Microwave-Assisted One-Pot Synthesis of Dibenzo[*b*,*d*]oxepines *via* Domino C–C Coupling and Cyclo-condensation Pathway

Pradip S. Waghmare, and Gedu Satyanarayana*

Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi, Sangareddy, Telangana - 502284, India.

Phone: (040) 2301 6251; Fax: (040) 2301 6003/32, E-mail: gvsatya@chy.iith.ac.in

Table of Contents:

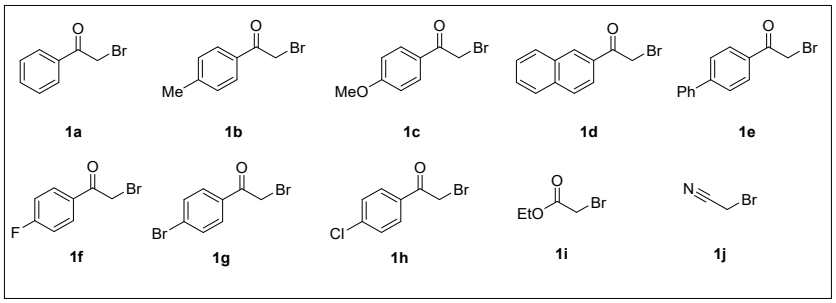
EXPERIMENTAL SECTION

General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) and 600 (600 MHz) spectrometers at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δH = 0.00 ppm) or $CHCl_3$ (δH = 7.26 ppm). ^{13}C{1H} NMR spectra were recorded on Bruker Avance 400 (101 MHz) and 600 (151 MHz) spectrometers at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δC = 77.16 ppm (central line of triplet)]. In the ^{13}C{1H} NMR, the nature of carbons (C, CH, CH_2, and CH_3) was determined by recording the DEPT-135 spectra and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^{1}H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, dd = doublet of doublet, m = multiplet, and brs = broad singlet. The assignment of signals was confirmed by 1H, ^{13}C{^{1}H} CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode. Melting points are recorded using the Tempo and Mettler FP1 melting point apparatus in capillary tubes and are uncorrected. A single crystal of **3aa** was selected and mounted on an Oxford SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 298 K during data collection. Using Olex2, the structure was solved with Olex2.solve, structure solution program using direct methods, and refined with the olex2. Refinement package using Gauss-Newton minimization. All small-scale dry reactions were carried out using Schlenk tubes under an inert atmosphere. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Reactions generally run under argon or a nitrogen atmosphere. Solvents were distilled before use; petroleum ether with a boiling range of 60 to 80 °C was used. Palladium-catalyzed reactions were done in DMF and EtOH. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per gram of crude material). The microwave irradiation experiments were carried out in a dedicated CEM- Discover monomode microwave apparatus, operating at a frequency of 2.45 GHz with continuous irradiation power from 0 to 300 W and utilization of the standard absorbance level of 100 W. The reactions were carried out in 10 mL glass tubes, sealed with a Teflon septum, and placed in the microwave cavity. The reactions were irradiated at the required set temperature for the stipulated time and then cooled to ambient temperature with air jet cooling. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Reactions were generally run

under argon or a nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 60 to 80 °C was used. $Pd(OAc)_2$, potassium carbonate, $Pd(PPh_3)_4$, and Caesium Carbonate were purchased from Sigma-Aldrich and used as received. Substituted 2-formylphenyl boronic acids, 2-indophenols, 2-bromophenols, and 2-bromoacetophenones were purchased from TCI/local sources and used as received. Acme's silica gel (100–200 mesh) was used for column chromatography (approximately 20 g per gram of crude material).

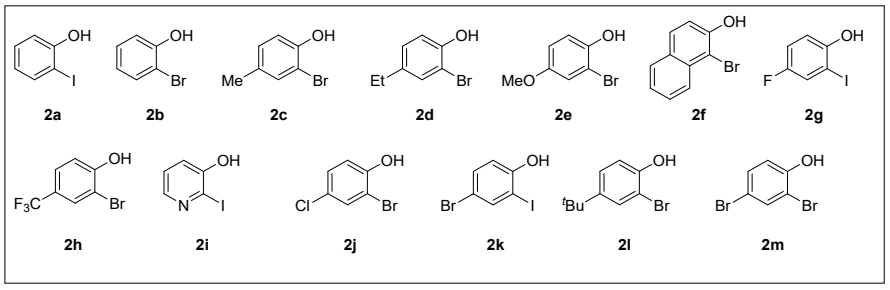
The following 2-bromo-1-phenylethan-1-ones/2-bromoacetonitrile/ethyl 2-bromoacetates (**1a-1j**) are purchased and used as received, as shown in Table-1S.

Table-1S: 2-Bromo-1-phenylethan-1-ones/2-bromoacetonitrile/ethyl 2-bromoacetates (**1a-1j**).



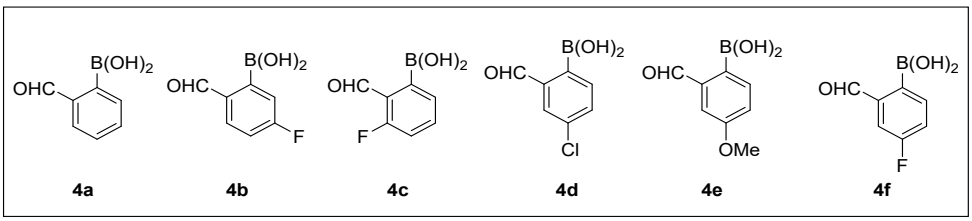
The following 2-bromophenols/2-iodophenols (**2a–2m**) are purchased and used as received, as shown in Table-2S.

Table-2S: 2-Bromophenols/ 2-Iodophenols (**2a–2m**).



The following 2-formylphenyl boronic acids **4a**-**4f** are purchased and used as received, as shown in Table 3S.

Table-3S: Different 2-formylphenyl boronic acids (**4a–4f**).



General Procedure – 1 (GP-1) for the Preparation of *o*-Alkylphenyl ethers/2-(2-bromophenoxy)acetonitrile/alkyl 2-(2-bromophenoxy)acetate (3a-3t):

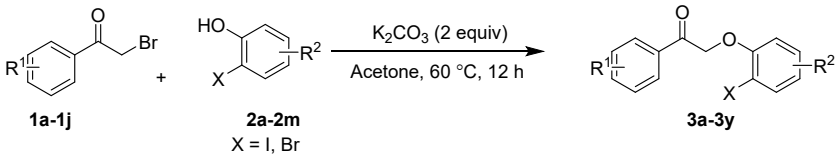
In an oven-dried round-bottom flask equipped with a magnetic stir bar, were added 2-bromophenols/2-iodophenols **2a-2m** (1 mmol) in acetone (2 mL), 2-bromo-1-phenylethan-1-ones/2-bromoacetonitrile/ethyl 2-bromoacetates **1a-1j** (1 mmol), and K_2CO_3 (2 mmol). The resultant reaction mixture was stirred in an oil bath preheated to 60 °C for 12 h. The progress of the reaction was monitored by thin-layer chromatography. The reaction was cooled to room temperature, quenched with 70 mL of water, and extracted with ethyl acetate (3 × 50 mL). The combined organic layers solution was washed with a brine solution and dried over anhydrous sodium sulphate. The solvent was removed in vacuo, and the residue was purified by chromatography (petroleum ether/ ethyl acetate: 99:01 to 90:10) furnished the products **3a-3x** (76%-90%) as white/yellow solids or oil.

General Procedure - 2 (GP-2) General strategy for the preparation of dibenzo[*b*,*d*]oxepins (5aa-5le):

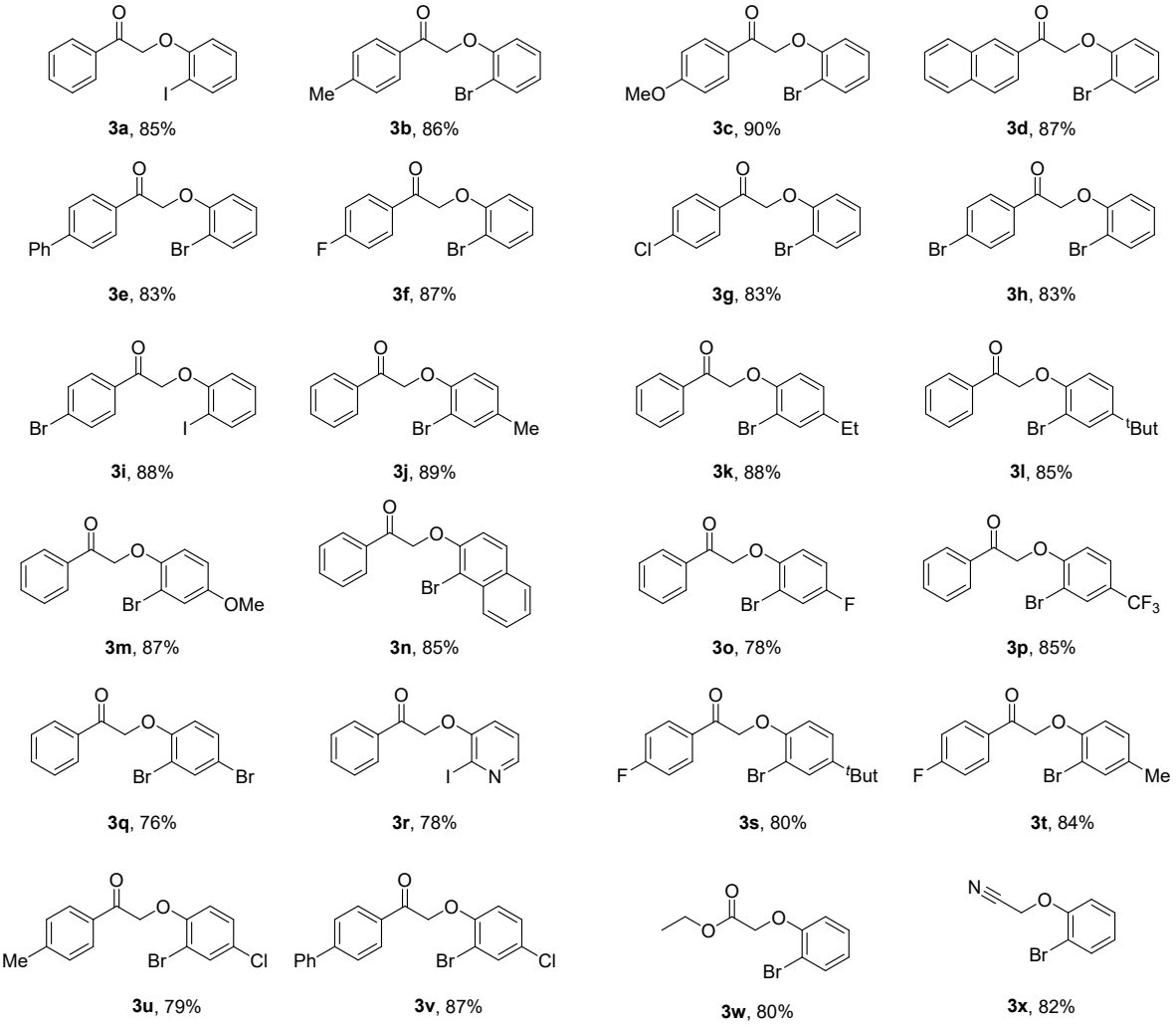
To an oven-dried 10 mL glass tube sealed with Teflon septum equipped with a magnetic stir bar, were added 2-(2-bromophenoxy)-1-phenylethan-1-ones **3a-3x** (0.2 mmol), (2-formylphenyl)boronic acid **4a-4f** (0.3 mmol), followed by $Pd(PPh_3)_4$ (5 mol%), Cs_2CO_3 (4 mmol) and solvent DMF:EtOH (3:1, 2 mL), at room temperature under inert atmosphere. The resultant reaction mixture was subjected to microwave irradiation at 120 °C for 15 min with 100 W in a closed vessel. The completion of the reaction was monitored by TLC (98:02 to 75:25 hexane and ethyl acetate). The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with a brine solution, dried (Na_2SO_4), and filtered. Evaporation of organic solvents under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished dibenzo[*b,d*]oxepine **5aa-5le** (70% to 94%) as a colourless/brown/greenish liquid, colourless gel, *or* white solid.

The following starting material is reported in the literature excluding **3i**, **3k**, **3l**, **3p**, **3t**, **3u**, **3v**, **3s**, and **3w** (Table 3S).

Table-4S: Keto-ethers (**3a-3x**).[1]



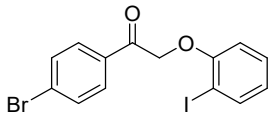
1a-1j + **2a-2m** (X = I, Br) → **3a-3y**



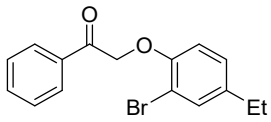
[a]**Reaction conditions**: all reactions were performed using **1a-1j** (0.1 mmol), **2a-2m** (0.1 mmol), K_2CO_3 (2 equiv), acetone (5 mL), 60 °C, 3 h. [b]Isolated yields of **3a-3x**.

Reference:

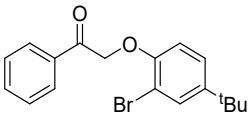
(1) Kishore, D. R.; Satyanarayana, G. Intermolecular Sonogashira Coupling and Intramolecular 5-Exo-Dig Cycloisomerization Cascade: A One-Pot Pathway for Accessing (3-Benzylbenzofuran-2-Yl)(Phenyl)Methanones. *J. Org. Chem.* **2022**, *87* (15), 10158–10172. https://doi.org/10.1021/acs.joc.2c01101.



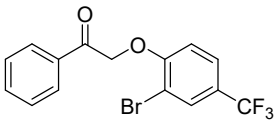
1-(4-Bromophenyl)-2-(2-iodophenoxy)ethan-1-one (3i): GP- 1 was carried out with **1g** (278 mg, 1 mmol) **2a** (220 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol), and acetone (5 mL) at 60 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 90/10) furnished the product **3i** (366 mg, 88%) as a white solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**1g**) = 0.40, R_f (**2a**) = 0.30, R_f (**3i**) = 0.50, UV detection. Melting point: 58-60 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3065, 2922, 1699, 1582, 1221, 1014, 970, 821, 750 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.89 (dd, J = 8.7, 1.9 Hz, 2H), 7.76 (dd, J = 8.0, 1.6 Hz, 1H), 7.61 (dd, J = 8.7, 1.9 Hz, 2H), 7.23 (ddd, J = 8.3, 7.5, 1.6 Hz, 1H), 6.77 – 6.68 (m, 2H), 5.22 (s, 2H). **^{13}C**{^{1}H} **NMR** (151 MHz, $CDCl_3$) δ = 193.6, 156.6, 139.9, 133.0, 132.2 (2C), 130.1 (2C), 129.6, 129.3, 123.7, 112.5, 86.4, 72.0 ppm. **HRMS** (ESI) m/z: $[(M+Na)]^+$ Calcd for $C_{14}H_{10}{}^{79}BrINaO_2^+$ 438.8801; Found: 438.8770; Calcd for $C_{14}H_{10}{}^{81}BrINaO_2^+$ 440.8781; Found: 440.8752.



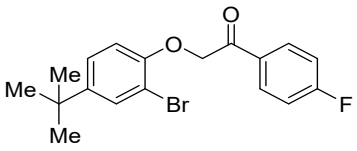
2-(2-Bromo-4-ethylphenoxy)-1-phenylethan-1-one (3k): GP-1 was carried out with **1a** (199 mg, 1 mmol), **2d** (201 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol), and acetone (5 mL) 60 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 90/10) furnished the product **3k** (280 mg, 88%) as a yellow oil. TLC (petroleum ether/ethyl acetate 98:2, R_f (**1a**) = 0.40, R_f (**2d**) = 0.50, R_f (**3k**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3748, 2964, 2343, 1701, 1598, 1494, 1224, 1085, 970, 810, 754, 688 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.02 (dd, J = 8.4, 1.3 Hz, 2H), 7.65 – 7.56 (m, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.39 (d, J = 2.1 Hz, 1H), 7.02 (dd, J = 8.4, 2.1 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 5.30 (s, 2H), 2.56 (q, J = 7.6 Hz, 2H), 1.19 (t, J = 7.6 Hz, 3H). **^{13}C** {^{1}H} **NMR** (151 MHz, $CDCl_3$) δ = 194.4, 152.7, 139.3, 134.5, 134.0, 133.0, 128.9 (2C), 128.4 (2C), 127.8, 114.1, 112.3, 72.3, 27.8, 15.6 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{16}H_{16}{}^{79}BrO_2^+$ 319.0328; Found: 319.0332; Calcd for $C_{16}H_{16}{}^{81}BrO_2^+$ 321.0308; Found: 321.0310.



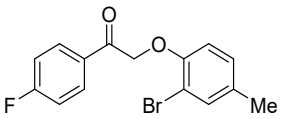
2-(2-Bromo-4-(tert-butyl)phenoxy)-1-phenylethan-1-one (3l): GP-1 was carried out with **1a** (199 mg, 1 mmol), **2l** (229 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol), and Acetone (5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **1v** (246 mg, 85%) as a colourless oil. TLC (petroleum ether/ethyl acetate 98:2, R_f (**1a**) = 0.40, R_f (**2l**) = 0.50, R_f (**3l**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3739, 3598, 2960, 2345, 2241, 2174, 1701, 1496, 1224, 1087, 971, 757, 693 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.77 (dd, J = 8.5, 1.4 Hz, 2H), 7.39 – 7.33 (m, 1H), 7.30 (d, J = 2.4 Hz, 1H), 7.27 – 7.21 (m, 2H), 6.95 (dd, J = 8.6, 2.4 Hz, 1H), 6.51 (d, J = 8.6 Hz, 1H), 5.05 (s, 2H), 1.01 (s, 9H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 194.42, 152.40, 146.33, 134.54, 134.06, 130.90, 128.9 (2C), 128.4(2C), 125.38, 113.68, 112.11, 72.22, 34.35, 31.4 (3C) ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{18}H_{20}{}^{79}BrO_2^+$ 347.0641; Found: 347.0643; Calcd for $C_{18}H_{20}{}^{81}BrO_2^+$ 349.0621; Found: 349.0623.



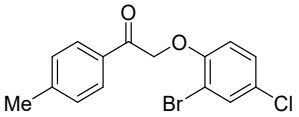
2-(2-Bromo-4-(trifluoromethyl)phenoxy)-1-phenylethan-1-one (3p): GP-1 was carried out with **1a** (199 mg, 1 mmol), **2h** (241 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol), and Acetone (5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 90/10) furnished the product **1x** (305 mg, 85%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, Rf (**1a**) = 0.40, R_f (**2h**) = 0.50, R_f (**3p**) = 0.50, UV detection. Melting point: 78-80 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} =3739, 3598, 2960, 2345, 2241, 2174, 1701, 1496, 1224, 1087, 971, 757, 693 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.00 (dd, J = 8.5, 1.4 Hz, 2H), 7.67 (dd, J = 8.2, 0.7 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.53 – 7.47 (m, 1H), 7.12 (dd, J = 8.2, 1.8 Hz, 1H), 7.01 (d, J = 1.6 Hz, 1H), 5.42 (s, 2H). **^{13}C**{^{1}H} **NMR** (101 MHz, $CDCl_3$) δ = 192.9, 154.9, 134.3, 134.2, 134.1, 130.90 (q, J_{C-F} = 32.9 Hz), 129.04, 128.2, 120.8 (q, J_{C-F} = 272.5 Hz), 119.55 (q, J_{C-F} = 3.8 Hz), 116.65, 110.27 (q, J_{C-F} = 3.8 Hz), 71.64 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{15}H_{11}{}^{79}BrF_3O_2^+$ 358.9889; Found: 358.9886; $C_{15}H_{11}{}^{81}BrF_3O_2^+$ 360.9869; Found: 360.9870.



