

Supporting Information

Efficient Synthesis of Spirooxazine-pyrans *via* Rhodium-catalyzed [3 + 3] Cascade Spiroannulation of Benzoxazines with 1-Diazonaphthalen-2(1*H*)-ones

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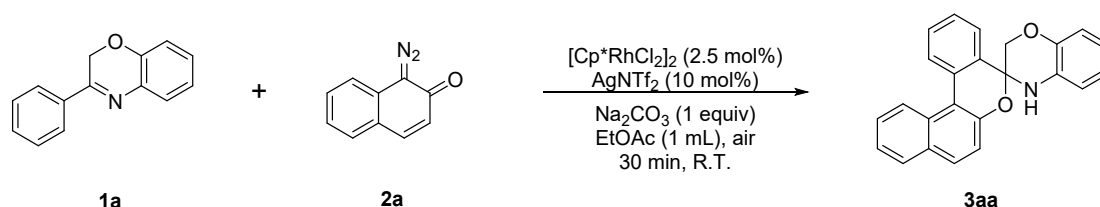
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1. General information

All manipulations were conducted under air atmosphere. Unless otherwise stated, all commercial materials and solvents were used directly without further purification. NMR spectra were measured on a 400 MHz Bruker spectrometer (^1H 400MHz, ^{13}C 100MHz, ^{19}F NMR 376 MHz) using CDCl_3 or $(\text{CD}_3)_2\text{SO}$ (spectra were referenced to the solvent peaks ^1H : residual $\text{CDCl}_3 = 7.26$ ppm, $(\text{CD}_3)_2\text{SO} = 2.50$ ppm; ^{13}C : $\text{CDCl}_3 = 77.00$ ppm, $(\text{CD}_3)_2\text{SO} = 39.52$ ppm) as the solvent. High-resolution mass spectra (HRMS) were measured on ESI-TOF. Infrared spectra were measured with a NICOLET iS 50 ATR spectrometer. Melting points were measured on a microscopic apparatus and were uncorrected. Column chromatography was performed on silica gel (70-230 mesh ASTM) using the reported eluents. Thin-layer chromatography (TLC) was carried out on 4×5 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254). Starting materials **1**¹ and **2**² were prepared according to the reported procedures.

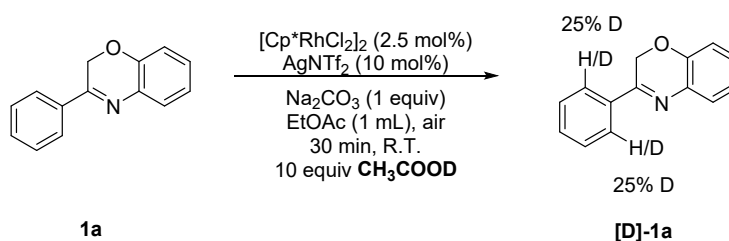
2. General catalytic procedure



A reaction tube (25 mL) equipped with a magnetic stirrer bar was charged with 3-phenyl-2*H*-benzo[*b*][1,4]oxazine **1a** (20.9 mg, 0.1 mmol), 1-diazonaphthalen-2(1*H*)-one **2a** (18.7 mg, 0.11 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (1.5 mg, 0.0025 mmol, 2.5 mol%), AgNTf_2 (3.9 mg, 0.01 mmol, 10 mol%), Na_2CO_3 (10.6 mg, 0.1 mmol, 1 equiv) and EtOAc (1.0 mL). The reaction mixture was stirred at room temperature for 30 minutes under air. After the solvent was removed under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 100:1 to 50:1) as eluent to give the corresponding compound **3aa**.

3. Mechanism exploration

(1) H/D exchange experiment



To a tube equipped with magnetic stir bar, 3-phenyl-2*H*-benzo[*b*][1,4]oxazine **1a** (20.9 mg, 0.1 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (1.5 mg, 0.0025 mmol), AgNTf_2 (3.9 mg, 0.01 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol, 1 equiv), CH_3COOD (10 equiv) were added in EtOAc (1.0 mL). The mixture was stirred at room temperature for 30 minutes. After the solvent was removed under reduced pressure, purification was performed by flash column chromatography on silica gel to give the corresponding product **[D]-1a**. The deuterium

incorporation was calculated based on ^1H NMR spectrum of **[D]-1a**.

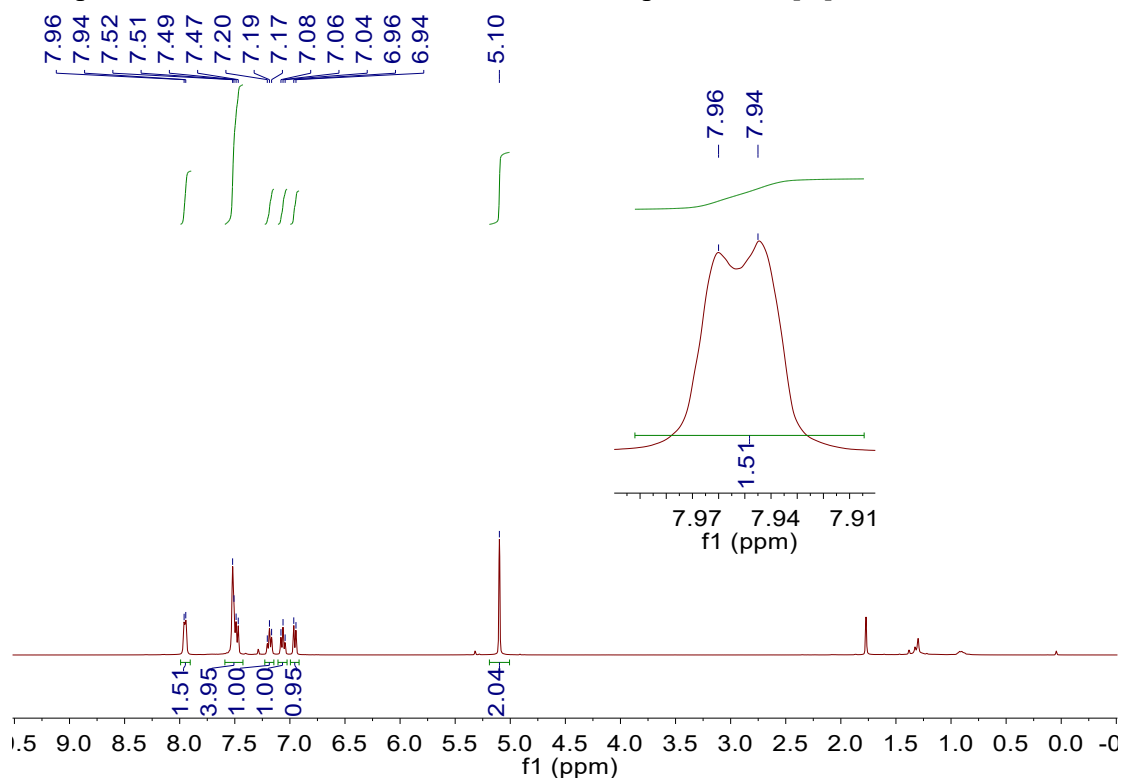
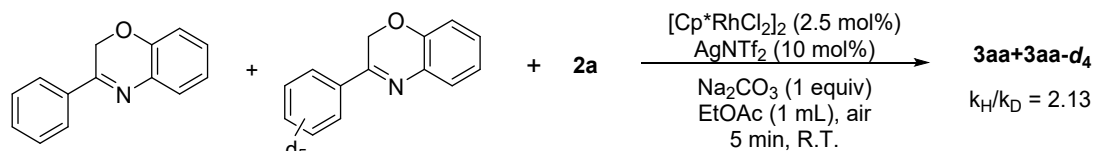


Figure S1. ^1H NMR spectrum of **[D]-1a**.

(2) Kinetic Isotope Effect (KIE) Study



A reaction tube (25 mL) equipped with a magnetic stirrer bar was charged with **1a** (20.9 mg, 0.1 mmol) and **1a-d₅** (21.4 mg, 0.1 mmol), 1-diazonaphthalen-2(1*H*)-one **2a** (18.7 mg, 0.11 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (1.5 mg, 0.0025 mmol, 2.5 mol%), AgNTf_2 (3.9 mg, 0.01 mmol, 10 mol%), Na_2CO_3 (10.6 mg, 0.1 mmol) and EtOAc (1.0 mL). The reaction mixture was stirred at room temperature for 30 minutes under air. After the solvent was removed under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 100:1 to 50:1) as eluent to give the corresponding compounds **3aa** and **3aa-d₅**. The KIE value was determined to be $k_{\text{H}}/k_{\text{D}} = 2.13$ on the basis of ^1H NMR analysis.

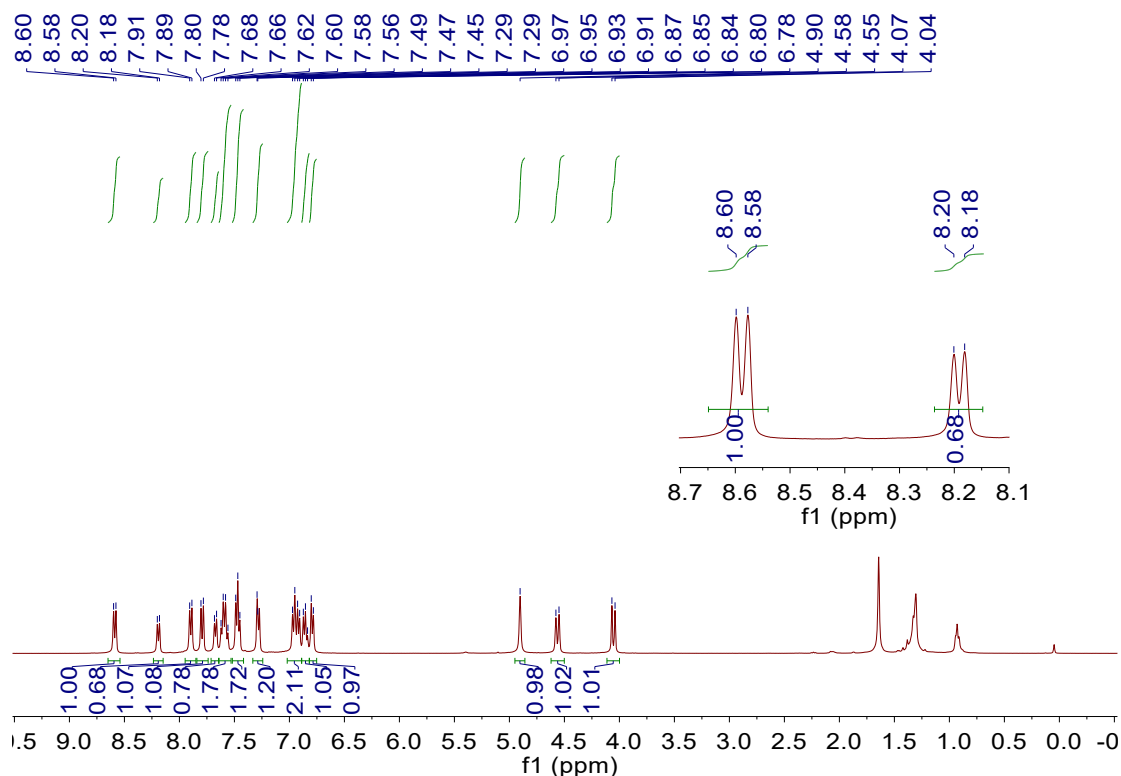
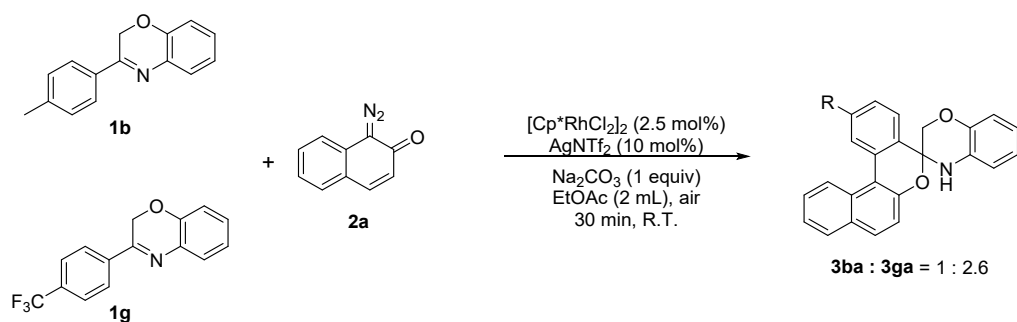


Figure S2. ^1H NMR spectrum of **3aa** and **3aa- d_5** .

(3) Competitive reaction



A sealed tube was charged with 3-(*p*-tolyl)-2*H*-benzo[*b*][1,4]oxazine (**1b**, 22.3 mg, 0.1 mmol), 3-(*p*-(trifluoromethyl)phenyl)-2*H*-benzo[*b*][1,4]oxazine (**1g**, 27.7 mg, 0.1 mmol), 1-diazonaphthalen-2(1*H*)-one **2a** (37.4 mg, 0.22 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), AgNTf_2 (7.8 mg, 0.02 mmol, 10 mol%), Na_2CO_3 (21.2 mg, 0.2 mmol, 1 equiv) and EtOAc (2.0 mL). The reaction mixture was stirred at room temperature for 30 minutes under air. After the solvent was removed under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 100:1 to 50:1) as eluent to give the corresponding compounds. The ratio of **3ba** and **3ga** was determined by ^1H NMR spectrum (1:2.6).

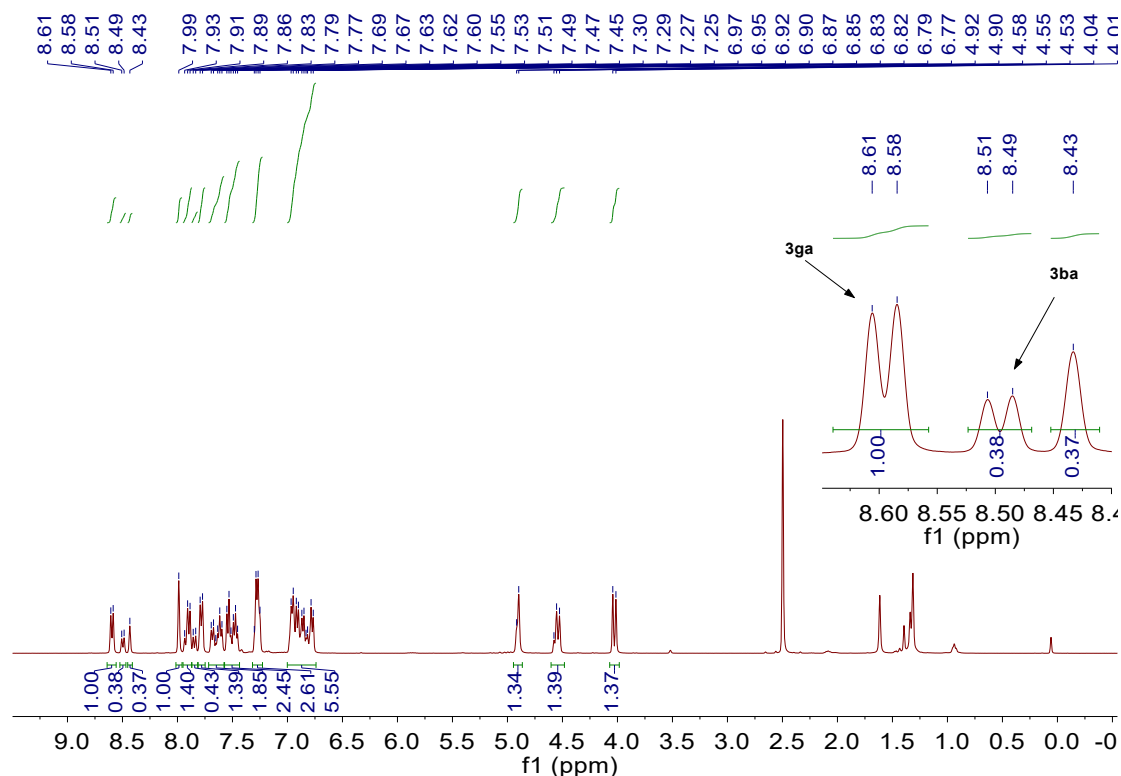
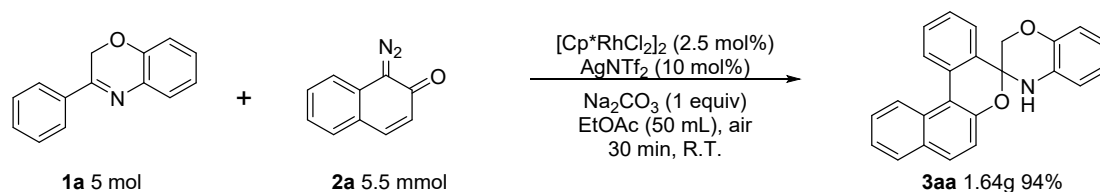


Figure S3. ^1H NMR spectrum of **3ba** and **3ga**.

4. Gram-scale experiment



A round-bottomed flask (100 mL) equipped with a magnetic stirrer bar was charged with 3-phenyl-2H-benzo[*b*][1,4]oxazine **1a** (1.05 g, 5 mmol), 1-diazonaphthalen-2(1H)-one **2a** (0.94 g, 5.5 mmol, 1.1 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (77.3 mg, 0.125 mmol, 2.5 mol%), AgNTf_2 (194.0 mg, 0.5 mmol, 10 mol%), Na_2CO_3 (528.5 mg, 5 mmol, 1 equiv) and EtOAc (50.0 mL). The reaction mixture was stirred at room temperature for 30 minutes under air. After the solvent was removed under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 100:1 to 50:1) as eluent to give the corresponding compound **3aa** (1.64 g, 94 %).

5. X-ray Crystallographic data of 3aa

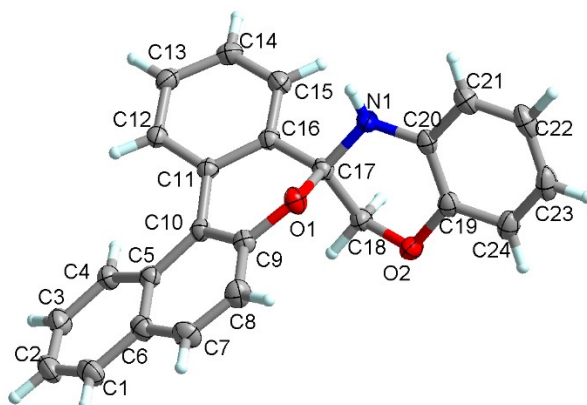


Figure S4. X-ray molecular structure of 3aa with the probability at 50% level.

The single crystal of compound **3aa** was prepared by the slow evaporation from the solution of DCM and pentane with the compound **3aa** at room temperature. The structure of **3aa** was determined by the single crystal X-ray diffraction. Further information could be found in the CIF file. The crystal data were deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC **2183290**. ORTEP view of complex Ellipsoids are represented at the 50% probability level.

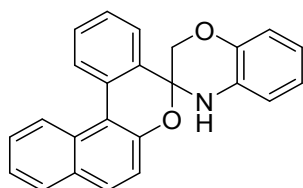
Table S1 Crystal data and structure refinement for 3aa.

Identification code	CCDC 2183290
Empirical formula	C ₂₄ H ₁₇ NO ₂
Formula weight	351.38
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	9.2178(2)
b/Å	10.5693(4)
c/Å	18.1416(5)
α/°	90
β/°	94.955(2)
γ/°	90
Volume/Å ³	1760.85(9)
Z	4
ρ _{calc} /cm ³	1.325
μ/mm ⁻¹	0.670
F(000)	736.0
Crystal size/mm ³	0.24 × 0.14 × 0.1
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	9.632 to 134.158

Index ranges	-11 ≤ h ≤ 6, -12 ≤ k ≤ 12, -19 ≤ l ≤ 21
Reflections collected	6450
Independent reflections	3137 [R _{int} = 0.0317, R _{sigma} = 0.0398]
Data/restraints/parameters	3137/0/249
Goodness-of-fit on F ²	1.024
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0479, wR ₂ = 0.1289
Final R indexes [all data]	R ₁ = 0.0640, wR ₂ = 0.1473
Largest diff. peak/hole / e Å ⁻³	0.17/-0.21

6. Characterization of Products

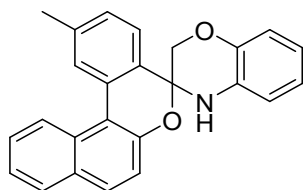
2*H*,4*H*-Spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3aa)



White solid. 33.0 mg, Yield: 94%, mp 182-184 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.60 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.53 (m, 2H), 7.47 (td, *J* = 7.6, 4.4 Hz, 2H), 7.31 – 7.26 (d, *J* = 8.8 Hz, 1H), 7.01 – 6.89 (m, 2H), 6.91 – 6.82 (m, 1H), 6.79 (dd, *J* = 7.7, 1.7 Hz, 1H), 4.90 (s, 1H), 4.57 (dd, *J* = 11.4, 2.5 Hz, 1H), 4.06 (d, *J* = 11.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃ ppm) δ 150.5, 143.5, 133.4, 130.9, 130.9, 130.9, 130.6, 130.0, 129.3, 129.1, 127.9, 127.1, 127.0, 124.4, 124.4, 124.0, 122.0, 120.2, 119.2, 116.7, 116.1, 115.9, 83.7, 66.3. IR (ATR) ν_{max}: 3369, 1588, 1500, 1486, 1425, 1303, 1288, 1224, 1206, 1036, 736 cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₄H₁₈NO₂ [M+H]⁺ 352.1332, found 352.1334.

2'-Methyl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3ba)

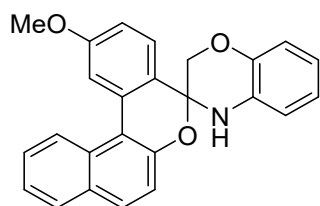


White solid. 26.6 mg, Yield: 73%, mp 183-185 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.60 (d, *J* = 8.6 Hz, 1H), 7.99 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 9.0 Hz, 2H), 7.00 – 6.88 (m, 2H), 6.85 (t, *J* = 7.1 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 4.91 (s, 1H), 4.54 (dd, *J* = 11.5, 2.4 Hz, 1H), 4.03 (d, *J* = 11.4 Hz, 1H), 2.49 (s, 3H). ¹³C NMR (100 MHz, CDCl₃ ppm) δ 150.6, 143.5, 139.1, 131.0, 130.9, 130.7, 130.4, 130.0, 129.1, 128.6, 127.6, 126.9, 124.5, 124.3, 123.9, 121.9, 120.2, 119.3, 116.7, 116.2, 115.9, 83.7, 66.4, 21.7. IR (ATR) ν_{max}: 3379,

2912, 1586, 1498, 1483, 1428, 1306, 1287, 1224, 1206, 809, 740 cm^{-1} . **HRMS (ESI)** m/z calcd for $\text{C}_{25}\text{H}_{20}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 366.1489, found 366.1491.

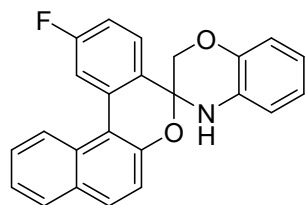
2'-Methoxy-2H,4H-spiro[benzo[b][1,4]oxazine-3,5'-dibenzo[c,f]chromene] (3ca)



White solid. 24.0 mg, Yield: 63%, mp 185-186 °C. column chromatography eluent, EtOAc/PE = 1:50

^1H NMR (400 MHz, CDCl_3 ppm) δ 8.60 (d, $J = 8.6$ Hz, 1H), 7.89 (d, $J = 8.1$ Hz, 1H), 7.79 (d, $J = 8.7$ Hz, 1H), 7.69 (s, 1H), 7.60 (t, $J = 7.7$ Hz, 1H), 7.54 (d, $J = 8.5$ Hz, 1H), 7.47 (t, $J = 7.4$ Hz, 1H), 7.27 (d, $J = 8.9$ Hz, 1H), 6.99 – 6.87 (m, 3H), 6.89 – 6.81 (m, 1H), 6.77 (d, $J = 7.5$ Hz, 1H), 4.94 (s, 1H), 4.52 (dd, $J = 11.6, 2.4$ Hz, 1H), 3.99 (d, $J = 11.4$ Hz, 1H), 3.88 (s, 3H). **^{13}C NMR** (100 MHz, CDCl_3 ppm) δ 160.2, 150.9, 143.5, 131.8, 131.0, 131.0, 130.8, 130.0, 129.2, 127.1, 125.9, 125.7, 124.3, 124.0, 121.9, 120.2, 119.3, 116.6, 115.9, 115.9, 113.2, 112.6, 83.8, 66.5, 55.5. **IR** (ATR) ν_{max} : 3329, 2916, 1590, 1483, 1420, 1294, 1236, 1225, 1206, 1039, 732, 531 cm^{-1} . **HRMS (ESI)** m/z calcd for $\text{C}_{25}\text{H}_{20}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 382.1438, found 382.1439.

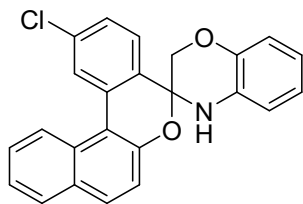
2'-Fluoro-2H,4H-spiro[benzo[b][1,4]oxazine-3,5'-dibenzo[c,f]chromene] (3da)



White solid. 35.4 mg, Yield: 96%, mp 212-214 °C. column chromatography eluent, EtOAc/PE = 1:100 \rightarrow 1:50

^1H NMR (400 MHz, CDCl_3 ppm) δ 8.53 (d, $J = 8.6$ Hz, 1H), 7.93 – 7.84 (m, 2H), 7.81 (d, $J = 8.8$ Hz, 1H), 7.69 – 7.58 (m, 2H), 7.48 (t, $J = 7.5$ Hz, 1H), 7.26 (d, $J = 8.8$ Hz, 1H), 7.14 (td, $J = 8.3, 2.5$ Hz, 1H), 6.98 – 6.90 (m, 2H), 6.86 (t, $J = 7.5$ Hz, 1H), 6.80 (d, $J = 7.6$ Hz, 1H), 4.87 (s, 1H), 4.53 (dd, $J = 11.4, 2.5$ Hz, 1H), 4.00 (d, $J = 11.4$ Hz, 1H). **^{13}C NMR** (100 MHz, CDCl_3 ppm) δ 163.4 (d $J = 246.8$ Hz), 151.0, 143.5, 132.8 (d $J = 9.1$ Hz), 131.6, 130.8, 130.7, 129.8, 129.3, 129.1 (d $J = 2.6$ Hz), 127.5, 126.5 (d $J = 9.1$ Hz), 124.2, 123.9, 122.0, 120.5, 119.1, 116.7, 116.0, 115.1 (d, $J = 2.1$ Hz), 114.5 (d $J = 21.9$ Hz), 113.8 (d $J = 24.2$ Hz), 83.7, 66.3. **^{19}F NMR** (376 MHz, CDCl_3 ppm) δ -111.61. **IR** (ATR) ν_{max} : 3358, 2292, 1591, 1501, 1472, 1418, 1307, 1221, 1049, 730 cm^{-1} . **HRMS (ESI)** m/z calcd for $\text{C}_{24}\text{H}_{17}\text{FNO}_2$ $[\text{M}+\text{H}]^+$ 370.1238, found 370.1239.

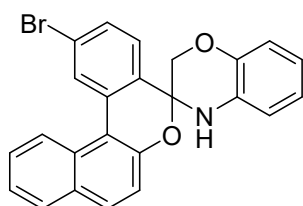
2'-Chloro-2H,4H-spiro[benzo[b][1,4]oxazine-3,5'-dibenzo[c,f]chromene] (3ea)



White solid. 34.6 mg, Yield: 90%, mp 209-211 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.51 (d, *J* = 8.6 Hz, 1H), 8.14 (d, *J* = 2.0 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.39 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 6.93 (q, *J* = 7.5 Hz, 2H), 6.86 (td, *J* = 7.5, 1.7 Hz, 1H), 6.78 (d, *J* = 7.4 Hz, 1H), 4.88 (s, 1H), 4.52 (dd, *J* = 11.5, 2.5 Hz, 1H), 3.98 (d, *J* = 11.5 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃ ppm) δ 151.0, 143.45, 135.5, 132.3, 131.6, 131.5, 130.8, 130.7, 129.7, 129.3, 127.7, 127.5, 126.7, 126.0, 124.3, 123.9, 122.0, 120.5, 119.1, 116.7, 116.0, 114.9, 83.6, 66.0. **IR** (ATR) ν_{\max} : 3367, 2916, 1587, 1494, 1473, 1302, 1217, 736, 724 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇ClNO₂ [M+H]⁺ 386.0492, found 386.0491. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇³⁷ClNO₂ [M+H]⁺ 388.0913, found 388.0913.

