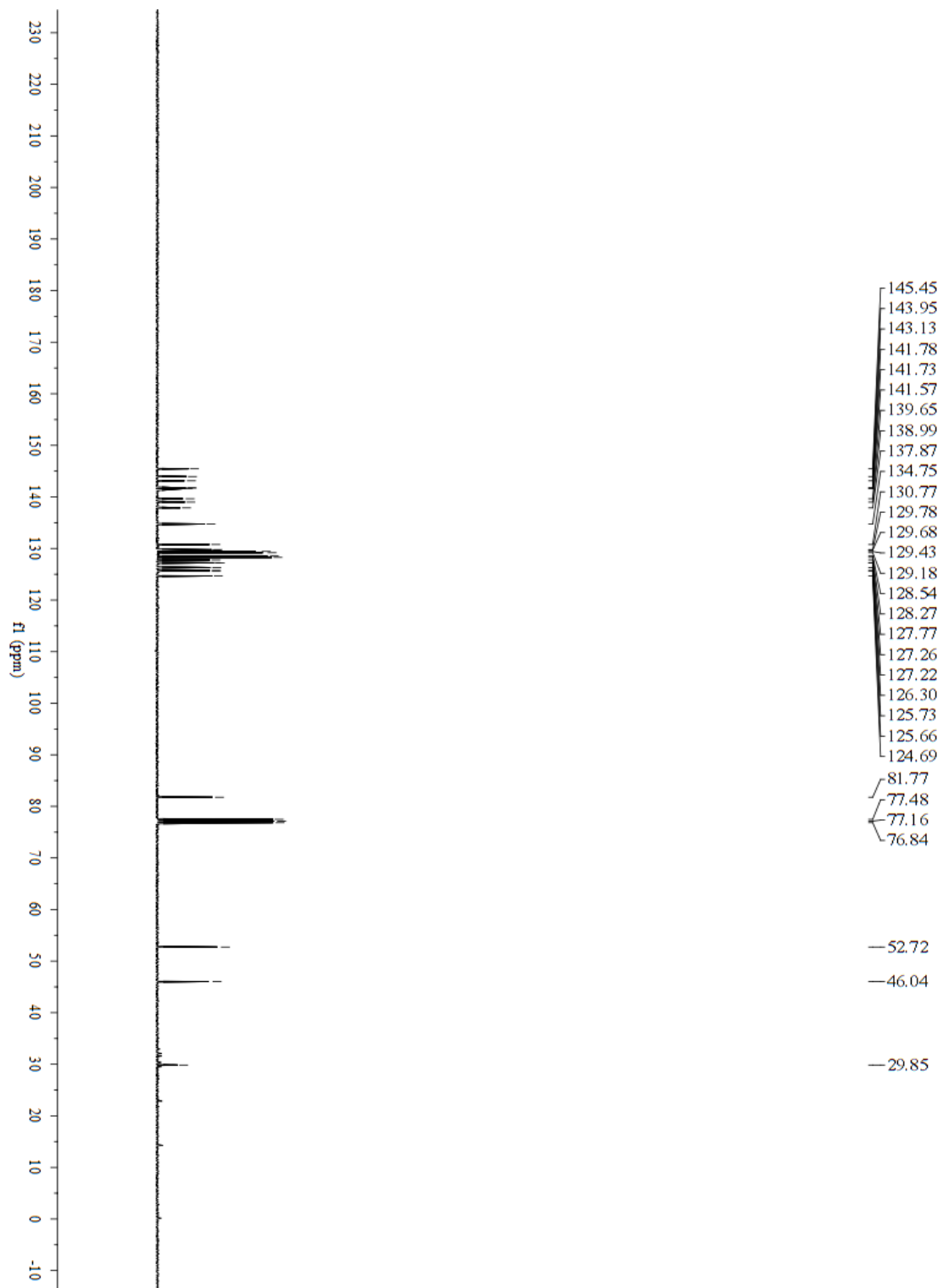


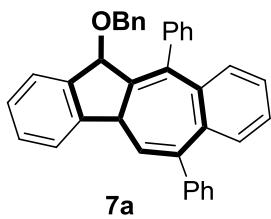
6a
¹H NMR (400 MHz, CDCl₃)



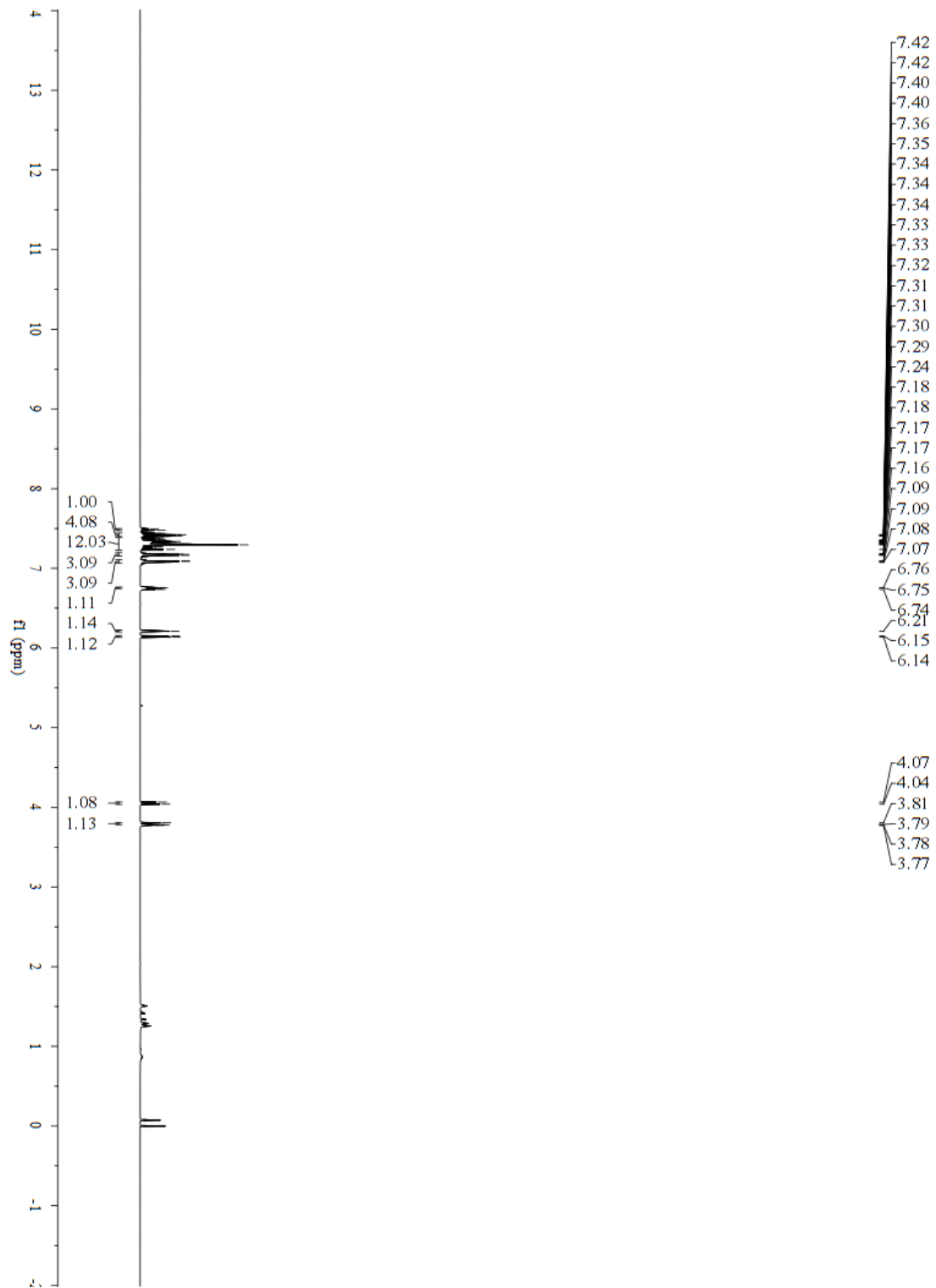


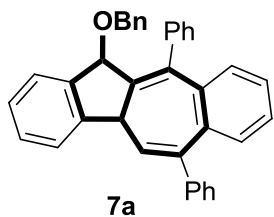
^{13}C NMR (100 MHz, CDCl_3)