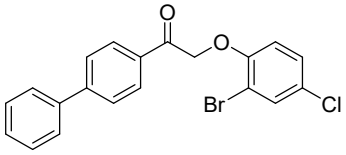
2-(2-Bromo-4-(*tert*-butyl)phenoxy)-1-(4-fluorophenyl)ethan-1-one (3s): GP-1 was carried out with **1f** (217 mg, 1 mmol), **2l** (229 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol), and Acetone (5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 90/10) furnished the product **3s** (246 mg, 80%) as a colourless oil. TLC (petroleum ether/ethyl acetate 98:2, R_f (**1f**) = 0.40, R_f (**2l**) = 0.50, R_f (**3s**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3055, 2918, 1695, 1602, 1226, 1099, 985, 758 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.10 – 7.96 (m, 2H), 7.48 (d, J = 2.4 Hz, 1H), 7.14 (dd, J = 8.6, 2.4 Hz, 1H), 7.12–7.05 (m, 2H), 6.69 (d, J = 8.6 Hz, 1H), 5.16 (s, 2H), 1.20 (s, 9H). **^{13}C**{^{1}H} **NMR** (101 MHz, $CDCl_3$) δ = 193.3, 166.3 (d, $J_{C\text{-}F}$ = 256.3 Hz), 152.2, 146.5, 131.3 (d, $J_{C\text{-}F}$ = 9.5 Hz, 2C), 131.0 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.9, 125.4, 116.1 (d, J = 21.9 Hz, 2C), 113.5, 112.0, 72.3, 72.3, 31.4 (3C) ppm. **HRMS** (ESI) m/z: $[(M+Na)]^+$ Calcd for $C_{18}H_{18}{}^{79}BrFNaO_2^+$ 387.0366; Found: 387.0370; Calcd for $C_{18}H_{18}{}^{81}BrFNaO_2^+$ 389.0346; Found: 389.0359.



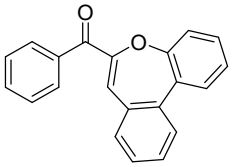
2-(2-Bromo-4-methylphenoxy)-1-(4-fluorophenyl)ethan-1-one (3t): GP-1 was carried out with **1f** (217 mg, 1 mmol), **2c** (187 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol), and Acetone (5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 90/10) furnished the product **3t** (271 mg, 84%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**1f**) = 0.40, R_f (**2c**) = 0.50, R_f (**3t**) = 0.50, UV detection. Melting point: 60-62 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3711, 3640, 3529, 2702, 2343, 2246, 2125, 2039, 1700, 1495, 1232, 756, 687 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.11 – 8.03 (m, 2H), 7.36 – 7.33 (m, 1H), 7.17 – 7.11 (m, 2H), 7.01 – 6.95 (m, 1H), 6.72 (d, J = 8.3 Hz, 1H), 5.22 (s, 1H), 2.24 (s, 3H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 193.1, 166.2 (d, $J_{C\text{-}F}$ = 256.1 Hz), 152.3, 134.1, 132.9, 131.3 (d, $J_{C\text{-}F}$ = 9.5 Hz), 130.9 (d, $J_{C\text{-}F}$ = 3.0 Hz), 128.9, 116.0 (d, $J_{C\text{-}F}$ = 21.9 Hz), 113.8, 112.0, 72.2, 20.2 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{15}H_{13}{}^{79}BrFO_2^+$ 323.0077; Found: 323.0074; Calcd for $C_{15}H_{13}{}^{81}BrFO_2^+$ 325.0057; Found: 325.0056.



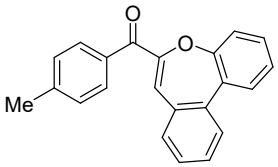
2-(2-Bromo-4-chlorophenoxy)-1-(*p*-tolyl)ethan-1-one (3u): GP-1 was carried out with **1b** (213 mg, 1 mmol), **2j** (207 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol), and Acetone (5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 90/10) furnished the product **3u** (267 mg, 79%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**1b**) = 0.40, R_f (**2j**) = 0.50, R_f (**3u**) = 0.50, UV detection. Melting point: 78-80 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} =2922, 1695, 1604, 1475, 1226, 1087, 970, 809 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.78 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 2.5 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.03 (dd, J = 8.8, 2.5 Hz, 1H), 6.61 (d, J = 8.8 Hz, 1H), 5.19 (s, 2H), 2.31 (s, H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 193.1, 153.5, 145.1, 133.0, 131.7, 129.6, 128.3 (2C), 128.2 (2C), 126.94, 114.4, 112.8, 71.8, 21.8 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{15}H_{13}{}^{79}BrClO_2^+$ 338.9782; Found: 338.9787; $[(M+H)]^+$ Calcd for $C_{15}H_{13}{}^{81}BrClO_2^+$ 340.9761; Found: 340.9763.



1-([1,1'-Biphenyl]-4-yl)-2-(2-bromo-4-chlorophenoxy)ethan-1-one (3v): GP-1 was carried out with **1e** (275 mg, 1 mmol), **2j** (207 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol), and Acetone (5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 90/10) furnished the product **3v** (384 mg, 87%) as a yellow viscous oil. TLC (petroleum ether/ethyl acetate 98:2, R_f (**1e**) = 0.40, R_f (**2j**) = 0.50, R_f (**3v**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3066, 2857, 1694, 1600, 1476, 1229, 973, 735, 694, cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.09 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H), 7.64 (dd, J = 7.1, 1.4 Hz, 2H), 7.56 (d, J = 2.5 Hz, 1H), 7.50 (d, J = 7.1 Hz, 1H), 7.53 – 7.345 (m, 2H), 7.45 – 7.37 (m, 1H), 7.19 (dd, J = 8.8, 2.5 Hz, 1H), 6.77 (d, J = 8.8 Hz, 1H), 5.35 (s, 2H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 193.4, 153.6, 146.9, 139.7, 133.3, 132.9, 129.2 (2C), 129.0 (2C), 128.7, 128.4, 127.6 (2C), 127.4 (2C), 127.3, 114.6, 113.0, 72.2 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{20}H_{15}{}^{79}BrClO_2^+$ 400.9938; Found: 400.9942; Calcd for $C_{20}H_{15}{}^{81}BrClO_2^+$ 402.9918; Found: 402.9930.

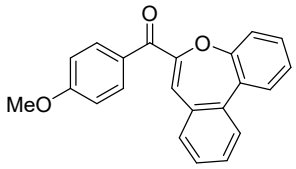


Dibenzo[*b,d*]oxepin-6-yl(phenyl)methanone (5aa): GP-2 was carried out with **3a** (67 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5aa** (55 mg, 94%) as a white crystalline solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3a**) = 0.40, R_f (**5aa**) = 0.50, UV detection. Melting point: 128-130 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3846, 3747, 3629, 3358, 3251, 2347, 2231, 2172, 2134, 1905, 1664, 1526, 1261, 759 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.91 – 7.86 (m, 2H), 7.67 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.52 – 7.43 (m, 4H), 7.39 (td, *J* = 7.5, 1.3 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.26 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.17 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.14 (s, 1H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 190.3, 159.9, 154.7, 138.5, 137.3, 132.7, 132.5, 132.4, 130.7, 129.97, 129.8, 129.6, 129.5 (2C), 129.2, 128.8, 128.3 (2C), 127.9, 125.9, 121.9 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{21}H_{15}O_2^+$ 299.1067; Found: 299.1066.

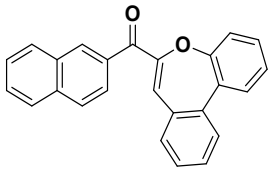


Dibenzo[*b,d*]oxepin-6-yl(*p*-tolyl)methanone (5ba): GP-2 was carried out with **3b** (61 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ba** (56 mg, 90%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**1b**) = 0.40, R_f (**5ba**) = 0.50, UV detection. Melting point: 128-130 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3734, 3582, 3052, 2359, 1655, 1609, 1485, 1434, 1274, 1196, 966, 758 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.2 Hz, 2H), 7.65 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.44 (td, *J* = 7.6, 1.5 Hz, 1H), 7.37 (td, *J* = 7.5, 1.3 Hz, 1H), 3.34 – 7.25 (m, 4H), 7.24 (td, *J* = 7.5, 1.4 Hz, 1H), 7.17 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.12 (s, 1H), 2.43 (s, 3H). **^{13}C**{^{1}H} **NMR** (101 MHz, $CDCl_3$) δ = 189.9, 160.1, 154.9, 143.3, 138.5, 134.6, 132.8, 132.6, 130.75, 130.0, 129.9, 129.8 (2C), 129.5, 129.2, 129.1 (2C), 128.3,

127.91, 125.9, 121.9, 21.8 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{22}H_{17}O_2^+$ 313.1223; Found: 313.1223.

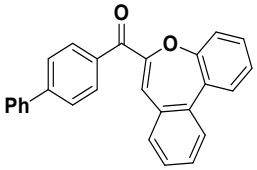


Dibenzo[*b,d*]oxepin-6-yl(4-methoxyphenyl)methanone (5ca): GP-2 was carried out with **3c** (64 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ca** (60 mg, 93%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f(**3c**) = 0.50, R_f(**5ca**) = 0.50, UV detection. Melting point: 98-100 °C. **IR** (MIR-ATR, 4000-600 cm−1) ν_{max} = 3738, 3604, 3061, 2354, 1650, 16001497, 1435, 1259, 1177, 965, 762 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99 (d, J = 8.9 Hz, 2H), 7.67 (dd, J = 7.8, 1.0 Hz, 1H), 7.51 (dd, J = 7.7, 1.7 Hz, 1H), 7.46 (td, J = 7.6, 1.6 Hz, 1H), 7.39 (td, J = 7.5, 1.3 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.25 (td, J = 7.5, 1.4 Hz, 1H), 7.15 (dd, J = 7.9, 1.4 Hz, 1H), 7.15 (s, 1H), 6.98 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 188.6, 163.4, 160.1, 155.3, 138.5, 132.8, 132.7, 132.3 (2 C), 130.7, 130.0, 129.8, 129.7, 129.4, 129.2, 127.9, 127.4, 125.9, 121.7, 113.6 (2 C), 55.6 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{22}H_{17}O_3^+$ 329.1172; Found: 329.1172.

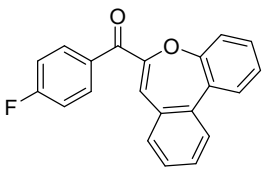


Dibenzo[*b,d*]oxepin-6-yl(naphthalen-1-yl)methanone (5da): GP-2 was carried out with **3d** (68 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5da** (52 mg, 76%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3d**) = 0.50, R_f (**5da**) = 0.50, UV detection. Melting point: 80-82 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3059, 2320, 1732, 1653, 1481, 1435, 1283, 1195, 942, 761 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.48 (s, 1H), 7.97 – 7.93 (m, 2H),

7.91 (d, J = 8.8 Hz, 1H), 7.69 (dd, J = 7.8, 0.9 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.59 – 7.55 (m, 1H), 7.55 – 7.50 (m, 1H), 7.47 (dd, J = 7.7, 1.4 Hz, 1H), 7.40 (td, J = 7.5, 1.3 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.29 (dd, J = 7.8, 1.7 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.23 (s, 1H), 7.14 (dd, J = 7.9, 1.5 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 190.1, 160.1, 155.1, 138.6, 135.3, 134.6, 132.8, 132.6, 132.37, 131.2, 130.9, 130.1, 129.9, 129.7, 129.6, 129.3, 128.7, 128.46, 128.3, 128.0, 127.9, 126.9, 126.0, 125.7, 121.9 ppm. **HRMS** (ESI) m/z: $[(M+(-H_2O)]^+$ Calcd for $C_{25}H_{14}O^+$ 330.1044; Found: 330.1049.

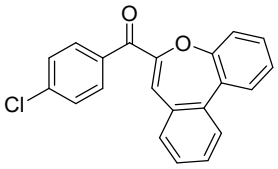


[1,1'-Biphenyl]-4-yl(dibenzo[*b,d*]oxepin-6-yl)methanone (5ea): GP-2 was carried out with **3e** (73 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl 100/00 to 95/05) furnished the product **5ea** (63 mg, 86%) as a light orange-coloured oil. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3e**) = 0.40, R_f (**5ea**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3808, 3737, 3599, 3052, 2925, 2356, 1658, 1605, 1487, 1273, 1198, 968, 755 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.01 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H), 7.71 – 7.64 (m, 3H), 7.54 – 7.46 (m, 4H), 7.45 – 7.39 (m, 2H), 7.38 – 7.32 (m, 2H), 7.27 (td, J = 7.5, 1.4 Hz, 1H), 7.21 (s, 1H) , 7.20 (dd, J = 8.0, 1.3 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 189.8, 160.1, 154.9, 145.3, 140.0, 138.6, 136.0, 132.8, 132.6, 130.9, 130.4 (2 C), 130.1, 129.9, 129.6, 129.2, 129.1 (2 C), 128.5, 128.3, 127.9, 127.4 (2 C), 127.0 (2 C), 125.9, 121.9 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{27}H_{19}O_2^+$ 375.1380; Found: 375.1367.

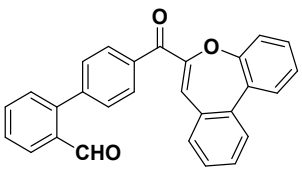


Dibenzo[*b,d*]oxepin-6-yl(4-fluorophenyl)methanone (5fa): GP-2 was carried out with **3f** (61 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min.

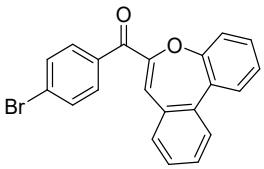
Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5fa** (49 mg, 79%) as a yellow oil. TLC (petroleum ether/ethyl acetate 98:2, Rf (**3f**) = 0.40, R_f (**5fa**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3737, 3547, 3041, 2348, 2139, 2095, 1662, 1602, 1498, 1274, 1219, 968, 765 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.68 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.48 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1H), 2.36 – 7.30 (m, 2H), 7.26 (dd, 7.5, 1.5 Hz, 1H), 7.22 – 7.14 (m, 3H), 7.09 (dd, *J* = 7.9, 1.4 Hz, 1H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 188.6, 165.5 (d, *J* = 254.1 Hz), 160.0, 154.8, 138.6, 133.4 (d, *J* = 3.1 Hz), 132.7, 132.6, 132.4 (d, *J* = 9.1 Hz) (2C), 130.9, 130.2, 129.9, 129.7, 129.3, 128.3, 128.0, 126.1, 121.8, 115.6 (d, *J* = 21.8 Hz) (2C) ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{21}H_{14}FO_2^+$ 317.0972; Found 317.0972.



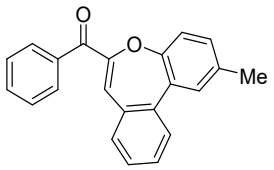
(4-Chlorophenyl)(dibenzo[*b,d*]oxepin-6-yl)methanone (5ga): GP-2 was carried out with **3g** (65 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ga** (51 mg, 78%) as a light greenish oil. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3g**) = 0.40, R_f (**5ga**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} =3741, 2351, 2081, 1660, 1594, 1486, 1434, 1272, 1999, 1094, 967, 760 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 8.7 Hz, 2H), 7.68 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.38 (m, 1H), 7.34 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.30 (dd, *J* = 11.5, 1.7 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.17 (s, 1H), 7.09 (dd, *J* = 7.9, 1.4 Hz, 1H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 188.8, 159.9, 154.6, 138.9, 138.6, 135.5, 132.6, 132.5, 131.2 (2C), 130.9, 130.1, 129.9, 129.8, 129.2, 128.7 (2C), 128.5 128.0, 126.0, 121.7 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{21}H_{14}ClO_2^+$ 333.0677; Found 333.0675.



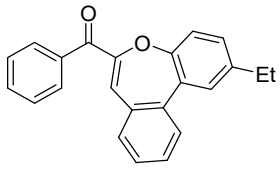
4'-(Dibenzo[*b,d*]oxepine-6-carbonyl)-[1,1'-biphenyl]-2-carbaldehyde (5ha): GP-2 was carried out with **3h** (74 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 90/10) furnished the product **5ha** (37 mg, 50%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**5h**) = 0.50, R_f (**5ha**) = 0.50, UV detection. Melting point: 162-164 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3868, 3458, 3068, 2354, 2161, 2039, 1696, 1599, 1267, 764 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 10.05 (s, 1H), 7.92 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.70 – 7.57 (m, 3H), 7.56 – 7.44 (m, 6H), 7.42 (td, *J* = 7.4, 1.5 Hz, 1H), 7.4 – 732 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.19 (s, 1H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 192.3, 190.3, 160.0, 154.7, 144.9, 137.8, 137.3, 135.6, 133.9, 133.8, 132.8, 132.7 (2C), 131.7, 131.3, 131.0, 130.9, 129.8, 129.7 (2C), 129.3, 128.9, 128.5 (2C), 128.4, 128.2, 127.9, 122.1 ppm. **HRMS** (ESI) m/z: $[(M+K)]^+$ Calcd for $C_{28}H_{18}KO_3^+$ 441.0888; Found: 441.0869.



(4-Bromophenyl)(dibenzo[*b,d*]oxepin-6-yl)methanone (5ia): GP-2 was carried out with **3i** (83 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ia** (51 mg, 68%) as a yellow oil. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3i**) = 0.40, R_f (**5ia**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3062, 2926, 1659, 1585, 1480, 1435, 1273, 1200, 967, 757 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.74 – 7.71 (m, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.46 – 7.38 (m, 2H), 7.31 (d, *J* = 7.6, 7.4,1.2 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.20 (d, *J* = 1.4, 7.6, 7.4 Hz, 1H), 7.09 (s, 1H), 7.01 (dd, *J* = 8.0, 1.2 Hz, 1H). **^{13}C**{^{1}H} **NMR** (151 MHz, $CDCl_3$) δ = 189.0, 159.9, 154.6, 138.6, 136.0, 132.6, 132.5, 131.7 (2C), 131.3 (2C), 130.9, 130.2, 129.9, 129.8, 129.3, 128.6, 128.0, 127.6, 126.1, 121.8 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{21}H_{14}{}^{79}BrO_2^+$ 377.0172; Found: 377.0182; Calcd for $C_{21}H_{14}{}^{81}BrO_2^+$ 379.0151; Found: 379.0156.

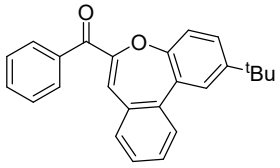


(2-Methyldibenzo[*b,d*]oxepin-6-yl)(phenyl)methanone (5ja): GP-2 was carried out with **3j** (60 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (4:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ja** (56 mg, 91%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3j**) = 0.50, R_f (**5ja**) = 0.50, UV detection. Melting point: 110-112 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3057, 1658, 1491, 1441, 1273, 1197, 966, 760, 715 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.89 (dd, J = 8.4, 1.4 Hz, 2H), 7.68 (dd, J = 7.8, 0.9 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.54 – 7.43 (m, 3H), 7.38 (td, J = 7.5, 1.3 Hz, 1H), 7.31 (dd, J = 7.7, 1.5 Hz, 2H), 7.16 – 7.12 (m, 2H), 7.06 (d, J = 8.2 Hz, 1H), 2.38 (s, 3H). **^{13}C**{^{1}H} **NMR** (101 MHz, $CDCl_3$) δ = 190.4, 158.0, 154.9, 138.7, 137.5, 135.4, 132.8, 132.4, 132.1, 130.8, 130.5, 130.4, 129.6 (2C), 129.6, 129.1, 128.8, 128.4 (2C), 127.8, 121.6, 21.0 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{22}H_{17}O_2^+$ 313.1223; Found: 313.1224.