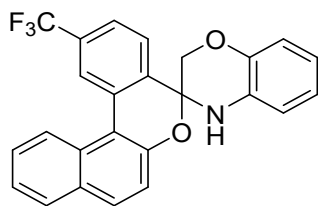
2'-Bromo-2H,4H-spiro[benzo[b][1,4]oxazine-3,5'-dibenzo[c,f]chromene] (3fa)



White solid. 39.8 mg, Yield: 93%, mp 186-188 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.50 (d, *J* = 8.5 Hz, 1H), 8.29 (d, *J* = 1.7 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.57 – 7.45 (m, 3H), 7.25 (d, *J* = 8.8 Hz, 1H), 6.98 – 6.89 (m, 2H), 6.90 – 6.82 (m, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 4.88 (s, 1H), 4.52 (dd, *J* = 11.5, 2.5 Hz, 1H), 3.98 (d, *J* = 11.5 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃ ppm) δ 151.0, 143.5, 132.6, 132.0, 131.7, 130.8, 130.6, 130.6, 129.7, 129.6, 129.3, 127.6, 126.2, 124.3, 123.9, 123.7, 122.1, 120.5, 119.1, 116.7, 116.1, 114.8, 83.7, 66.0. **IR** (ATR) ν_{\max} : 3352, 2916, 1588, 1500, 1477, 1427, 1301, 1278, 1228, 1215, 1046, 741, 545 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇BrNO₂ [M+H]⁺ 430.0437, found 430.0437. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇⁸¹BrNO₂ [M+H]⁺ 432.0417, found 432.0420.

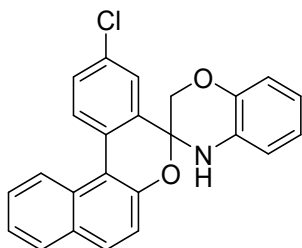
2'-(Trifluoromethyl)-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3ga)



White solid. 39.8 mg, Yield: 95%, mp 187-189 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, DMSO-*d*₆ ppm) δ 8.45 (d, *J* = 8.6 Hz, 1H), 8.35 (s, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 9.1 Hz, 1H), 7.92 (s, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 6.90 – 6.78 (m, 3H), 6.71 (t, *J* = 5.0 Hz, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 4.07 (d, *J* = 11.6 Hz, 1H). **¹³C NMR** (100 MHz, DMSO-*d*₆ ppm) δ 151.3, 143.0, 136.9, 132.3, 132.1, 131.3, 130.8, 130.1 (q *J* = 32.0 Hz), 129.8, 129.7, 128.4, 126.9, 124.9 (q *J* = 3.4 Hz), 124.8, 124.5 (q *J* = 272.4 Hz), 123.9, 122.83 (q *J* = 3.6 Hz), 122.3, 119.3, 119.3, 116.4, 115.9, 115.0, 84.1, 65.9. **¹⁹F NMR** (376 MHz, DMSO-*d*₆ ppm) δ -61.24. **IR** (ATR) ν_{\max} : 3339, 1593, 1500, 1427, 1327, 1226, 1124, 1036, 922, 825, 746 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₅H₁₇F₃NO₂ [M+H]⁺ 420.1206, found 420.1209.

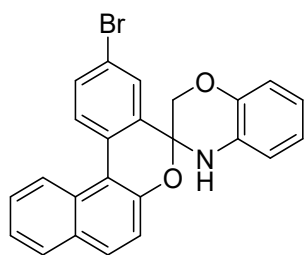
3'-Chloro-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3ha)



White solid. 37.8 mg, Yield: 98%, mp 191-193 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.48 (d, *J* = 8.7 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.69 (s, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 3.1 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 2H), 6.90 – 6.78 (m, 2H), 4.85 (s, 1H), 4.52 (d, *J* = 11.5 Hz, 1H), 3.98 (d, *J* = 11.4 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃ ppm) δ 150.5, 143.5, 135.0, 133.7, 131.2, 130.9, 130.6, 129.7, 129.4, 129.2, 129.2, 128.2, 127.2, 124.9, 124.2, 124.1, 122.1, 120.6, 119.1, 116.7, 116.1, 115.3, 83.4, 65.9. **IR** (ATR) ν_{\max} : 3345, 2917, 2844, 1588, 1498, 1478, 1245, 1228, 1210, 1031, 815, 740 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₆ClNO₂Na [M+Na]⁺ 408.0762, found 408.0762. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇³⁷ClNO₂ [M+H]⁺ 388.0913, found 388.0915.

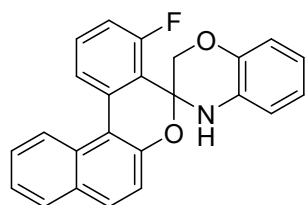
3'-Bromo-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3ia)



White solid. 42.6 mg, Yield: 99%, mp 219-221 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.47 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.85 – 7.75 (m, 2H), 7.68 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 2H), 6.91 – 6.78 (m, 2H), 4.85 (s, 1H), 4.51 (dd, *J* = 11.5, 2.6 Hz, 1H), 3.97 (d, *J* = 11.5 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃ ppm) δ 150.5, 143.5, 135.2, 132.3, 131.3, 130.9, 130.6, 129.7, 129.6, 129.2, 128.4, 127.8, 127.3, 124.2, 124.1, 122.1, 121.6, 120.6, 119.1, 116.7, 116.1, 115.3, 83.3, 65.9. **IR** (ATR) ν_{max} : 3353, 1595, 1501, 1476, 1427, 1300, 1275, 1230, 1209, 1039, 806, 737, 538 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇BrNO₂ [M+H]⁺ 430.0437, found 430.0436. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇⁸¹BrNO₂ [M+H]⁺ 432.0417, found 432.0418.

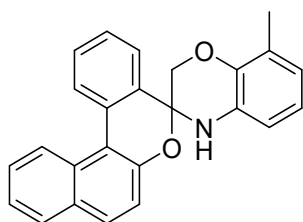
4'-Fluoro-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3ja)



White solid. 35.4 mg, Yield: 96%, mp 183-184 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.57 (d, *J* = 8.6 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.52 (m, 2H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.15 (dd, *J* = 11.4, 8.3 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.80 (td, *J* = 8.3, 7.7, 4.2 Hz, 2H), 6.45 (d, *J* = 6.9 Hz, 1H), 5.10 (s, 1H), 4.89 – 4.77 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃ ppm) δ 158.6 (d *J* = 249.0 Hz), 150.0, 143.6, 132.7 (d *J* = 4.4 Hz), 131.3, 130.9, 130.3 (d *J* = 9.4 Hz), 129.8, 129.8, 129.2, 127.2, 124.3, 124.2, 123.3 (d *J* = 3.1 Hz), 121.9, 120.1, 120.0 (d *J* = 13.7 Hz), 119.7, 116.9, 115.9 (d *J* = 2.9 Hz), 115.3, 115.1 (d *J* = 23.9 Hz), 82.0 (d *J* = 5.1 Hz), 68.4 (d *J* = 14.6 Hz). **¹⁹F NMR** (376 MHz, CDCl₃ ppm) δ -112.50. **IR** (ATR) ν_{max} : 3329, 2914, 1608, 1595, 1438, 1300, 1274, 1237, 1199, 1042, 1022, 737 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇FNO₂ [M+H]⁺ 370.1238, found 370.1238.

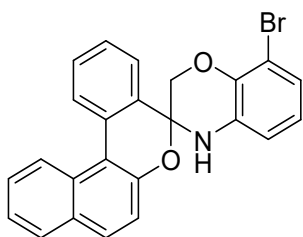
8-Methyl-2H,4H-spiro[benzo[b][1,4]oxazine-3,5'-dibenzo[c,f]chromene] (3ka)



White solid. 28.8 mg, Yield: 79%, mp 210-212 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.59 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.59 (q, *J* = 8.3 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.9 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 4.86 (s, 1H), 4.63 (d, *J* = 11.4 Hz, 1H), 4.05 (d, *J* = 11.4 Hz, 1H), 2.27 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃ ppm) δ 150.7, 141.7, 133.5, 130.8, 130.8, 130.6, 130.5, 130.0, 129.2, 129.1, 127.9, 127.0, 127.0, 126.2, 124.4, 124.3, 124.0, 121.9, 121.2, 119.4, 116.1, 113.6, 83.7, 66.4, 15.7. **IR** (ATR) ν_{\max} : 3360, 2917, 1592, 1482, 1434, 1428, 1303, 1292, 1228, 1205, 1028, 753 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₅H₂₀NO₂ [M+H]⁺ 366.1489, found 366.1489.

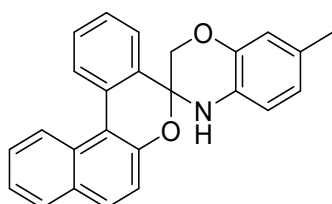
8-Bromo-2H,4H-spiro[benzo[b][1,4]oxazine-3,5'-dibenzo[c,f]chromene] (3la)



White solid. 36.4 mg, Yield: 85%, mp 215-217 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.57 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.67 – 7.54 (m, 3H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.29 (s, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.78 (t, *J* = 7.9 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 4.96 (d, *J* = 2.4 Hz, 1H), 4.69 (dd, *J* = 11.4, 2.4 Hz, 1H), 4.10 (d, *J* = 11.4 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃ ppm) δ 150.23, 140.5, 132.8, 132.1, 130.9, 130.9, 130.6, 129.9, 129.4, 129.1, 127.9, 127.1, 127.0, 124.4, 124.2, 124.1, 123.9, 122.5, 119.2, 116.0, 114.9, 110.6, 83.2, 66.9. **IR** (ATR) ν_{\max} : 3392, 2917, 1588, 1477, 1424, 1307, 1216, 1199, 1033, 713, 538 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇BrNO₂ [M+H]⁺ 430.0437, found 430.037. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇⁸¹BrNO₂ [M+H]⁺ 432.0417, found 432.0417.

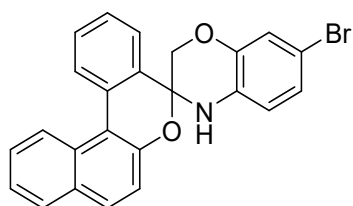
7-Methyl-2H,4H-spiro[benzo[b][1,4]oxazine-3,5'-dibenzo[c,f]chromene] (3ma)



White solid. 32.5 mg, Yield: 89%, mp 160-162 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.58 (d, *J* = 8.6 Hz, 1H), 8.18 (d, *J* = 7.9 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.58 (q, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 2.1 Hz, 1H), 6.78 (s, 1H), 6.71 (q, *J* = 7.9 Hz, 2H), 4.78 (s, 1H), 4.54 (d, *J* = 11.4 Hz, 1H), 4.03 (d, *J* = 11.4 Hz, 1H), 2.31 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃ ppm) δ 150.6, 143.3, 133.5, 130.8, 130.8, 130.6, 130.0, 129.9, 129.2, 129.1, 128.3, 127.9, 127.0, 126.9, 124.4, 124.0, 122.4, 119.2, 117.2, 116.1, 115.7, 83.8, 66.4, 20.7. **IR** (ATR) ν_{\max} : 3347, 2920, 1592, 1510, 1443, 1315, 1229, 1035, 824, 744 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₅H₂₀NO₂ [M+H]⁺ 366.1489, found 366.1489.

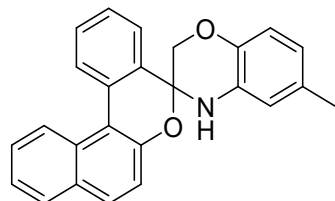
7-Bromo-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3na)



White solid. 41.2 mg, Yield: 96%, mp 192-193 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.57 (d, *J* = 8.6 Hz, 1H), 8.18 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.60 (dt, *J* = 15.4, 7.9 Hz, 3H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 1H), 7.09 (s, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 4.89 (s, 1H), 4.54 (d, *J* = 11.4 Hz, 1H), 4.03 (d, *J* = 11.4 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃ ppm) δ 150.3, 144.2, 132.9, 130.9, 130.9, 130.5, 130.2, 129.9, 129.4, 129.1, 127.9, 127.1, 127.1, 124.6, 124.4, 124.2, 124.1, 119.7, 119.1, 116.9, 116.1, 111.6, 83.2, 66.4. **IR** (ATR) ν_{\max} : 3370, 2917, 1594, 1496, 1445, 1405, 1304, 1280, 1037, 818, 785, 735, 534 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇BrNO₂ [M+H]⁺ 430.0438, found 430.0438. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇⁸¹BrNO₂ [M+H]⁺ 432.0417, found 432.0418.

6-Methyl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3oa)

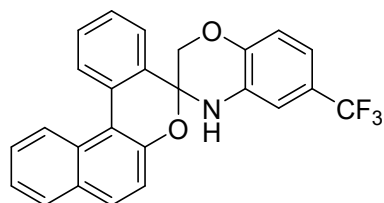


White solid. 29.9 mg, Yield: 82%, mp 229-231 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.59 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.69 – 7.53 (m, 3H), 7.46 (q, *J* = 7.1 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.66 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.61 (s, 1H), 4.84 (s, 1H), 4.54 (dd, *J* = 11.5, 2.5 Hz, 1H), 4.02 (d, *J* = 11.4 Hz,

1H), 2.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃ ppm) δ 150.6, 141.3, 133.5, 131.5, 130.8, 130.8, 130.5, 130.5, 129.9, 129.2, 129.1, 127.9, 127.0, 124.4, 124.4, 124.0, 120.8, 119.3, 116.4, 116.4, 116.1, 83.8, 66.4, 20.8. IR (ATR) ν_{max}: 3342, 1593, 1487, 1455, 1375, 1293, 1230, 1213, 1035, 941, 746 cm⁻¹. HRMS (ESI) m/z calcd for C₂₅H₂₀NO₂ [M+H]⁺ 366.1489, found 366.1489.

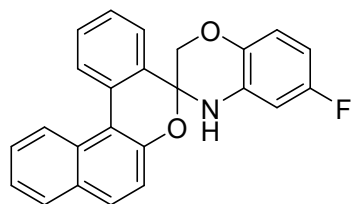
6-(Trifluoromethyl)-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3pa)



White solid. 39.3 mg, Yield: 93%, mp 237-239 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.58 (d, *J* = 8.6 Hz, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.62 (m, 3H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.22 (m, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 7.07 – 6.97 (m, 2H), 5.03 (s, 1H), 4.60 (d, *J* = 11.5 Hz, 1H), 4.07 (d, *J* = 11.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃ ppm) δ 150.2, 146.1, 132.7, 131.2, 131.0, 130.9, 130.5, 129.9, 129.5, 129.1, 128.0, 127.2, 127.1, 124.4, 124.3 (q, *J* = 272.3 Hz), 124.1 (q, *J* = 32.5 Hz), 124.2, 119.0, 117.5 (q, *J* = 3.93 Hz), 116.7, 116.1, 112.9 (q, *J* = 3.8 Hz), 83.1, 66.5. ¹⁹F NMR (376 MHz, CDCl₃ ppm) δ -61.67. IR (ATR) ν_{max}: 3348, 2928, 2847, 1616, 1593, 1480, 1334, 1207, 1159, 1034, 1102, 943, 745 cm⁻¹. HRMS (ESI) m/z calcd for C₂₅H₁₇F₃NO₂ [M+H]⁺ 420.1206, found 420.1209.

6-Fluoro-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3qa)

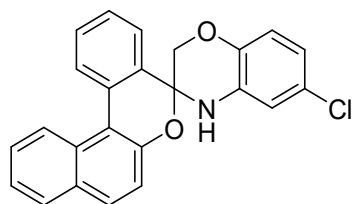


White solid. 33.8 mg, Yield: 90%, mp 213-215 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.58 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.60 (m, 3H), 7.47 (q, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 1H), 6.87 (t, *J* = 7.1 Hz, 1H), 6.53 (q, *J* = 9.0 Hz, 2H), 4.97 (s, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.00 (d, *J* = 11.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃ ppm) δ 158.0 (d, *J* = 239.0 Hz), 150.27, 139.46, 133.00, 131.7 (d, *J* = 10.8 Hz), 130.92, 130.50, 129.90, 129.36, 129.14, 127.92, 127.12, 127.07, 124.40, 124.19, 124.11, 119.12, 117.1 (d, *J* = 9.4 Hz), 116.08, 106.2 (d, *J* = 23.2 Hz), 102.7 (d, *J* = 27.0 Hz), 83.32, 66.39. ¹⁹F NMR (376 MHz, CDCl₃ ppm) δ -121.56. IR (ATR) ν_{max}: 3374, 2915, 1613, 1587, 1511, 1480, 1380, 1310, 1300, 1227, 1198, 1031, 987, 789 cm⁻¹. HRMS

(ESI) m/z calcd for $C_{24}H_{17}FNO_2$ $[M+H]^+$ 370.1238, found 370.1239.

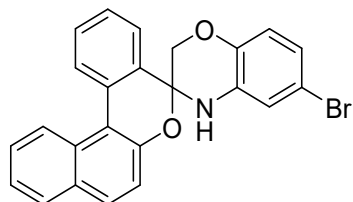
6-Chloro-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3ra)



White solid. 35.5 mg, Yield: 92%, mp 217-219 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

1H NMR (400 MHz, $CDCl_3$ ppm) δ 8.57 (d, $J = 8.6$ Hz, 1H), 8.19 (d, $J = 7.9$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.80 (d, $J = 8.8$ Hz, 1H), 7.59 (q, $J = 8.2$ Hz, 3H), 7.48 (m, 2H), 7.31 – 7.21 (m, 1H), 6.86 (d, $J = 8.4$ Hz, 1H), 6.83 – 6.73 (m, 2H), 4.95 (s, 1H), 4.54 (d, $J = 11.4$ Hz, 1H), 4.01 (d, $J = 11.4$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 142.1, 132.9, 132.0, 130.9, 130.9, 130.5, 129.9, 129.4, 129.1, 128.0, 127.1, 127.1, 126.6, 124.4, 124.2, 124.1, 120.0, 119.1, 117.6, 116.1, 115.6, 83.2, 66.4. IR (ATR) ν_{max} : 3343, 2912, 2844, 1610, 1592, 1501, 1472, 1378, 1282, 1229, 1211, 1037, 943, 746 cm^{-1} . HRMS (ESI) m/z calcd for $C_{24}H_{17}ClNO_2$ $[M+Na]^+$ 408.0762, found 408.0764. HRMS (ESI) m/z calcd for $C_{24}H_{17}^{37}ClNO_2$ $[M+H]^+$ 388.0913, found 388.0916.

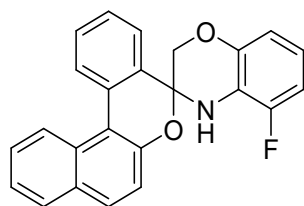
6-Bromo-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3sa)



White solid. 40.7 mg, Yield: 95%, mp 248-249 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

1H NMR (400 MHz, $CDCl_3$ ppm) δ 8.57 (d, $J = 8.6$ Hz, 1H), 8.18 (d, $J = 7.8$ Hz, 1H), 7.89 (d, $J = 8.1$ Hz, 1H), 7.80 (d, $J = 8.8$ Hz, 1H), 7.59 (q, $J = 8.2$ Hz, 3H), 7.46 (q, $J = 6.8$ Hz, 2H), 7.26 (d, $J = 8.8$ Hz, 1H), 6.97 – 6.88 (m, 2H), 6.81 (d, $J = 8.4$ Hz, 1H), 4.94 (s, 1H), 4.54 (d, $J = 11.4$ Hz, 1H), 4.01 (d, $J = 11.4$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$ ppm) δ 150.2, 142.6, 132.9, 132.4, 130.9, 130.9, 130.5, 129.9, 129.4, 129.1, 128.0, 127.1, 127.1, 124.4, 124.2, 124.1, 122.9, 119.0, 118.4, 118.0, 116.1, 113.8, 83.2, 66.4. IR (ATR) ν_{max} : 3353, 2966, 2922, 1590, 1492, 1467, 1443, 1283, 1232, 1210, 1036, 751, 536 cm^{-1} . HRMS (ESI) m/z calcd for $C_{24}H_{17}BrNO_2$ $[M+H]^+$ 430.0437, found 430.0437. HRMS (ESI) m/z calcd for $C_{24}H_{17}^{81}BrNO_2$ $[M+H]^+$ 432.0417, found 432.0416.

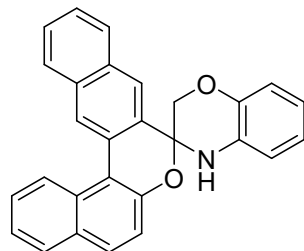
5-Fluoro-2H,4H-spiro[benzo[b][1,4]oxazine-3,5'-dibenzo[c,f]chromene] (3va)



White solid. 36.1 mg, Yield: 98%, mp 184-185 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.60 (d, *J* = 8.6 Hz, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.61 (q, *J* = 7.2 Hz, 2H), 7.49 (q, *J* = 6.9 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 1H), 6.78 (d, *J* = 6.2 Hz, 3H), 5.07 (s, 1H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.02 (d, *J* = 11.4 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃, ppm) δ 151.8 (d *J* = 239.2 Hz), 150.3, 144.8 (d *J* = 5.4 Hz), 133.0, 130.9, 130.6, 129.9, 129.5, 129.1, 128.0, 127.1, 127.1, 124.6, 124.4, 124.1, 120.3 (d *J* = 15.5 Hz), 119.1, 118.7 (d *J* = 9.0 Hz), 116.1, 112.1 (d *J* = 2.6 Hz), 108.2 (d *J* = 18.3 Hz), 82.8, 66.3. **¹⁹F NMR** (376 MHz, CDCl₃, ppm) δ -136.06. **IR** (ATR) ν_{max} : 3389, 2914, 1594, 1482, 1304, 1291, 1232, 1195, 1058, 1030, 749 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇FNO₂ [M+H]⁺ 370.1238, found 370.1239.

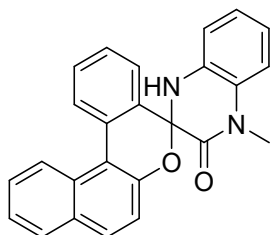
2H,4H-Spiro[benzo[b][1,4]oxazine-3,8'-benzo[f]naphtho[2,3-c]chromene] (3wa)



White solid. 39.3 mg, Yield: 98%, mp 194-196 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.70 (d, *J* = 8.6 Hz, 1H), 8.45 (s, 1H), 8.10 (s, 1H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.83 (dd, *J* = 16.9, 8.4 Hz, 2H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 1H), 6.96 (ddd, *J* = 17.7, 7.7, 1.6 Hz, 2H), 6.92 – 6.81 (m, 3H), 5.06 (s, 1H), 4.59 (dd, *J* = 11.5, 2.5 Hz, 1H), 4.03 (d, *J* = 11.5 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃, ppm) δ 150.8, 143.6, 133.6, 132.8, 132.4, 131.1, 131.0, 130.8, 130.3, 129.2, 128.1, 128.0, 127.6, 127.2, 127.1, 126.5, 126.1, 124.5, 124.1, 122.0, 120.3, 119.4, 116.7, 116.2, 116.0, 84.1, 66.6. **IR** (ATR) ν_{max} : 3360, 2977, 2909, 1588, 1498, 1429, 1311, 1294, 1229, 1207, 1038, 739 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₈H₂₀NO₂ [M+H]⁺ 402.1489, found 402.1491.

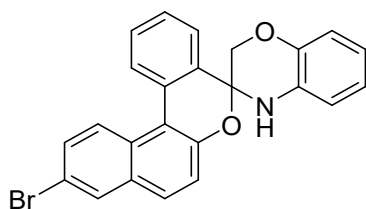
4'-Methyl-1',4'-dihydro-3'*H*-spiro[dibenzo[*c,f*]chromene-5,2'-quinoxalin]-3'-one (3xa)



Yellow solid. 37.0 mg, Yield: 98%, mp 194-196 °C. column chromatography eluent, EtOAc/PE = 1:20 → 1:5

¹H NMR (400 MHz, DMSO-*d*₆ ppm) δ 9.21 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.56 – 7.43 (m, 2H), 7.37 (q, *J* = 8.3, 7.9 Hz, 3H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.16 (dt, *J* = 15.3, 7.5 Hz, 2H), 7.03 (dd, *J* = 17.3, 8.3 Hz, 2H), 3.48 (s, 3H). **¹³C NMR** (100 MHz, DMSO-*d*₆ ppm) δ 156.1, 154.2, 151.7, 137.6, 136.6, 134.1, 133.4, 132.5, 132.2, 130.6, 130.3, 129.3, 129.2, 128.7, 128.1, 128.0, 126.7, 126.0, 125.2, 123.5, 122.6, 120.9, 118.3, 114.8, 29.4. **IR** (ATR) ν_{max} : 3062, 2912, 1664, 1648, 1585, 1467, 1298, 1226, 1032, 745 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₅H₁₉N₂O₂ [M+H]⁺ 379.1441, found 379.1441.

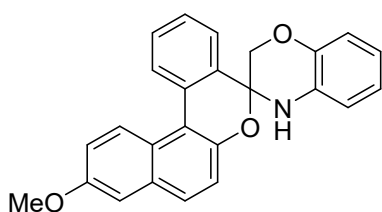
10'-Bromo-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3ab)



White solid. 41.6 mg, Yield: 97%, mp 203-205 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.43 (d, *J* = 9.1 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 8.02 (s, 1H), 7.71 – 7.61 (m, 3H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 6.99 – 6.89 (m, 2H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 4.88 (s, 1H), 4.51 (d, *J* = 11.4 Hz, 1H), 4.03 (d, *J* = 11.2 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃ ppm) δ 150.7, 143.4, 133.4, 132.1, 131.0, 130.8, 130.1, 130.1, 129.8, 129.4, 128.4, 128.2, 126.9, 126.2, 124.5, 122.0, 120.4, 117.6, 116.7, 116.4, 115.9, 83.9, 66.3. **IR** (ATR) ν_{max} : 3371, 2912, 1584, 1498, 1481, 1427, 1307, 1231, 1203, 1038, 736, 533 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇BrNO₂ [M+H]⁺ 430.0437, found 430.0438. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇⁸¹BrNO₂ [M+H]⁺ 432.0417, found 432.0417.

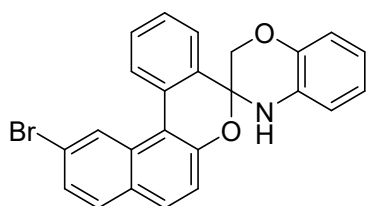
10'-Methoxy-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3ac)



White solid. 36.5 mg, Yield: 96%, mp 162-164 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl₃ ppm) δ 8.48 (d, *J* = 9.0 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 9.7 Hz, 2H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.34 – 7.17 (m, 3H), 7.00 – 6.89 (m, 2H), 6.85 (t, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 4.90 (s, 1H), 4.55 (d, *J* = 11.3 Hz, 1H), 4.04 (d, *J* = 11.4 Hz, 1H), 3.98 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃ ppm) δ 156.1, 148.9, 143.5, 133.6, 132.1, 131.0, 130.6, 129.5, 129.2, 127.9, 127.0, 125.9, 125.0, 124.4, 121.9, 120.2, 119.6, 119.1, 116.7, 116.5, 115.9, 107.5, 83.5, 66.3, 55.4. **IR** (ATR) ν_{\max} : 3376, 2920, 1603, 1500, 1472, 1429, 1309, 1236, 1284, 1204, 1030, 744 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₅H₂₀NO₃ [M+H]⁺ 382.1438, found 382.1438.

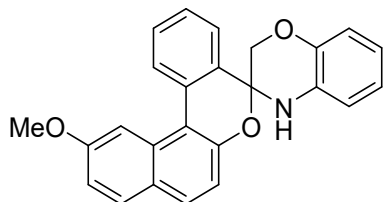
11'-Bromo-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3ad)



White solid. 42.0 mg, Yield: 98%, mp 180-182 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, DMSO-*d*₆ ppm) δ 8.62 (s, 1H), 8.05 (d, *J* = 7.7 Hz, 1H), 7.93 (dd, *J* = 18.3, 8.6 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.65 – 7.52 (m, 3H), 7.27 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.87 – 6.76 (m, 3H), 6.68 (s, 1H), 4.42 (d, *J* = 11.6 Hz, 1H), 4.03 (d, *J* = 11.3 Hz, 1H). **¹³C NMR** (100 MHz, DMSO-*d*₆ ppm) δ 151.6, 143.0, 133.4, 132.3, 131.7, 131.1, 130.0, 129.7, 129.3, 128.6, 127.4, 126.7, 126.5, 125.5, 122.2, 121.5, 120.1, 119.1, 116.4, 115.8, 115.7, 84.4, 66.4. **IR** (ATR) ν_{\max} : 3347, 1610, 1499, 1426, 1308, 1273, 1226, 1206, 1033, 740, 543 cm⁻¹. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇BrNO₂ [M+H]⁺ 430.0437, found 430.0439. **HRMS (ESI)** *m/z* calcd for C₂₄H₁₇⁸¹BrNO₂ [M+H]⁺ 432.0417, found 432.0420.