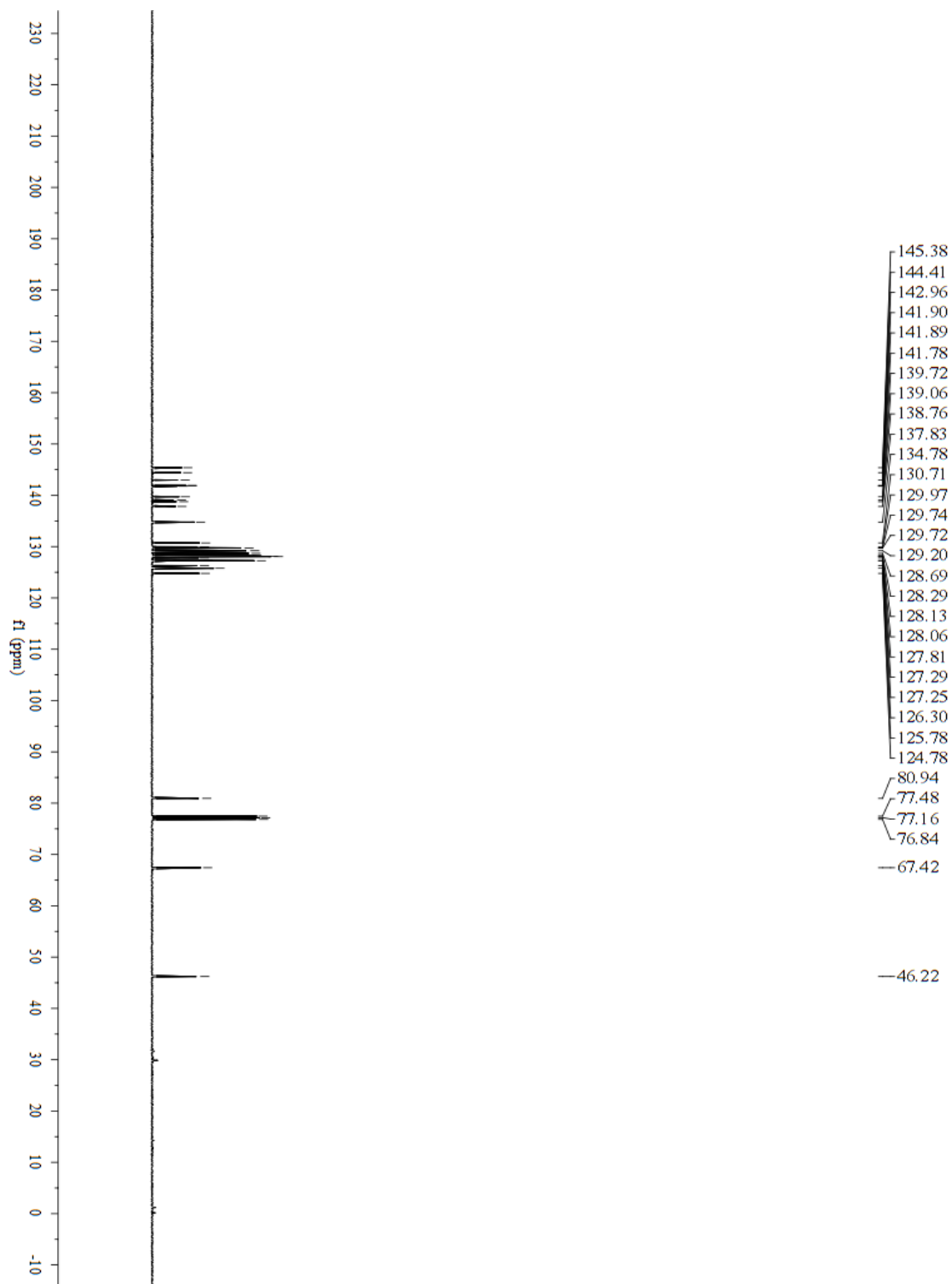


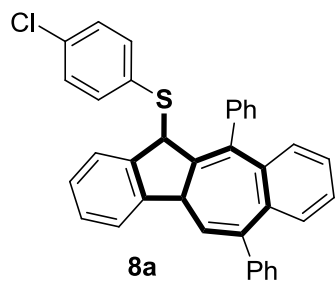
7a
¹H NMR (400 MHz, CDCl₃)



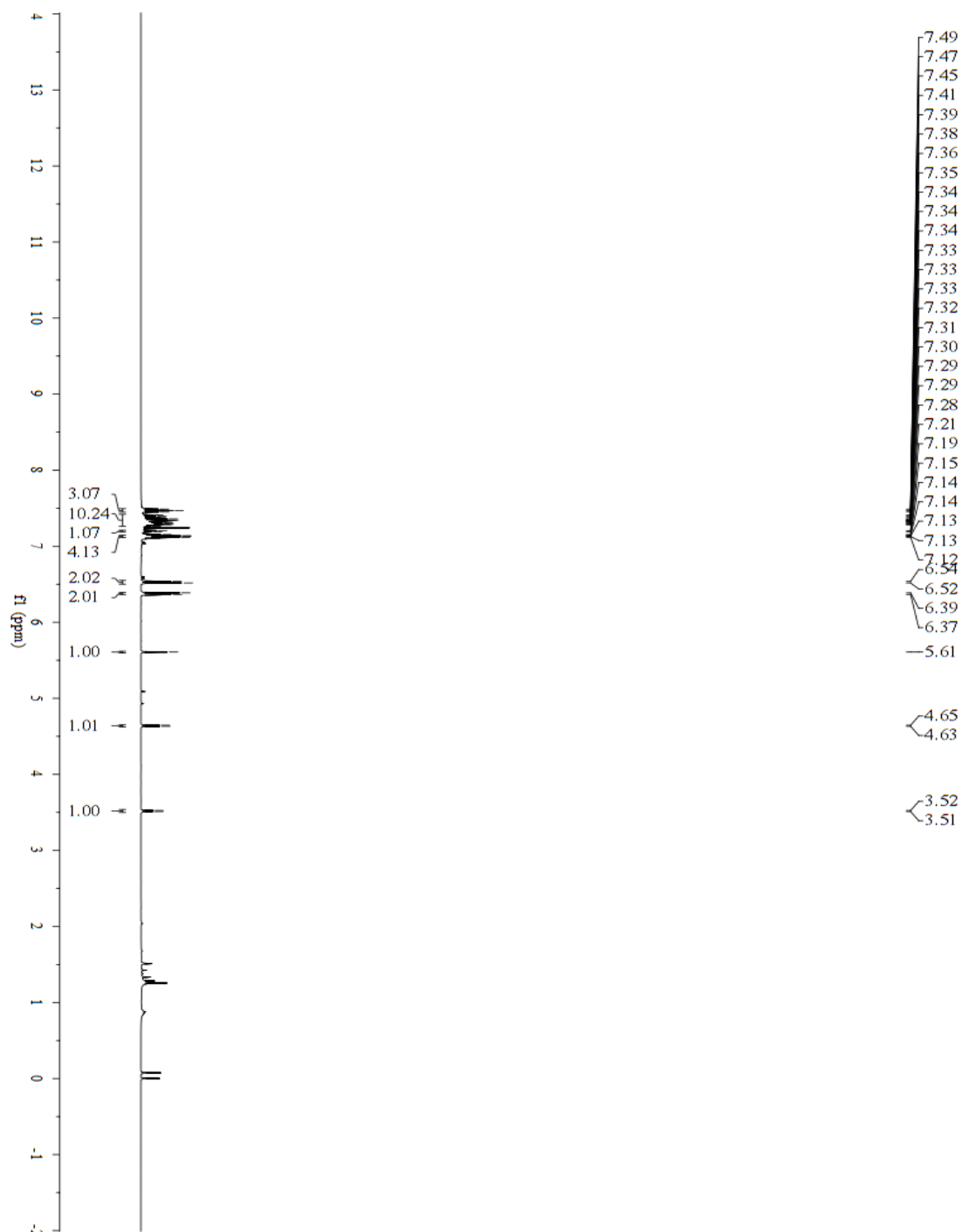


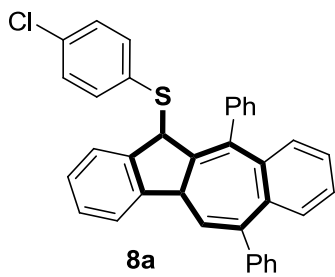
¹³C NMR (100 MHz, CDCl₃)