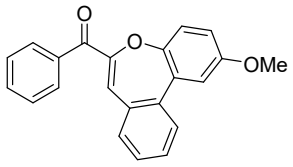


(2-(Tert-butyl)dibenzo[*b,d*]oxepin-6-yl)(phenyl)methanone (5ka): GP-2 was carried out with **3k** (63 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ka** (59 mg, 92%) as a white solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3k**) = 0.40, R_f (**5ka**) = 0.50, UV detection. Melting point: 104-106 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3058, 2927, 1658, 11491, 1444, 1405, 1272, 1197, 966, 712 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.90 (dd, J = 8.4, 1.4 Hz, 2H), 7.70 (dd, J = 7.8, 0.8 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.54 – 7.44 (m, 3H), 7.39 (td, J = 7.5,

1.3 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.17 (dd, J = 8.2, 2.2 Hz, 1H), 7.14 (s, 1H), 7.10 (d, J = 8.2 Hz, 1H), 2.68 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.6 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 190.4, 158.1, 154.9, 141.8, 138.8, 137.5, 132.8, 132.4, 132.2, 130.8, 129.6 (2C), 129.6, 129.3, 129.3, 129.2, 128.8, 128.4 (2C), 127.8, 121.6, 28.5, 15.8 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{23}H_{19}O_2^+$ 327.1380; Found: 327.1377.

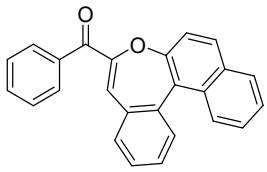


(2-(Tert-butyl)dibenzo[*b,d*]oxepin-6-yl)(phenyl)methanone (5la): GP-2 was carried out with **3l** (69 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5la** (63 mg, 90%) as a yellow oil. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3l**) = 0.40, R_f (**5la**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3059, 2959, 1660, 1492, 1273, 1207, 967, 834, 760 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.89 (dd, J = 8.4, 1.4 Hz, 2H), 7.70 (dd, J = 7.7, 0.7 Hz, 1H), 7.63 – 7.55 (m, 1H), 7.53 – 7.45 (m, 4H), 7.39 (td, J = 7.6, 1.3 Hz, 1H), 7.35 (dd, J = 8.5, 2.4 Hz, 1H), 7.32 (dd, J = 7.6, 1.4 Hz, 1H), 7.13 (s, 1H), 7.09 (d, J = 8.5 Hz, 1H), 1.35 (s, 9H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 190.4, 157.9, 154.9, 148.7, 139.1, 137.5, 132.9, 132.4, 131.7, 130.8, 129.7 (2C), 129.6, 129.2, 128.80, 128.4 (2C), 127.8, 127.0, 126.9, 121.2, 34.7, 31.6 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{25}H_{23}O_2^+$ 355.1693; Found: 355.1680.

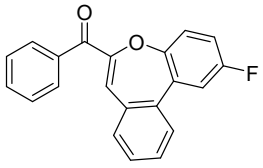


(2-Methoxydibenzo[*b,d*]oxepin-6-yl)(phenyl)methanone (5ma): GP-2 was carried out with **3m** (59.66 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ma** (55 mg, 84%) as a yellow crystalline solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3m**) = 0.40, R_f (**5ma**) = 0.50, UV detection.

Melting point: 116-118 °C. **IR** (MIR-ATR, 4000-600 $cm^{-1)}$ ν_{max} = 3652, 3075, 2353, 1738, 1657, 1611, 1485, 1441, 1282, 1156, 981, 762 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.86 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.67 – 7.54 (m, 2H), 7.52 – 7.47 (m, 2H), 7.47 – 7.42 (m, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.34 (td, *J* = 7.4, 1.3 Hz, 1H), 7.29 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.12 (s, 1H), 6.84 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.75 (d, *J* = 2.6 Hz, 1H), 3.80 (s, 3H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 190.5, 161.4, 160.8, 154.2, 138.5, 137.6, 132.4, 132.2, 130.9, 130.4, 129.7, 129.6 (3C), 128.8, 128.4 (2C), 127.3, 124.9, 112.7, 106.9, 55.7 ppm. **HRMS** (ESI) m/z: $[(M+Na)]^+$ Calcd for $C_{22}H_{16}NaO_3^+$ 351.0992; Found: 351.0978.

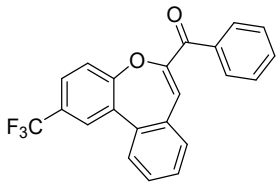


Benzo[*d*]naphtho[1,2-*b*]oxepin-2-yl(phenyl)methanone (5na): GP-2 was carried out with **3n** (68 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5na** (48 mg, 70%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3n**) = 0.40, R_f (**5na**) = 0.50, UV detection. Melting point: 114-116 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3061, 2351, 1658, 1281, 1206, 977, 752 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.07 – 8.00 (m, 1H), 7.92 – 7.84 (m, 3H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.43 (m, 7H), 7.36 (d, *J* = 8.9 Hz, 1H), 7.25 (s, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 190.0, 160.1, 156.6, 137.3, 136.4, 134.4, 132.7, 132.5, 132.5, 132.3, 130.2, 130.2, 129.6 (2C), 129.5, 128.5, 128.4 (2C), 128.05, 127.6, 126.8 (2C), 125.8, 125.3, 121.3 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{25}H_{17}O_2^+$ 349.1223; Found: 349.1222.

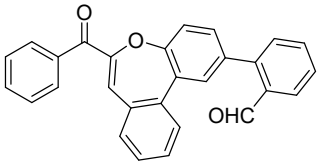


(2-Fluorodibenzo[*b,d*]oxepin-6-yl)(phenyl)methanone (5oa): GP-2 was carried out with **3o** (61 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min.

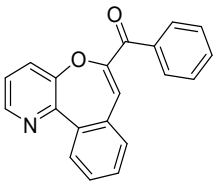
Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5oa** (51 mg, 82%) as a white viscous oil. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3o**) = 0.40, R_f (**5oa**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3936, 3874, 3604, 2449, 2358, 2235, 2162, 1952, 1516, 1094, 1027, 778 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.80 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.57 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.56 – 7.49 (m, 1H), 7.45 – 7.39 (m, 4H), 7.35 (td, *J* = 7.5, 1.4 Hz, 1H), 7.26 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.22 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 7.13 (s, 1H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 190.2, 158.5, 154.7, 137.2, 134.1, 132.7, 132.7, 131.2, 130.9, 129.9, 129.7, 129.6, 129.6 (2C), 129.2, 128.8, 128.6, 128.5 (2C), 127.9, 123.3, 77.2, 1.2 ppm. **HRMS** (ESI) m/z: $[(M]^+$ Calcd for $C_{21}H_{13}FO_2^+$ 316.0894; Found: 316.0892.



Phenyl(2-(trifluoromethyl)dibenzo[*b,d*]oxepin-6-yl)methanone (5pa): GP-2 was carried out with **3p** (71 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5pa** (56 mg, 78%) as a light-yellow oil. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3p**) = 0.40, R_f (**5pa**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3059, 2959, 1660, 1491, 1272, 1207, 967, 759, 711 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 8.4 Hz, 2H), 7.68 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.55 – 7.42 (m, 5H), 7.36 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.14 (s, 1H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 190.0, 159.8, 154.6, 137.1, 137.1, 136.1, 132.8, 132.7, 131.9 (q, $J_{C\text{-}F}$ = 33.2 Hz), 131.0, 130.5, 129.9, 129.6 (2C), 129.5, 128.9, 128.7, 128.5 (2C), 123.7 (q, $J_{C\text{-}F}$ = 272.3 Hz), 122.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 119.4 (q, $J_{C\text{-}F}$ = 3.7 Hz) ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{22}H_{14}F_3O_2^+$ 367.0940; Found: 403. 367.0912.

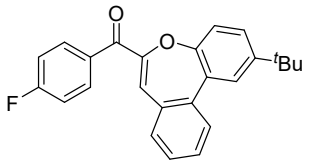


2-(6-Benzoyldibenzo[*b,d*]oxepin-2-yl)benzaldehyde (5qa): GP-2 was carried out with **3q** (74 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5qa** (66 mg, 83%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3q**) = 0.40, R_f (**5qa**) = 0.50, UV detection. Melting point: 126-128 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3060, 2926, 1686, 1602, 1270, 1201, 1131, 966, 833, 760 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 10.05 (d, J = 0.7 Hz, 1H), 8.03 (dd, J = 7.8, 1.2 Hz, 1H), 7.92 (dd, J = 8.4, 1.4 Hz, 2H), 7.71 – 7.57 (m, 3H), 7.55 – 7.49 (m, 4H), 7.48 – 7.44 (m, 2H), 7.42 (td, J = 7.4, 1.4 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.30 (d, J = 8.2 Hz, 1H), 7.19 (s, 1H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 192.2, 190.2, 160.0, 154.6, 144.1, 137.8, 137.2, 135.5, 133.8 (2C), 132.8, 132.6 (2C), 131.7, 131.3, 130.9, 130.9, 129.8, 129.6 (2C), 129.3, 128.9, 128.4 (2C), 128.3, 128.1, 127.9, 122.1 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{28}H_{19}O_3^+$ 403.1329; Found: 403.1310.

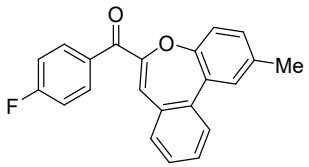


Benzo[4,5]oxepino[3,2-*b*]pyridin-6-yl(phenyl)methanone (5ra): GP-2 was carried out with **3r** (67 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ra** (47 mg, 80%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3r**) = 0.40, R_f (**5ra**) = 0.50, UV detection. Melting point: 88-90 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3466, 3059, 2353, 1656, 1439, 1269, 1190, 966, 801 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.54 (dd, J = 4.6, 1.5 Hz, 1H), 8.21 (dd, J = 7.9, 1.3 Hz, 1H), 7.87 (dd, J = 8.3, 1.3 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.57 – 7.42 (m, 5H), 7.35 – 7.28 (m, 2H), 7.11 (s, 1H). **^{13}C**{^{1}H} **NMR** (101 MHz, $CDCl_3$) δ = 190.2, 155.7, 153.8, 149.9, 146.8, 137.8, 137.2, 132.7, 132.2, 130.7, 130.2, 129.9, 129.7, 129.5 (2C), 129.54, 129.1,

128.5 (2C), 124.5 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{20}H_{14}NO_2^+$ 300.1019; Found: 300.1007.

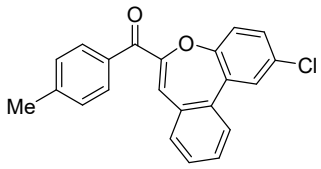


[1,1'-Biphenyl]-4-yl(2-chlorodibenzo[*b,d*]oxepin-6-yl)methanone (5sa): GP-2 was carried out with **3s** (80 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5sa** (59 mg, 73%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f(**3s**) = 0.40, R_f (**5sa**) = 0.50, UV detection. Melting point: 136-138 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3060, 1656, 1605, 1480, 1268, 1196, 964, 846, 745 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99 (dd, J = 8.5, 1.9 Hz, 2H), 7.73 (dd, J = 8.5, 1.9 Hz, 2H), 7.70 – 7.61 (m, 3H), 7.54 – 7.46 (m, 4H), 7.46 – 7.39 (m, 2H), 7.36 (dd, J = 7.6, 1.4 Hz, 1H), 7.30 (dd, J = 8.6, 2.6 Hz, 1H), 7.19 (s, 1H), 7.15 (d, J = 8.6 Hz, 1H). **^{13}C**{^{1}H} **NMR** (101 MHz, $CDCl_3$) δ = 189.5, 158.5, 154.8, 145.5, 139.9, 137.2, 135.8, 134.1, 132.8, 131.2, 130.9, 130.3 (2C), 129.8, 129.7, 129.6, 129.2, 129.2 (2C), 128.6, 128.4, 127.4 (2C), 127.1 (2C), 123.2 ppm.

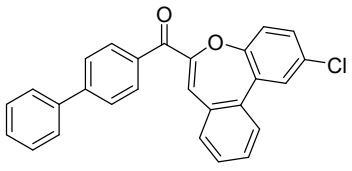


(2-(tert-butyl)dibenzo[*b,d*]oxepin-6-yl)(4-fluorophenyl)methanone (5ta): GP-2 was carried out with **3s** (73 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ta** (56 mg, 76%) as a light-yellow oil. TLC (petroleum ether/ethyl acetate 98:2, R_f(**3t**) = 0.40, R_f (**5ta**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2924, 1659, 1599, 1497, 1270, 1227, 1204, 967, 838, 757 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.01 – 7.93 (m, 2H), 7.69 (d, J = 7.5 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.40 (ddd, J = 7.6, 7.5, 1.2 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.21 – 7.11

(m, 2H), 7.01 (d, J = 8.5 Hz, 1H), 1.34 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 188.7, 157.9, 155.0, 148.9, 140.7, 140.2, 139.2, 133.53 (d, J_{C-F} = 3.3 Hz), 132.8, 132.4 (d, J_{C-F} = 9.0 Hz), 131.7, 130.8, 129.6, 129.1, 128.2, 127.9, 127.0, 126.9, 121.0, 115.4 (d, J_{C-F} = 21.9 Hz), 34.7, 31.6 ppm. **HRMS** (ESI) m/z: $[(M+K)]^+$ Calcd for $C_{25}H_{21}FKO_2^+$ 411.1157; Found: 411.1150.

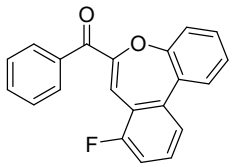


(4-Fluorophenyl)(2-methyldibenzo[*b,d*]oxepin-6-yl)methanone (5ua): GP-2 was carried out with **3u** (64 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ua** (54 mg, 82%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f(**3u**) = 0.40, R_f(**5ua**) = 0.50, UV detection. Melting point: 102-104 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3059, 2923, 1657, 1598, 1494, 1270, 1229, 1198, 975, 839, 754 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.02 – 7.90 (m, 2H), 8.02 – 7.90 (m, 1H), 7.47 (ddd, J = 7.8, 7.6, 1.4 Hz, 1H), 7.39 (ddd, J = 7.8, 7.6, 1.4 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.21 – 7.14 (m, 3H), 7.12 (dd, J = 8.2, 2.0 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 2.37 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 188.6, 165.45 (d, J_{C-F} = 254.0 Hz), 157.9, 154.9, 138.7, 135.6, 133.48 (d, J_{C-F} = 3.2 Hz), 132.7, 132.41 (d, J_{C-F} = 9.1 Hz) (2C), 132.1, 130.8, 130.6, 130.4, 129.6, 129.2, 128.2, 127.9, 121.4, 115.56 (d, J_{C-F} = 21.8 Hz) (2C), 21.0 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{22}H_{16}FO_2^+$ 331.1129; Found: 331.1133.

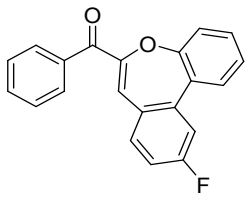


(2-Chlorodibenzo[b,d]oxepin-6-yl)(p-tolyl)methanone (5va): GP-2 was carried out with **3v** (67 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5va** (53 mg, 77%) as a yellow solid. TLC

(petroleum ether/ethyl acetate 98:2, R_f (**3v**) = 0.40, R_f (**5va**) = 0.50, UV detection. Melting point: 105-107 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3059, 1656, 1610, 1480, 1271, 1195, 964, 754 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.81 (dd, J = 8.2, 1.7 Hz, 2H), 7.64 (dd, J = 7.8, 1.1 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.42 (ddd, J = 7.6, 7.5, 1.4 Hz, 1H), 7.33 (dd, J = 7.6, 1.4 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.13 (d, J = 8.7 Hz, 1H), 7.11 (s, 1H), 2.45 (s, 3H). **^{13}C**{^{1}H} **NMR** (101 MHz, $CDCl_3$) δ = 189.6, 158.5, 154.9, 143.5, 137.1, 134.4, 134.1, 132.8, 131.0, 130.8, 129.8 (2C), 129.7, 129.6, 129.5, 129.1 (2C), 128.5, 128.1, 123.2, 21.8 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{22}H_{16}ClO_2^+$ 347.0833; Found: 347.0841.

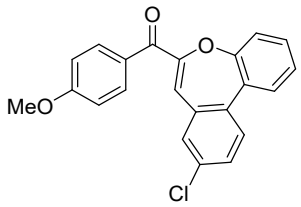


(10-Fluorodibenzo[*b,d*]oxepin-6-yl)(phenyl)methanone (5ab): GP-2 was carried out with **3a** (67 mg, 0.2 mmol), **4b** (50 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ab** (52 mg, 83%) as a white solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3a**) = 0.40, R_f (**5ab**) = 0.50, UV detection. Melting point: 82-84 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3842, 3638, 3526, 2345, 2240, 2127, 2034, 1942, 1661, 1448, 1263, 967, 753 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.88 (dd, J = 8.4, 1.4 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.53 – 7.45 (m, 3H), 7.41 – 7.34 (m, 21), 7.11 (s, 1H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 190.2, 163.1 (d, $J_{C\text{-}F}$ = 250.5 Hz), 159.7, 154.3, 141.0 (d, $J_{C\text{-}F}$ = 8.4 Hz), 137.3, 132.9 (d, $J_{C\text{-}F}$ = 8.8 Hz), 132.5, 131.6, 130.6, 129.9, 129.6 (2C), 128.9 (d, $J_{C\text{-}F}$ = 3.1 Hz) , 128.4 (2C), 128.0, 126.1, 122.1, 115.9 (d, $J_{C\text{-}F}$ = 22.9 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.9 Hz) ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd $C_{21}H_{14}FO_2^+$ 317.0972; Found: 317.0992.

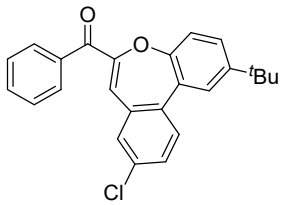


(8-Fluorodibenzo[*b,d*]oxepin-6-yl)(phenyl)methanone (5ac): GP-2 was carried out with **3a** (67 mg, 0.2 mmol), **4c** (50 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min.

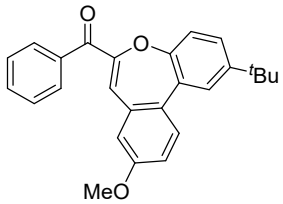
Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ac** (49 mg, 79%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3a**) = 0.50, R_f (**5ac**) = 0.50, UV detection. Melting point: 78-80 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3735, 3636, 3530, 3407, 2345, 2245, 2185, 2131, 2041, 1949, 1715, 1607, 1450, 1200, 967, 750 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.90 (dd, J = 8.4, 1.3 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.55 – 7.41 (m, 5H), 7.40 – 7.35 (m, 1H), 7.32 (d, J = 2.0 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.14 – 7.08 (m, 1H). **^{13}C**{^{1}H} **NMR** (101 MHz, $CDCl_3$) δ = 190.1, 160.2 (d, $J_{C\text{-}F}$ = 250.7 Hz), 160.0, 155.1, 140.2, 137.1, 132.7, 131.68 (d, $J_{C\text{-}F}$ = 2.4 Hz), 130.78 (d, $J_{C\text{-}F}$ = 9.4 Hz), 130.5, 130.0, 129.7 (2C), 128.4 (2C), 126.0, 124.73 (d, $J_{C\text{-}F}$ = 3.2 Hz), 121.4 (d, $J_{C\text{-}F}$ = 7.1 Hz), 121.12 (d, $J_{C\text{-}F}$ = 14.2 Hz), 114.2 (d, $J_{C\text{-}F}$ = 21.9 Hz) ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd $C_{21}H_{14}FO_2^+$ 317.0972; Found: 317.0949.