11'-Methoxy-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (3ae)

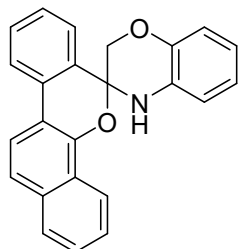


White solid. 36.5 mg, Yield: 96%, mp 227-229 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, DMSO-*d*₆ ppm) δ 8.27 (d, *J* = 7.9 Hz, 1H), 7.95 – 7.85 (m, 2H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.72 – 7.60 (m, 2H), 7.60 – 7.49 (m, 2H), 7.15 (d, *J* = 8.9 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 1H), 6.85 (q, *J* = 8.4 Hz, 3H), 6.69 (d, *J* = 7.6 Hz, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 3.96 (d, *J* = 17.1 Hz, 4H). **¹³C NMR** (100 MHz, DMSO-*d*₆ ppm) δ 159.0, 151.5, 143.0, 133.3, 132.5, 131.3, 131.1, 130.9, 130.6, 129.8, 128.1, 126.1,

126.0, 125.6, 122.1, 119.0, 116.8, 116.3, 116.1, 115.9, 115.5, 104.4, 84.1, 66.2, 55.6.
IR (ATR) ν_{max} : 3345, 1617, 1484, 1438, 1421, 1310, 1251, 1224, 1207, 1036, 749 cm^{-1} .
HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{20}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 382.1438, found 382.1439.

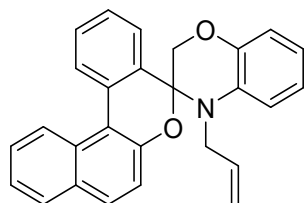
2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-dibenzo[*c,h*]chromene] (3af)



White solid. 33.7 mg, Yield: 96%, mp 188-190 °C. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

¹H NMR (400 MHz, CDCl_3 ppm) δ 8.17 (d, $J = 8.3$ Hz, 1H), 7.88 (d, $J = 8.3$ Hz, 2H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.53 (ddd, $J = 28.1, 13.0, 7.4$ Hz, 4H), 7.42 (q, $J = 7.5$ Hz, 2H), 7.03 – 6.93 (m, 2H), 6.89 (t, $J = 7.7$ Hz, 1H), 6.84 (d, $J = 7.7$ Hz, 1H), 4.99 (s, 1H), 4.50 (d, $J = 11.3$ Hz, 1H), 3.94 (d, $J = 11.3$ Hz, 1H). **¹³C NMR** (100 MHz, CDCl_3 ppm) δ 147.2, 143.6, 134.6, 131.3, 131.1, 131.1, 129.9, 128.2, 127.4, 127.0, 126.1, 126.0, 125.3, 122.6, 122.5, 121.8, 121.8, 120.9, 120.2, 116.6, 116.0, 115.4, 84.5, 67.9.
IR (ATR) ν_{max} : 3345, 2916, 1595, 1583, 1496, 1479, 1426, 1307, 1260, 1208, 1043, 734 cm^{-1} . **HRMS (ESI)** m/z calcd for $\text{C}_{24}\text{H}_{18}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 352.1332, found 352.1333.

4-allyl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,5'-dibenzo[*c,f*]chromene] (4aa)



Yellow liquid. 30.1 mg, Yield: 77%. column chromatography eluent, EtOAc/PE = 1:100 → 1:50

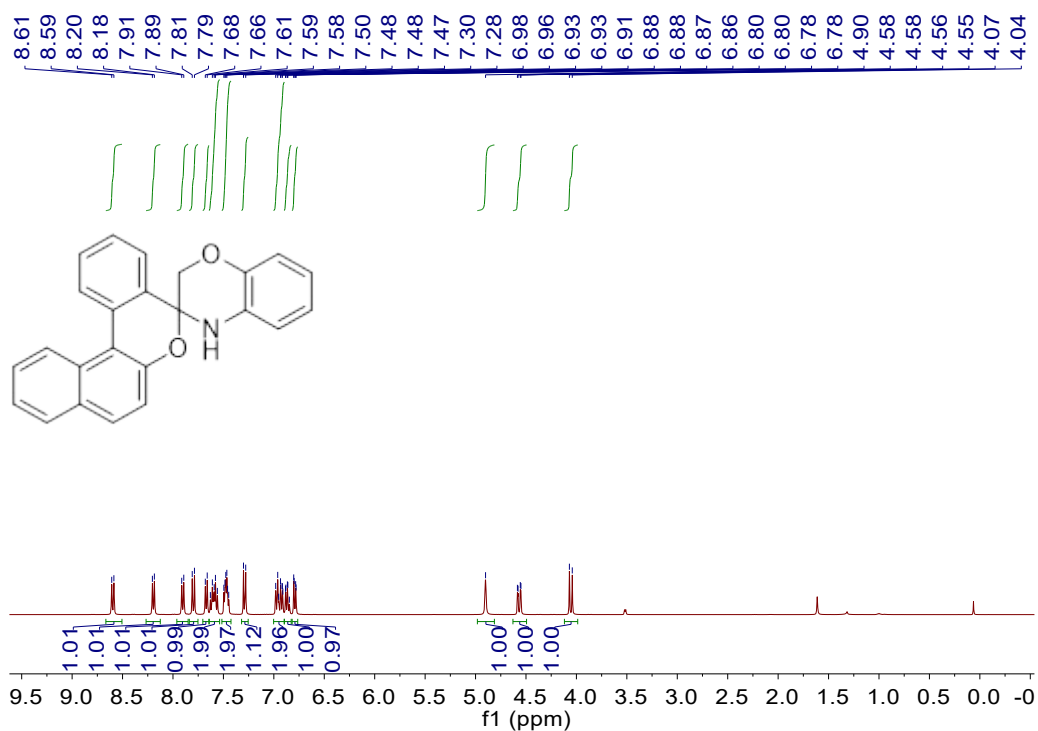
¹H NMR (400 MHz, CDCl_3 ppm) δ 8.04 (d, $J = 6.8$ Hz, 1H), 7.91 (d, $J = 9.0$ Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 7.60 (q, $J = 7.2, 6.6$ Hz, 2H), 7.48 (d, $J = 8.1$ Hz, 1H), 7.39 (m, 6.4 Hz, 4H), 7.32 (d, $J = 9.0$ Hz, 1H), 7.07 (t, $J = 7.7$ Hz, 1H), 6.98 (t, $J = 7.5$ Hz, 1H), 6.74 (d, $J = 7.9$ Hz, 1H), 5.91 (m, 1H), 5.19 (dd, $J = 28.9, 13.9$ Hz, 2H), 4.61 (d, $J = 4.9$ Hz, 2H), 4.02 (d, $J = 14.3$ Hz, 1H), 3.70 (d, $J = 14.3$ Hz, 1H). **¹³C NMR** (100 MHz, CDCl_3 ppm) δ 162.2, 153.0, 146.5, 139.0, 135.3, 134.5, 133.4, 133.2, 132.1, 130.3, 130.0, 129.0, 128.8, 128.3, 128.1, 128.0, 127.5, 127.2, 124.9, 124.0, 123.8, 122.2, 117.4, 115.4, 114.5, 69.7, 63.9. **IR** (ATR) ν_{max} : 3058, 2881, 1610, 1587, 1503, 1472, 1256, 1219, 1047, 1005, 984, 799, 752 cm^{-1} . **HRMS (ESI)** m/z calcd for $\text{C}_{27}\text{H}_{21}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 392.1645, found 392.1648.

7. References

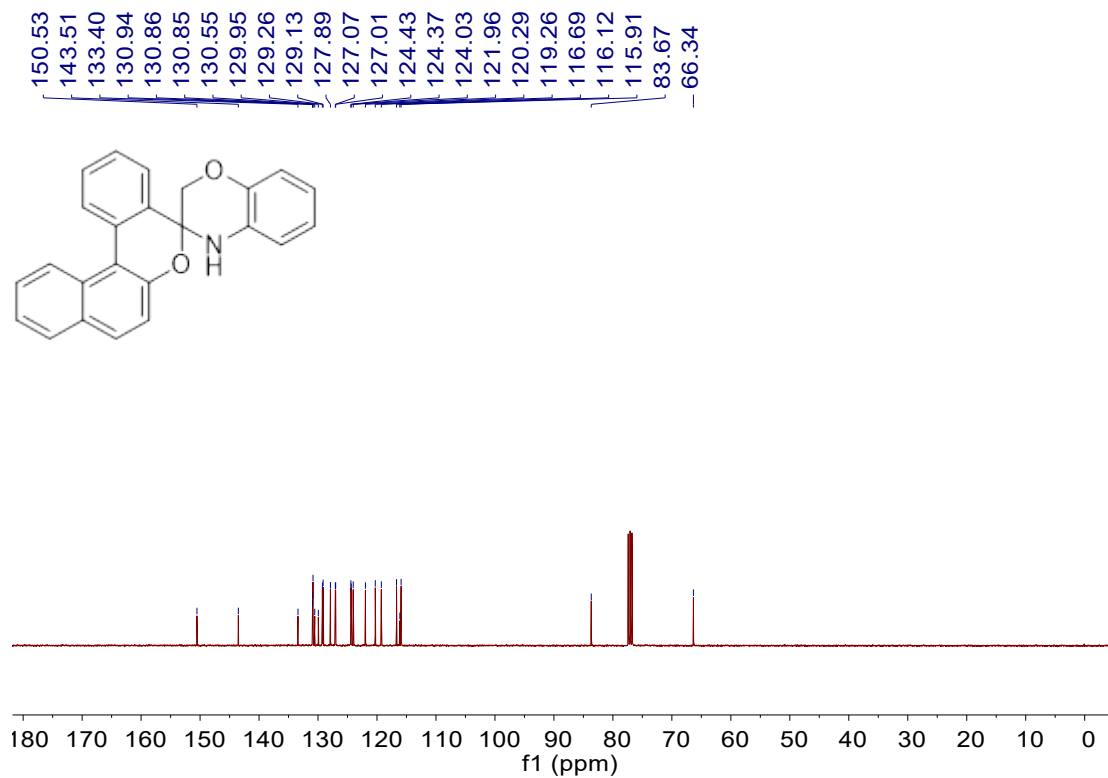
1. K. Gao, C.-B. Yu, D.-S. Wang and Y.-G. Zhou, *Adv. Synth. Catal.*, **2012**, 354, 483-488.
2. X. Han, L. Kong, J. Feng, X. Li, *Chem. Commun.*, **2020**, 56, 5528-5531;

8. Copies of NMR Spectra.

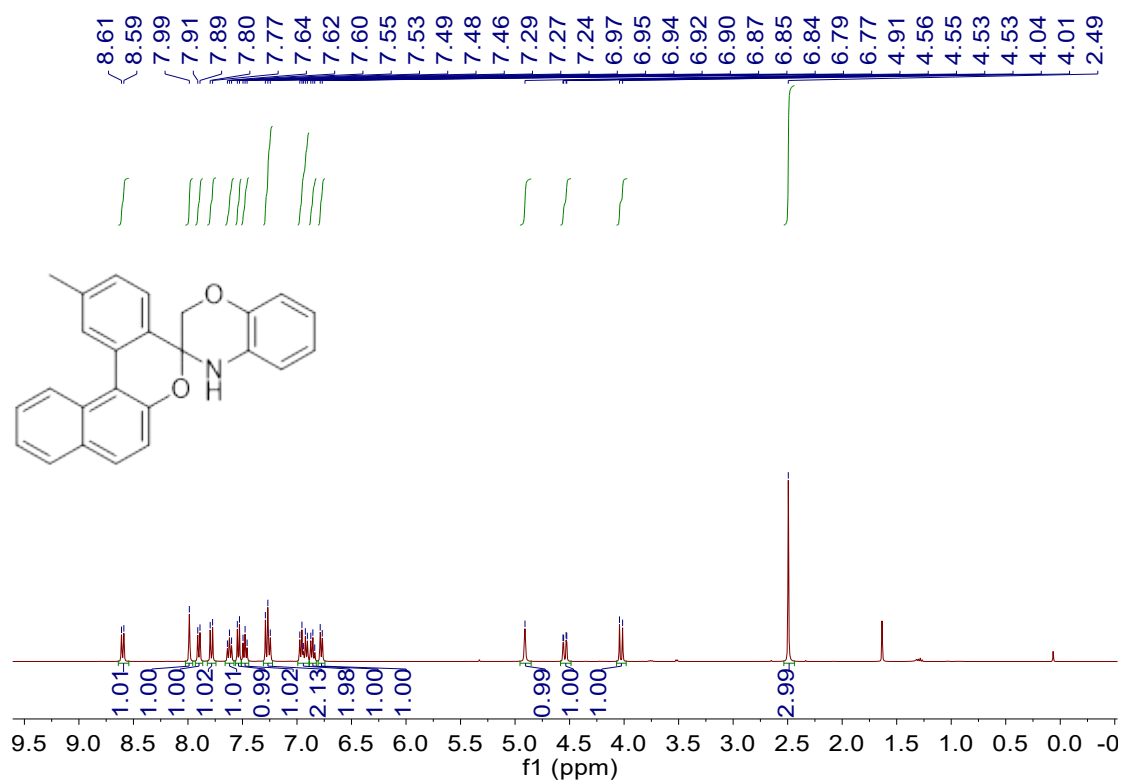
^1H NMR (CDCl_3) spectrum of **3aa**



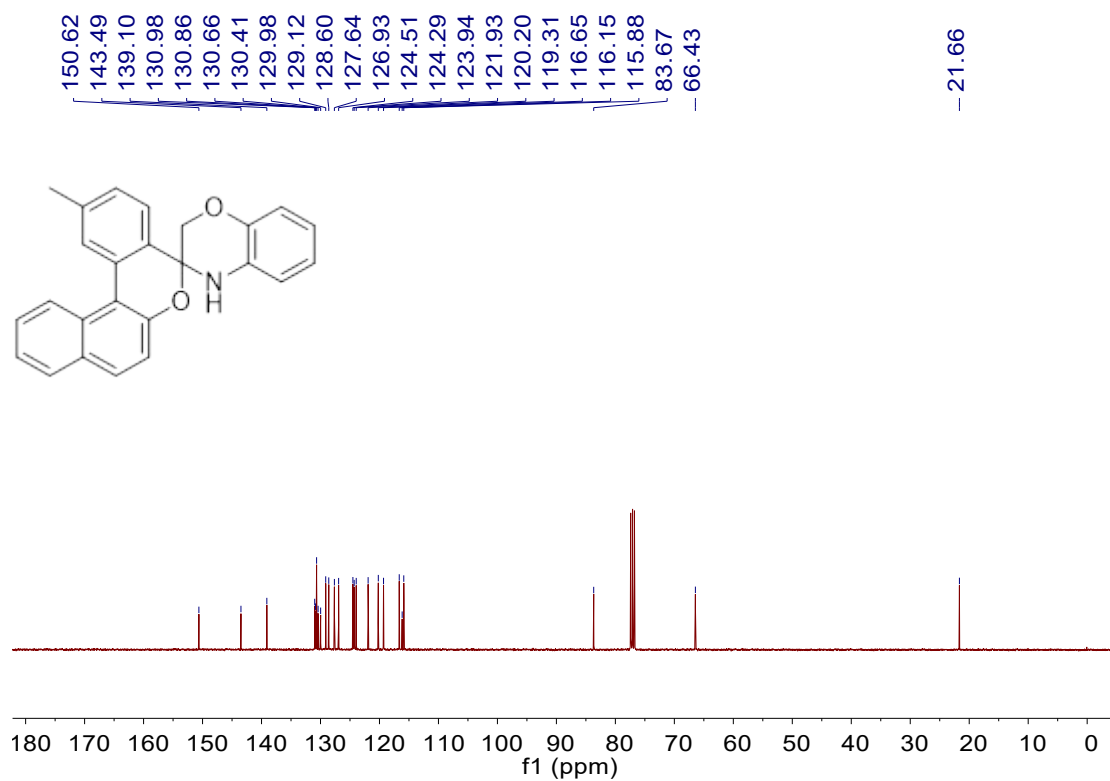
^{13}C NMR (CDCl_3) spectrum of **3aa**



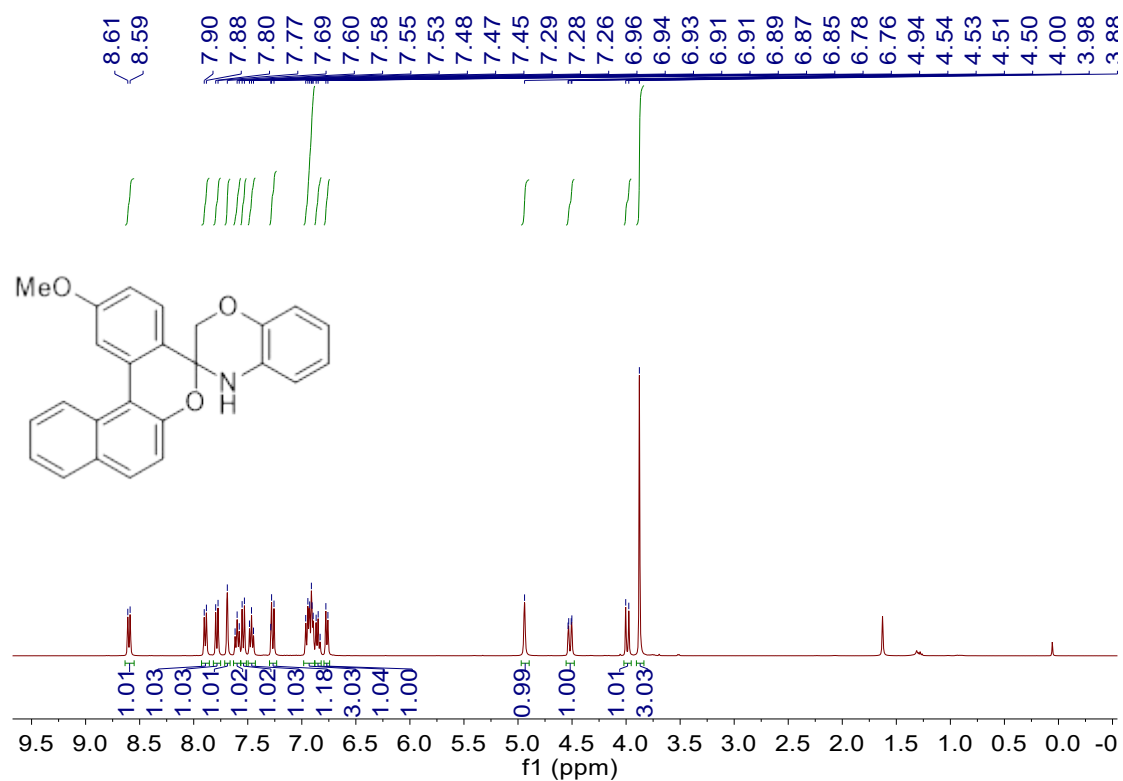
¹H NMR (CDCl₃) spectrum of **3ba**



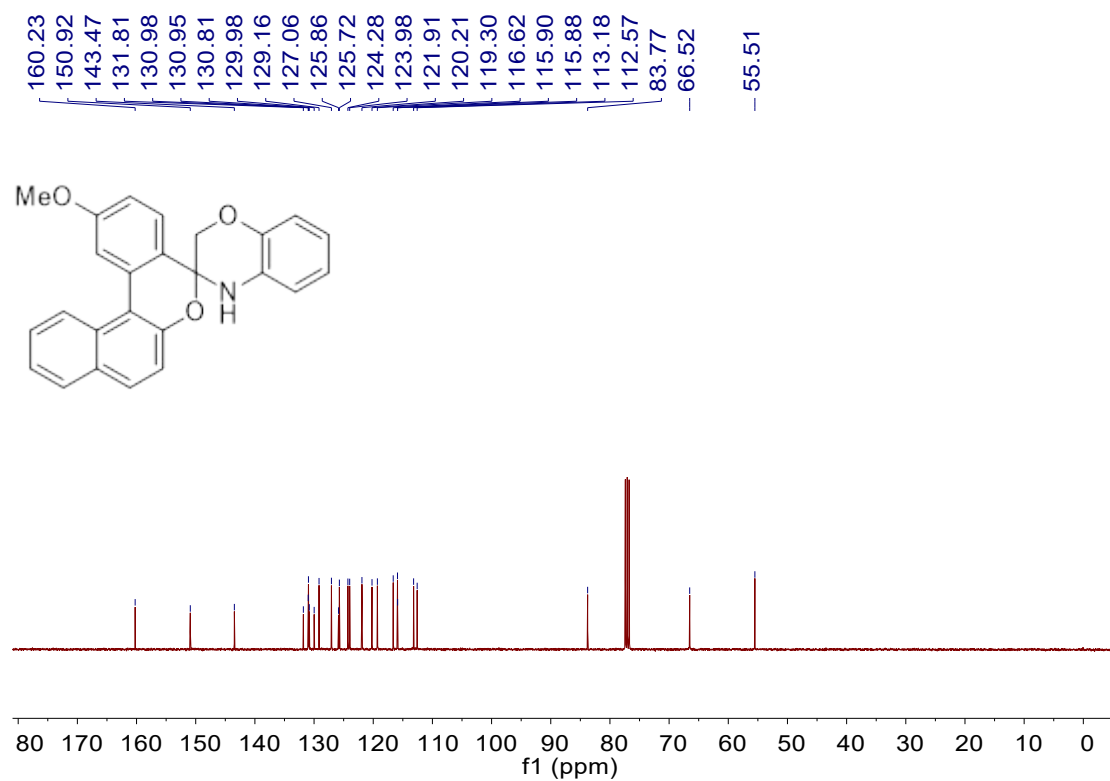
¹³C NMR (CDCl₃) spectrum of **3ba**



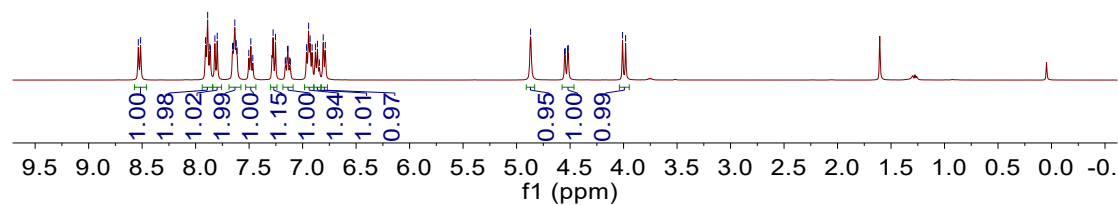
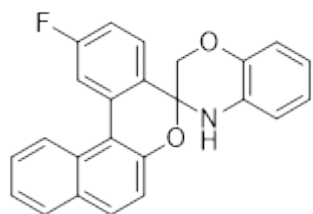
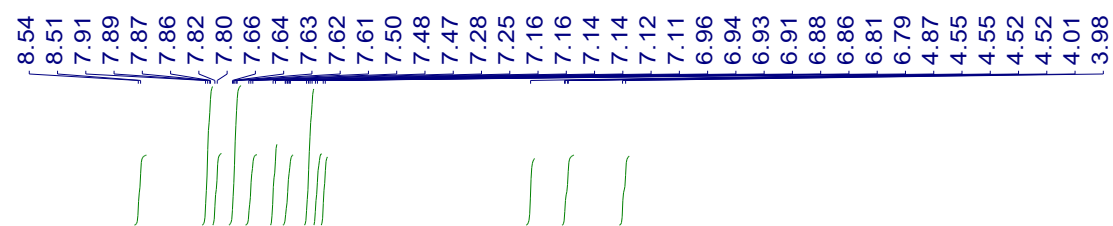
¹H NMR (CDCl₃) spectrum of **3ca**