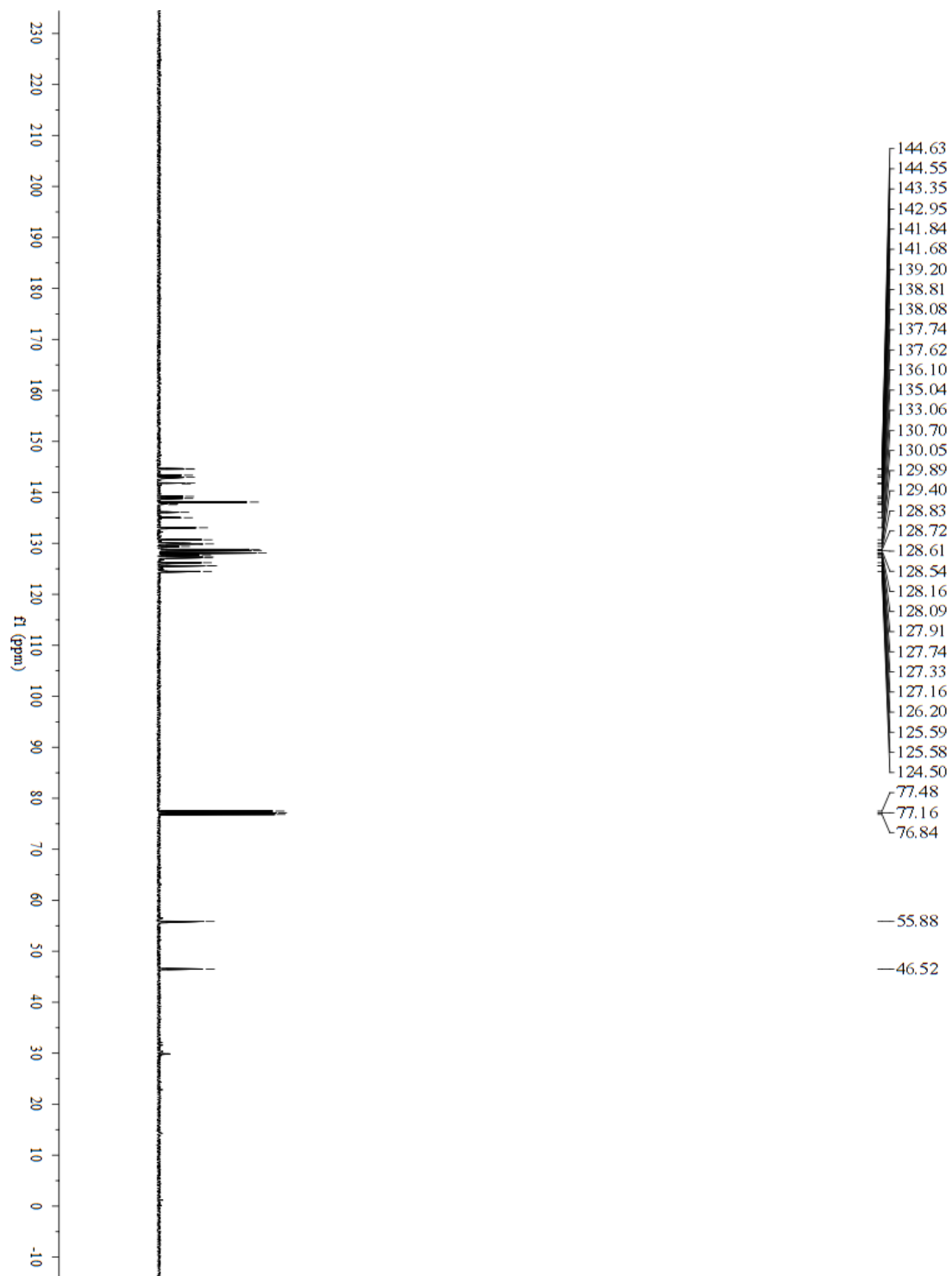


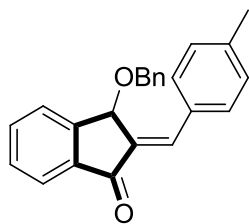
^{13}C NMR (100 MHz, CDCl_3)





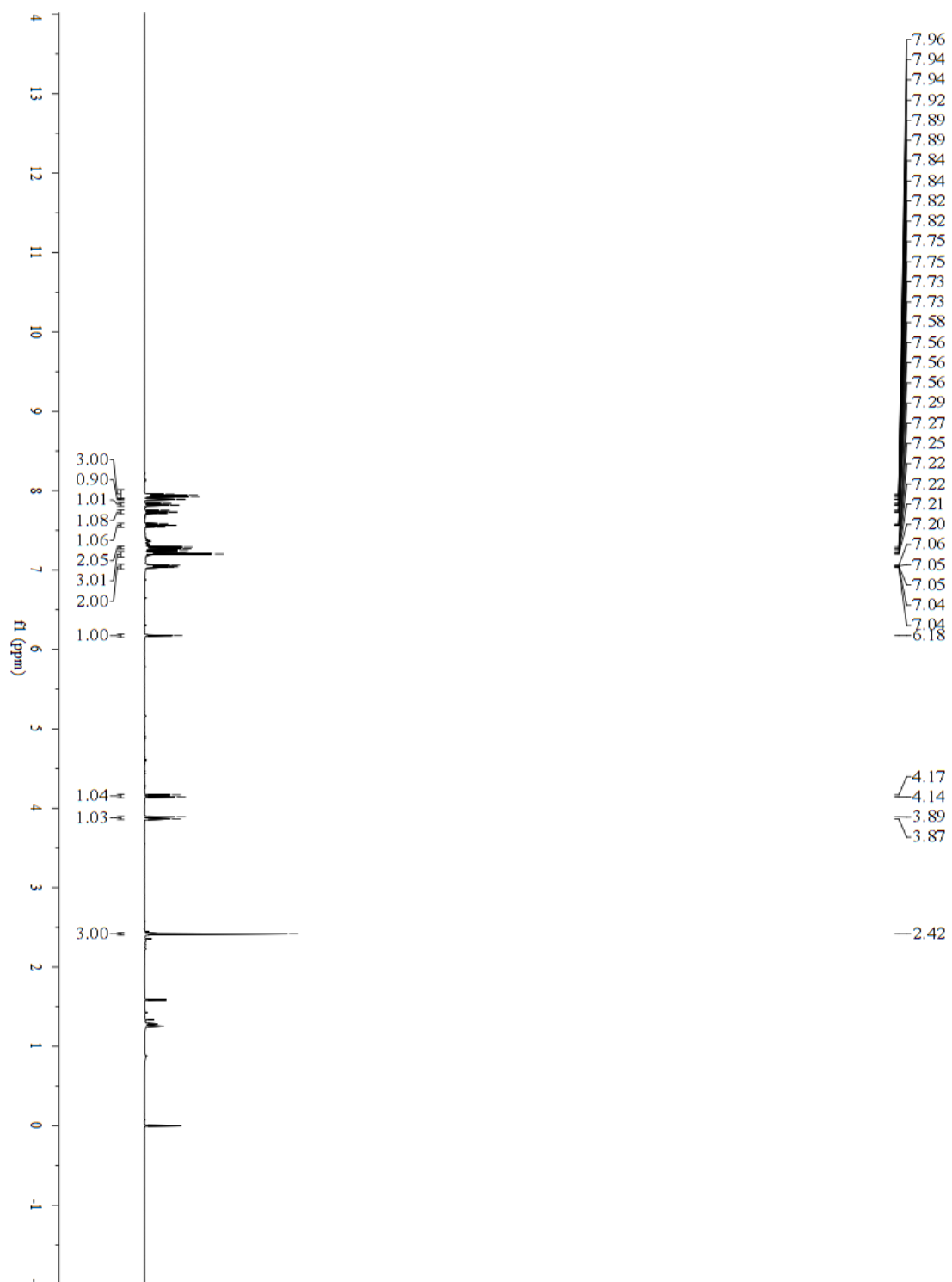
$^1\text{H NMR}$ (400 MHz, CDCl_3)