(9-Chlorodibenzo[*b,d*]oxepin-6-yl)(4-methoxyphenyl)methanone (5cd): GP-2 was carried out with **3c** (64 mg, 0.2 mmol), **4d** (55 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5cd** (50 mg, 70%) as a yellow oil. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3c**) = 0.40, R_f (**5cd**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3605, 2936, 1653, 1599, 1472, 1260, 1177, 970, 835, 764 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.97 (d, J = 8.9 Hz, 2H), 7.58 (d, J = 8.5 Hz, 1H), 7.45 (dd, J = 7.7, 1.7 Hz, 1H), 7.40 (dd, J = 8.5, 2.3 Hz, 1H), 3.36 – 7.28 (m, 2H), 7.27 – 7.21 (m, 1H), 7.13 (dd, J = 8.0, 1.3 Hz, 1H), 7.02 (s, 1H), 6.97 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H). **^{13}C**{^{1}H} **NMR** (100 MHz, $CDCl_3$) δ = 188.3, 163.5, 159.9, 156.0, 136.8, 134.5, 133.8, 132.3 (2C), 131.7, 130.5, 130.1 (2C), 129.8, 129.4, 129.3, 126.1, 125.7, 121.9, 113.7 (2C), 55.6 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{22}H_{16}ClO_3^+$ 363.0782; Found: 363.0784.

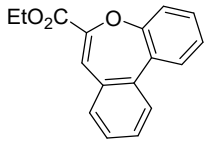


(2-(Tert-butyl)-9-chlorodibenzo[*b,d*]oxepin-6-yl)(phenyl)methanone (5ld): GP-2 was carried out with **3l** (69 mg, 0.2 mmol), **4d** (55 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ld** (68 mg, 90%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3l**) = 0.40, R_f (**5ld**) = 0.50, UV detection. Melting point: 108-110 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2958, 1734, 1661, 1486, 1270, 1206, 972, 711 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.88 (dd, J = 8.4, 1.4 Hz, 2H), 7.66 – 7.54 (m, 2H), 7.53 – 7.46 (m, 2H), 7.46 – 7.41 (m, 2H), 7.37 (dd, J = 8.5, 2.4 Hz, 1H), 7.31 (d, J = 2.2 Hz, 1H), 7.09 (d, J = 8.5 Hz, 1H), 7.03 (s, 1H), 1.34 (s, 9H). **^{13}C**{^{1}H} **NMR** (151 MHz, $CDCl_3$) δ = 190.2, 157.7, 155.6, 148.9, 137.5, 137.1, 134.4, 133.6, 132.66, 130.7, 130.5, 130.2, 129.6 (2C), 129.5, 128.4 (2C), 127.3, 127.1, 126.7, 121.4, 34.7, 31.6 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{25}H_{22}O_2^+$ 389.1303; Found: 389.1302.

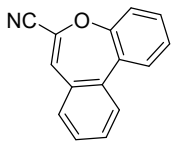


(2-(Tert-butyl)-9-methoxydibenzo[*b,d*]oxepin-6-yl)(phenyl)methanone (5le): GP-2 was carried out with **3l** (69 mg, 0.2 mmol), **4e** (54 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5le** (53 mg, 70%) as a yellow solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3l**) = 0.40, R_f (**5le**) = 0.50, UV detection. Melting point: 132-134 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2958, 1728, 1659, 1606, 1492, 1251, 1043,976, 833, 709 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.94 – 7.86 (m, 2H), 7.62 (d, J = 8.6 Hz, 1H), 7.58 (dt, J = 2.7, 1.7 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.44 (d, J = 2.4 Hz, 1H), 7.31 (dd, J = 8.5, 2.4 Hz, 1H), 7.09 (s, 1H), 7.06 (d, J = 8.5 Hz, 1H), 7.05 (dd, J = 8.7, 2.8 Hz, 1H), 6.83 (d, J = 2.7 Hz, 1H), 3.86 (s, 3H), 1.34 (s, 9H). **^{13}C**{^{1}H} **NMR** (151

MHz, $CDCl_3$) δ = 190.5, 159.1, 157.4, 154.8, 148.7, 137.5, 134.0, 132.5, 131.8, 131.46, 130.5, 129.7 (2C), 128.5, 128.4 (2C), 126.5, 126.3, 126.3, 121.1, 116.1, 114.9, 55.6, 34.7, 31.6 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{26}H_{25}O_3^+$ 385.1798; Found: 385.1805.

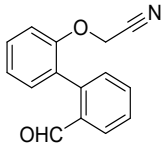


Ethyl dibenzo[*b,d*]oxepine-6-carboxylate (5wa): GP-2 was carried out with **3w** (51 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (13 0mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5wa** (45 mg, 86%) as a yellow oil. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3w**) = 0.50, R_f (**5wa**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3739, 3637, 3520, 2343, 2243, 2177, 2132, 1721, 1536, 1271, 757 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.66 (dd, J = 7.8, 1.1 Hz, 1H), 7.51 (dd, J = 7.7, 1.6 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.42 – 7.31 (m, 4H), 7.34 (s, 1H), 7.30 – 7.25 (m, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). **^{13}C**{^{1}H} **NMR** (151 MHz, $CDCl_3$) δ = 162.8, 160.2, 147.5, 138.5, 132.7, 132.5, 130.4, 130.1, 129.8, 129.3, 129.2, 127.9, 125.9, 125.9, 121.7, 61.7, 14.5 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{17}H_{15}O_3^+$ 267.1016; Found: 267.1003.

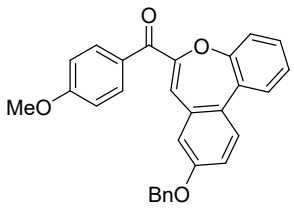


Dibenzo[*b,d*]oxepine-6-carbonitrile (5xa): GP-2 was carried out with **3x** (42 mg, 0.2 mmol), **4a** (45 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5xa** (29 mg, 68%) as a yellow gel. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3x**) = 0.40, R_f (**5xa**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3059, 2921, 2856, 2219, 1480, 1436, 1193, 1126, 1089, 759 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.65 (dd, J = 7.9, 0.8 Hz, 1H), 7.51 (dd, J = 7.8, 1.6 Hz, 1H), 7.48 (dd, J = 7.7, 1.4 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.33 (ddd, J = 7.6, 7.6 1.3 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.24 (dd, J = 8.0, 1.2 Hz, 1H), 6.87 (s, 1H). **^{13}C**{^{1}H} **NMR** (151 MHz, $CDCl_3$) δ = 159.6, 138.4, 131.6, 131.2,

130.9, 130.4, 130.4, 130.1 (2C), 129.9, 129.5, 128.1, 126.7, 121.3, 114.9 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd $C_{15}H_{10}NO^+$ 220.0757; Found: 220.0754.

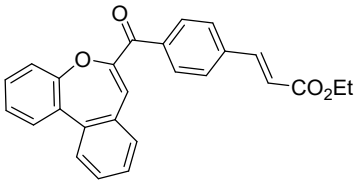


2-((2'-Formyl-[1,1'-biphenyl]-2-yl)oxy)acetonitrile (6xa): Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5xa** (12 mg, 20%) as a pink coloured solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3x**) = 0.40, R_f (**5xa**) = 0.50, UV detection. Melting point: 62-64 °C. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} =3630, 3467, 2344, 2182, 1696, 756 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.81 (d, J = 0.7 Hz, 1H), 8.01 (dd, J = 7.8, 1.3 Hz, 1H), 7.67 (td, J = 7.5, 1.5 Hz, 1H), 7.56 – 7.44 (m, 2H), 7.39 – 7.31 (m, 2H), 7.28 – 7.20 (m, 1H), 7.11 (dd, J = 8.3, 0.8 Hz, 1H), 4.65 (d, J = 5.1 Hz, 2H). **^{13}C** {^{1}H} **NMR** (101 MHz, $CDCl_3$) δ = 192.1, 153.5, 140.6, 134.0, 133.9, 132.3, 131.4, 130.3, 128.4, 128.3, 127.5, 123.7, 114.8, 112.8, 53.9 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{15}H_{12}NO_2^+$ 238.0863; Found: 238.0850.

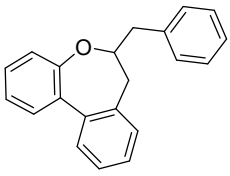


(9-(Benzyloxy)dibenzo[*b,d*]oxepin-6-yl)(4-methoxyphenyl)methanone (7ca): GP-2 was carried out with **3c** (64 mg, 0.2 mmol), **6a** (122 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 15 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5ma** (43 mg, 50%) as a yellow gel. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3m**) = 0.40, R_f (**5ma**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2925, 1597, 1494, 1251, 1171, 1029, 696 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99 (dd, J = 9.0, 2.1 Hz, 2H), 7.60 (d, J = 8.7 Hz, 1H), 7.49 – 7.39 (m, 5H), 7.38 – 7.35 (m, 1H), 7.30 – 7.25 (m, 1H), 7.25 – 7.20 (m, 1H), 7.12 – 7.07 (m, 3H), 6.98 (dd, J = 8.9, 2.1 Hz, 2H), 6.93 (d, J = 2.7 Hz, 1H), 5.13 (s, 2H), 3.90 (s, 3H). **^{13}C**{^{1}H} (101 MHz, $CDCl_3$) δ = 188.6, 163.4, 159.4, 158.4, 155.2, 136.7, 134.2, 132.5,

132.4 (2C), 131.4, 130.5, 129.7, 129.6, 129.2, 128.8 (2C), 128.3, 127.6 (2C), 127.1, 125.9, 121.8, 116.6, 116.0, 113.7 (2C), 70.3, 55.6 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd $C_{29}H_{23}O_4^+$ 435.1591; Found: 435.1592.



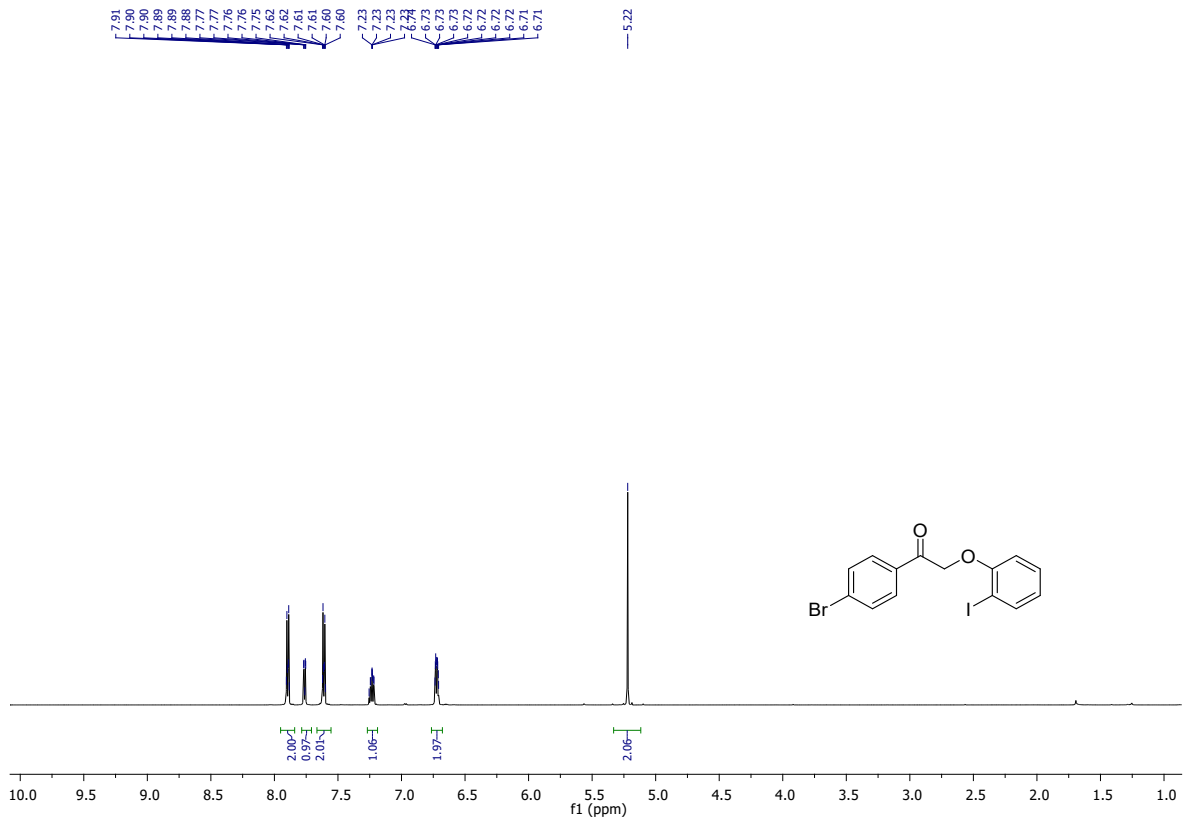
Ethyl (E)-3-(4-(dibenzo[*b,d*]oxepine-6-carbonyl)phenyl)acrylate (8ia): GP-4 was carried out with **5ia** (75 mg, 0.2 mmol), **7a** (30 mg, 0.3 mmol), $Pd(OAc)_2$ (11 mg, 5 mol%), PPh_3 10 (mol%) K_2CO_3 (130 mg, 0.8 mmol), and DMF (3 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 90/10) furnished the product **8aa** (46 mg, 60%) as a yellow gel. TLC (petroleum ether/ethyl acetate 98:2, R_f(**5ia**) = 0.40, R_f (**8aa**) = 0.50, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3060, 2980, 2929, 1710, 1646, 1268, 1173, 967, 761 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.86 (dd, J = 8.3, 1.7 Hz, 2H), 7.66 (d, J = 16.0 Hz, 1H), 7.61 (dd, J = 7.8, 1.0 Hz, 1H), 7.57 (d, J = 8.3 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.35 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H), 7.26 (ddd, J = 7.6, 7.3, 1.4 Hz, 1H), 7.17 (s, 1H), 7.11 (dd, J = 7.9, 1.4 Hz, 1H), 6.55 (d, J = 16.1 Hz, 1H), 4.36 – 4.18 (m, 2H), 4.36 – 4.18 (m, 1H). **^{13}C**{^{1}H} **NMR** (101 MHz, $CDCl_3$) δ = 190.9, 189.4, 166.7, 160.0, 154.7, 143.3, 138.7, 138.5, 138. 3, 132.7, 130.9, 130.3, 130.1 (2C), 129.9, 129.8, 129.3, 128.8, 128.0, 127.9, 127.1 (2C), 126.0, 121.8, 120.8, 60.9, 14.4 ppm. **HRMS** (ESI) m/z: $[(M+Na)]^+$ Calcd $C_{26}H_{20}NaO_4^+$ 419.1254; Found: 419.1251.



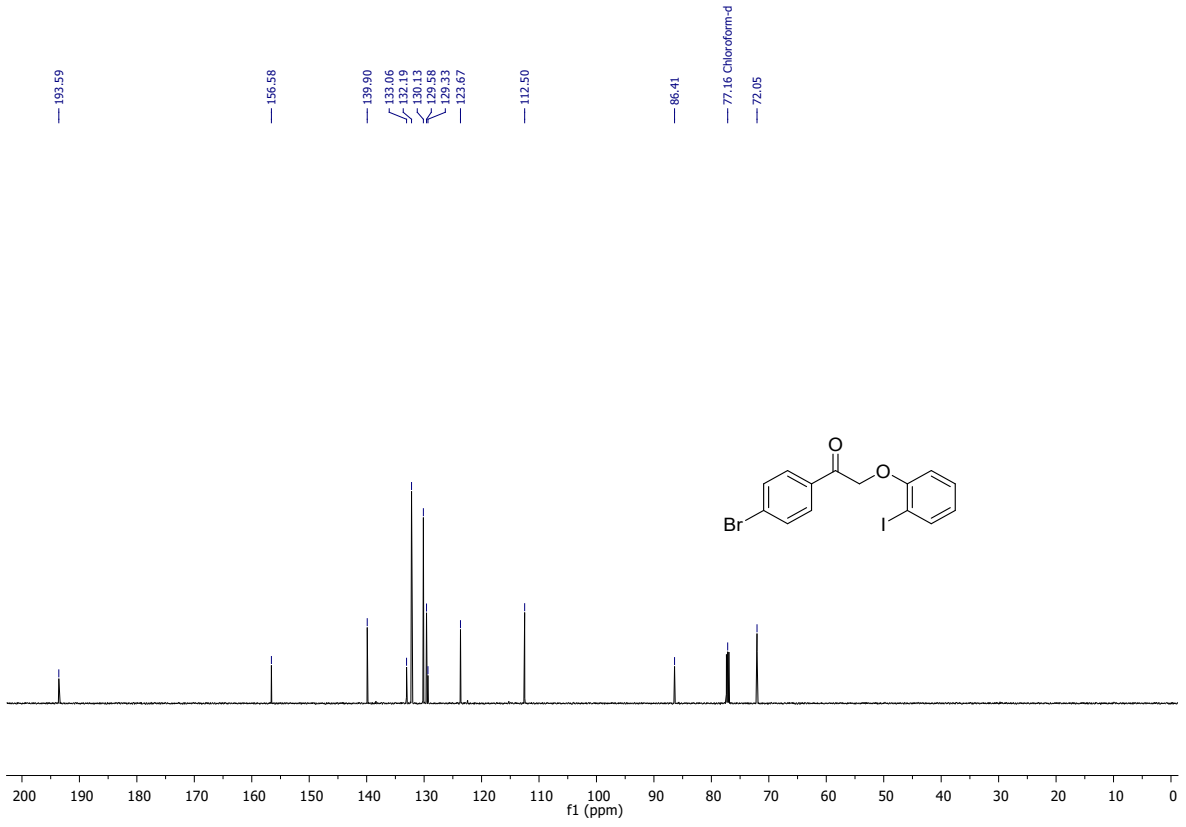
(S)-6-Benzyl-6,7-dihydrodibenzo[*b,d*]oxepine (9aa): Reaction was carried out with **5aa** (60 mg, 0.2 mmol), Pd/C (10 mg, 5 mol%), H_2 gas balloon, and MeOH (2 mL) at room temperature for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 98/02) furnished the product **9aa** (30 mg, 55%) as a colourless oil. TLC (petroleum ether/ethyl acetate 98:2, R_f(**5aa**) = 0.40, R_f (**9aa**) = 0.80, UV detection. **IR** (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3320, 2934, 1718, 1639, 1499, 1449, 1226, 755 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.49 (d, J = 7.6 Hz, 1H), 7.46 (dd, J = 7.5, 1.1 Hz, 1H), 7.41

(t, J = 7.5 Hz, 1H), 7.39 – 7.31 (m, 6H), 7.30 – 7.23 (m, 3H), 7.15 (d, J = 7.9 Hz, 1H), 4.97 – 4.81 (m, 1H), 3.23 (dd, J = 13.7, 6.2 Hz, 1H), 2.89 (dd, J = 13.7, 7.9 Hz, 1H), 2.77 (dd, J = 14.2, 5.2 Hz, 1H), 2.62 (dd, J = 14.2, 6.9 Hz, 1H). **^{13}C**{^{1}H} **NMR** (101 MHz, $CDCl_3$) δ = 153.5, 138.9, 138.36, 136.3, 135.4, 129.5 (2C), 129.3, 129.0, 128.9, 128.7 (2C), 128.1, 127.6, 127.5, 126.6, 124.7, 123.4, 89.7, 40.9, 36.9 ppm. **HRMS** (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{21}H_{19}O^+$ 287.1430; Found: 287.1450.