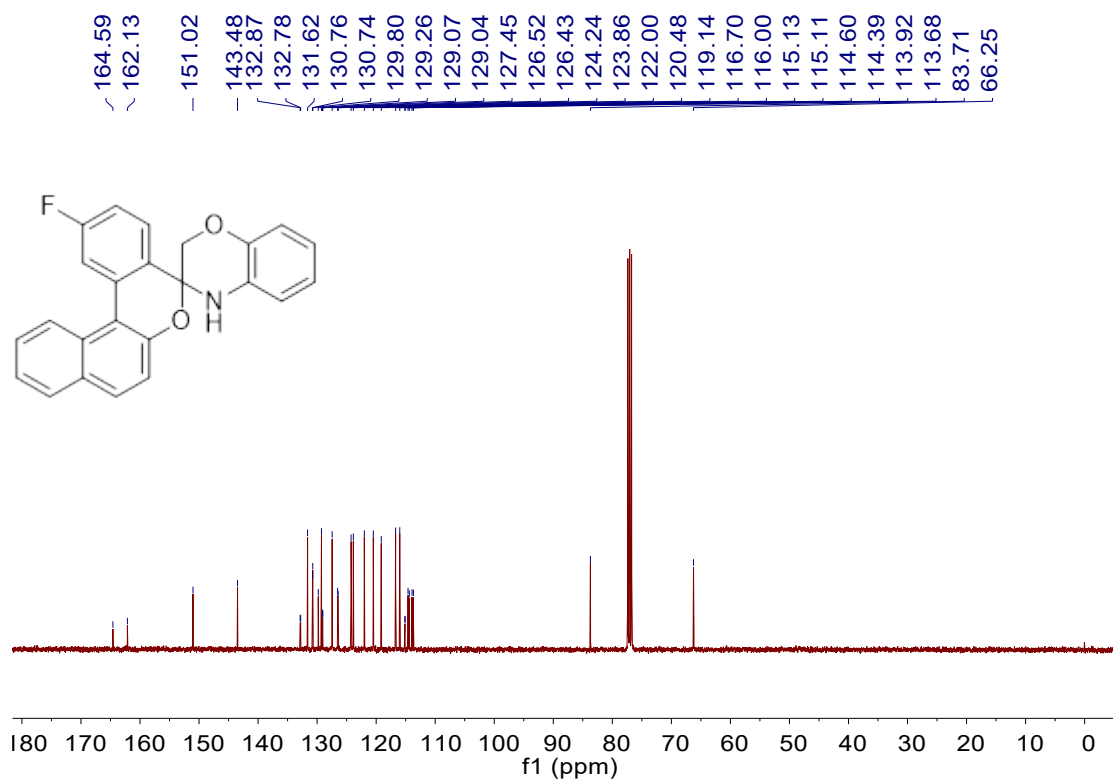
¹³C NMR (CDCl₃) spectrum of **3ca**



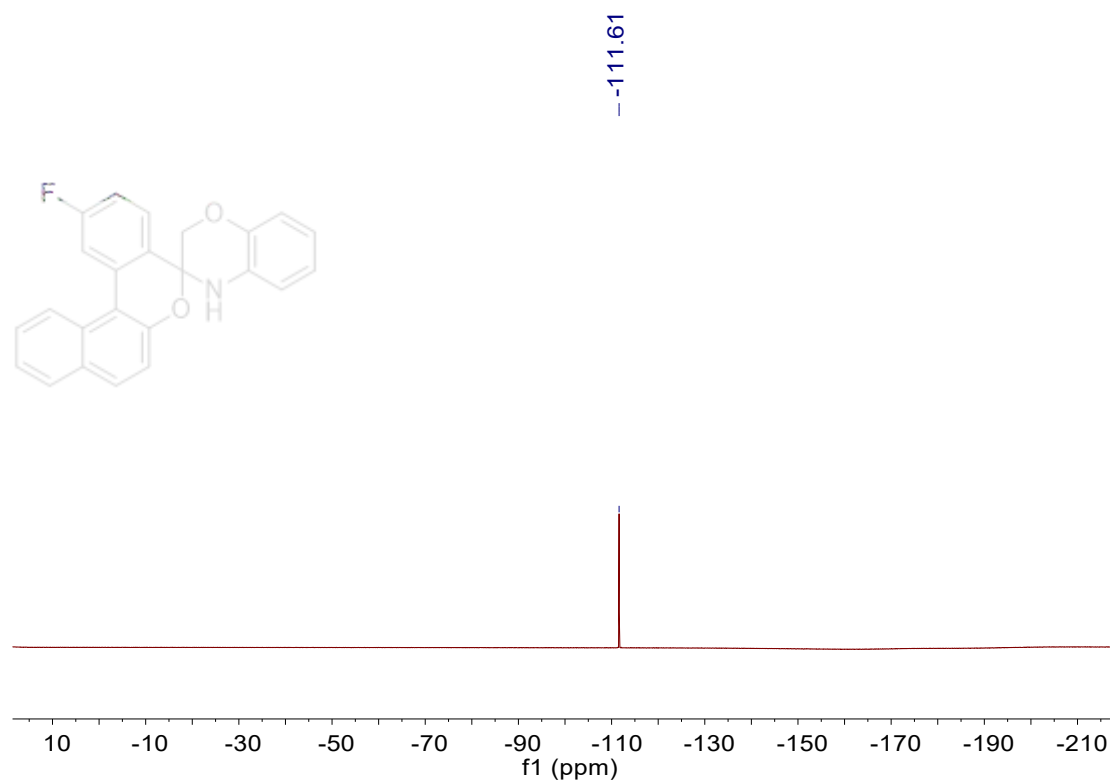
¹H NMR (CDCl₃) spectrum of **3da**



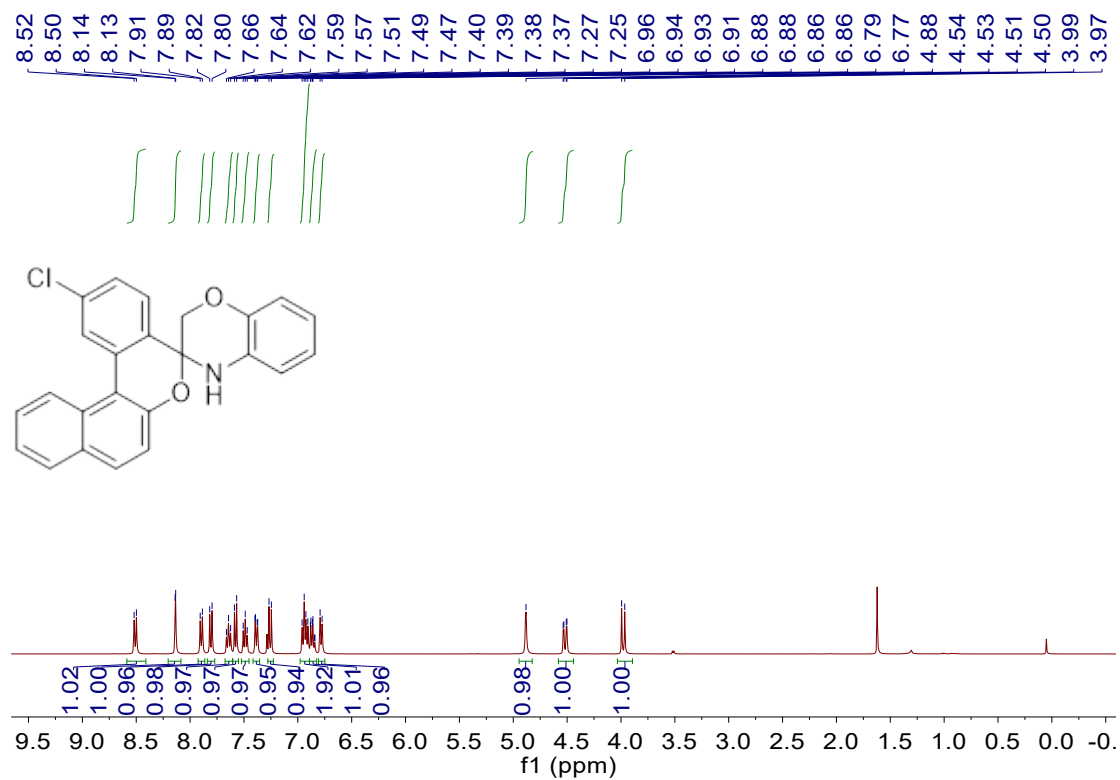
¹³C NMR (CDCl₃) spectrum of **3da**



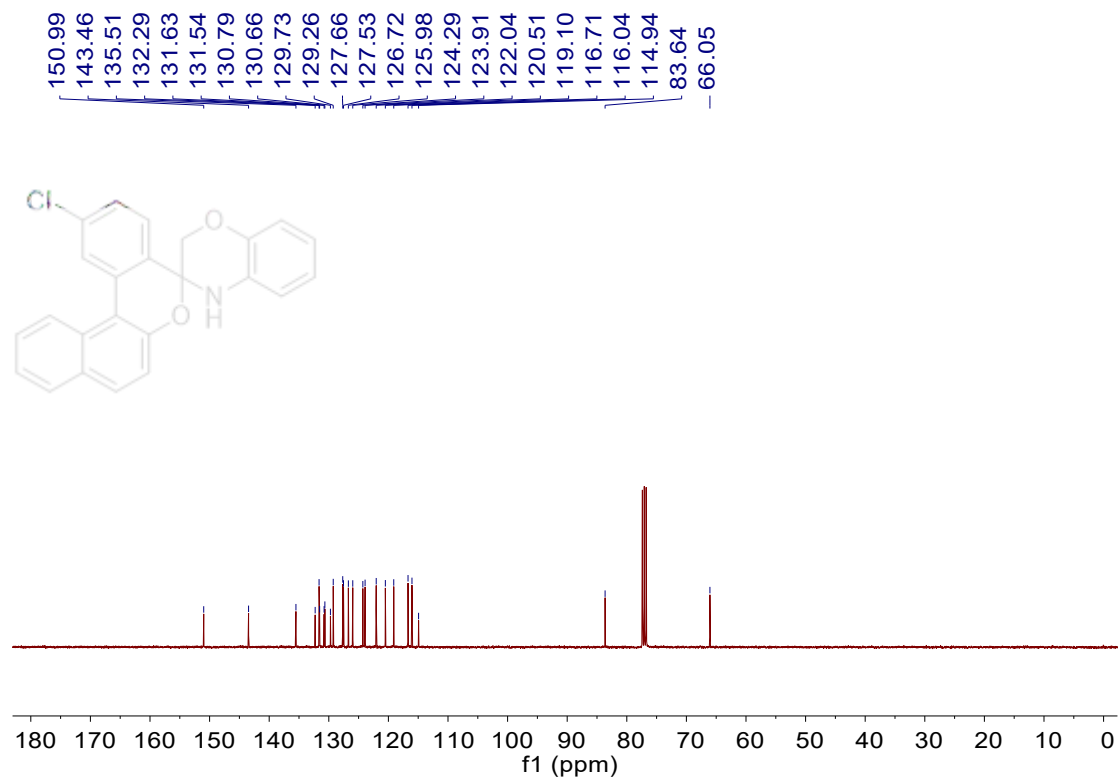
¹⁹F NMR (CDCl₃) spectrum of **3da**



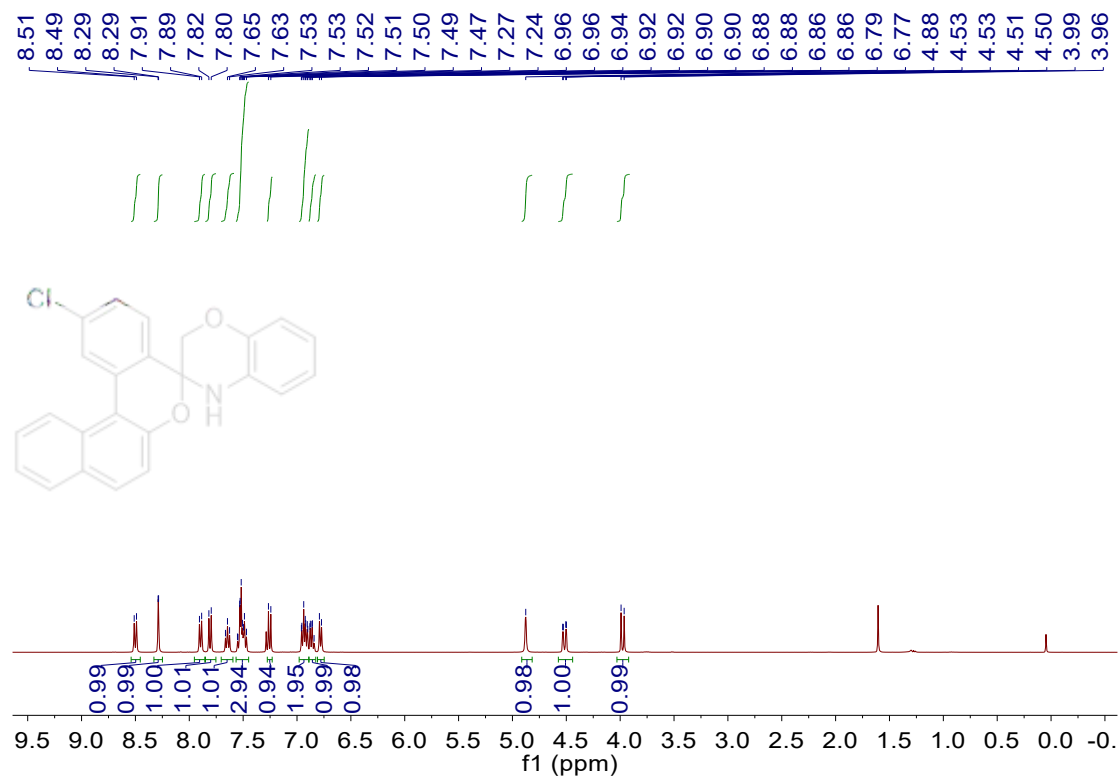
¹H NMR (CDCl₃) spectrum of **3ea**



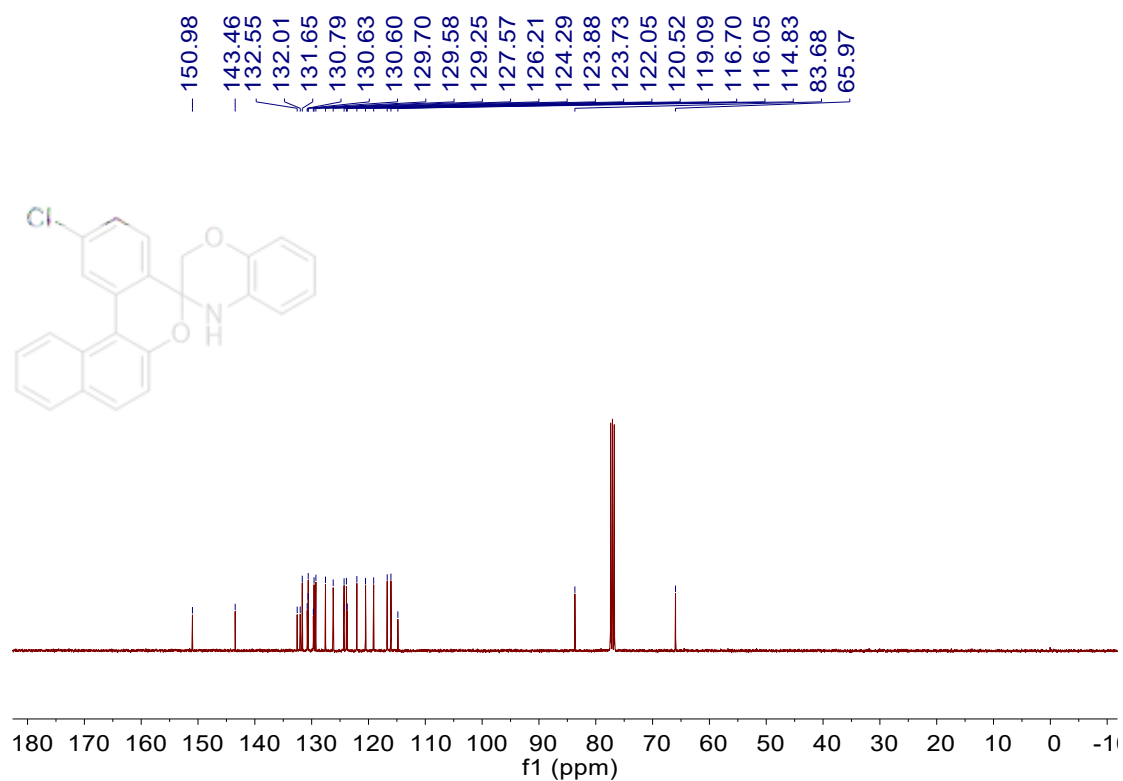
¹³C NMR (CDCl₃) spectrum of **3ea**



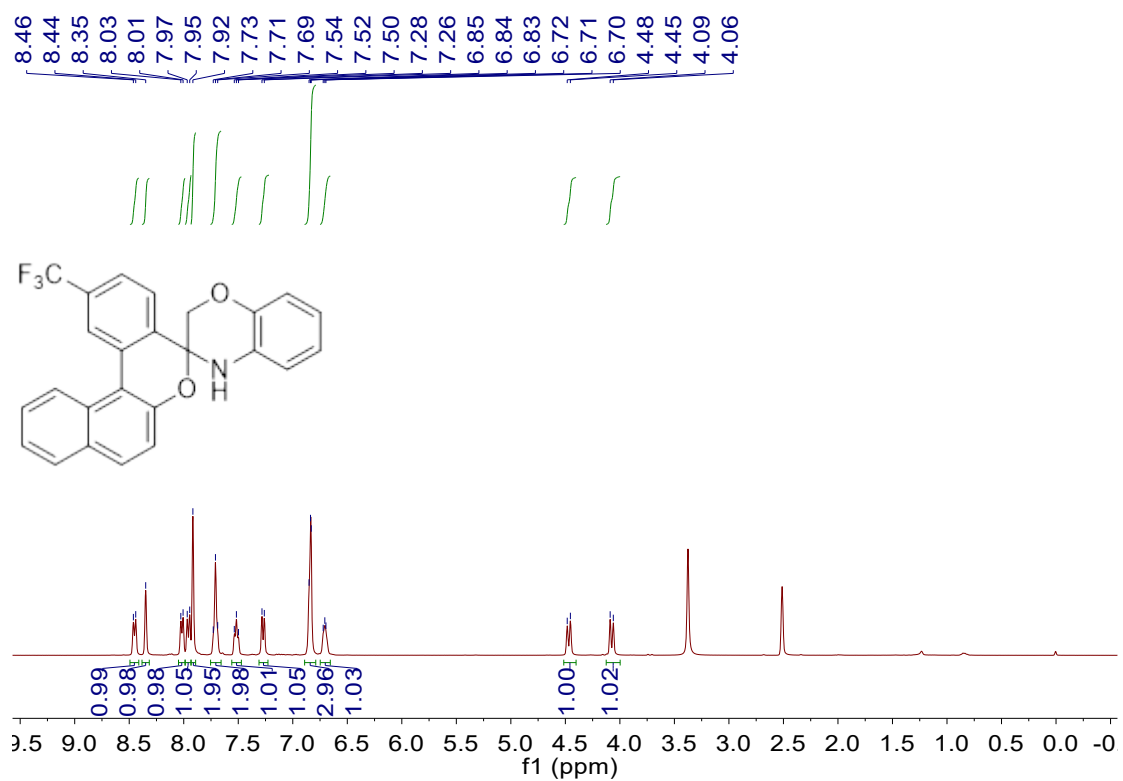
¹H NMR (CDCl₃) spectrum of **3fa**



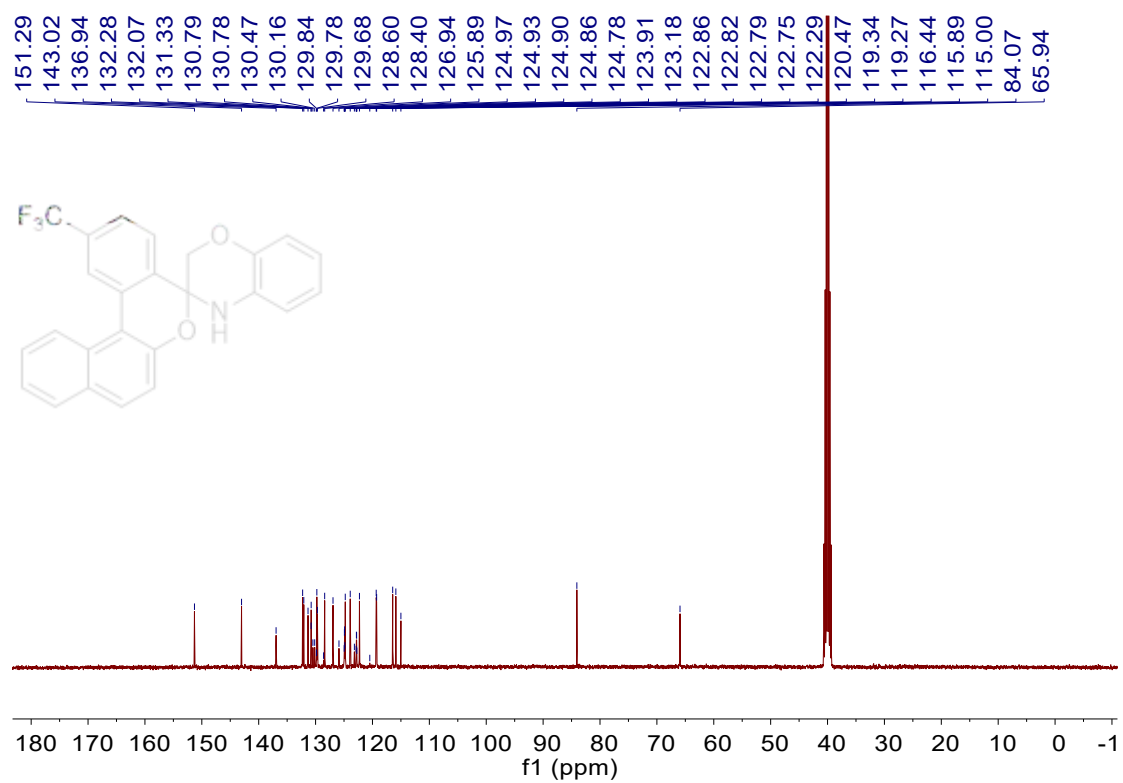
¹³C NMR (CDCl₃) spectrum of **3fa**



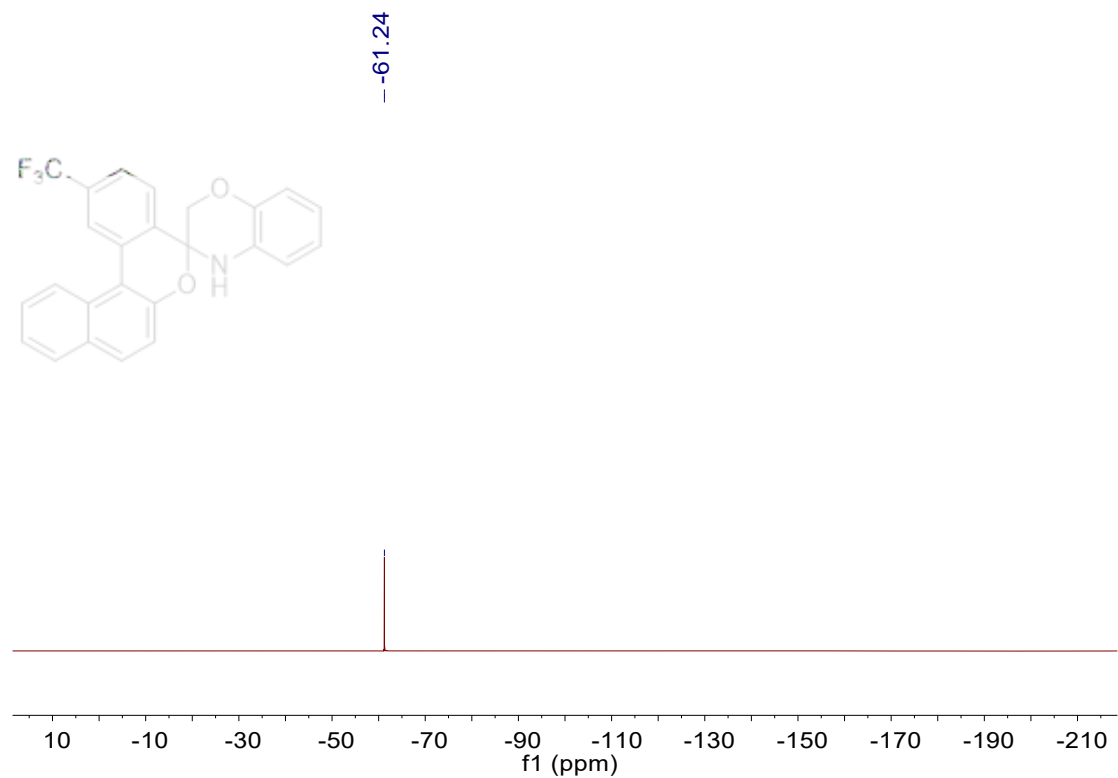
¹H NMR (DMSO-d₆) spectrum of **3ga**



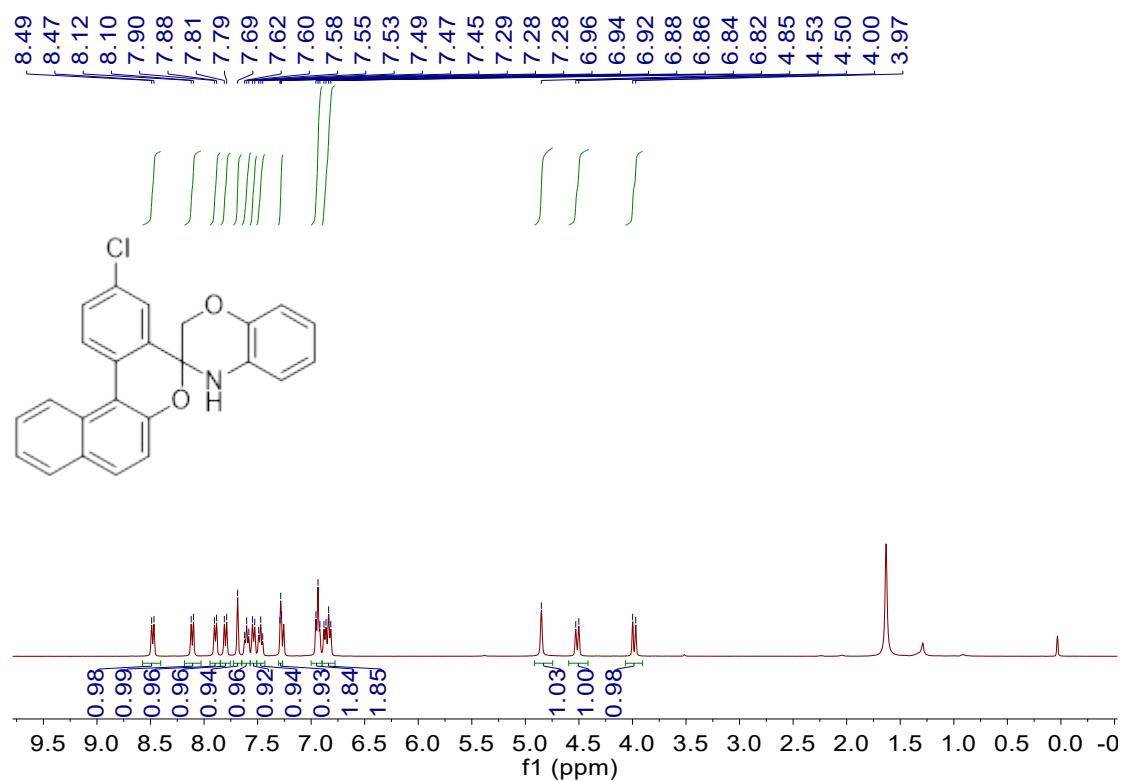
¹³C NMR (DMSO-*d*₆) spectrum of **3ga**



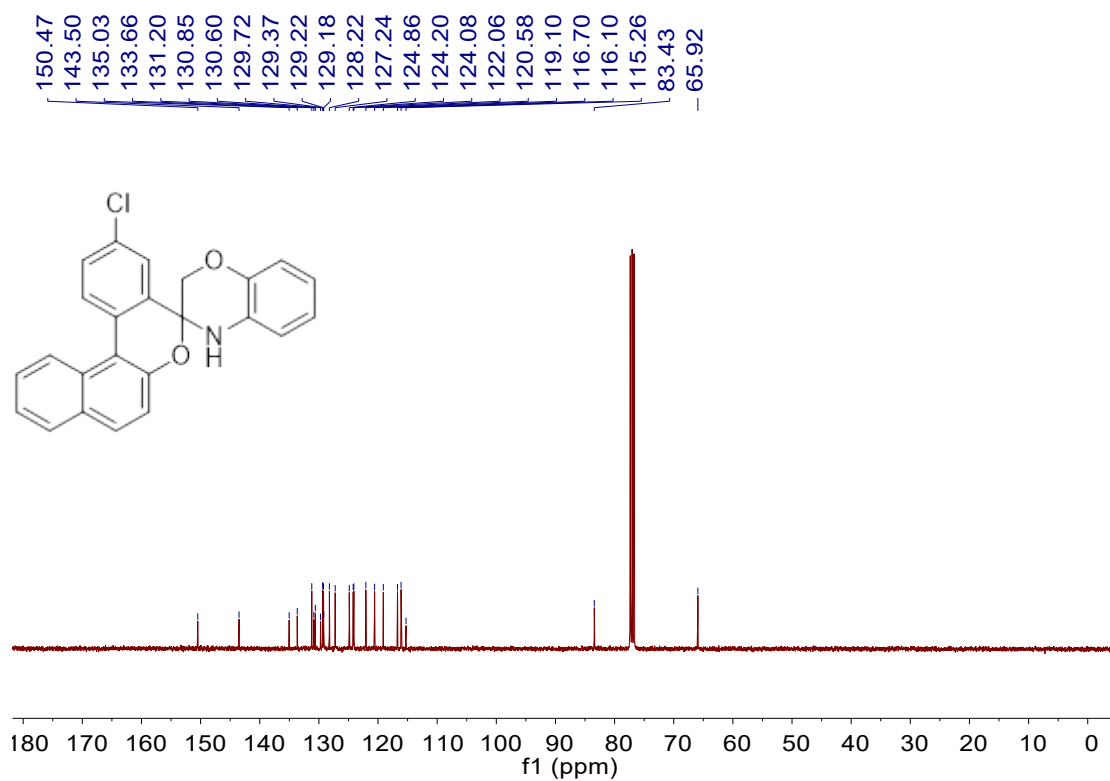
¹⁹F NMR (DMSO-*d*₆) spectrum of **3ga**