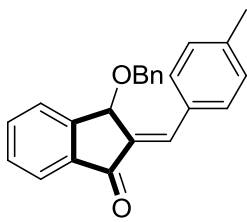




9a

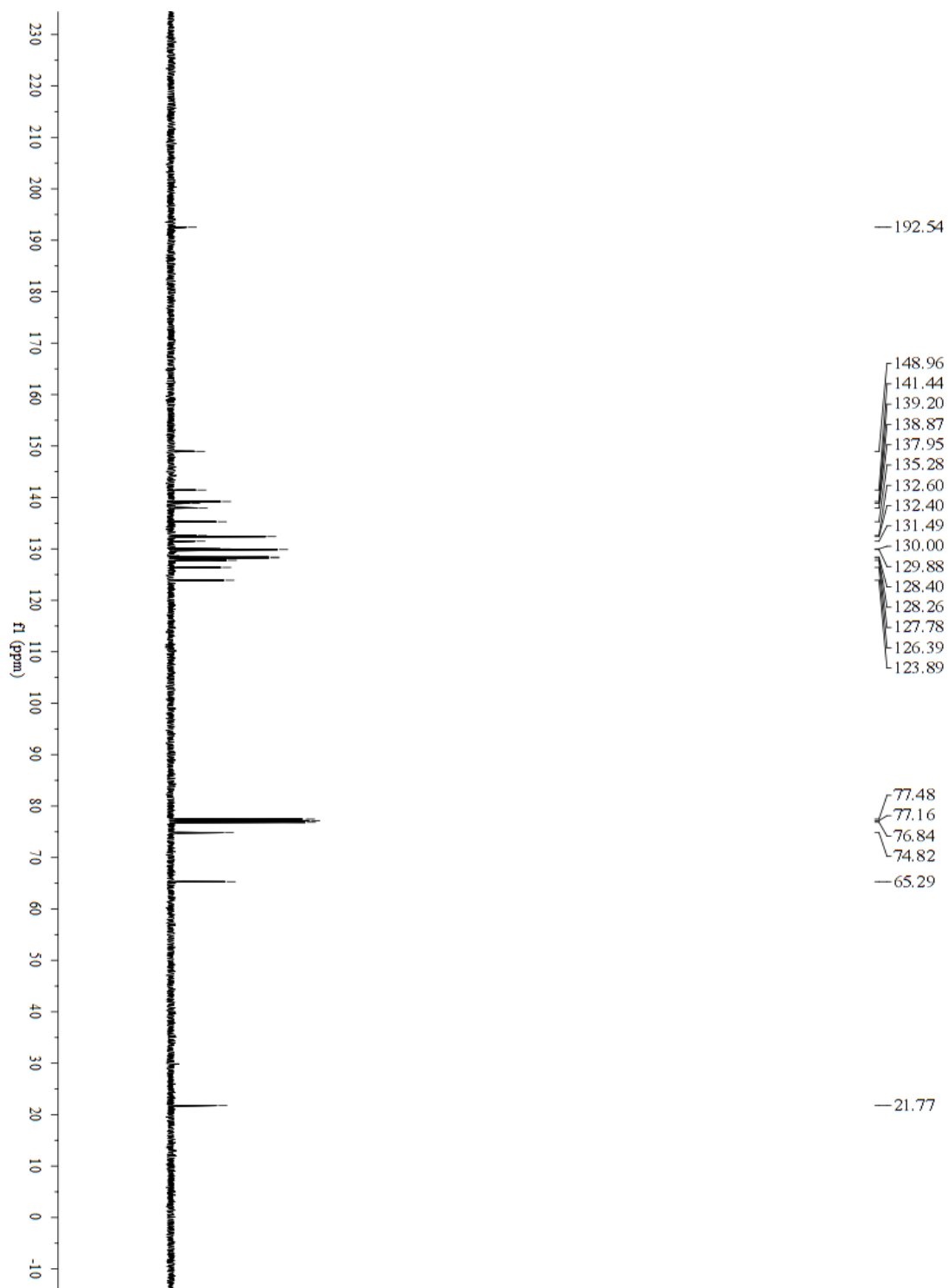
$^1\text{H NMR}$ (400 MHz, CDCl_3)

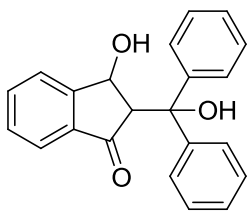




9a

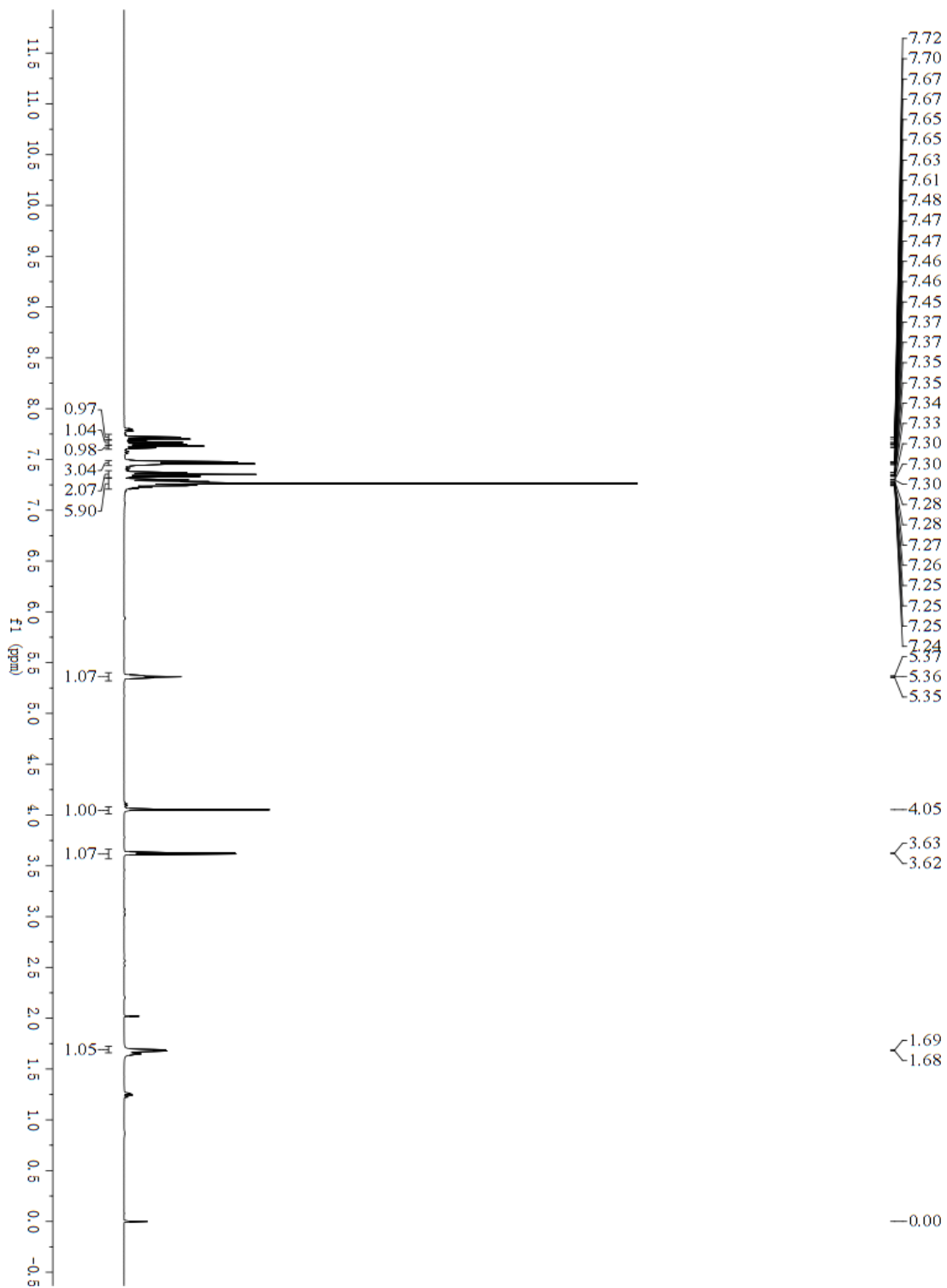
^{13}C NMR (100 MHz, CDCl_3)