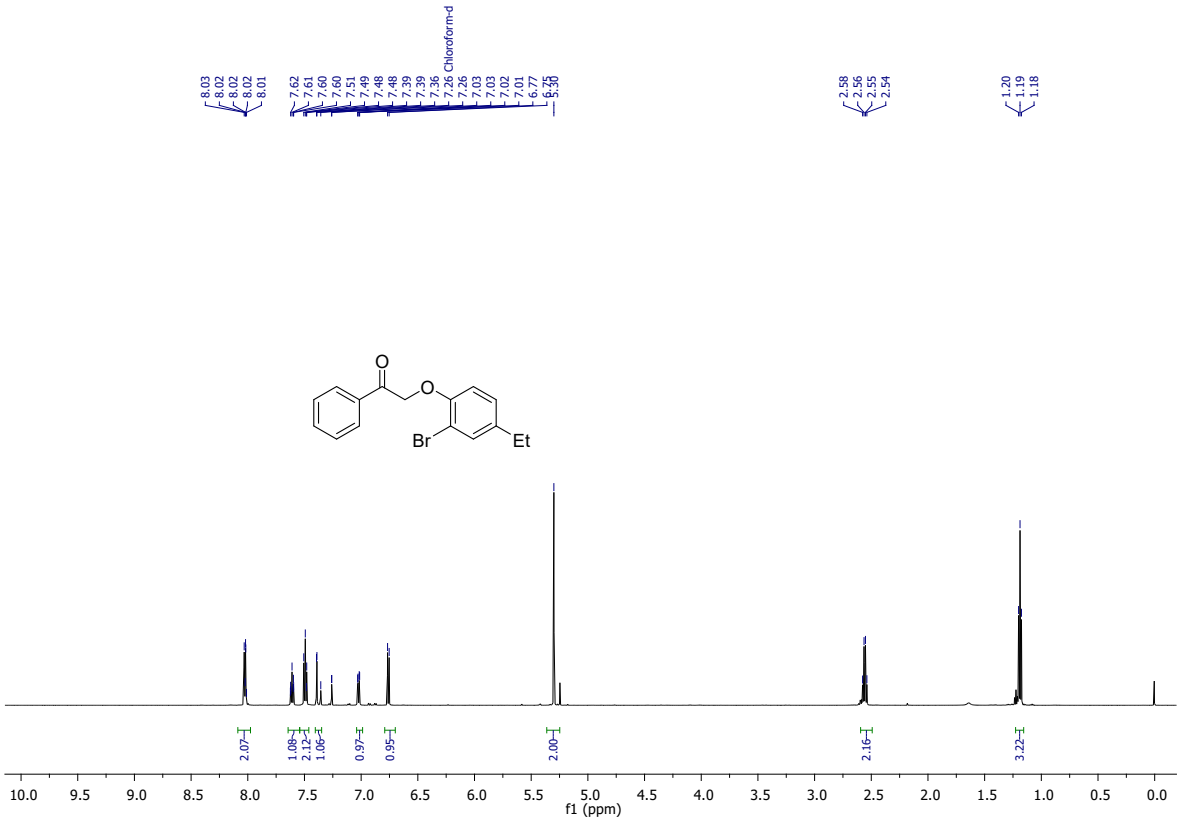
Gram scale reaction - Dibenzo[*b,d*]oxepin-6-yl(phenyl)methanone (5aa): GP-2 was carried out with **3a** (1000 mg, 2.9 mmol), **4a** (666 mg, 4.4 mmol), $Pd(PPh_3)_4$ (66 mg, 2 mol%), Cs_2CO_3 (1924 mg, 5.9 mmol), and DMF-EtOH (3:1, 2 mL) under microwave irradiation at 120 °C for 30 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100/00 to 95/05) furnished the product **5aa** (600 mg, 70%) as a white crystalline solid. TLC (petroleum ether/ethyl acetate 98:2, R_f (**3a**) = 0.40, R_f (**5aa**) = 0.50, UV detection.



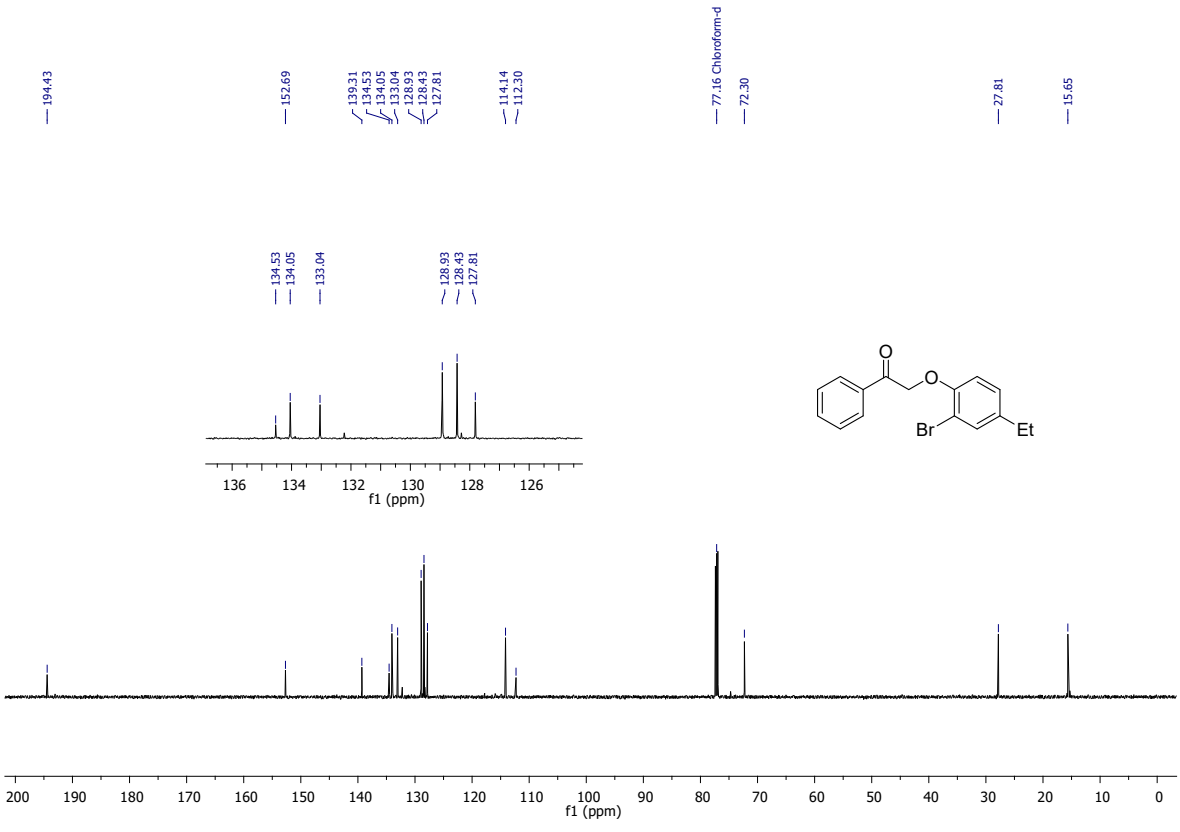
^{1}H NMR (400 MHz) spectrum of **3i** in $CDCl_3$



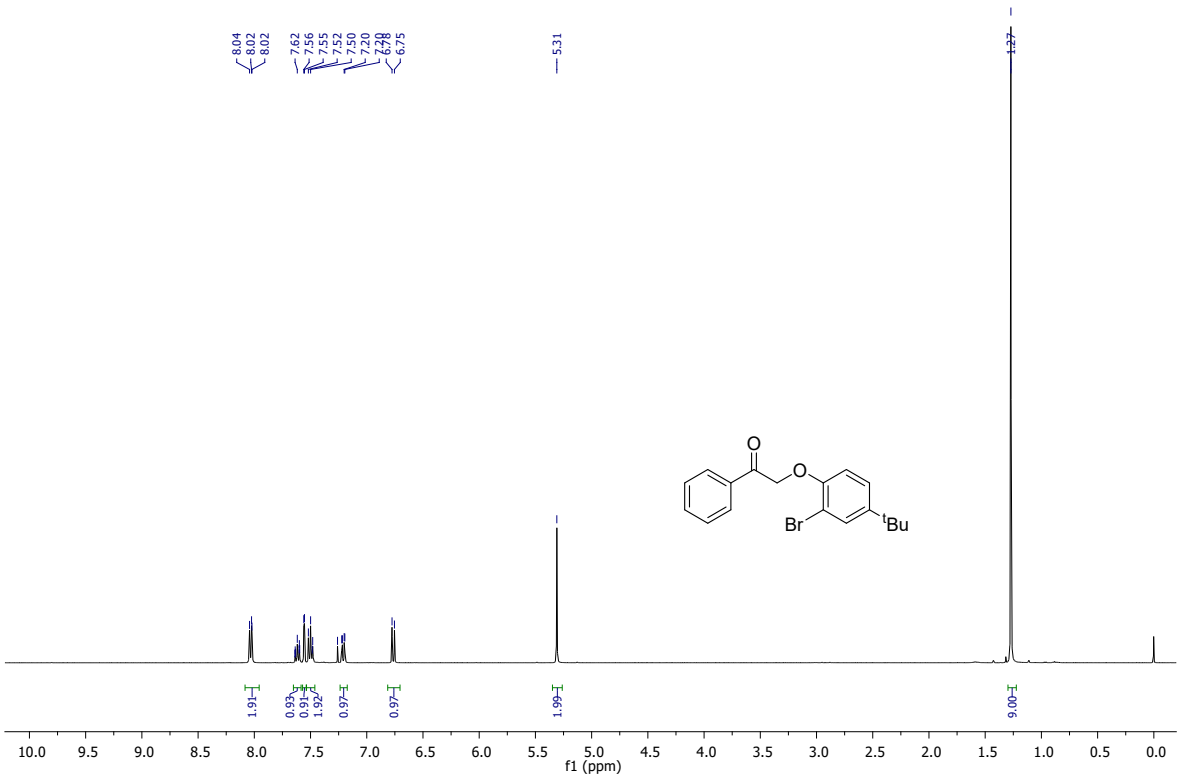
^{13}C{1H} NMR (100 MHz) spectrum of **3i** in $CDCl_3$



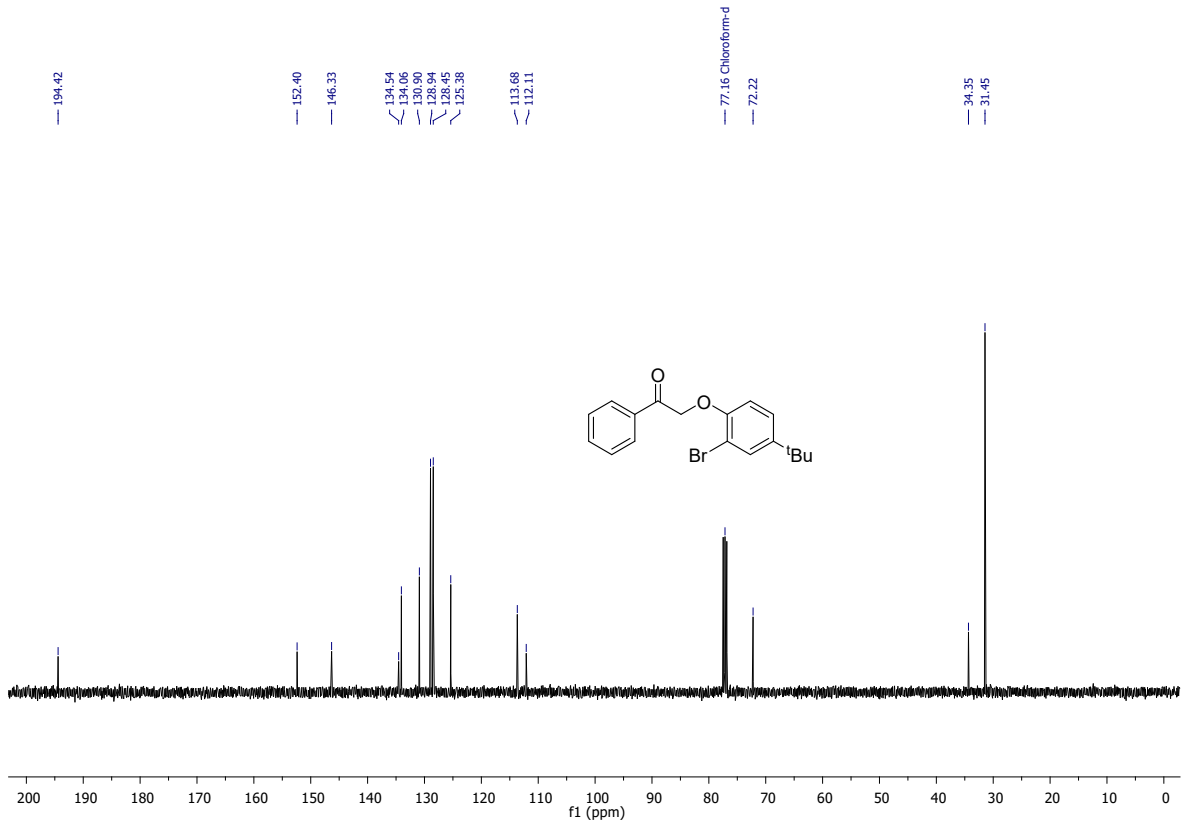
^{1}H NMR (400 MHz) spectrum of **3k** in $CDCl_3$



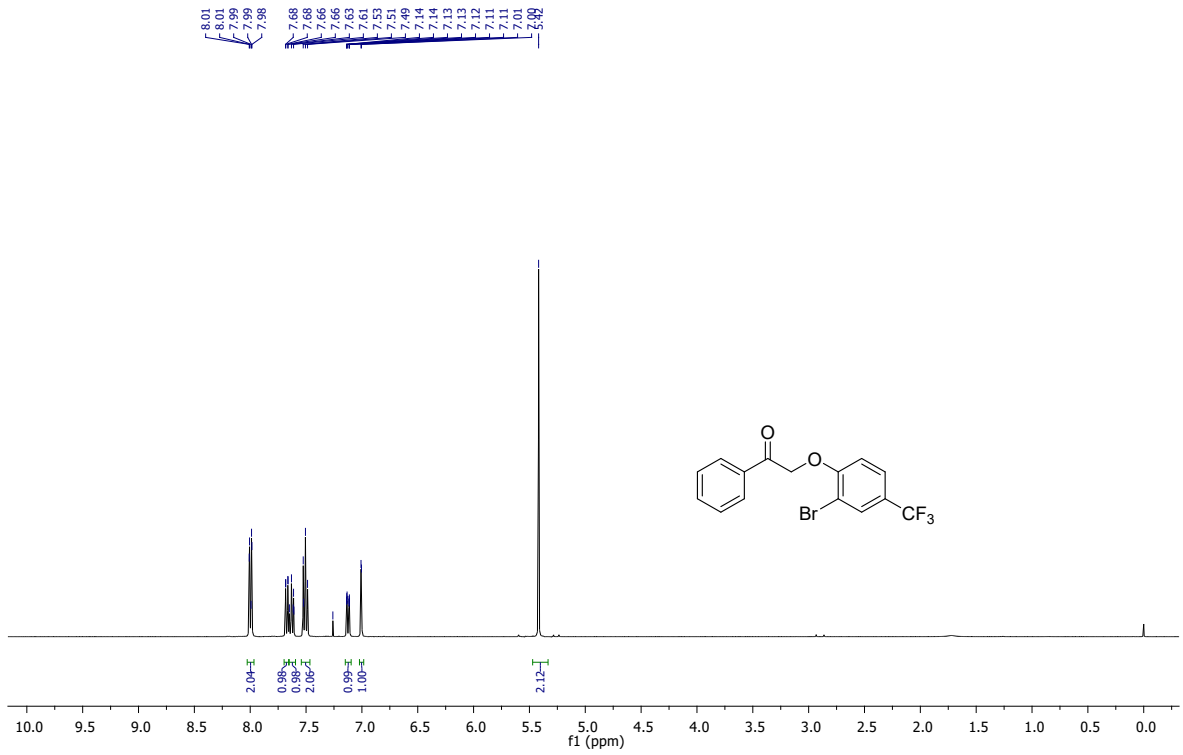
^{13}C{1H} NMR (100 MHz) spectrum of **3k** in $CDCl_3$



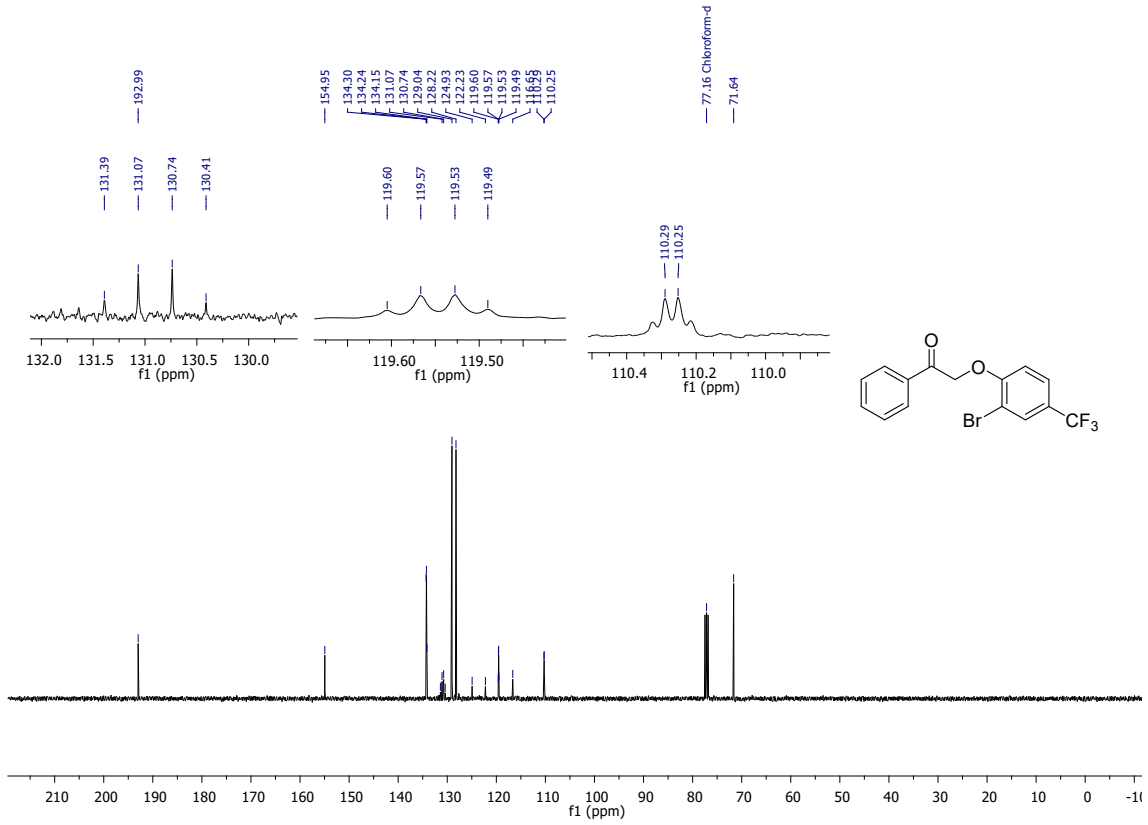
^{1}H NMR (400 MHz) spectrum of **3l** in $CDCl_3$