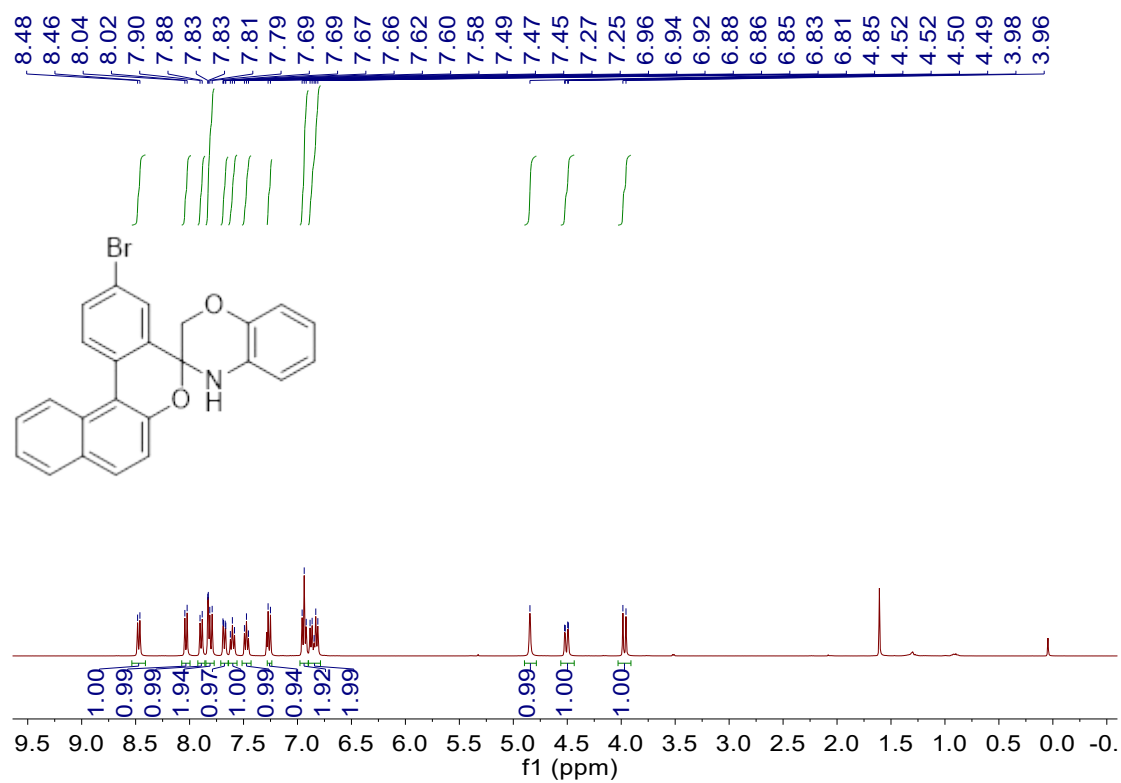
¹H NMR (CDCl₃) spectrum of **3ha**



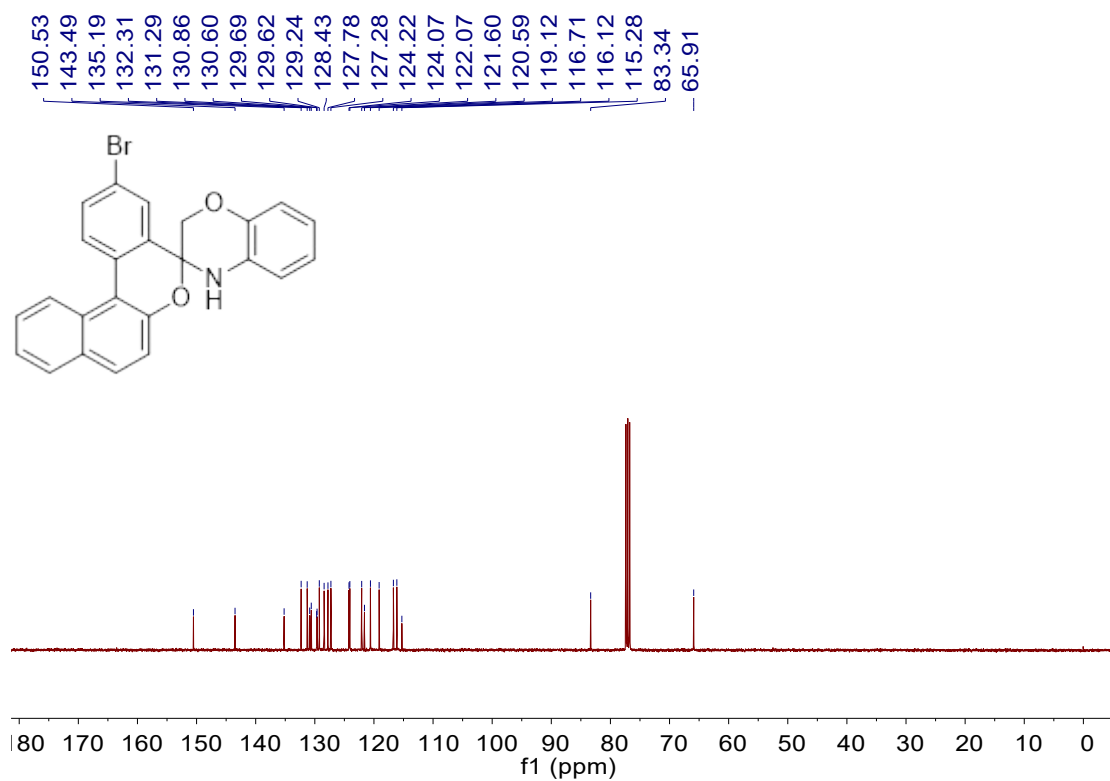
¹³C NMR (CDCl₃) spectrum of **3ha**



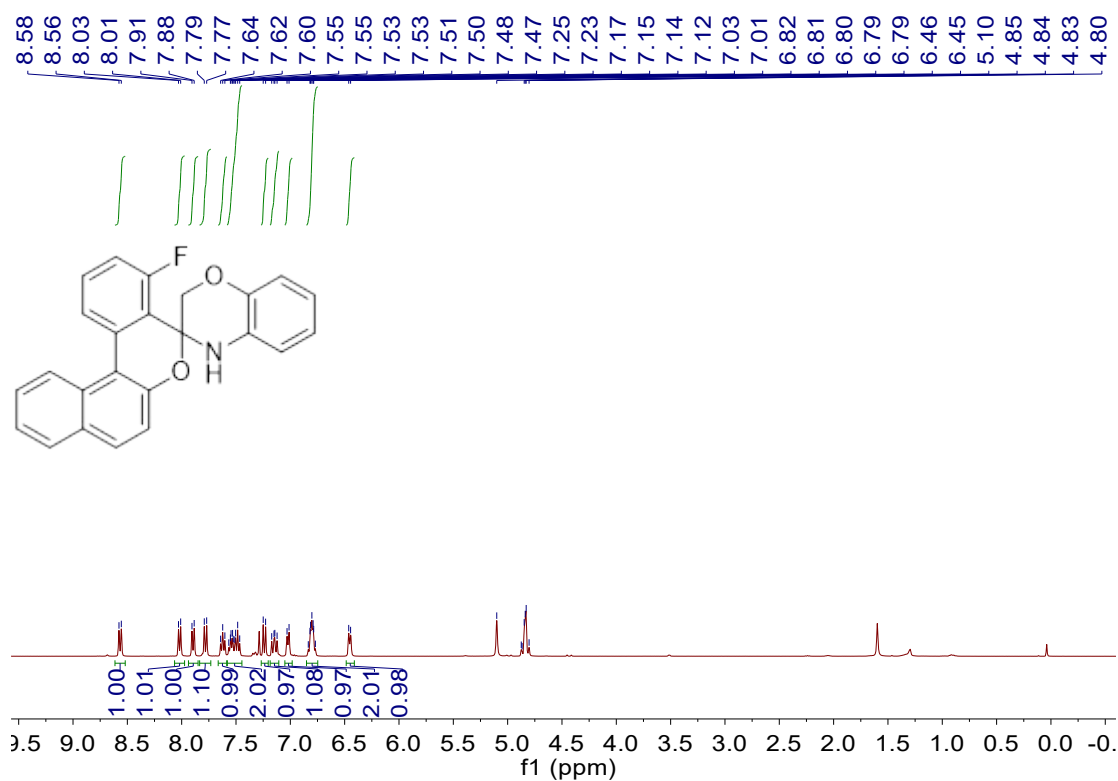
¹H NMR (CDCl₃) spectrum of **3ia**



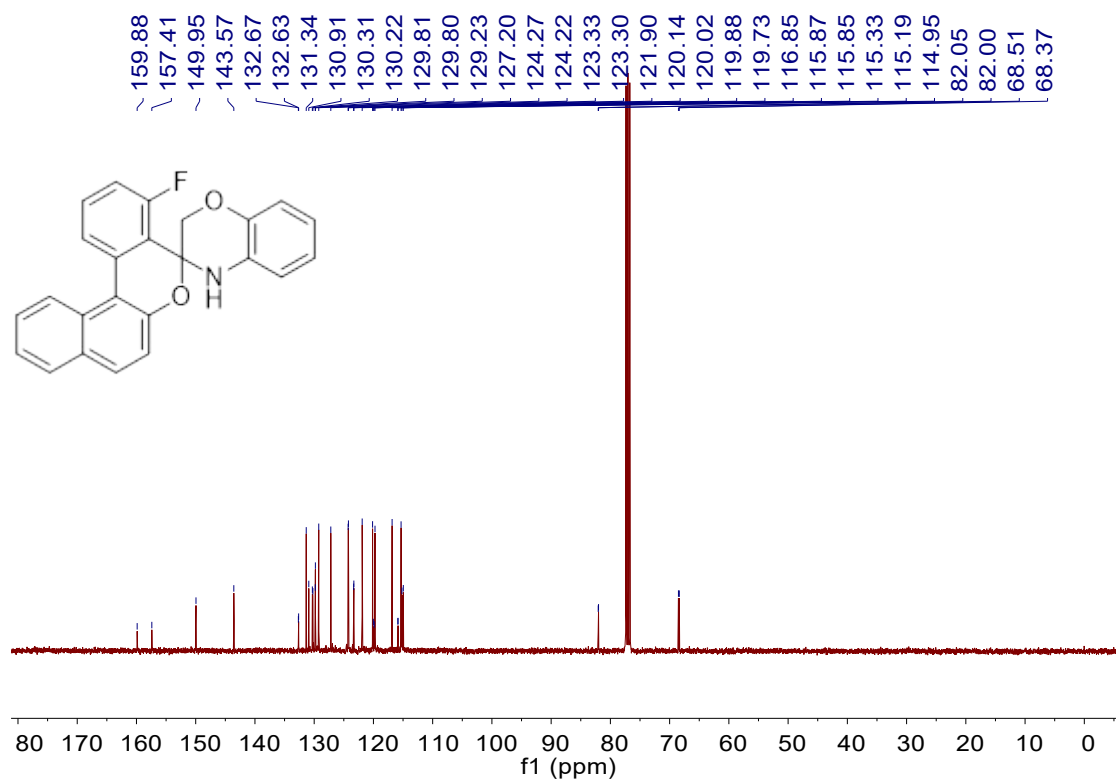
¹³C NMR (CDCl₃) spectrum of **3ia**



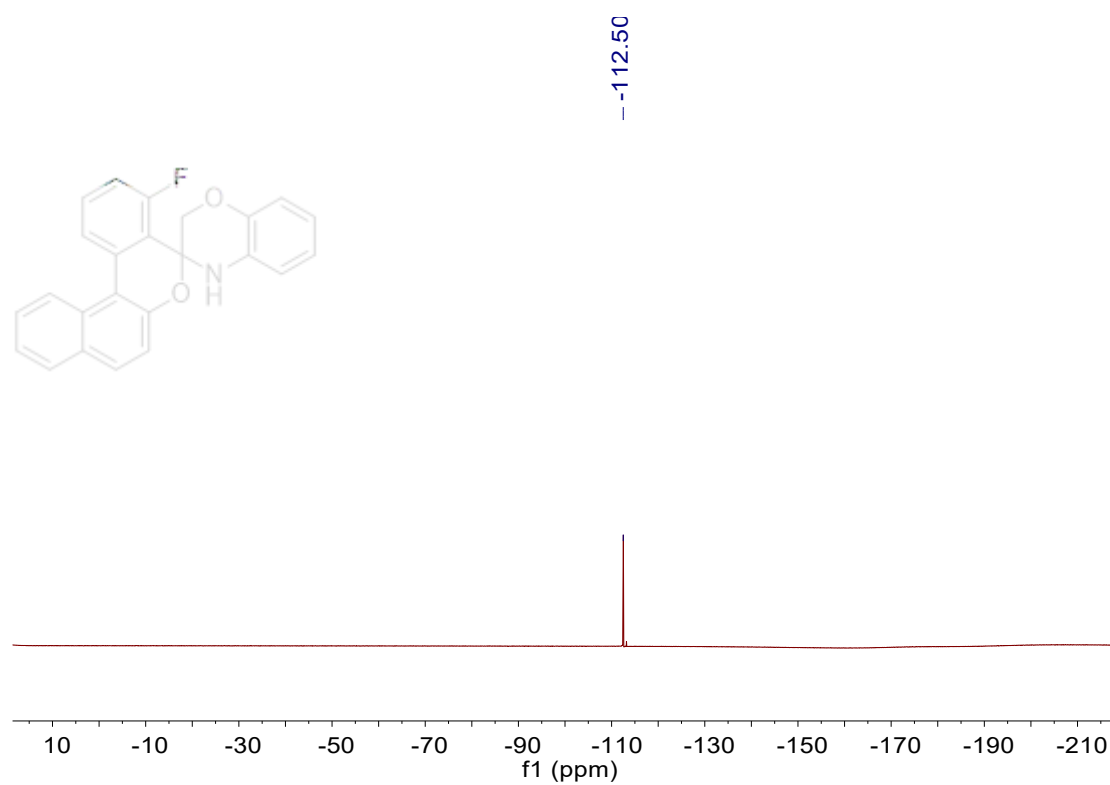
¹H NMR (CDCl₃) spectrum of **3ja**



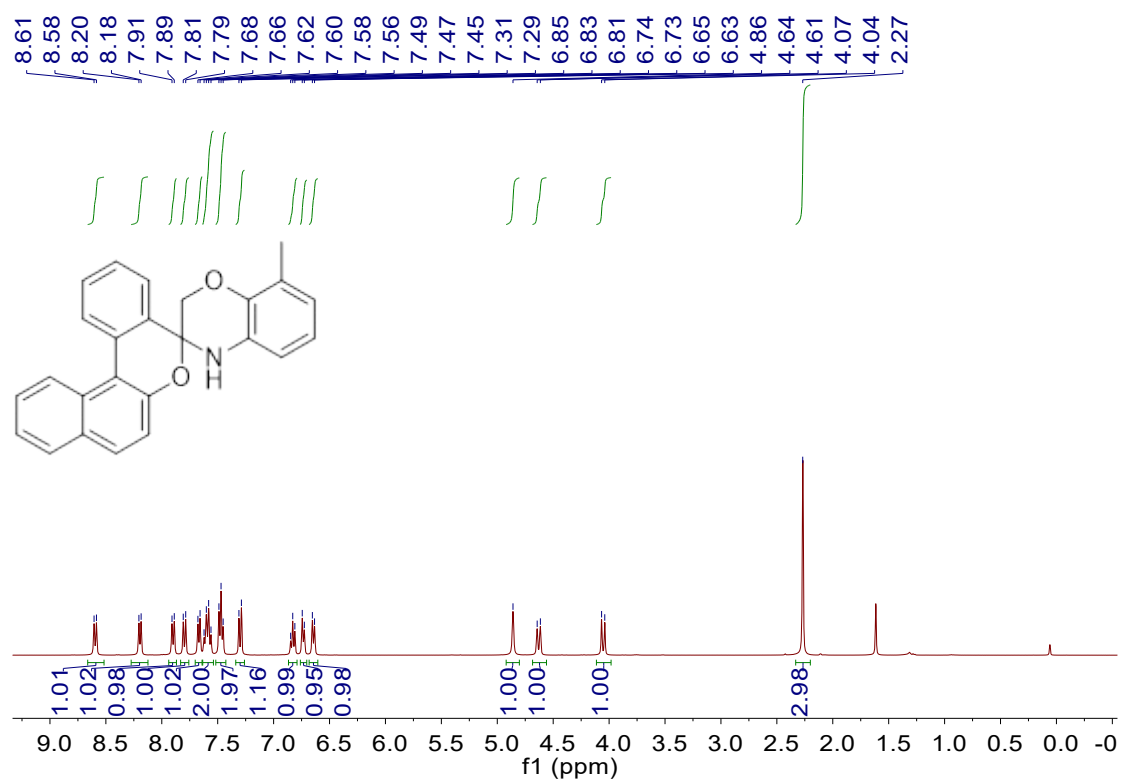
¹³C NMR (CDCl₃) spectrum of **3ja**



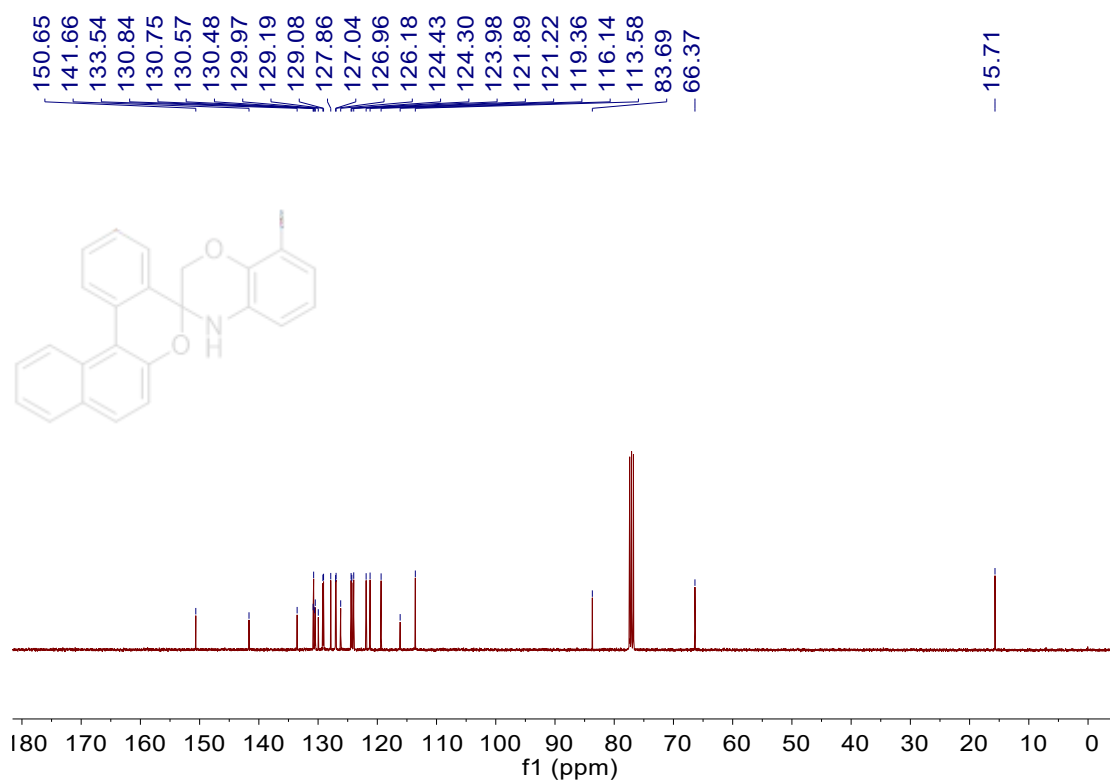
¹⁹F NMR (CDCl₃) spectrum of **3ja**



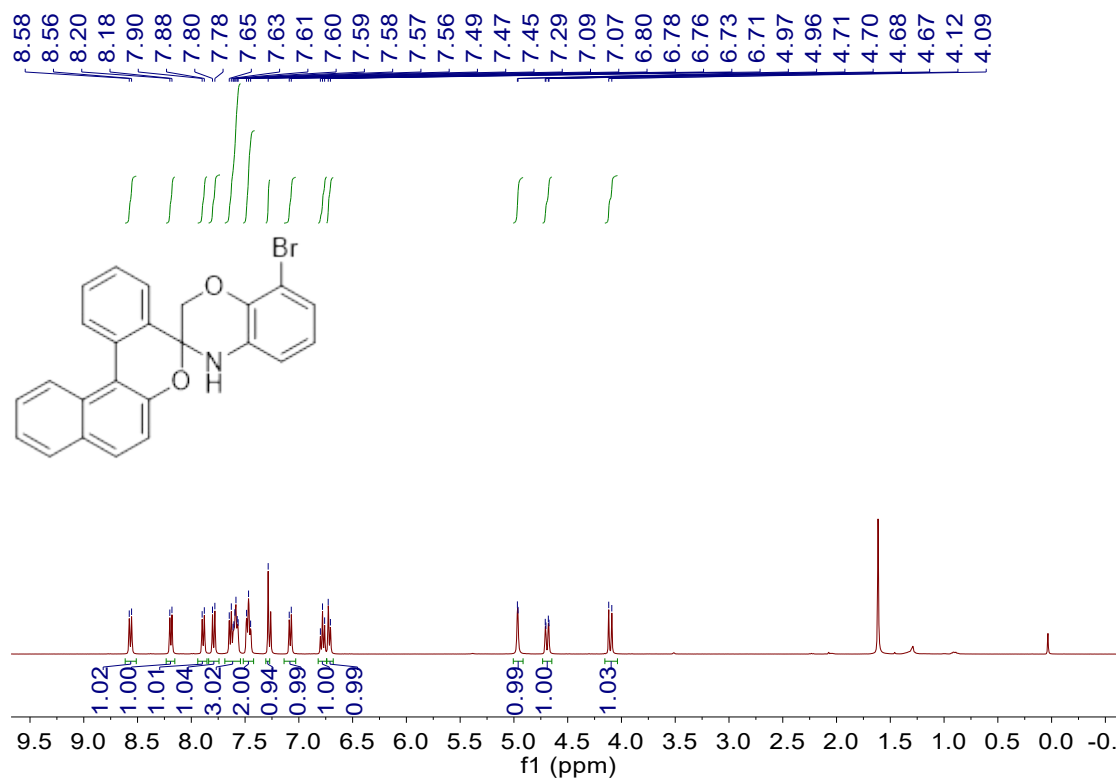
¹H NMR (CDCl₃) spectrum of **3ka**



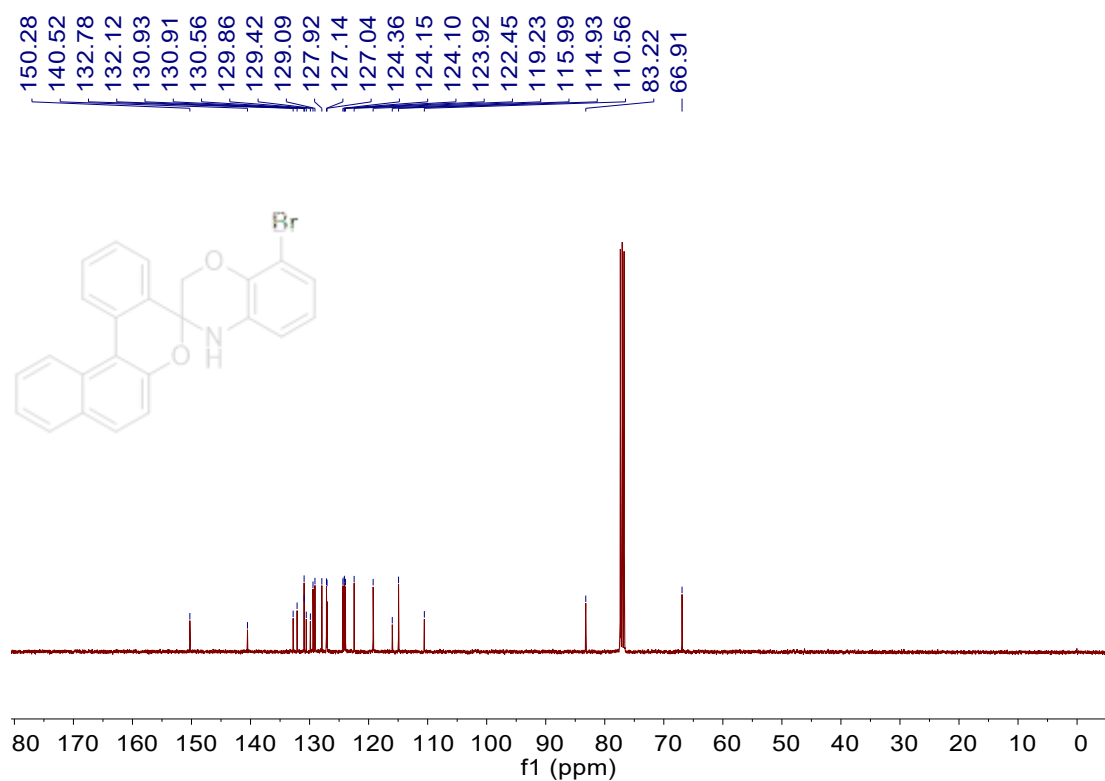
¹³C NMR (CDCl₃) spectrum of **3ka**



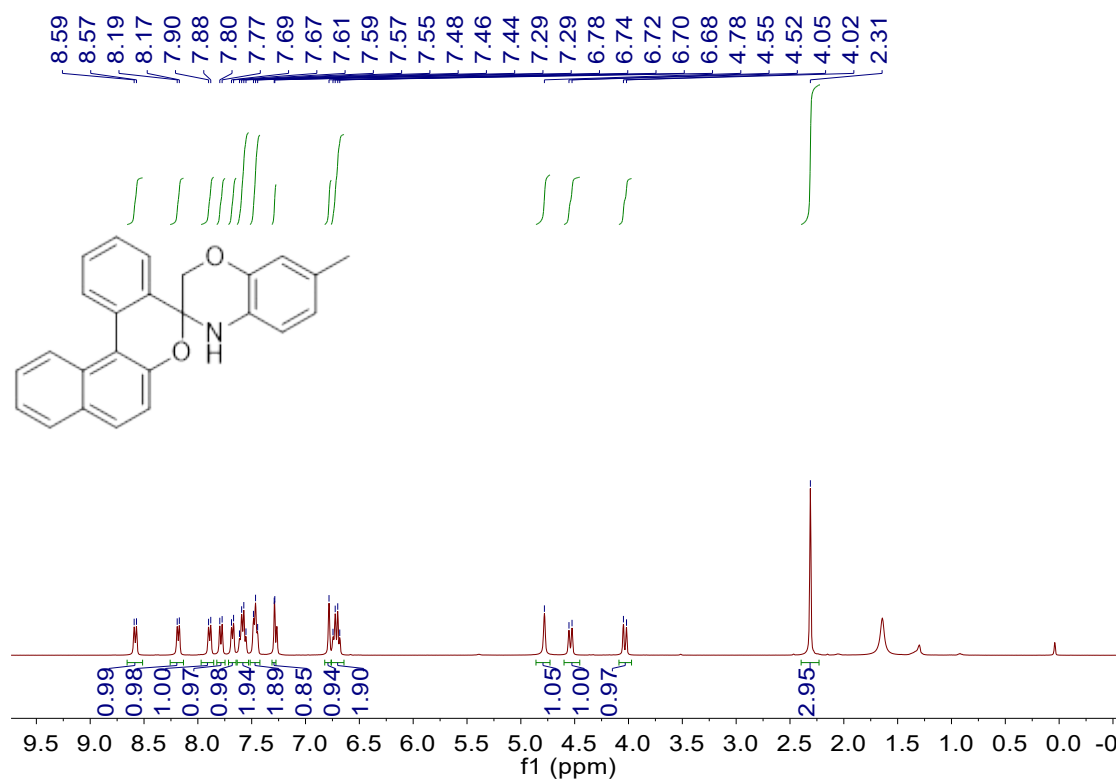
¹H NMR (CDCl₃) spectrum of **3la**



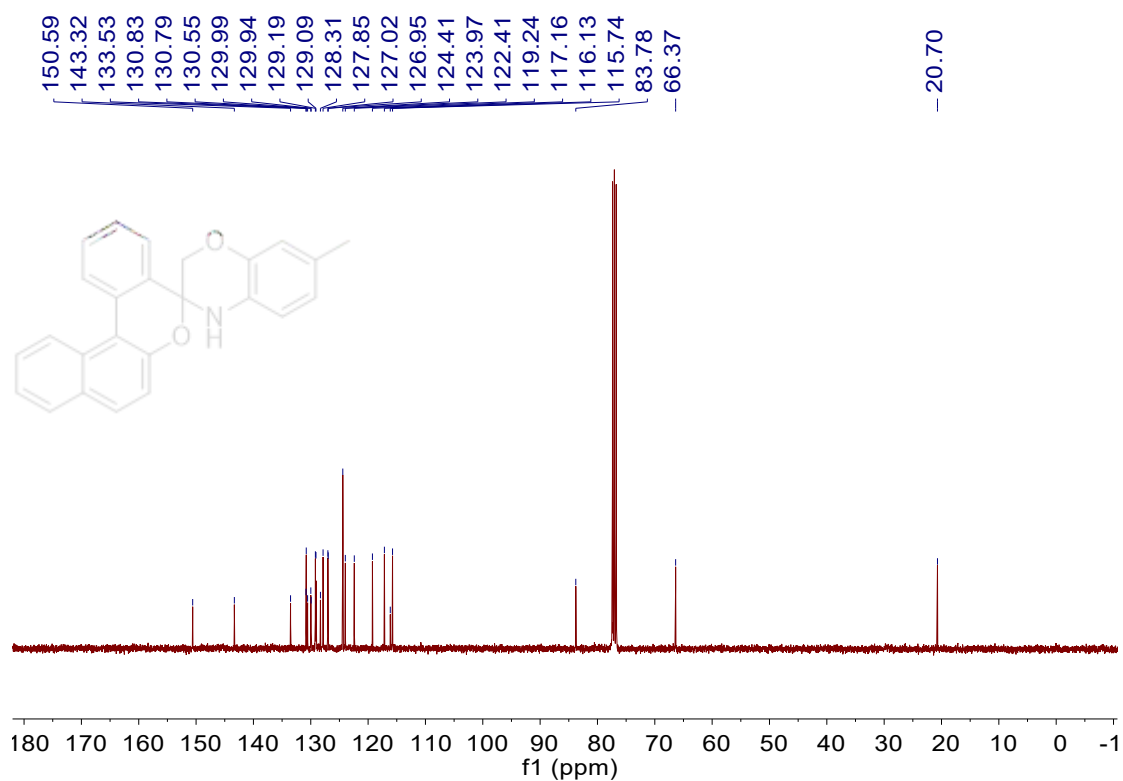
¹³C NMR (CDCl₃) spectrum of **3la**



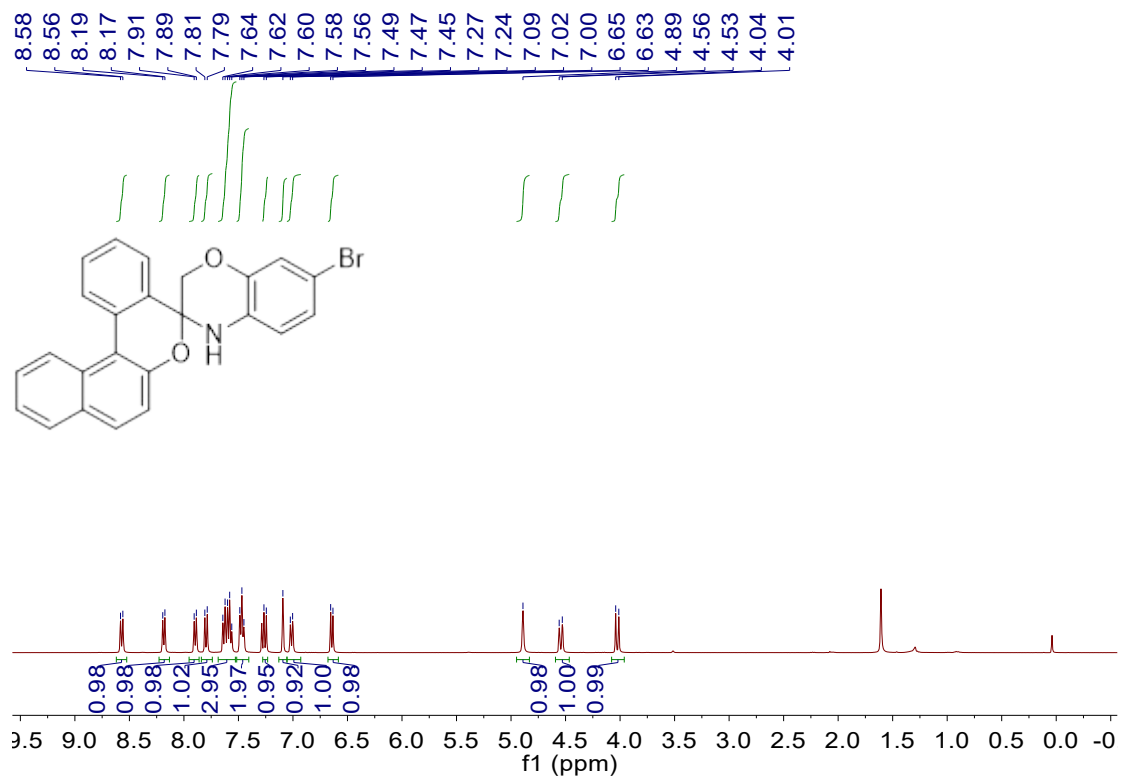