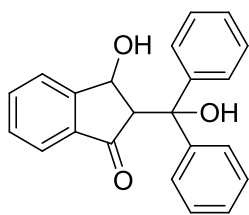




Int-2

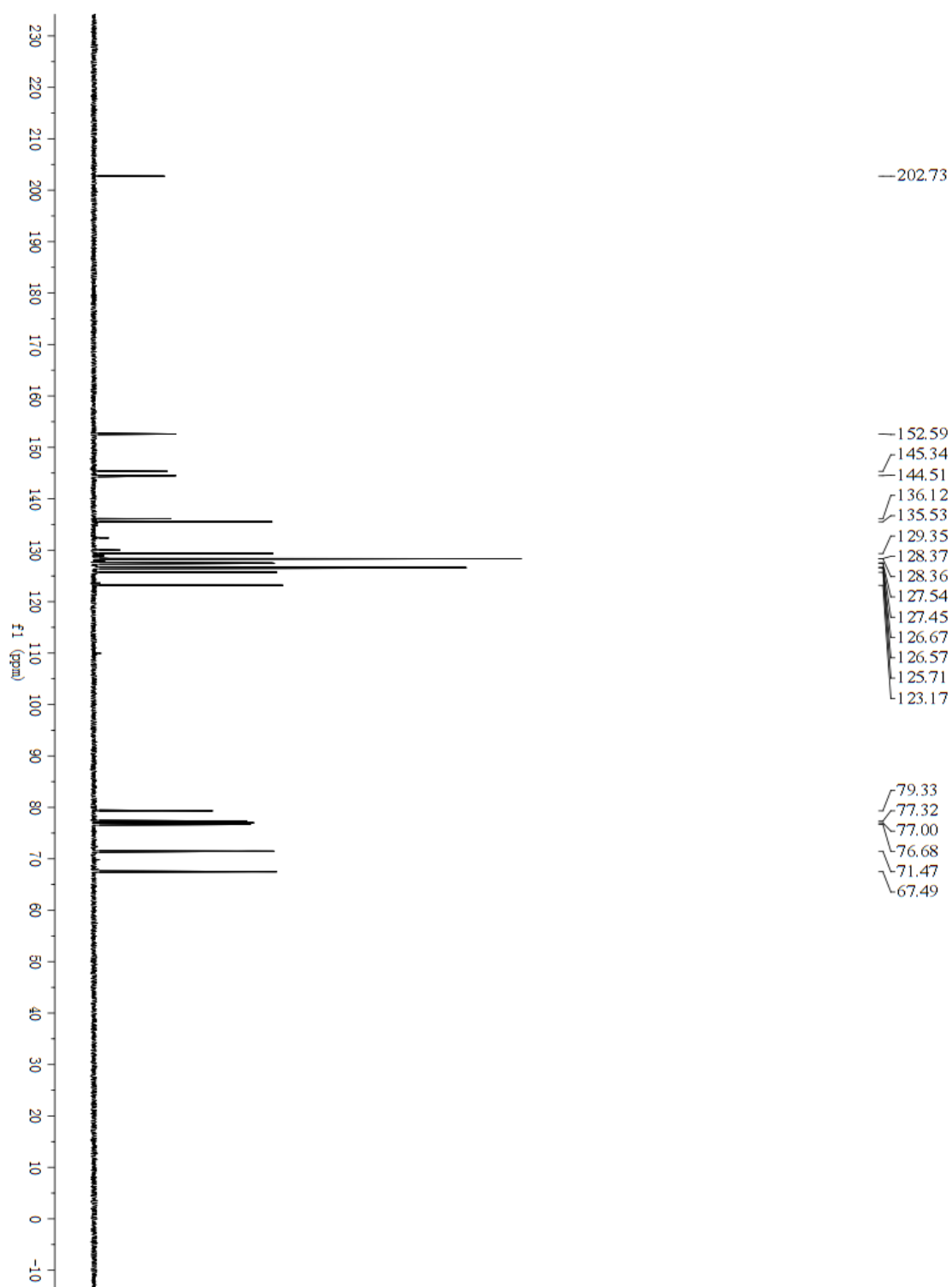
¹H NMR (400 MHz, CDCl₃)





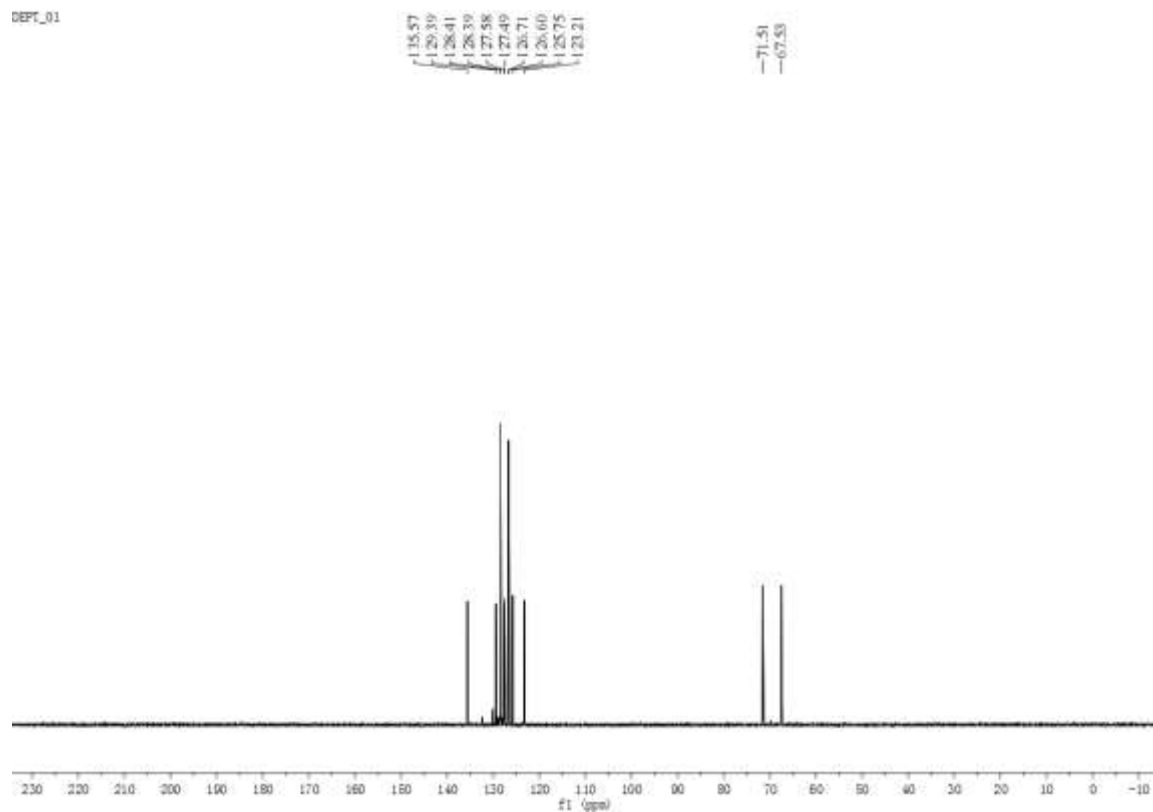
Int-2

^{13}C NMR (100 MHz, CDCl_3)