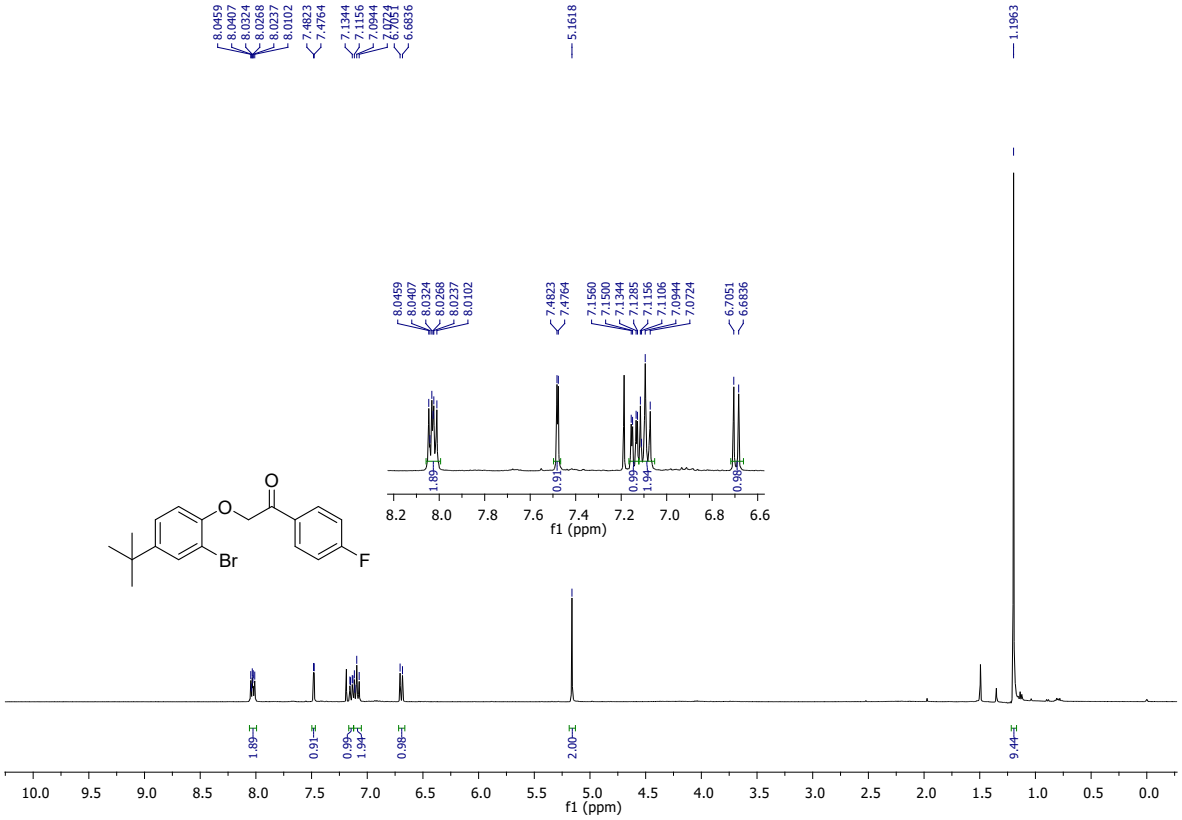
^{13}C{1H} NMR (100 MHz) spectrum of **3l** in $CDCl_3$



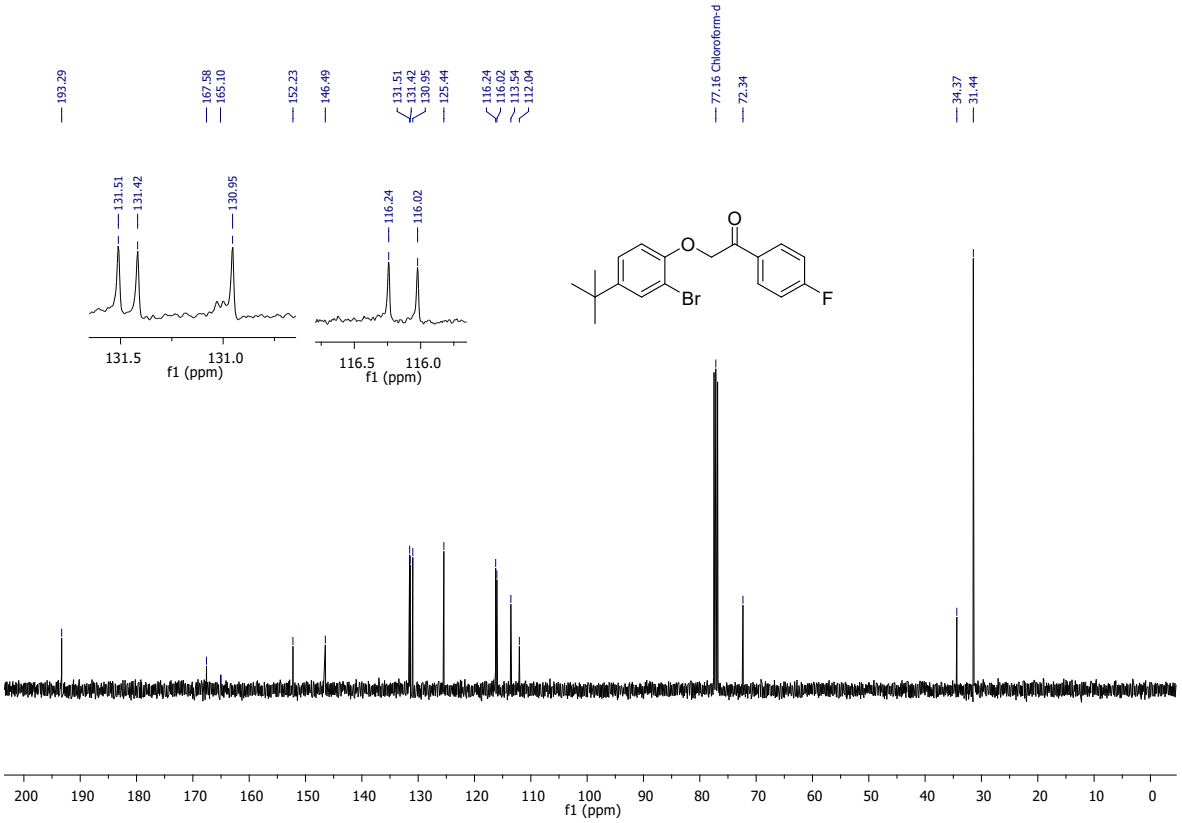
^{1}H NMR (400 MHz) spectrum of **3p** in $CDCl_3$



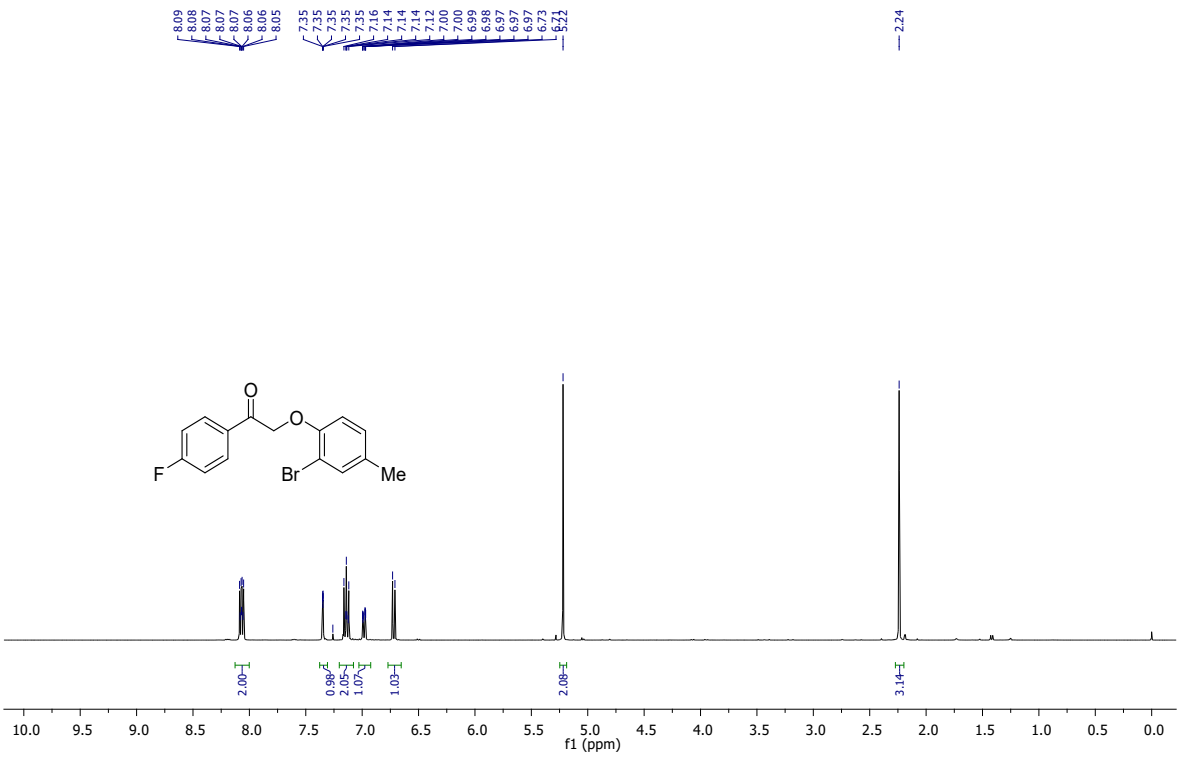
$^{13}C\{1H\}$ NMR (100 MHz) spectrum of **3p** in $CDCl_3$



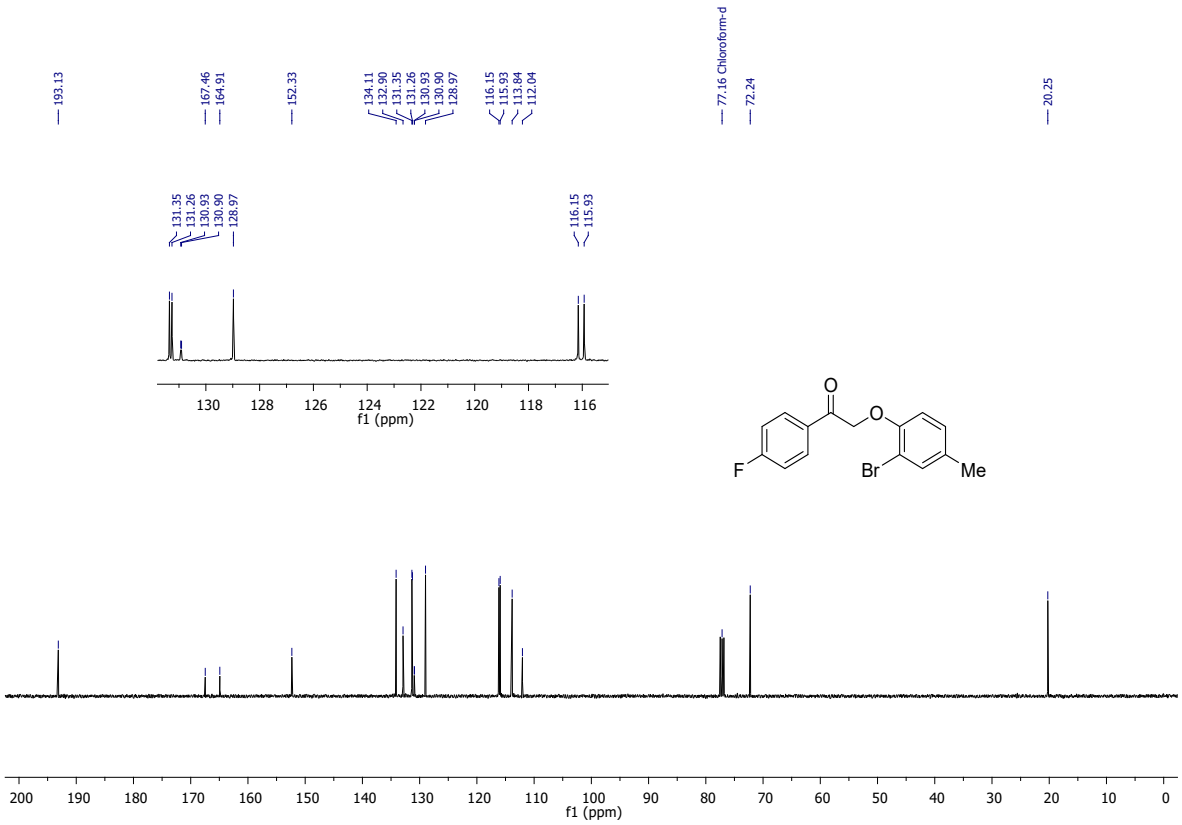
^{1}H NMR (400 MHz) spectrum of **3s** in $CDCl_3$



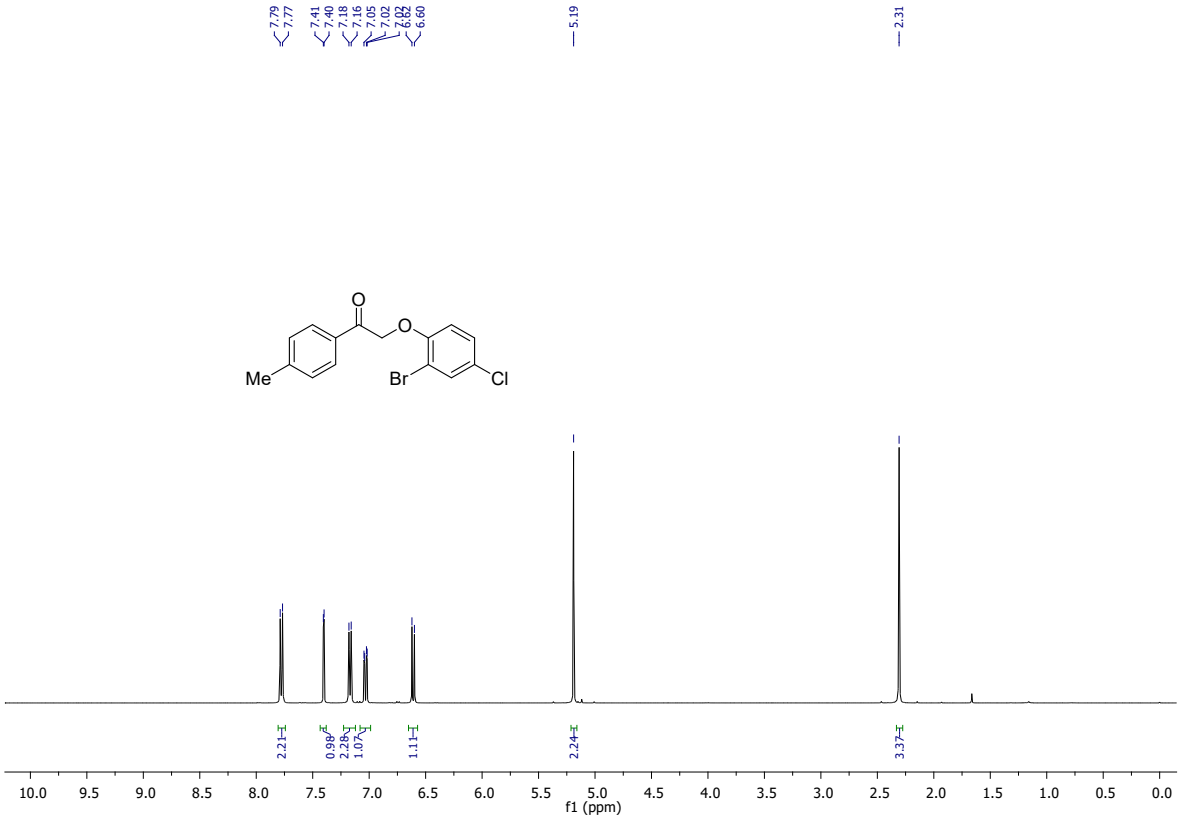
$^{13}C\{1H\}$ NMR (100 MHz) spectrum of **3s** in $CDCl_3$



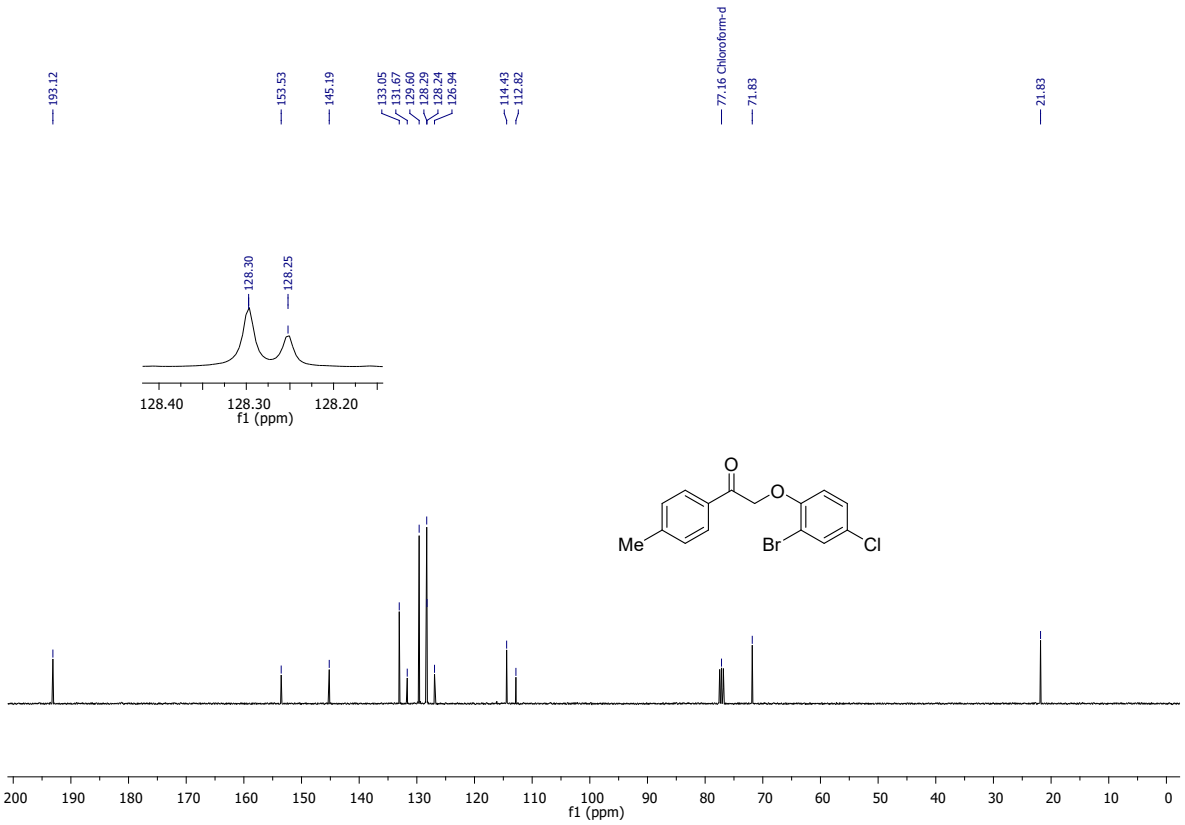
^{1}H NMR (400 MHz) spectrum of **3t** in $CDCl_3$