¹H NMR (CDCl₃) spectrum of **3ma**



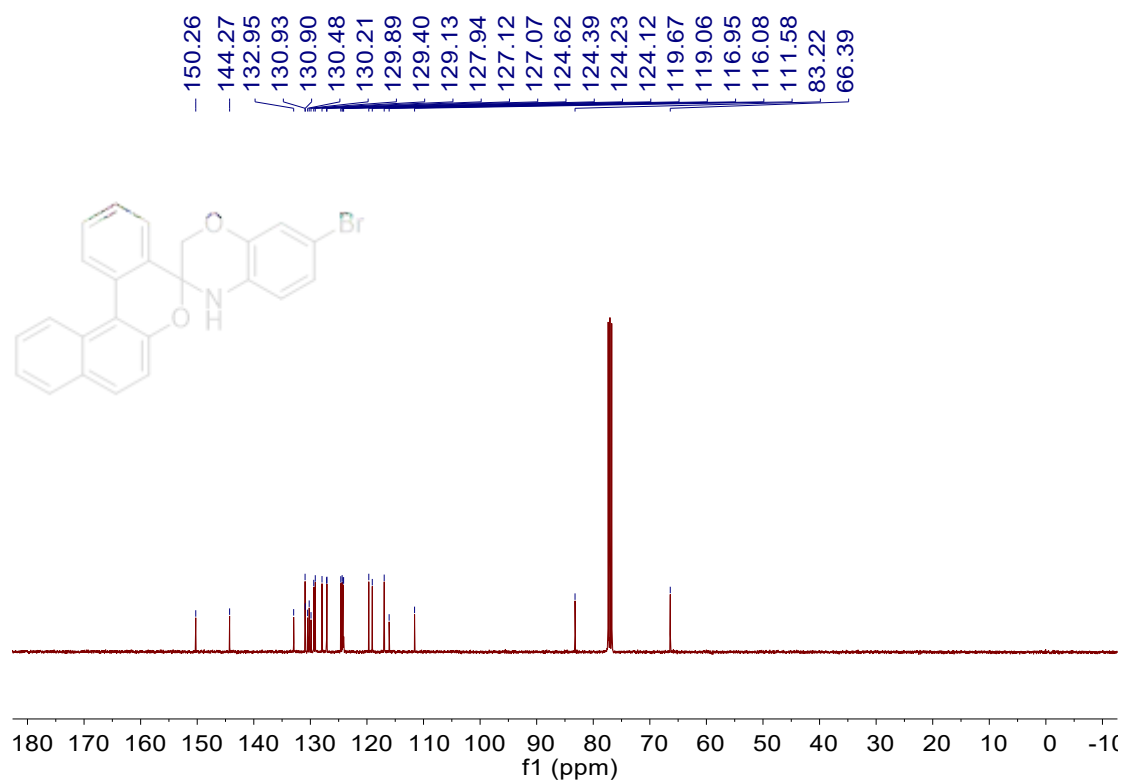
¹³C NMR (CDCl₃) spectrum of **3ma**



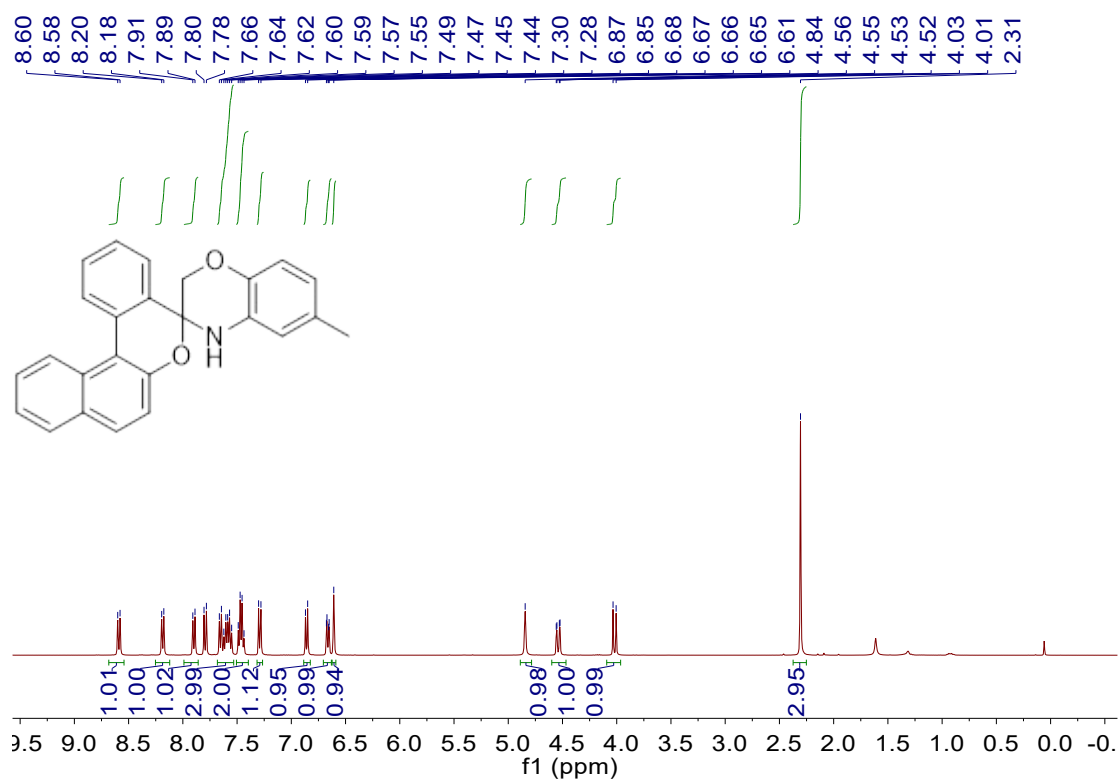
¹H NMR (CDCl₃) spectrum of **3na**



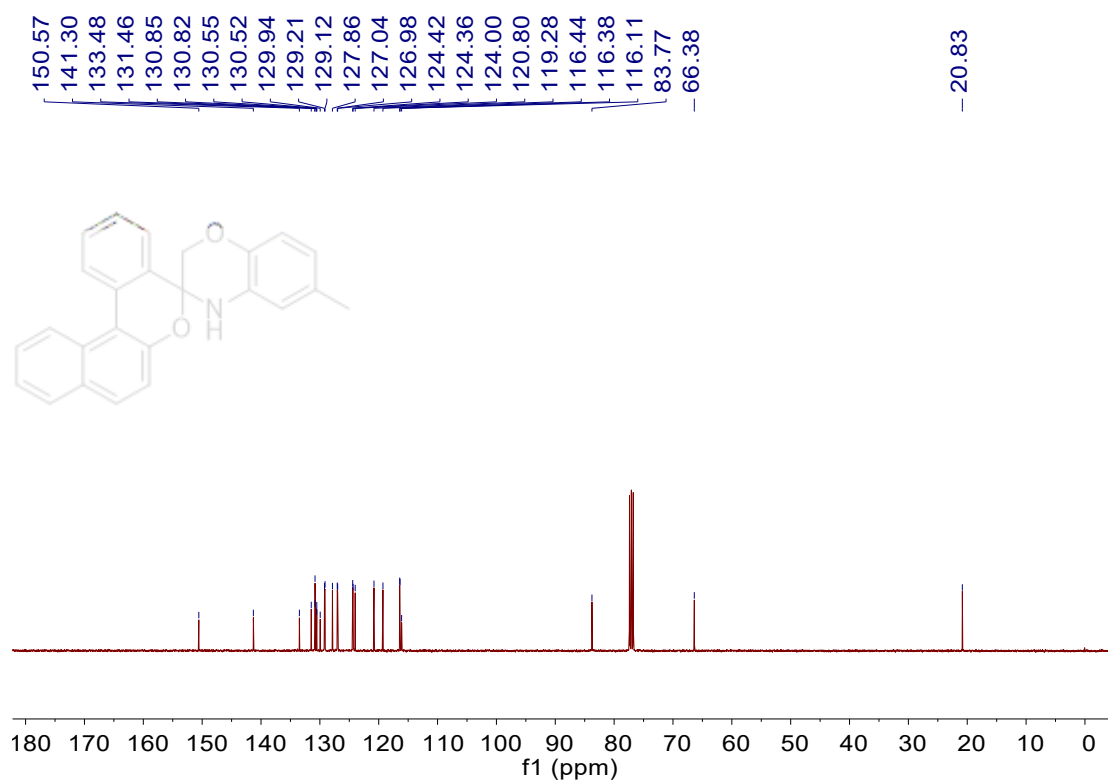
¹³C NMR (CDCl₃) spectrum of **3na**



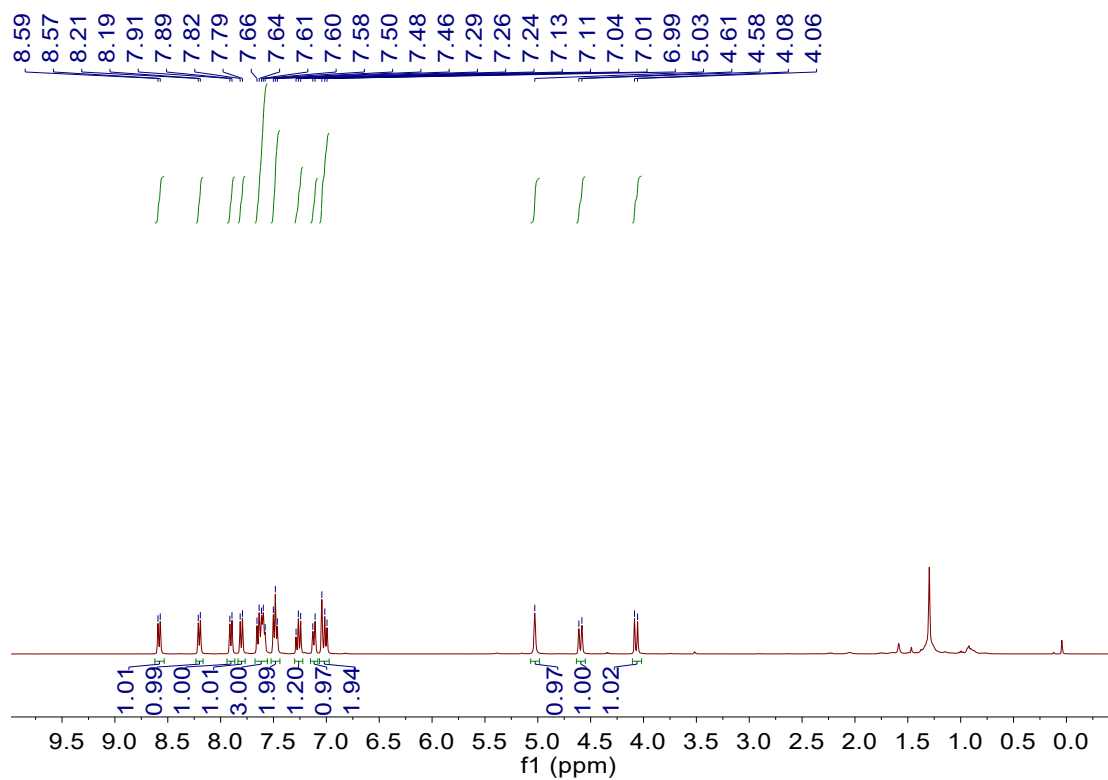
¹H NMR (CDCl₃) spectrum of **3oa**



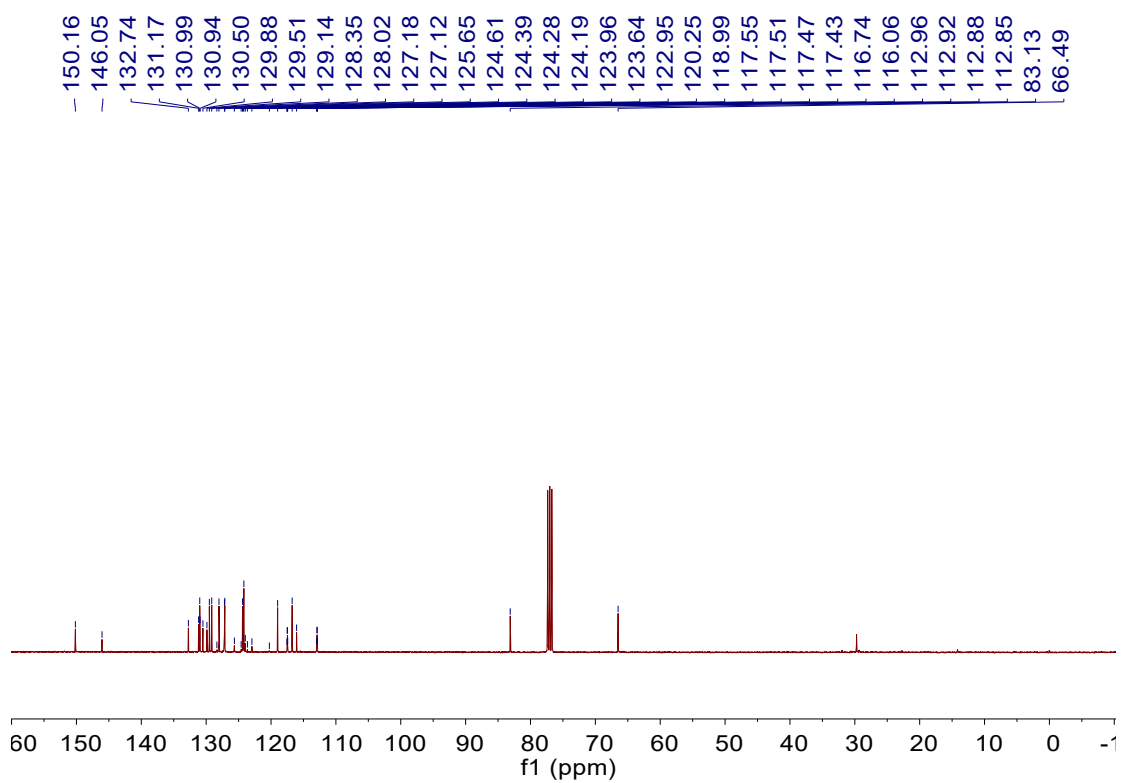
¹³C NMR (CDCl₃) spectrum of **30a**



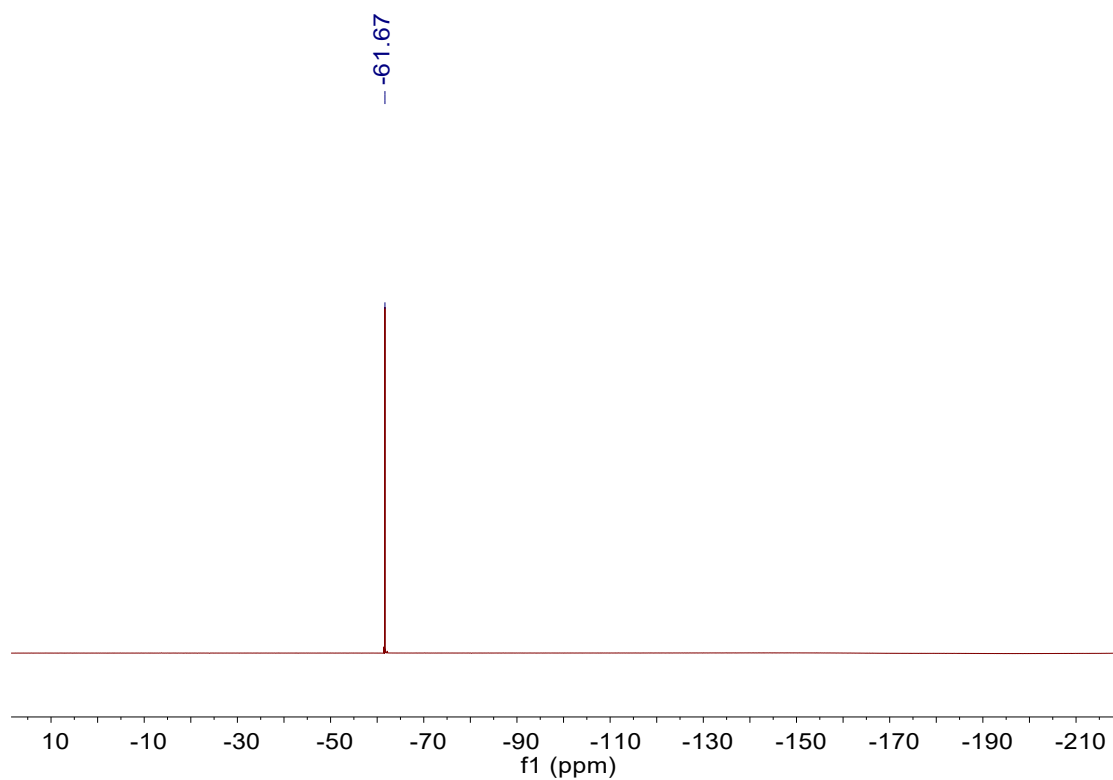
¹H NMR (CDCl₃) spectrum of **3pa**



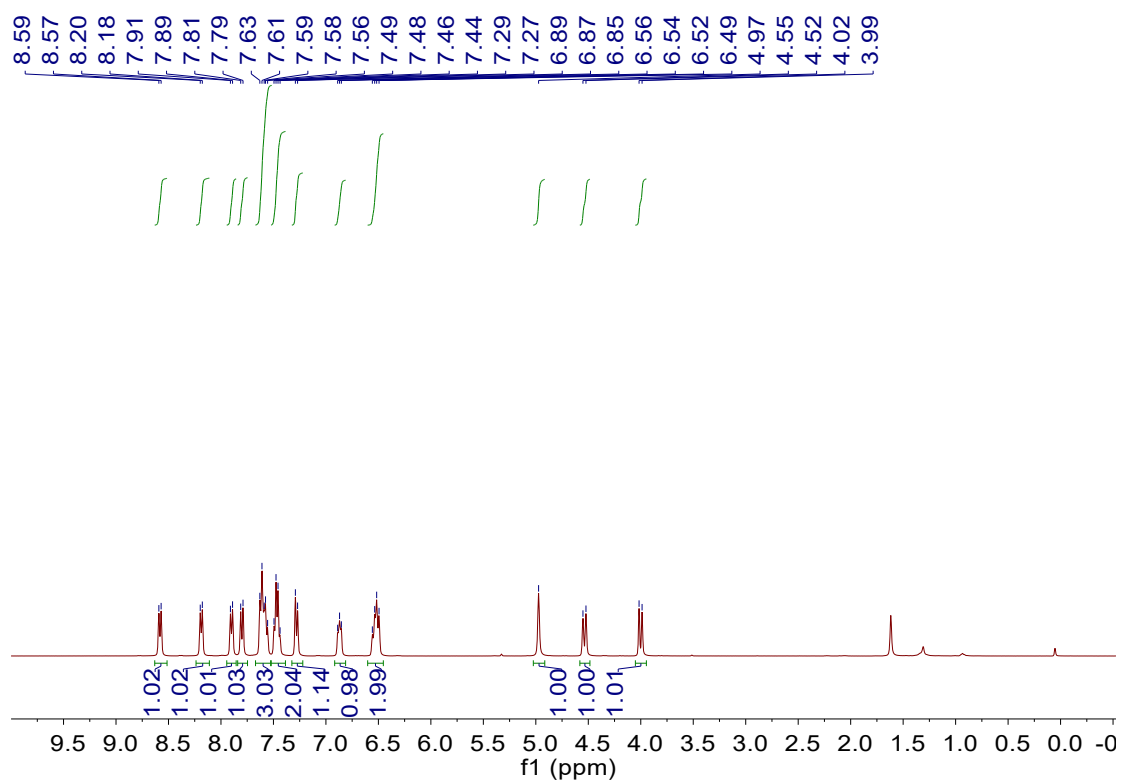
¹³C NMR (CDCl₃) spectrum of **3pa**



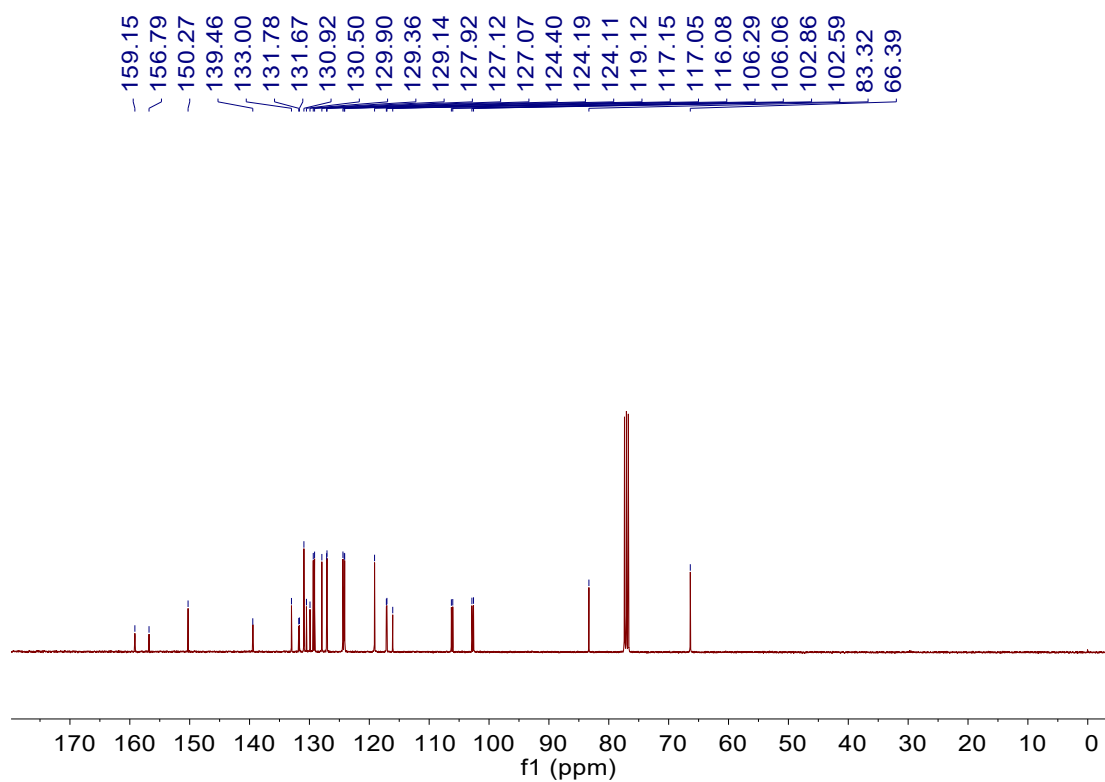
¹⁹F NMR (CDCl₃) spectrum of **3pa**



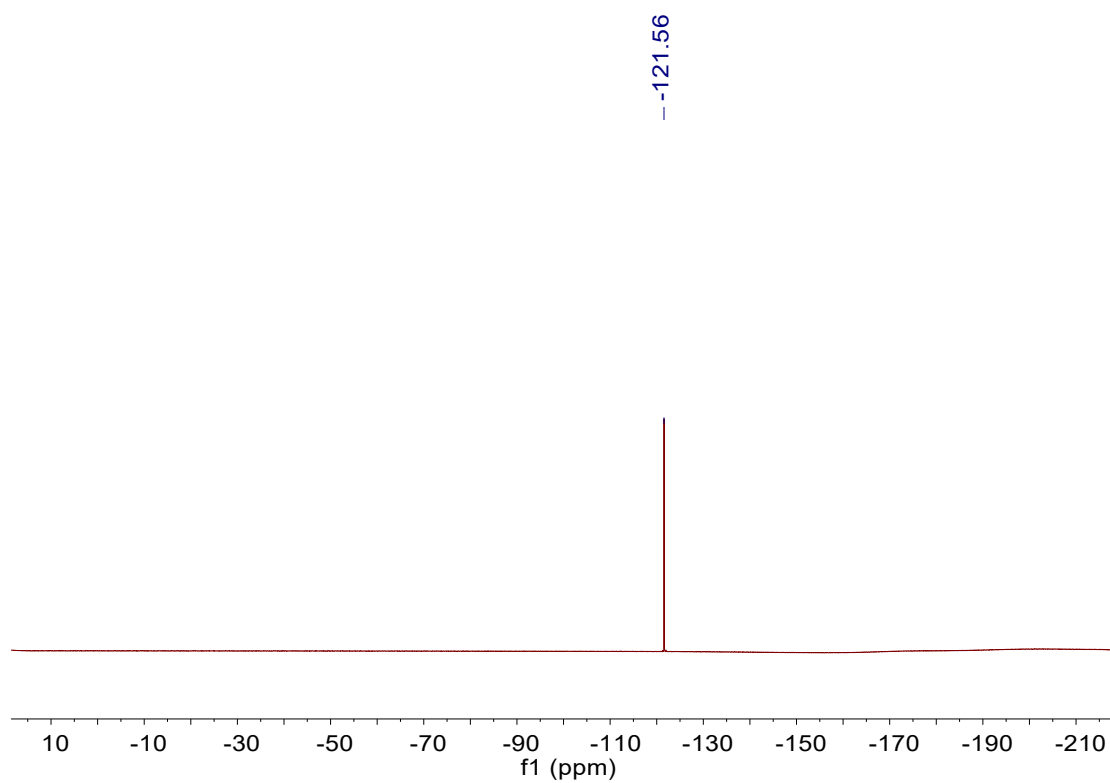
¹H NMR (CDCl₃) spectrum of **3qa**



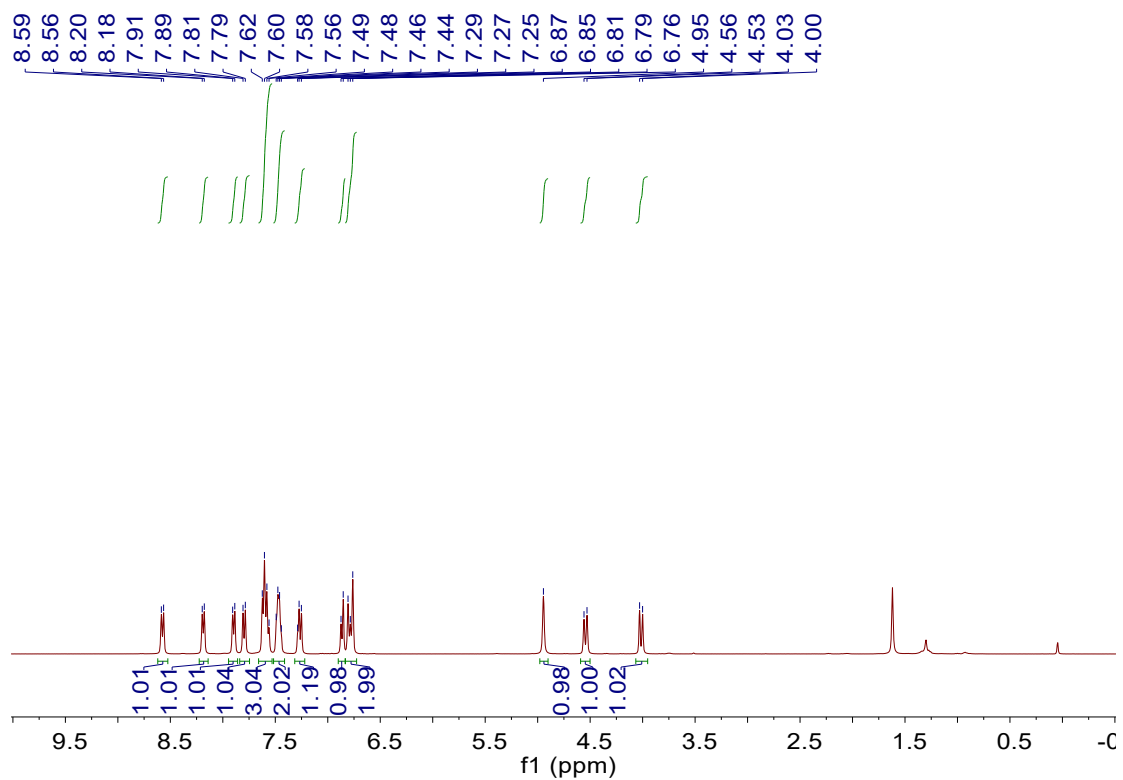
¹³C NMR (CDCl₃) spectrum of **3qa**



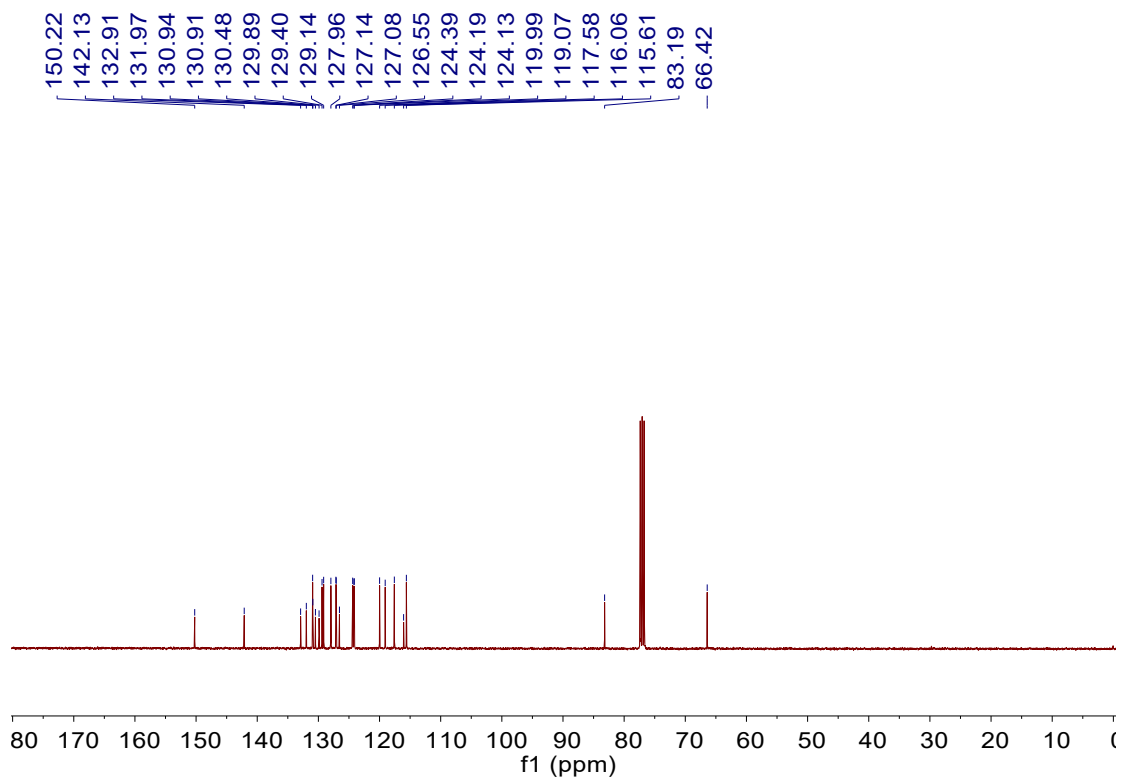
^{19}F NMR (CDCl_3) spectrum of **3qa**