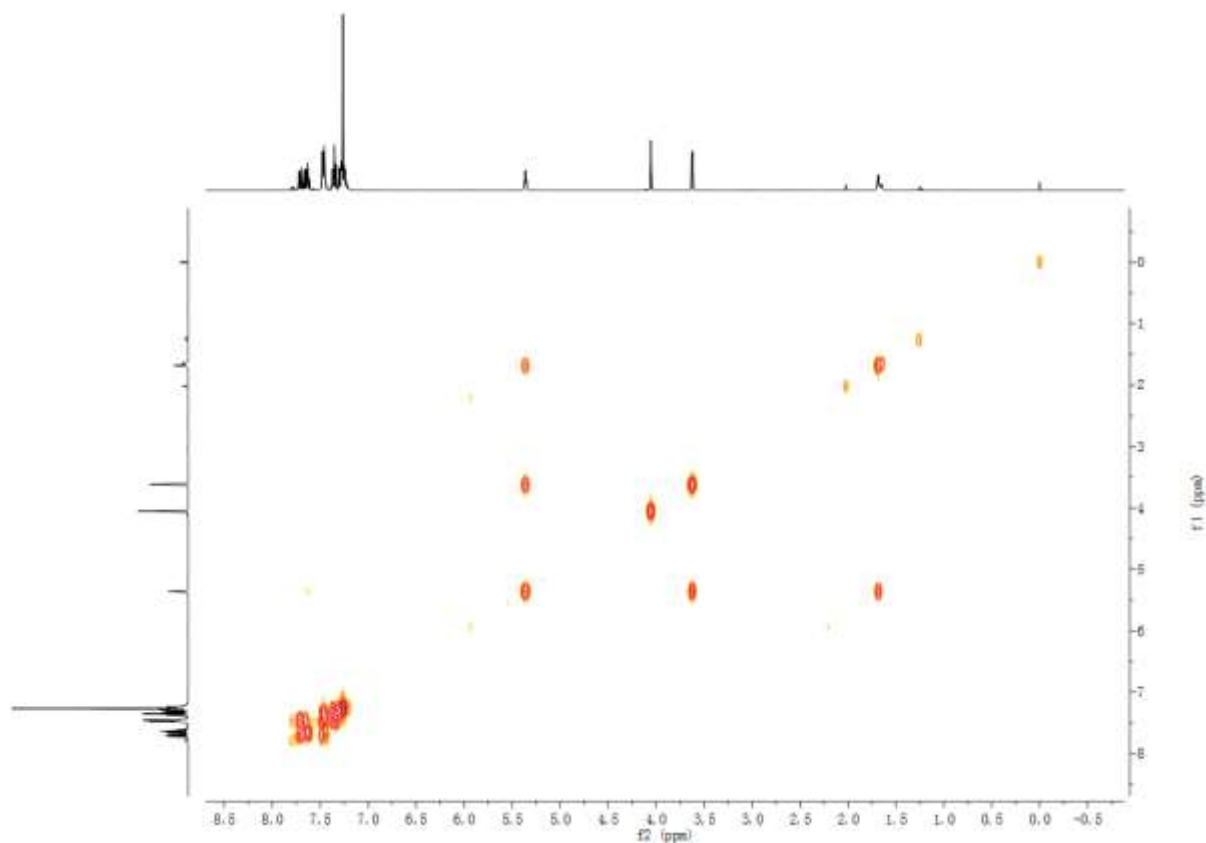


Int-2-DEPT

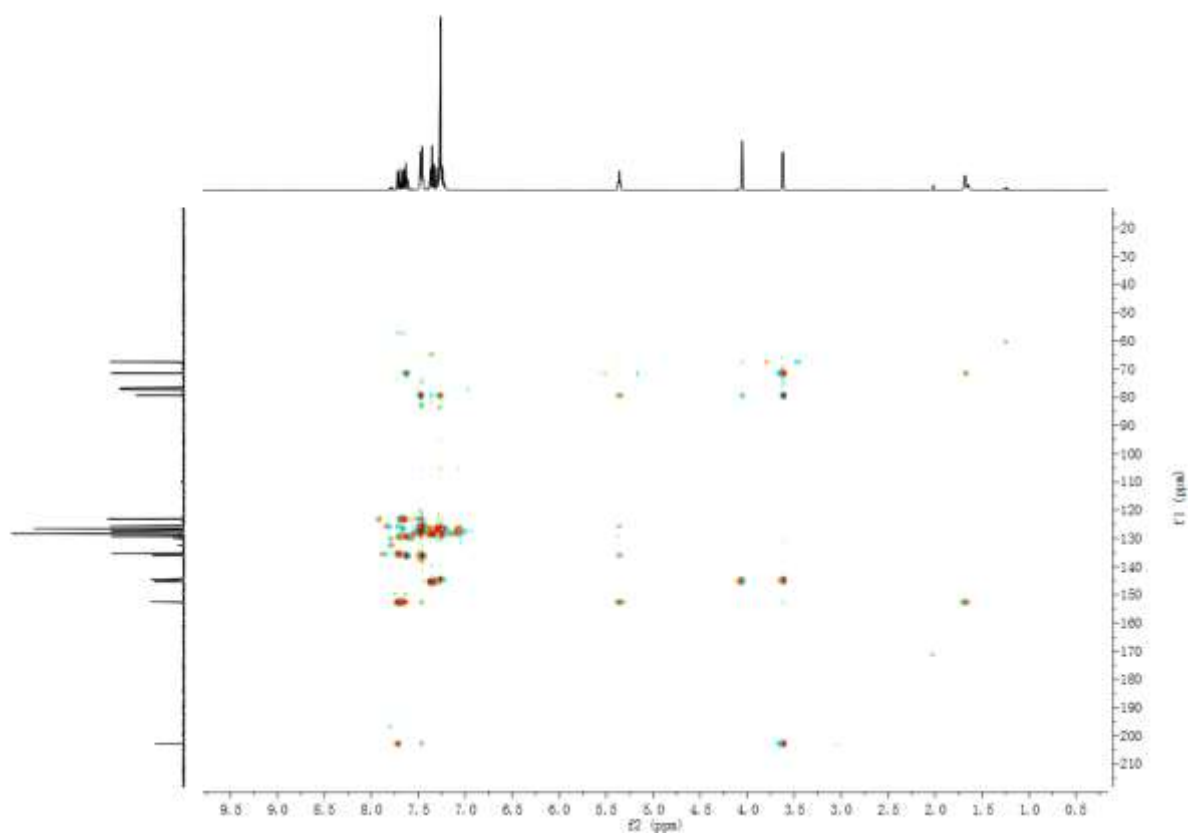
DEPT_01



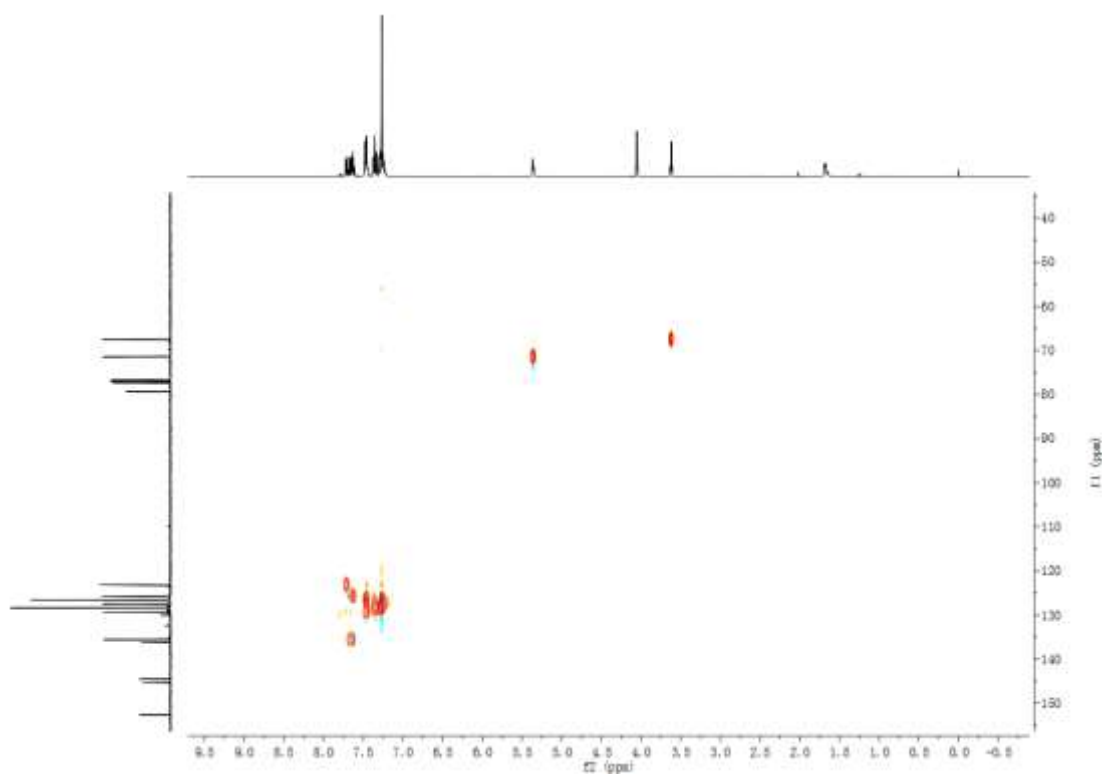
Int-2- ¹H-¹H COSY

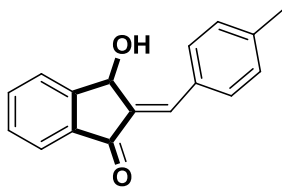


Int-2- HMBC



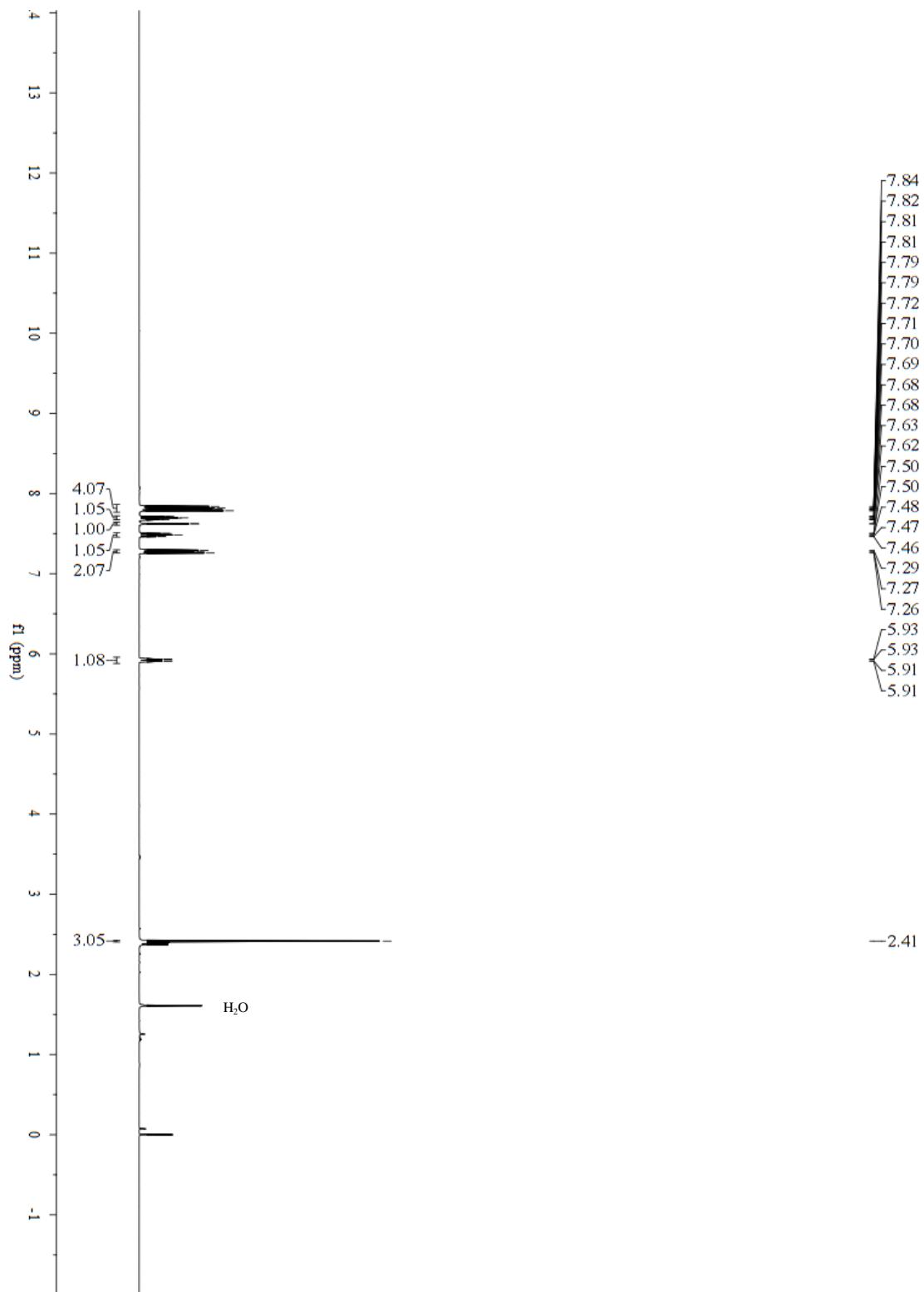
Int-2- HSQC

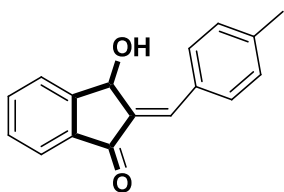