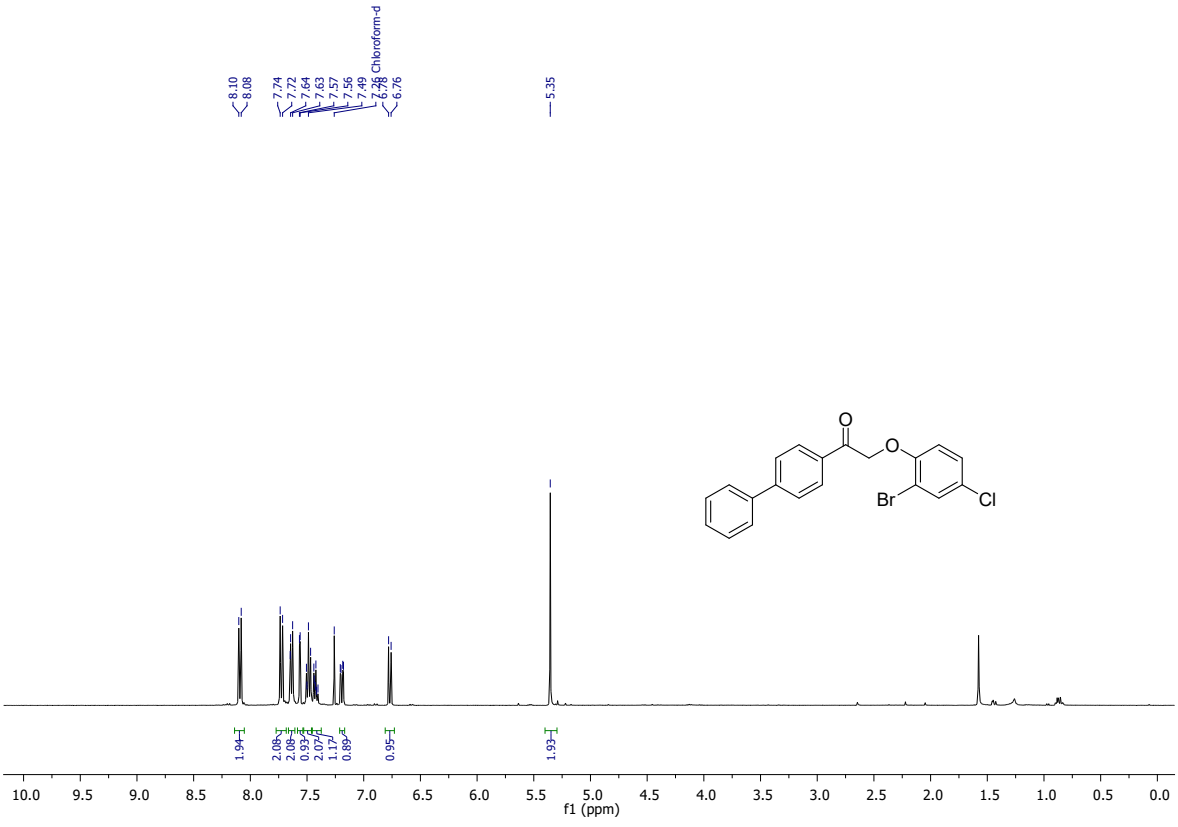
$^{13}C\{1H\}$ NMR (100 MHz) spectrum of **3t** in $CDCl_3$



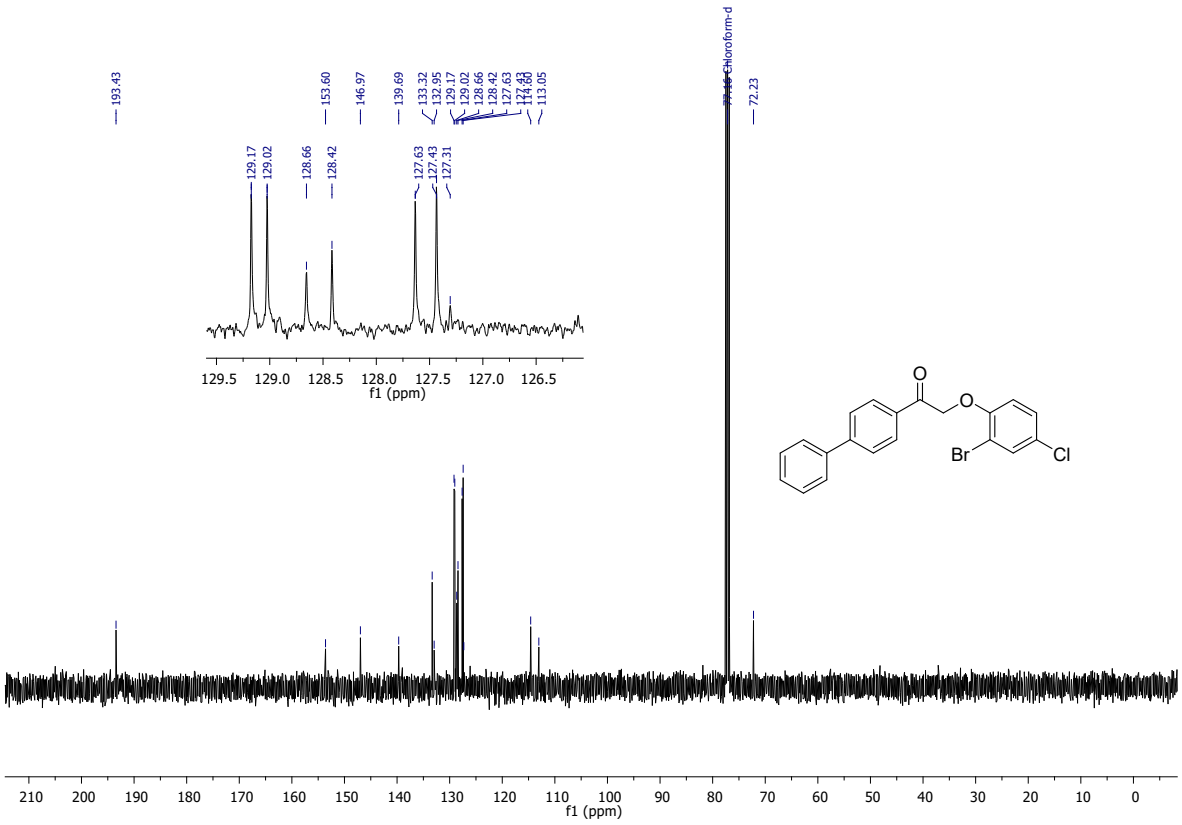
^{1}H NMR (400 MHz) spectrum of **3u** in $CDCl_3$



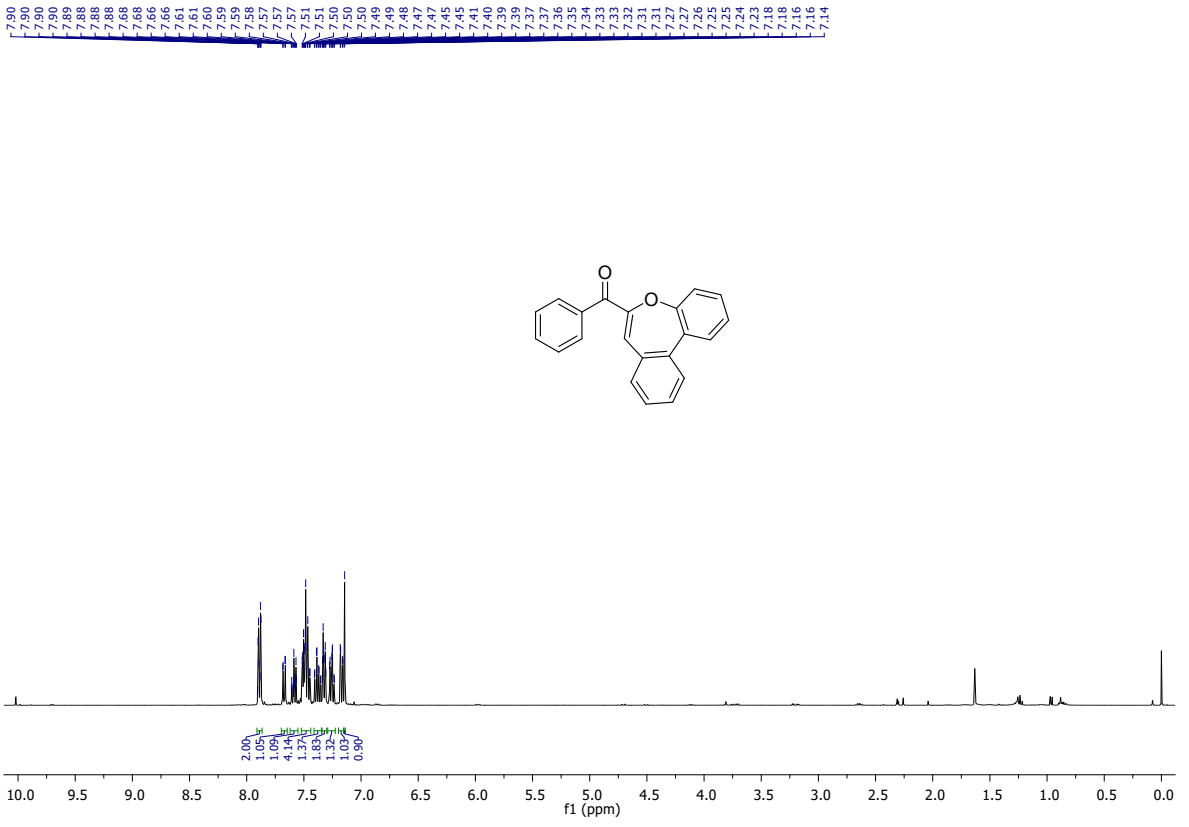
$^{13}C\{1H\}$ NMR (100 MHz) spectrum of **3u** in $CDCl_3$



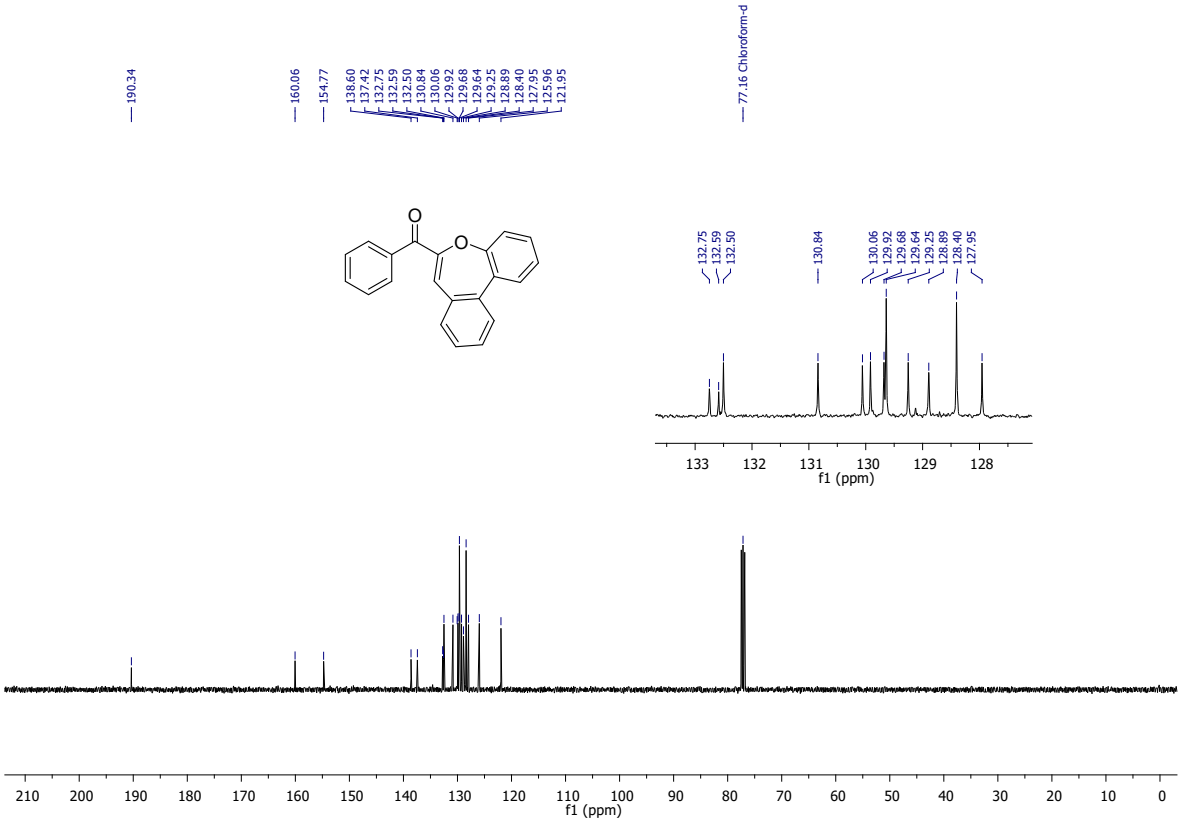
^{1}H NMR (400 MHz) spectrum of **3v** in $CDCl_3$



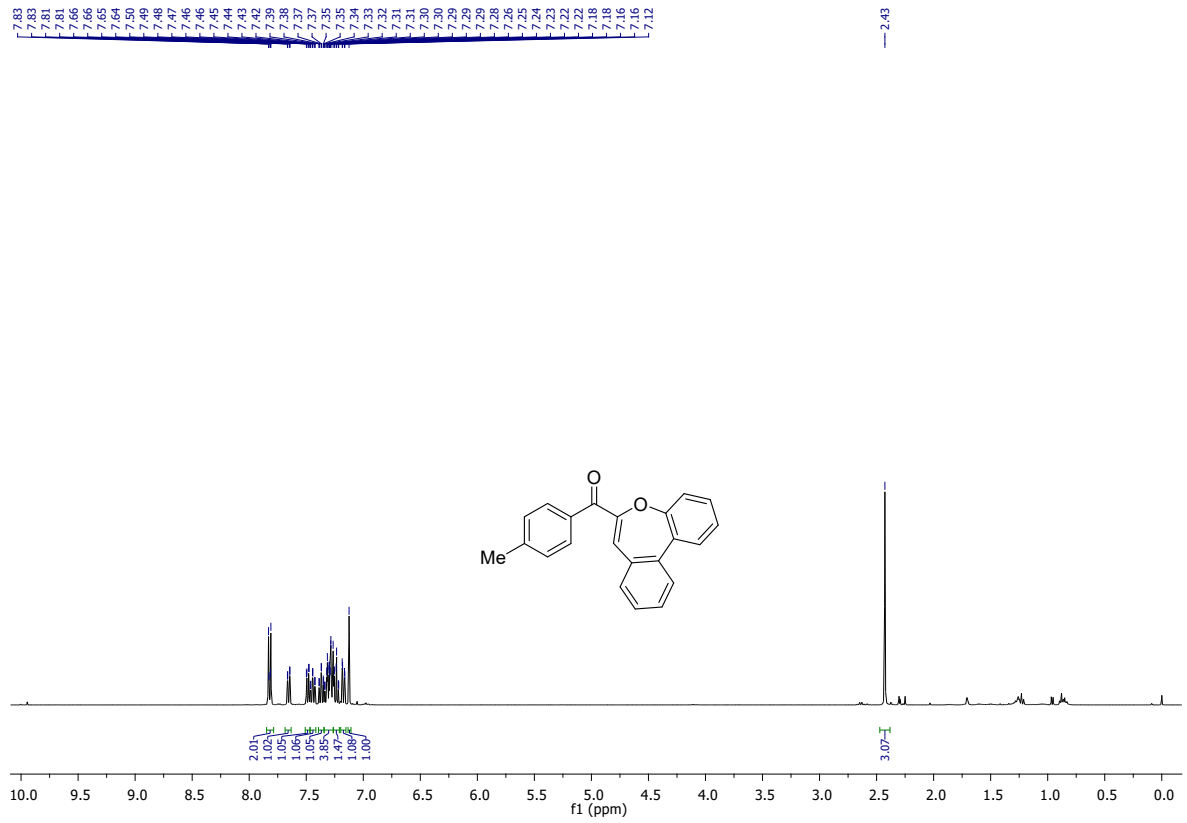
$^{13}C\{1H\}$ NMR (100 MHz) spectrum of **3v** in $CDCl_3$



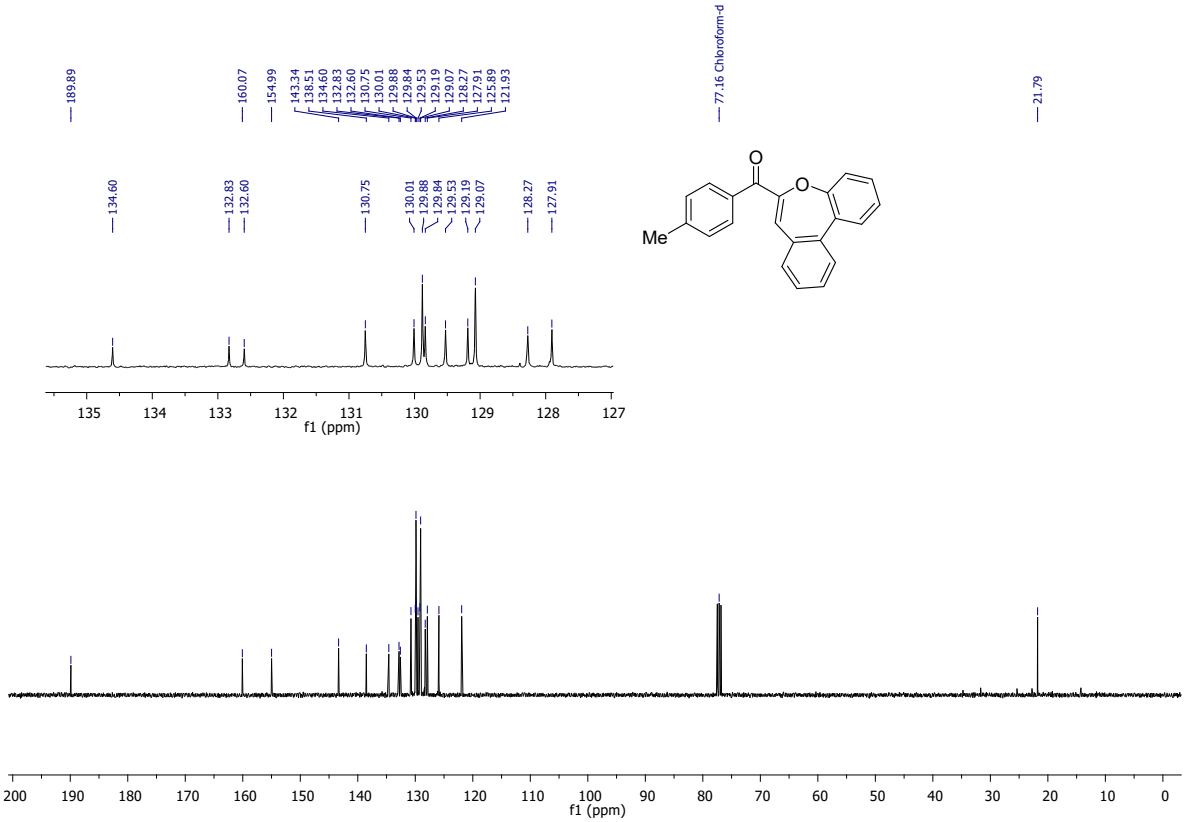
^{1}H NMR (400 MHz) spectrum of **5aa** in $CDCl_3$