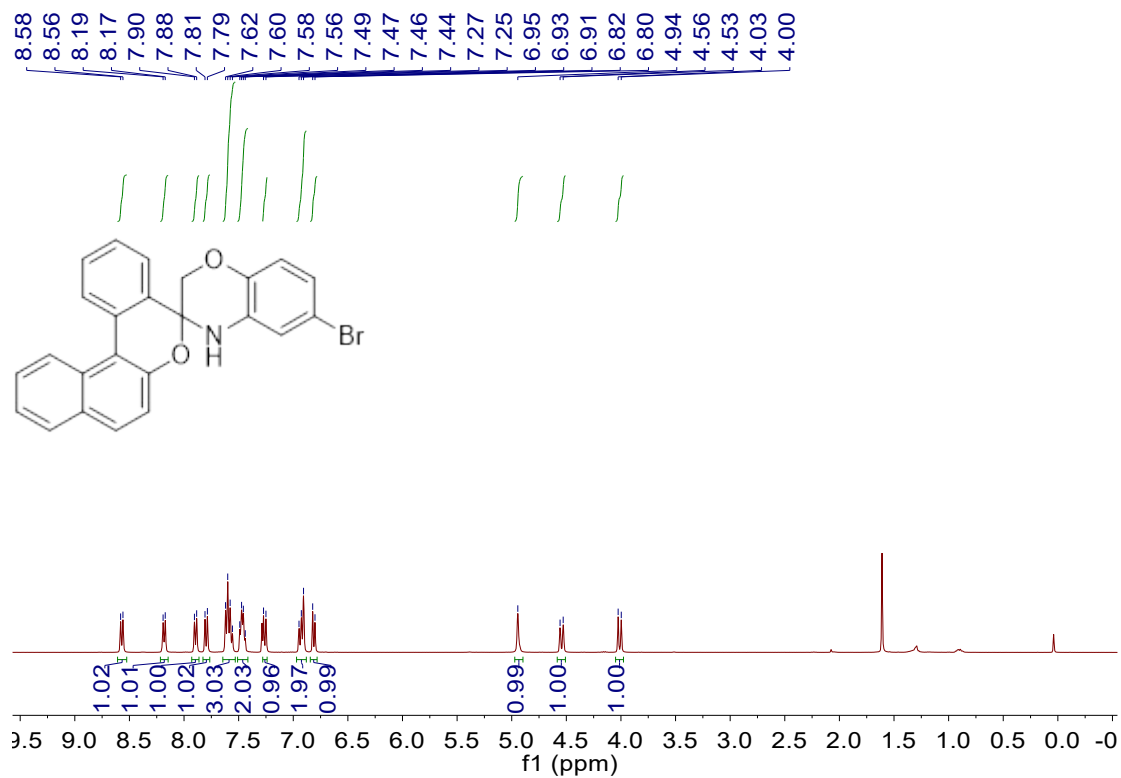
^1H NMR (CDCl_3) spectrum of **3ra**



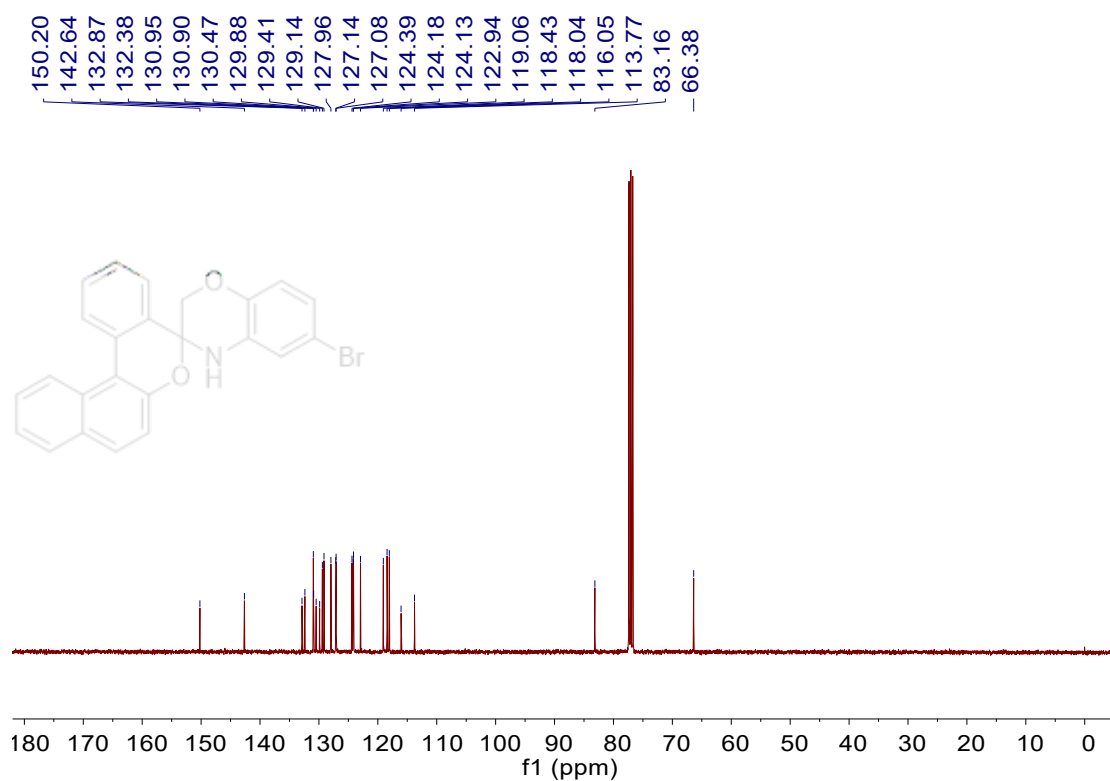
¹³C NMR (CDCl₃) spectrum of **3ra**



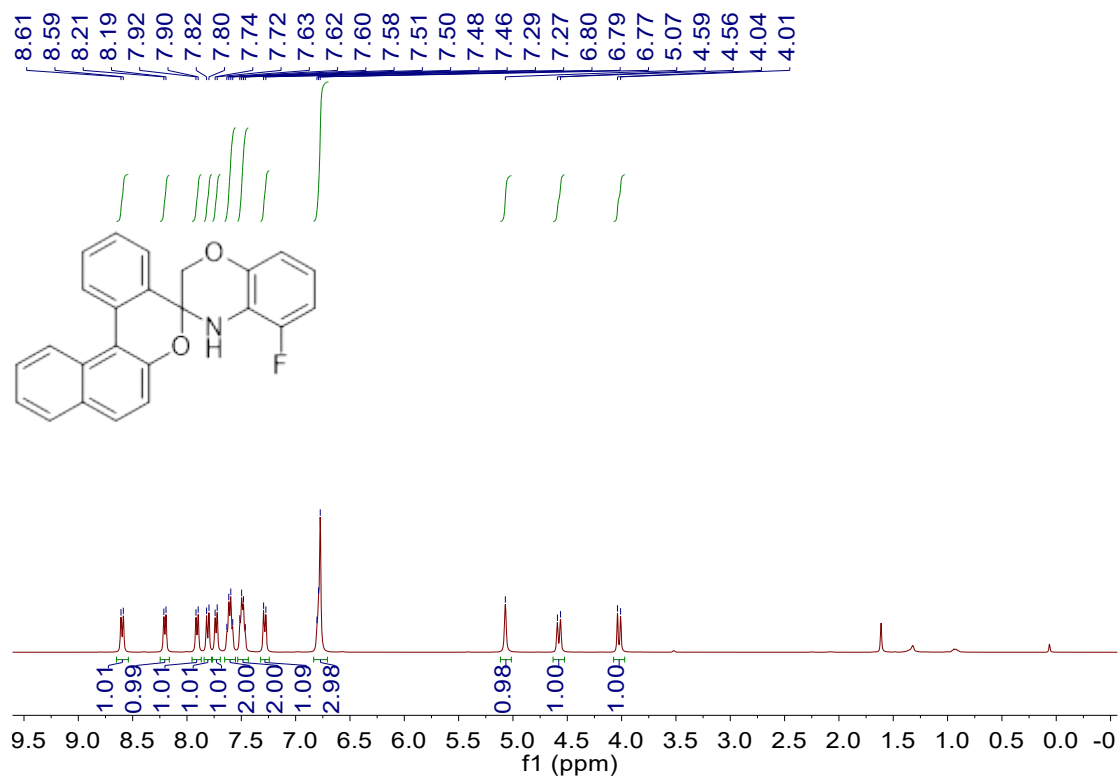
¹H NMR (CDCl₃) spectrum of **3sa**



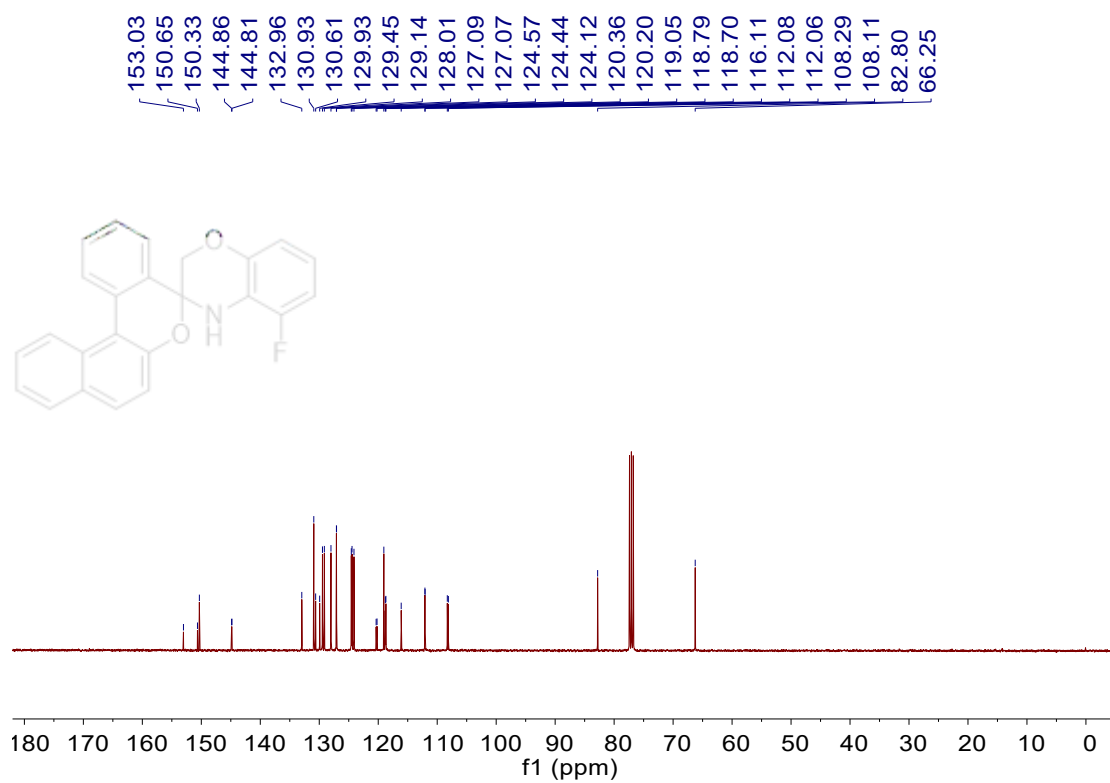
¹³C NMR (CDCl₃) spectrum of **3sa**



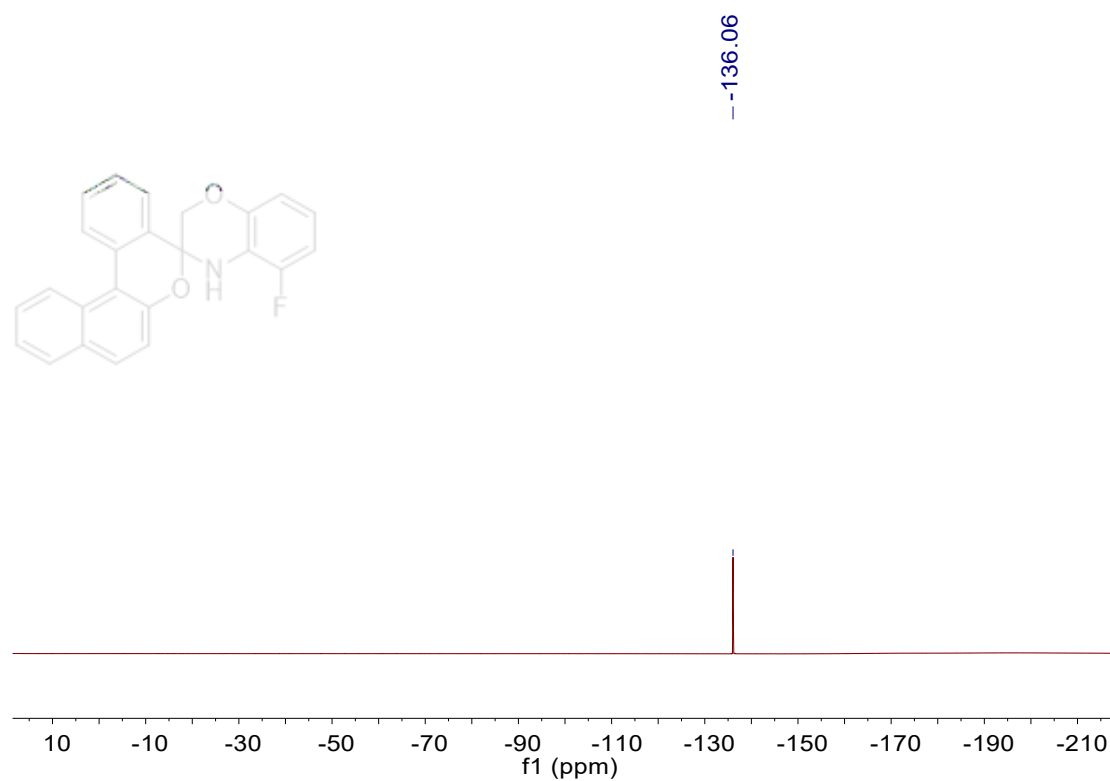
¹H NMR (CDCl₃) spectrum of **3va**



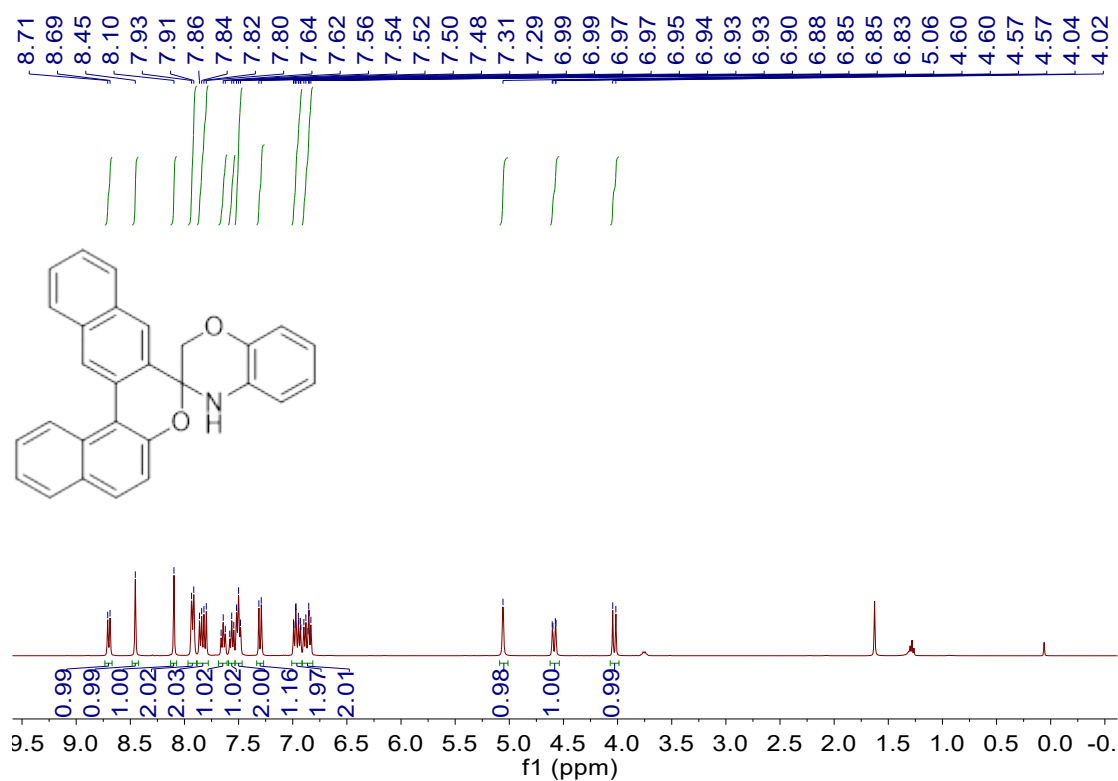
¹³C NMR (CDCl₃) spectrum of **3va**



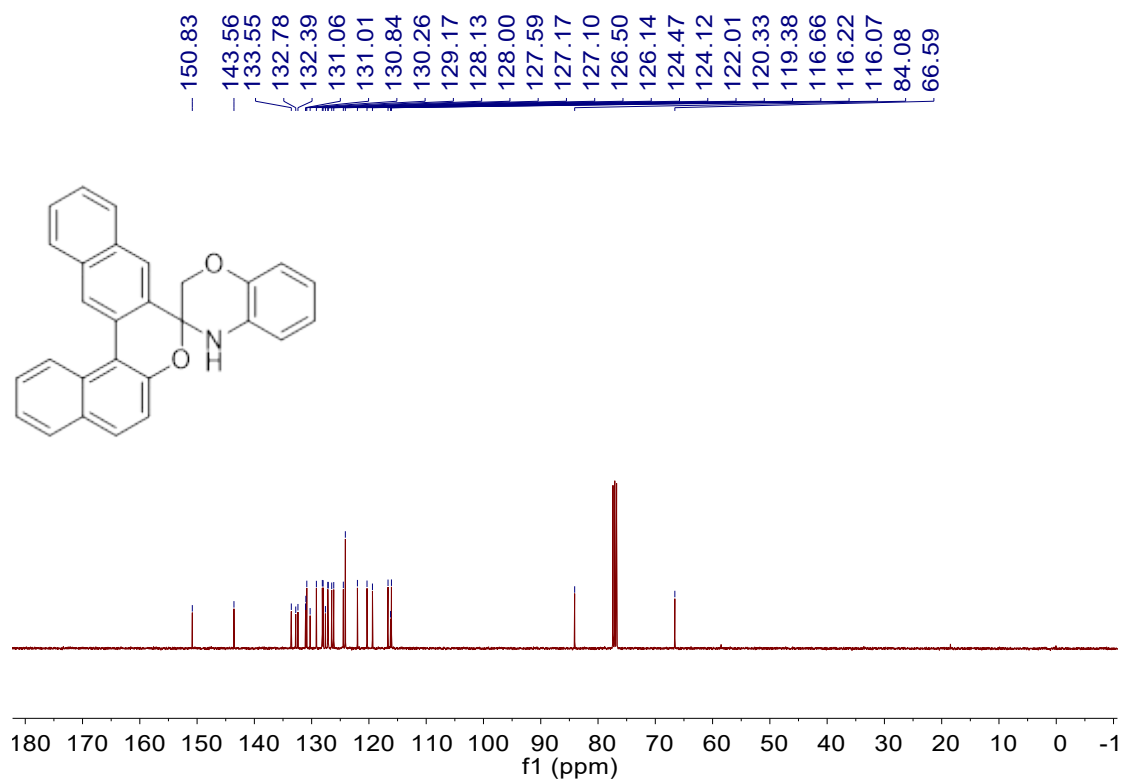
¹⁹F NMR (CDCl₃) spectrum of **3va**



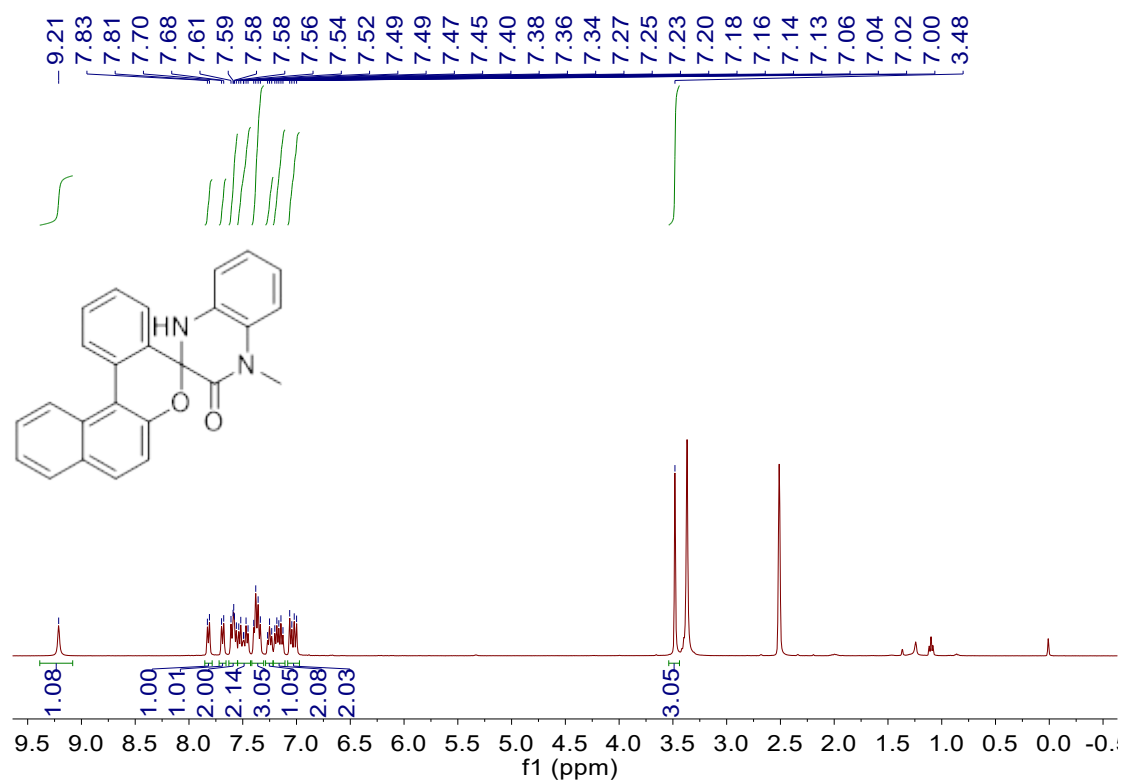
¹H NMR (CDCl₃) spectrum of **3wa**



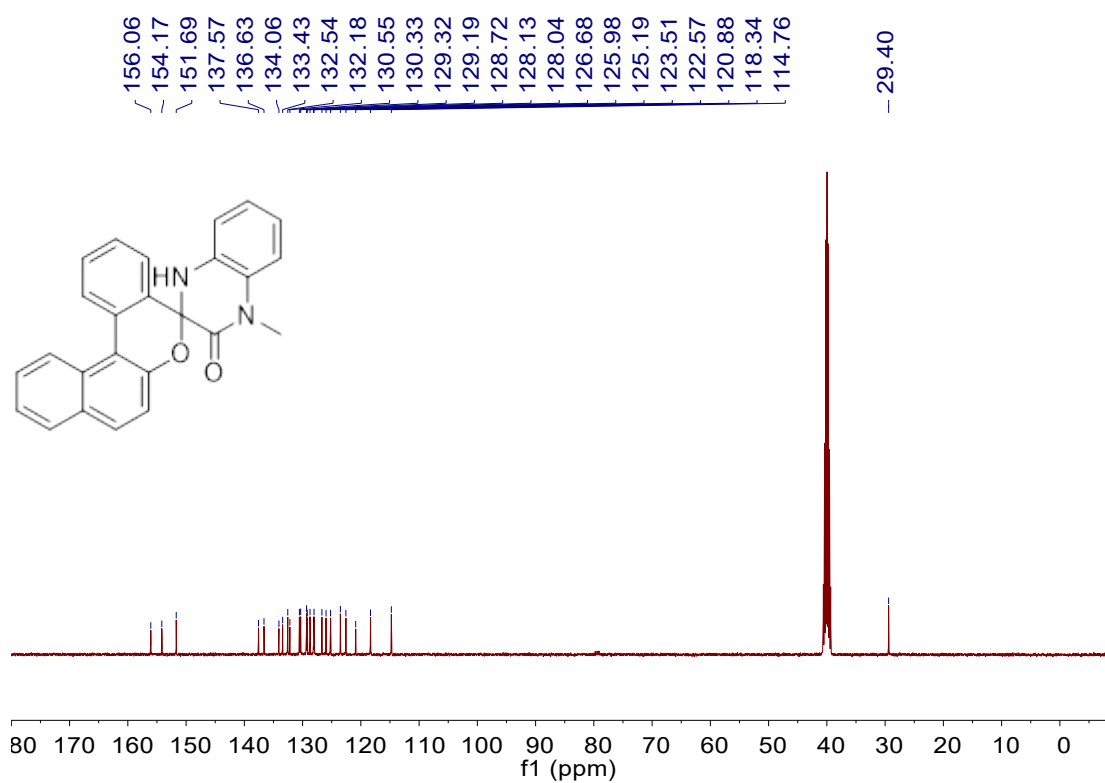
¹³C NMR (CDCl₃) spectrum of **3wa**



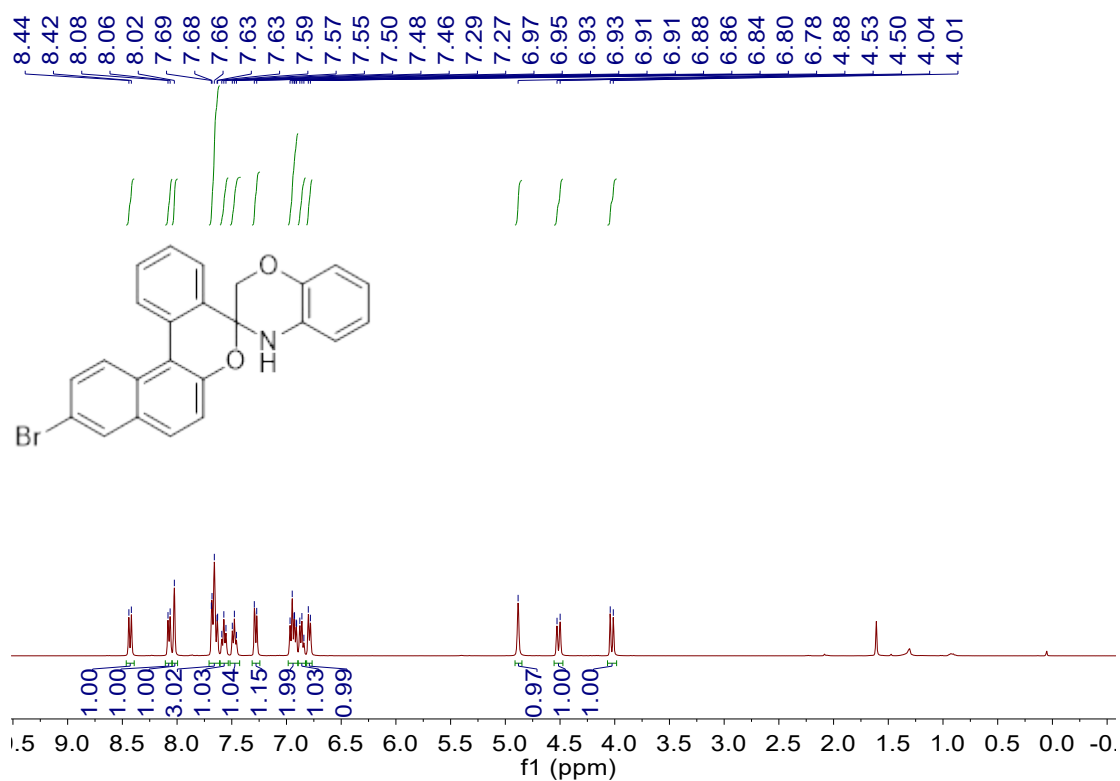
^1H NMR (DMSO- d_6) spectrum of **3xa**



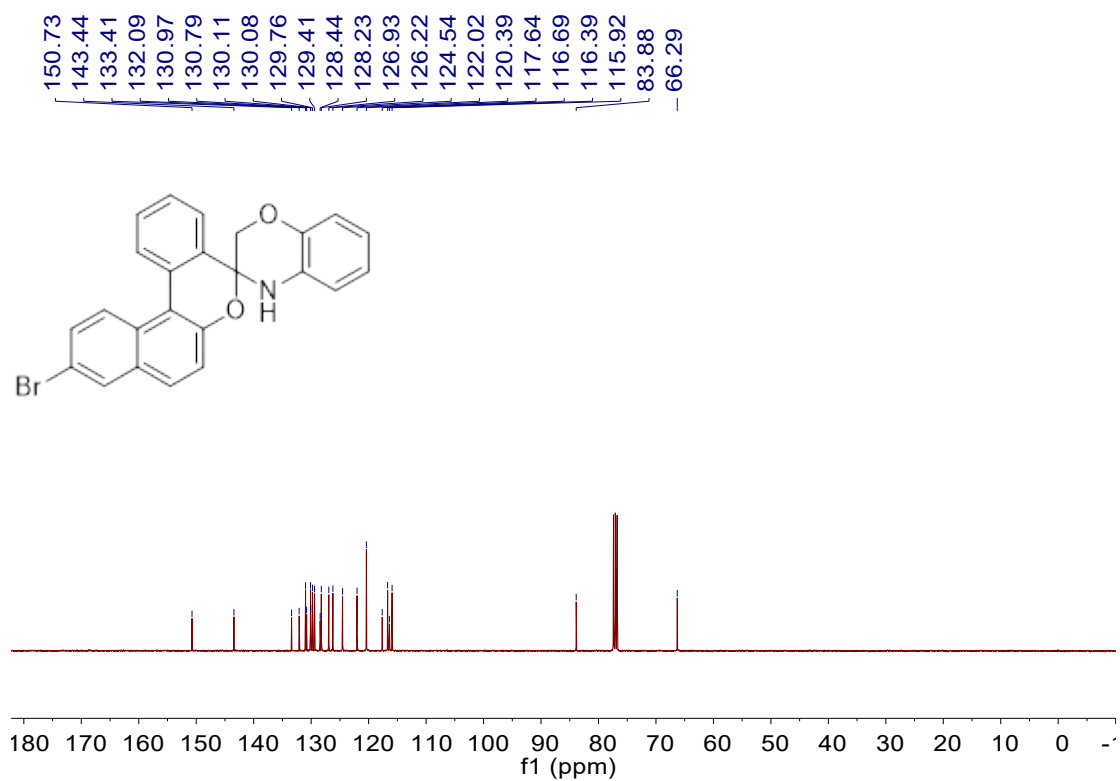
^{13}C NMR (DMSO- d_6) spectrum of **3xa**