Int-3

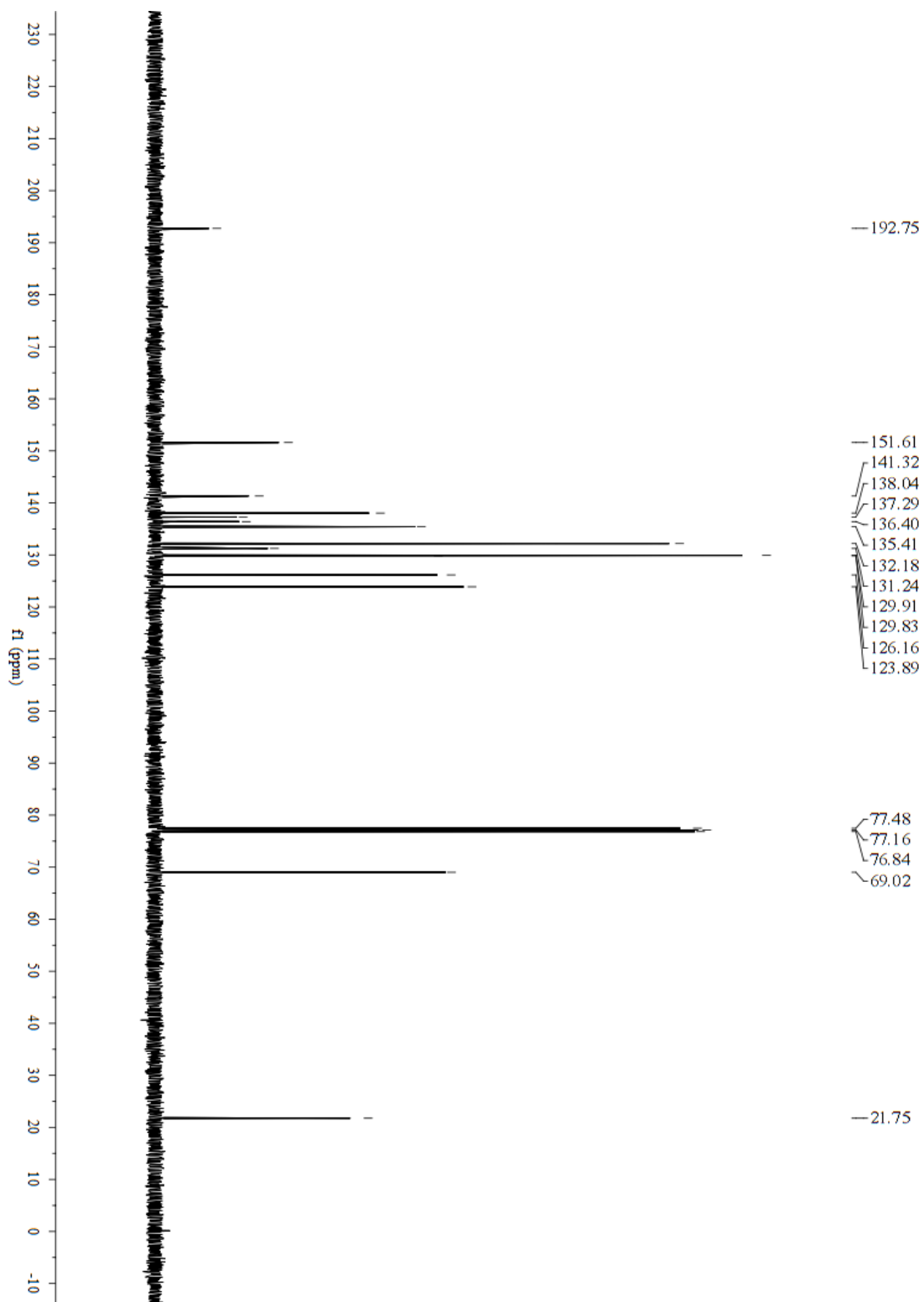
¹H NMR (400 MHz, CDCl₃)





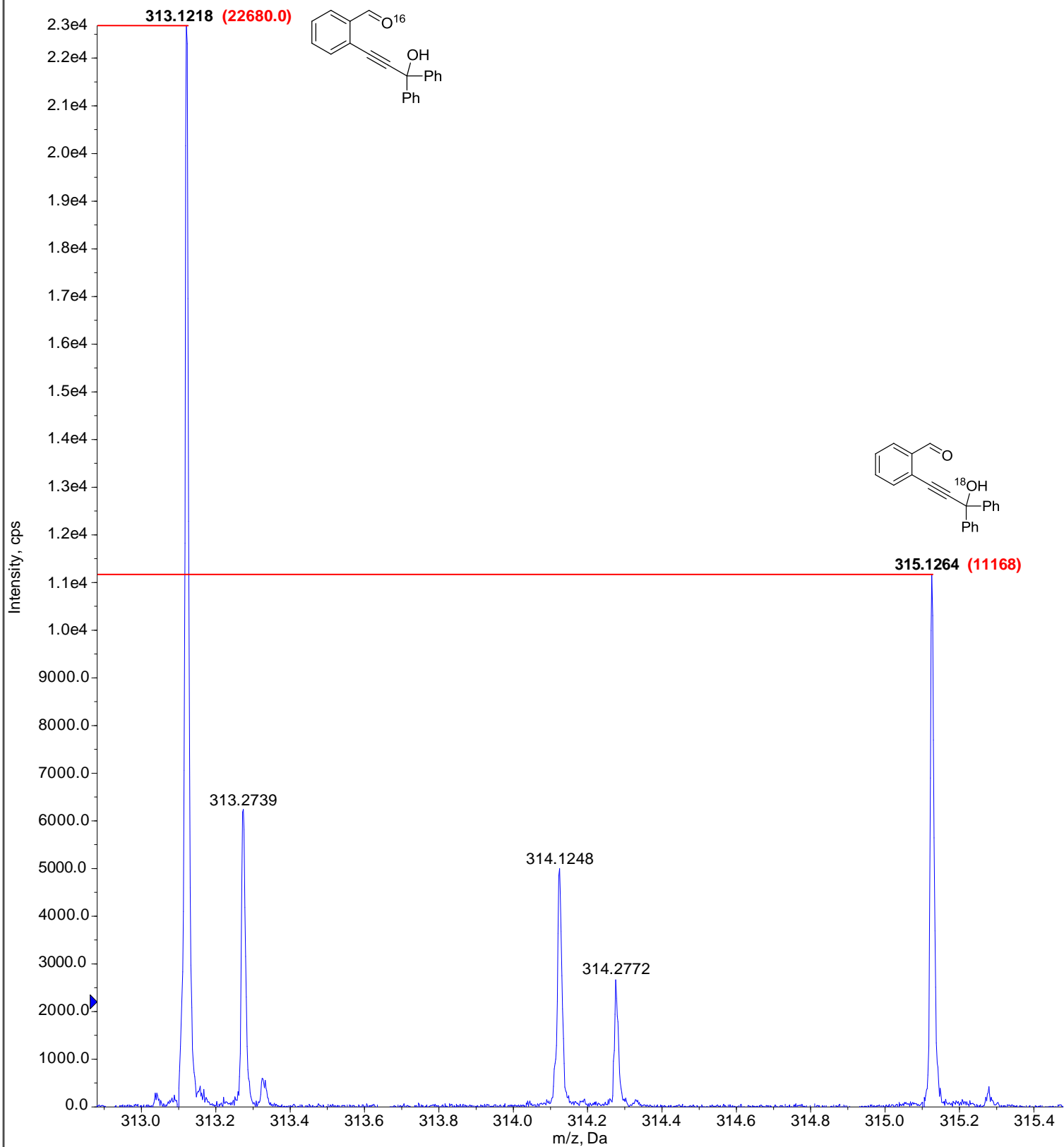
Int-3

^{13}C NMR (100 MHz, CDCl_3)



+TOF MS: 0.0791 min from Sample 1 (TuneSampleID) of P-Y-2-1.wiff
a=5.73261327690843470e-004, t0=3.39272797853219110e+000 (DuoSpray ())

Max. 3.1e4 cps.

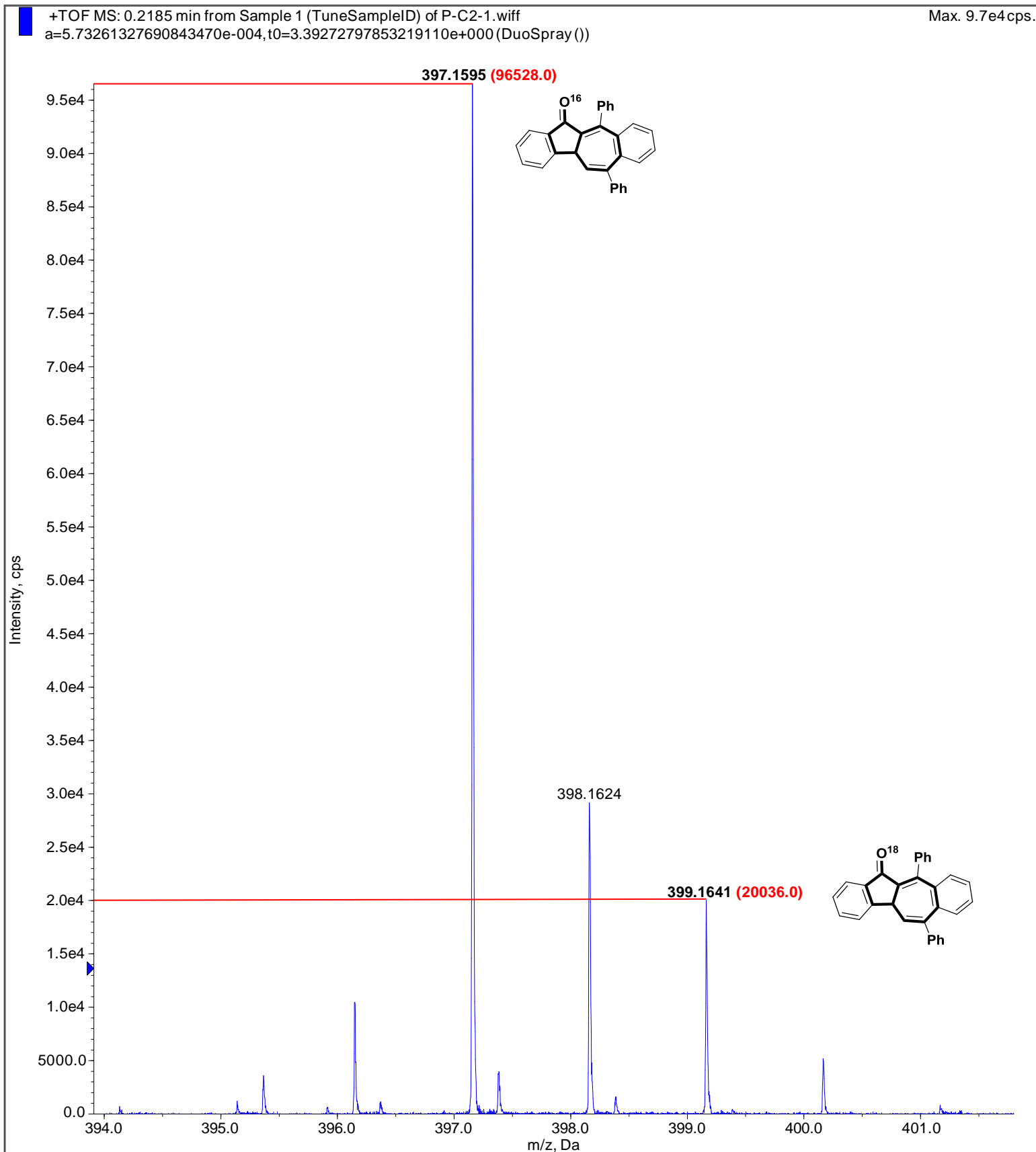


$1a-^{16}O : 1a-^{18}O \approx 2 : 1$

Model reaction:

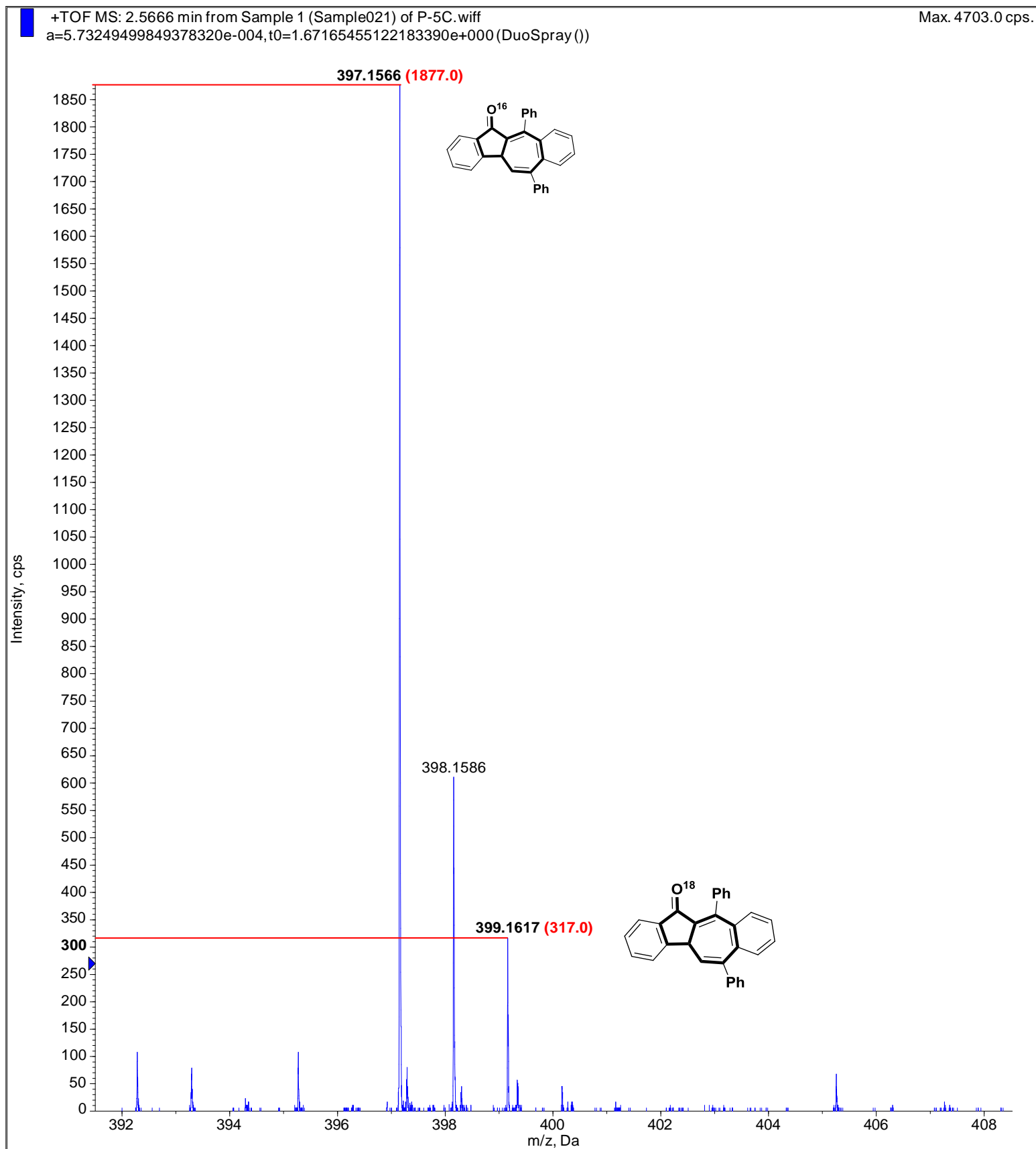
+TOF MS: 0.2185 min from Sample 1 (TuneSampleID) of P-C2-1.wiff
a=5.73261327690843470e-004, t0=3.39272797853219110e+000 (DuoSpray())

Max. 9.7e4 cps.



$3a\text{-}^{16}\text{O} : 3a\text{-}^{18}\text{O} \approx 5 : 1$

H₂O¹⁸ Experiment:



$3a\text{-}^{16}\text{O} : 3a\text{-}^{18}\text{O} \approx 6 : 1$