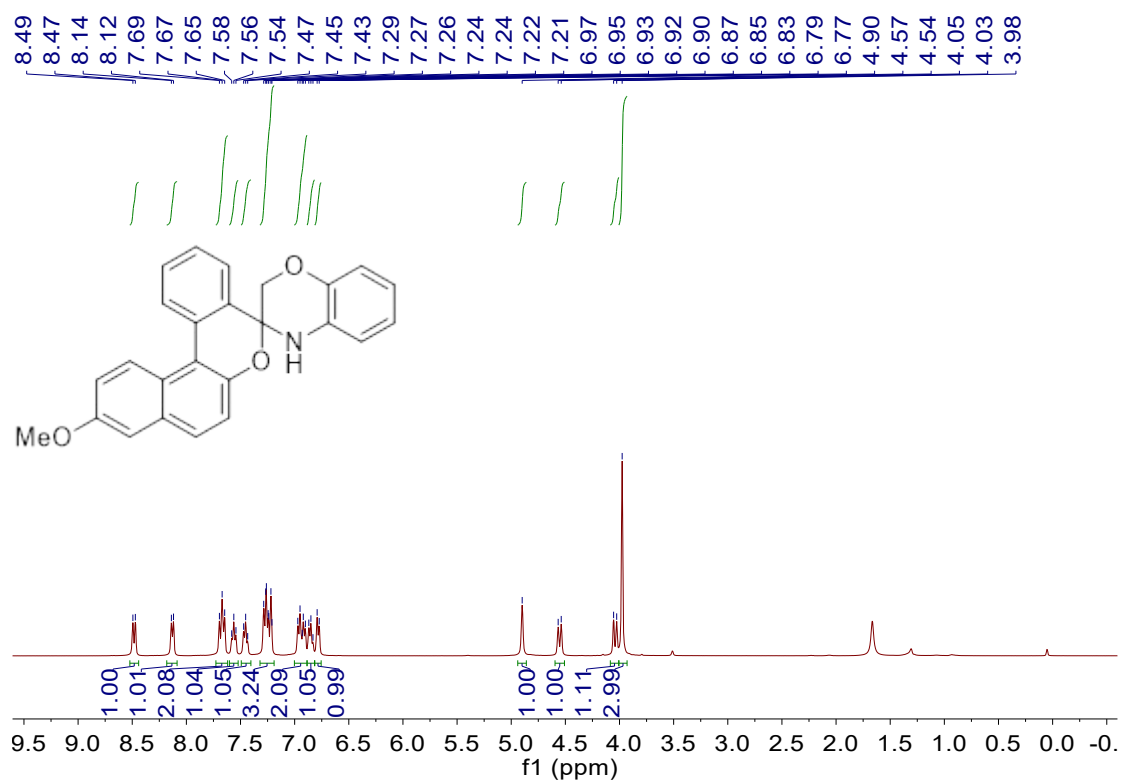
¹H NMR (CDCl₃) spectrum of **3ab**



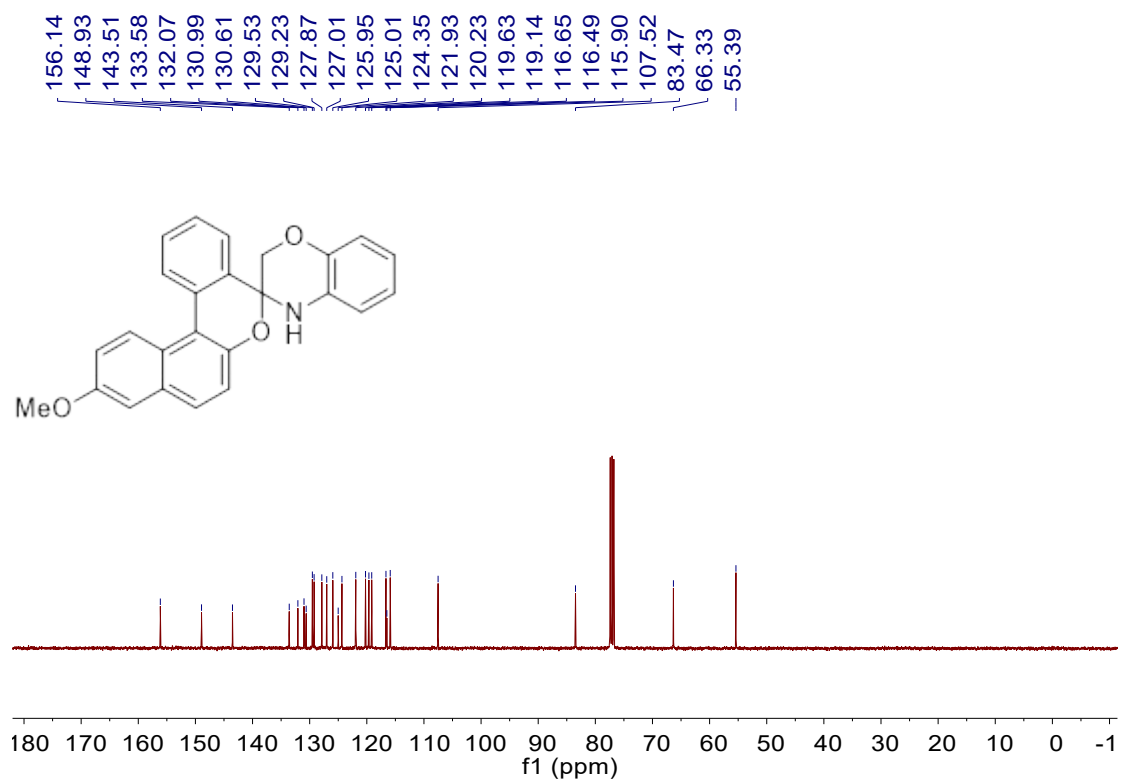
¹³C NMR (CDCl₃) spectrum of **3ab**



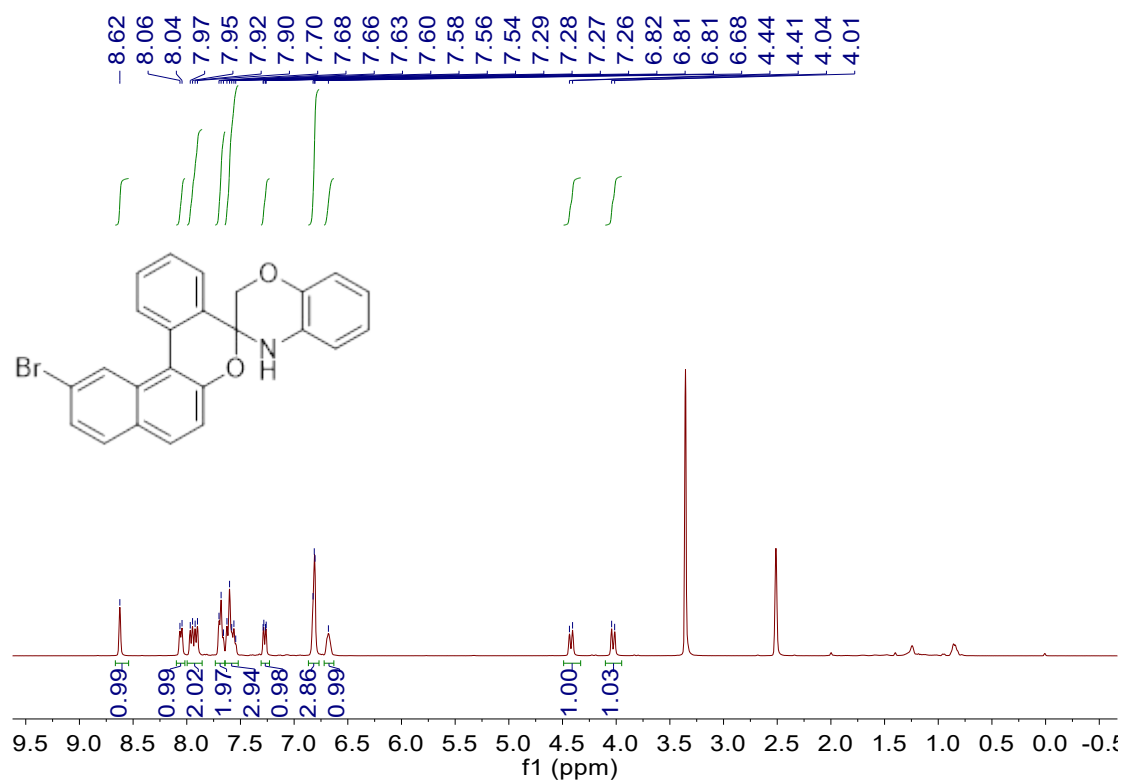
¹H NMR (CDCl₃) spectrum of **3ac**



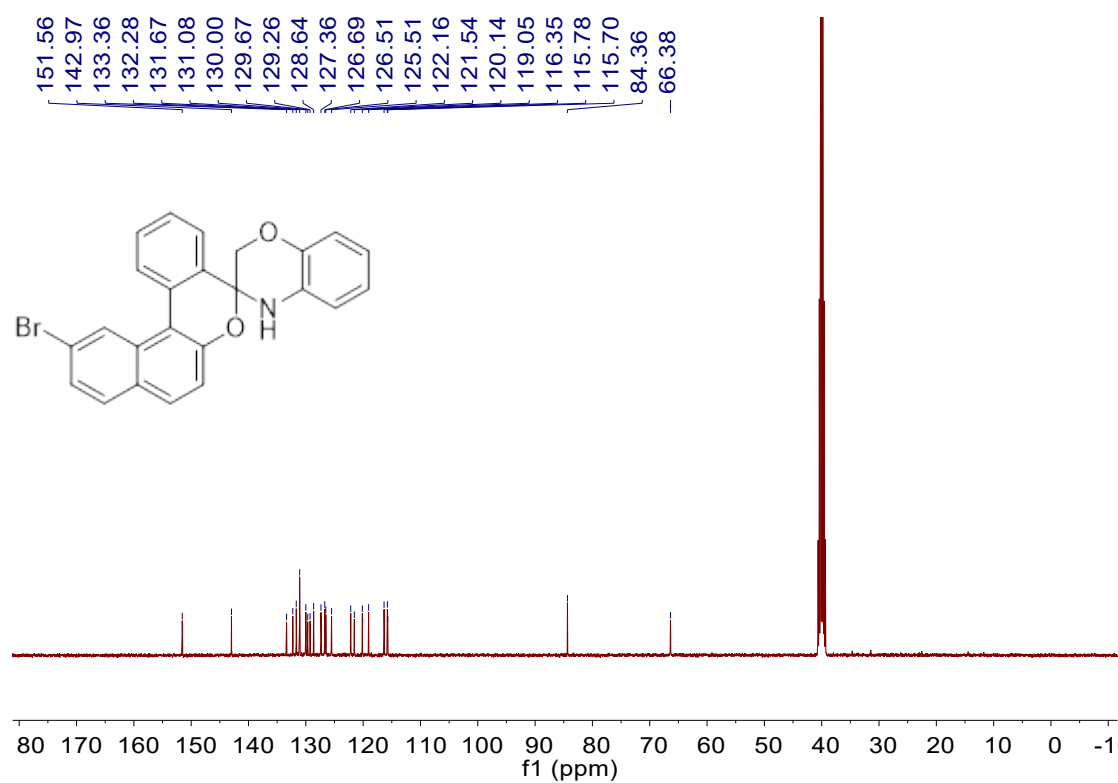
¹³C NMR (CDCl₃) spectrum of **3ac**



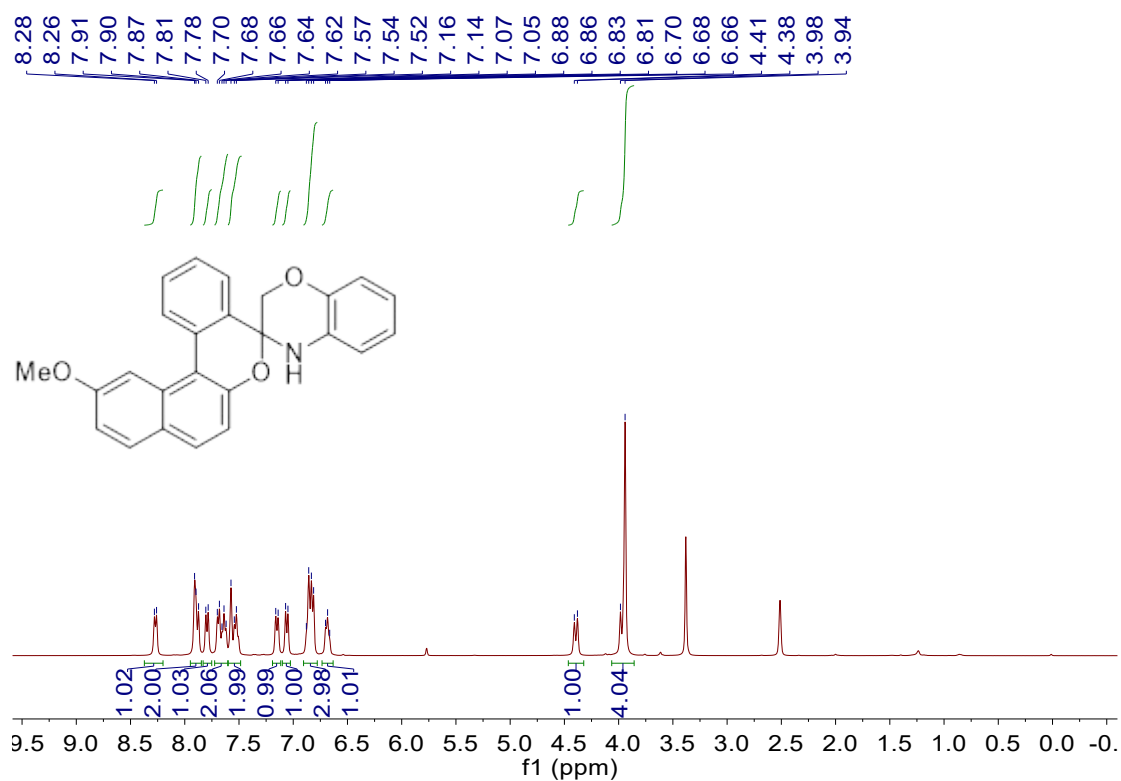
¹H NMR (DMSO-*d*₆) spectrum of **3ad**



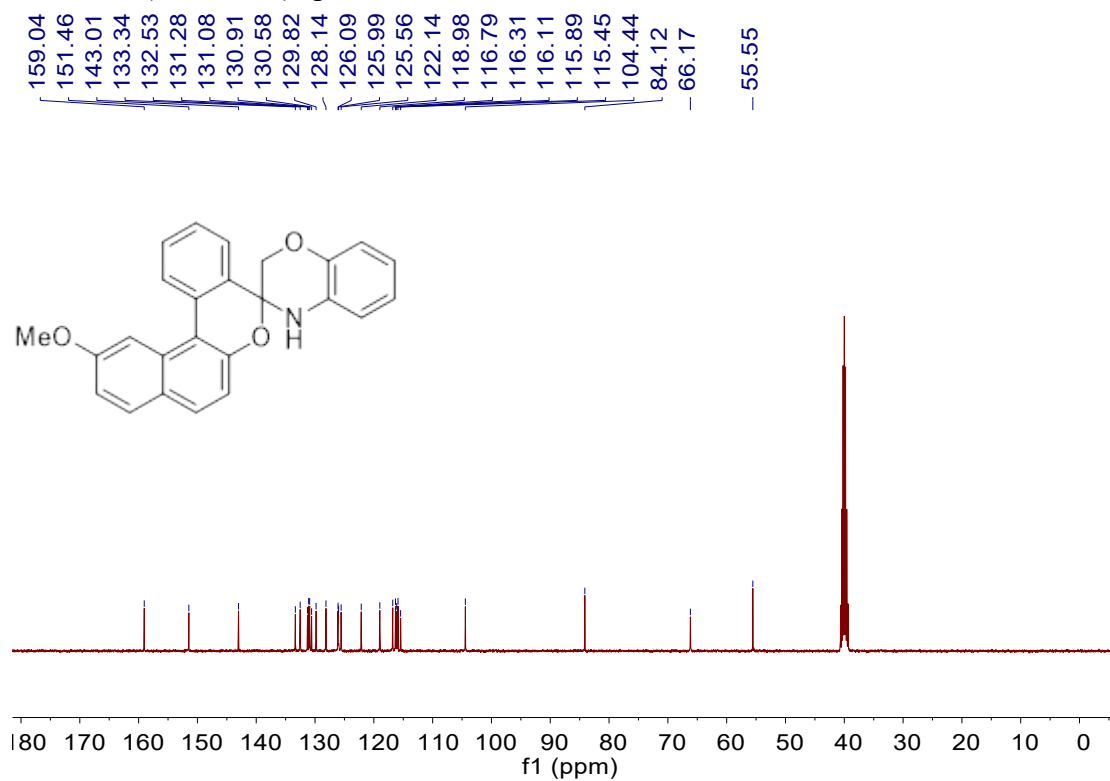
¹³C NMR (DMSO-*d*₆) spectrum of **3ad**



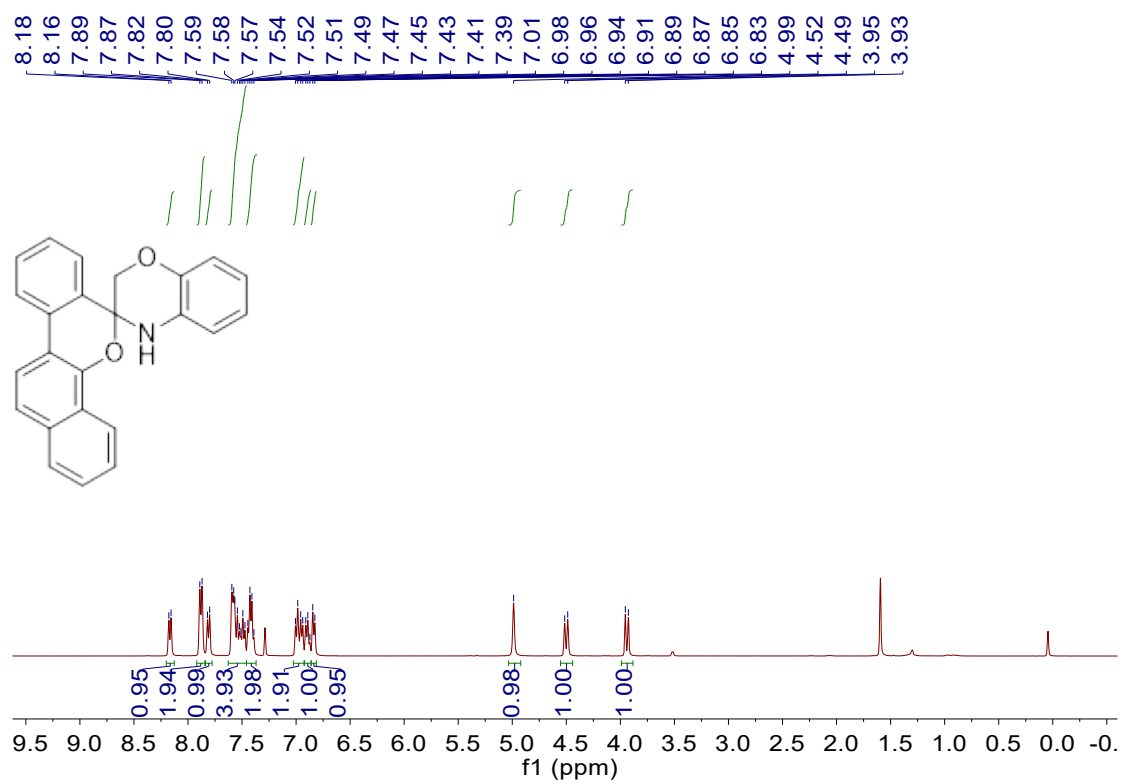
¹H NMR (DMSO-*d*₆) spectrum of **3ae**



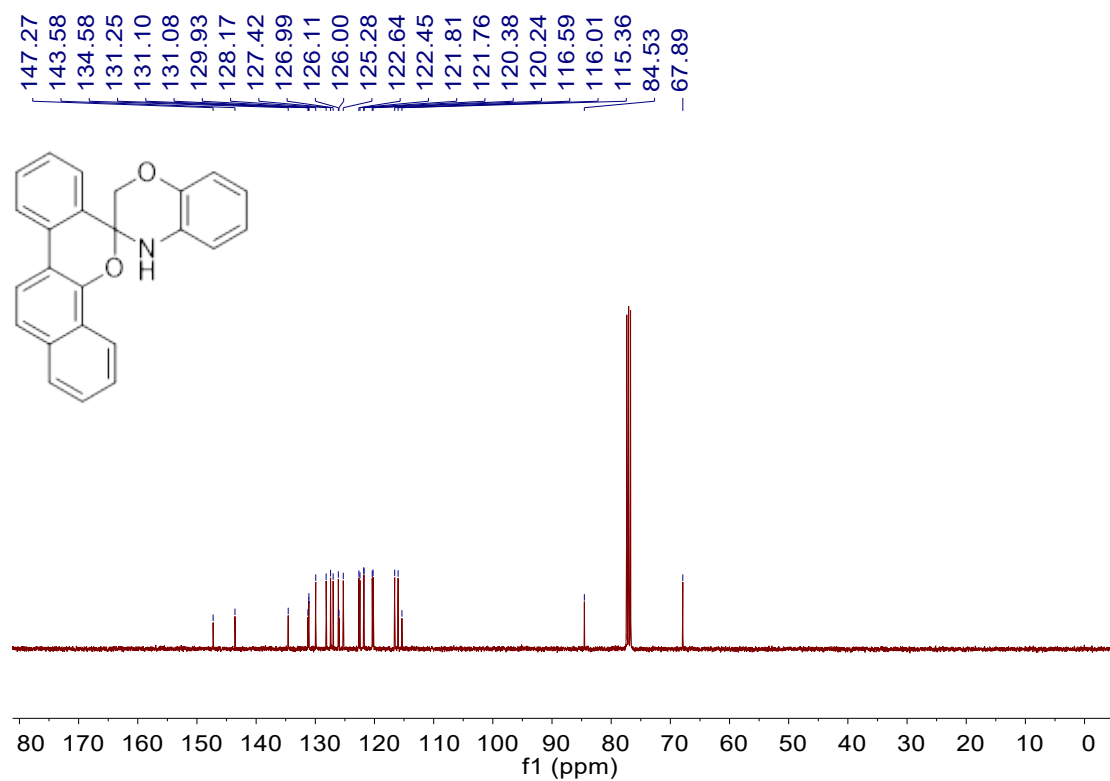
¹³C NMR (DMSO-*d*₆) spectrum of **3ae**



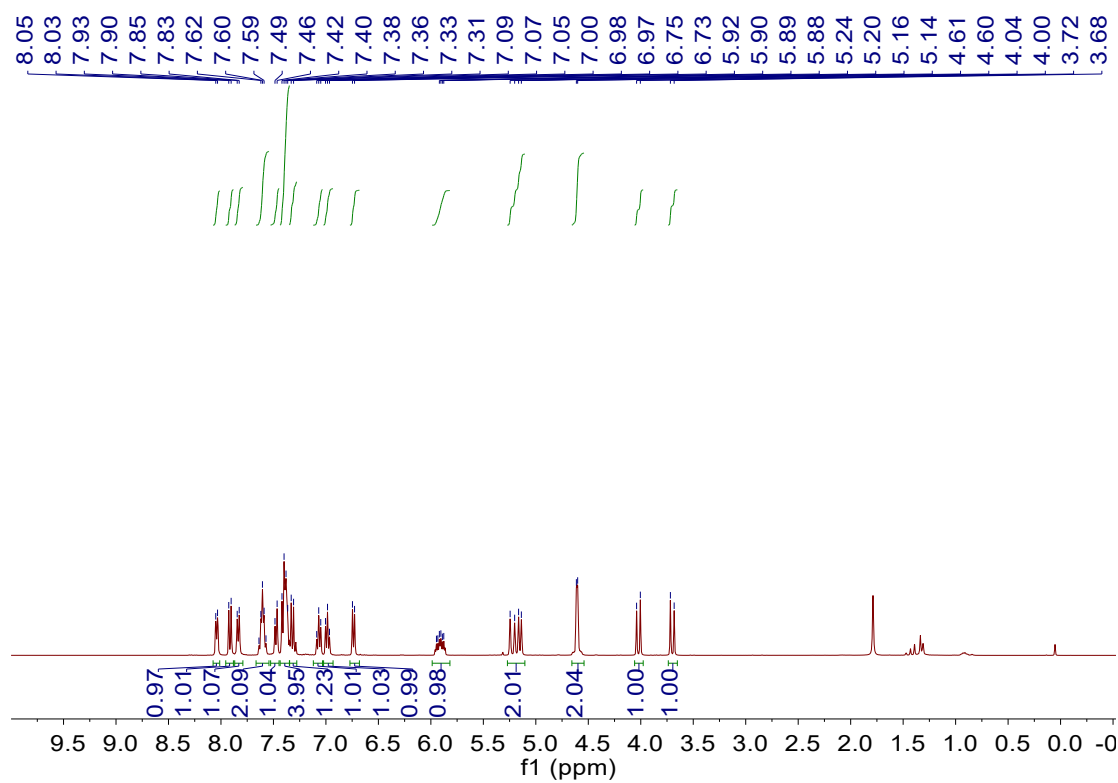
¹H NMR (CDCl₃) spectrum of **3af**



¹³C NMR (CDCl₃) spectrum of **3af**



¹H NMR (CDCl₃) spectrum of **4aa**



¹³C NMR (CDCl₃) spectrum of **4aa**