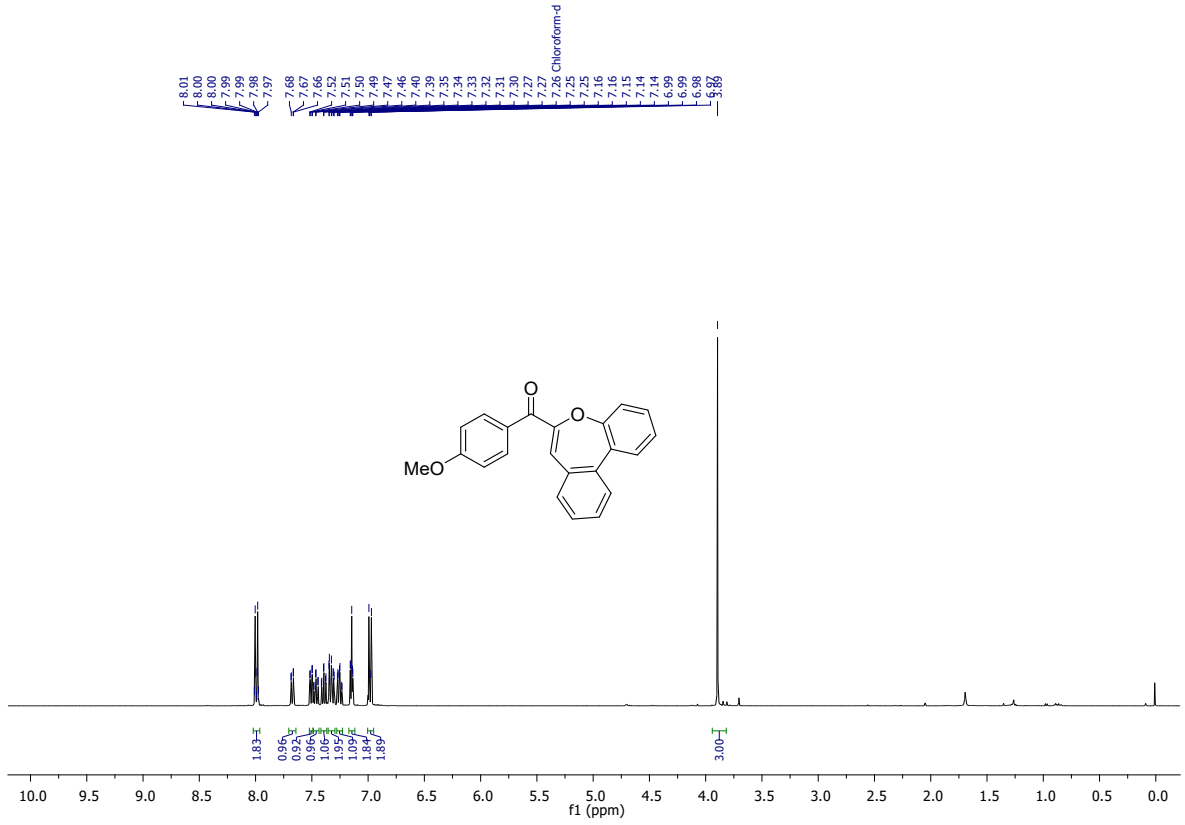
^{13}C{1H} NMR (100 MHz) spectrum of **5aa** in $CDCl_3$



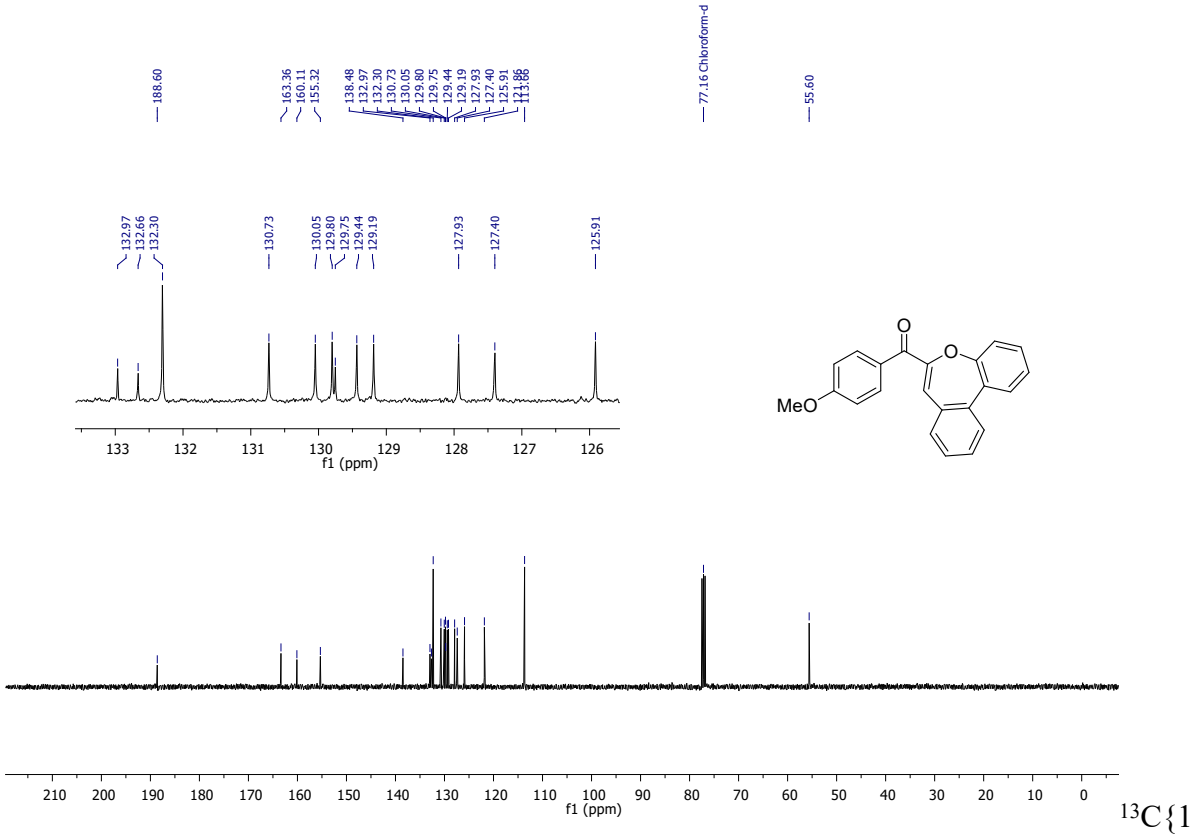
^{1}H NMR (400 MHz) spectrum of **5ba** in $CDCl_3$



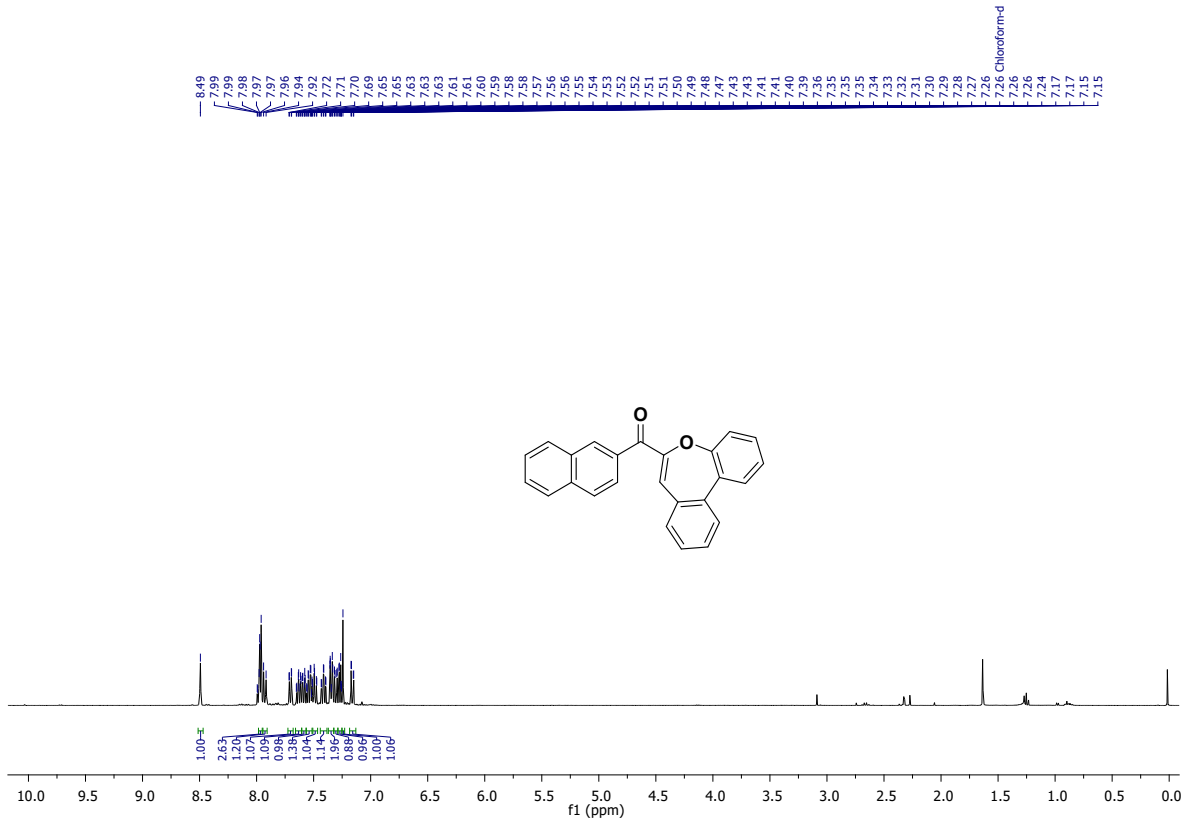
^{13}C{1H} NMR (100 MHz) spectrum of **5ba** in $CDCl_3$



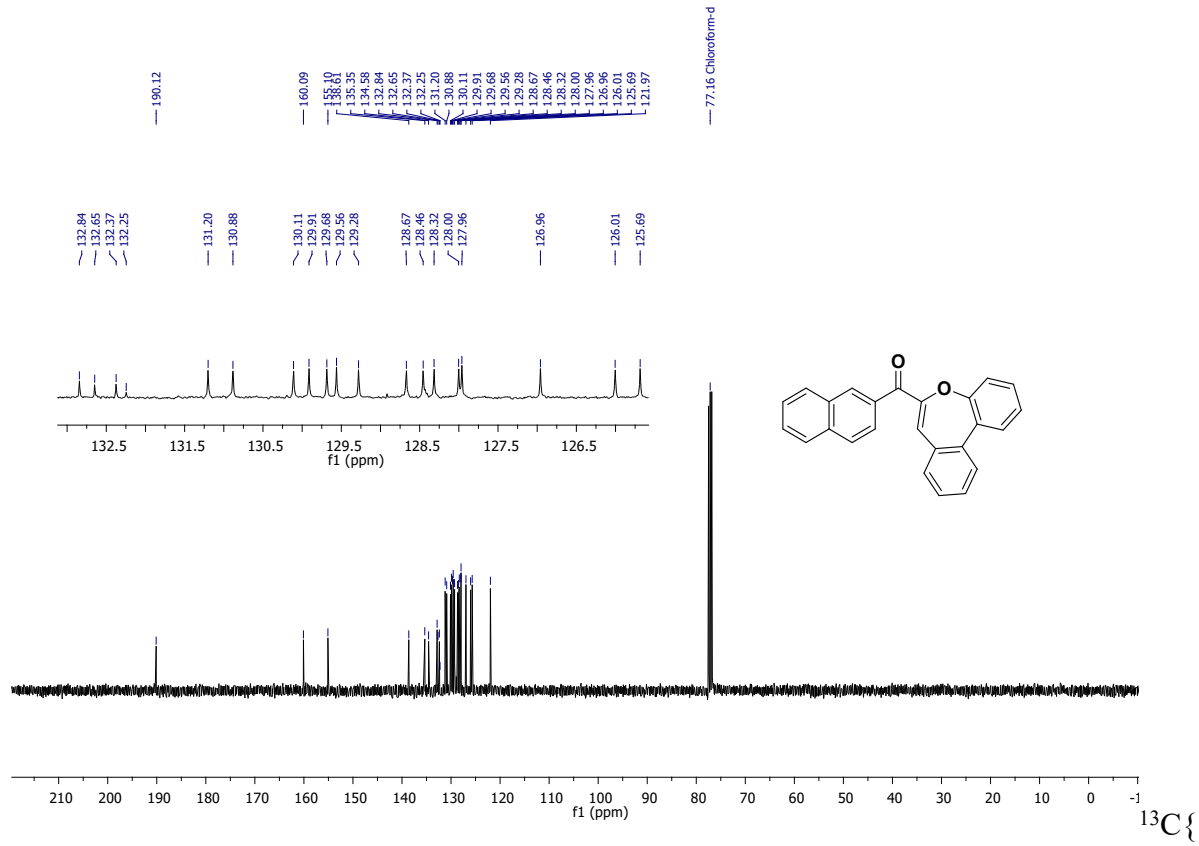
^{1}H NMR (400 MHz) spectrum of **5ca** in $CDCl_3$



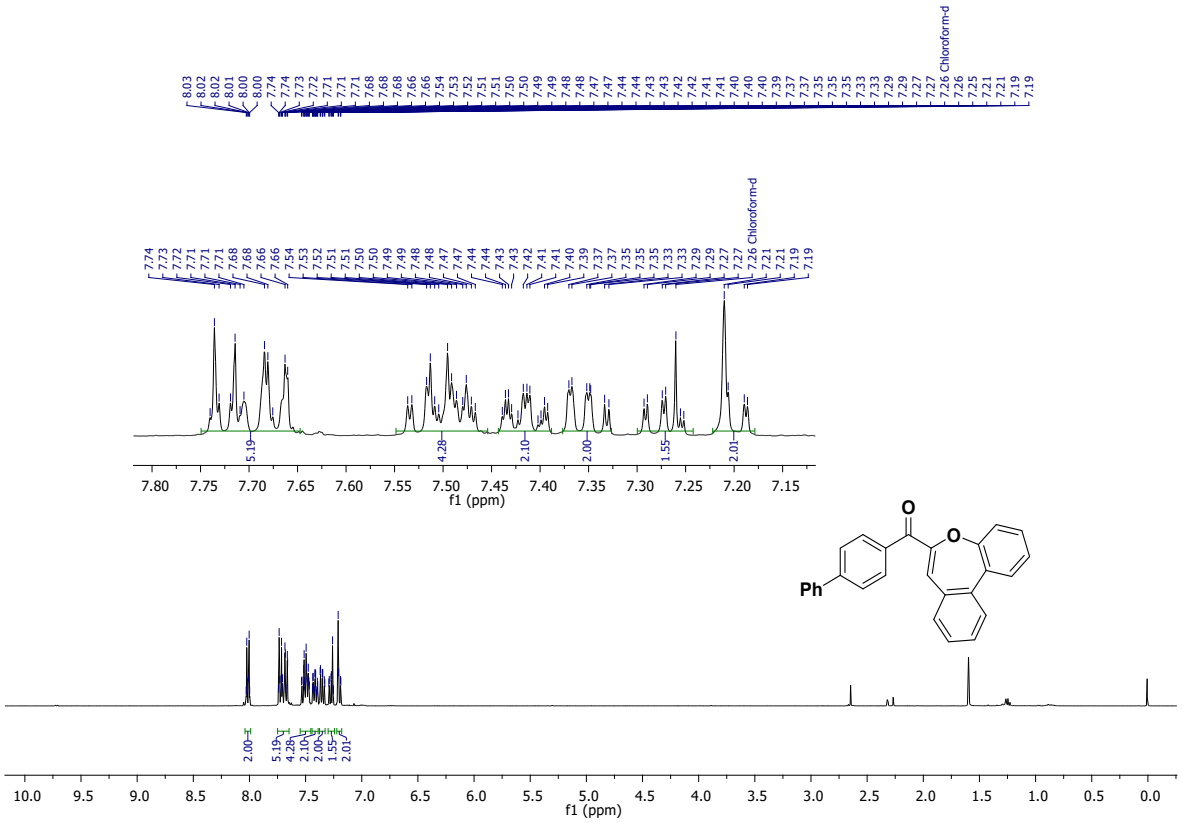
^{13}C{1H} NMR (100 MHz) spectrum of **5ca** in $CDCl_3$



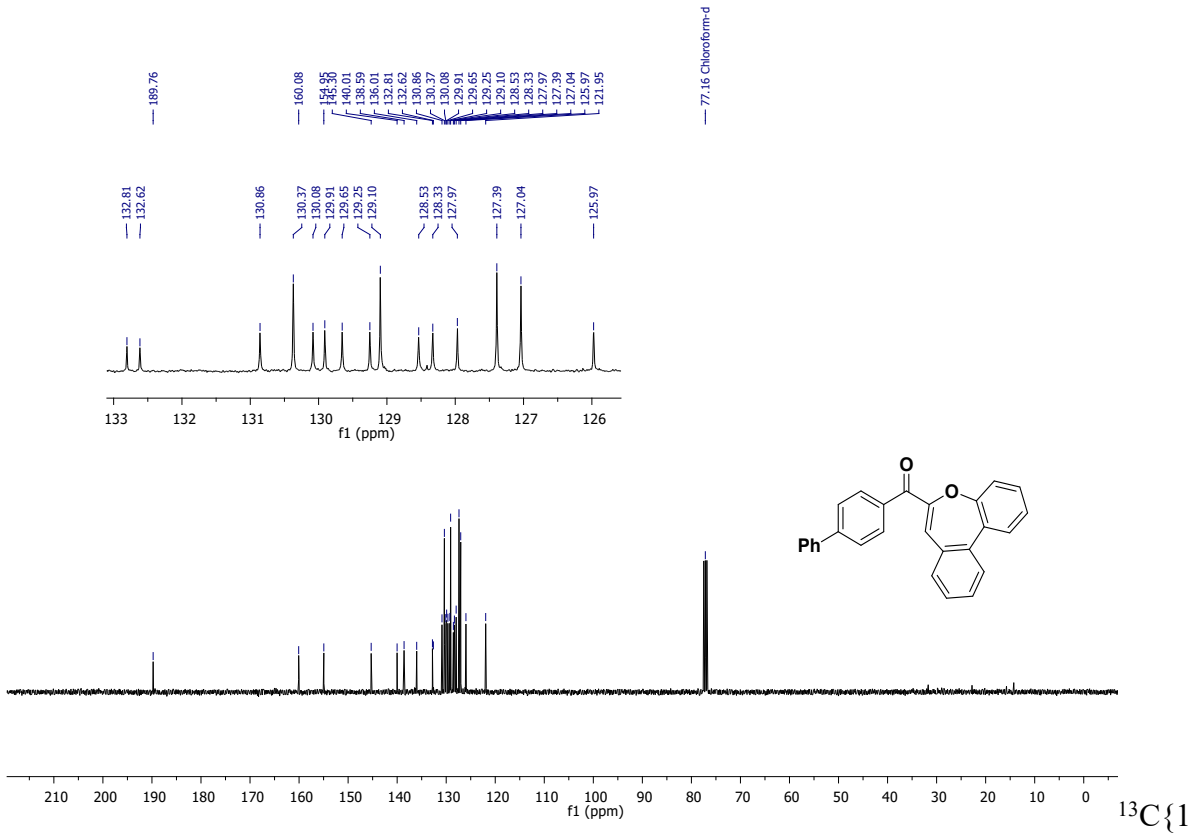
^{1}H NMR (400 MHz) spectrum of **5da** in $CDCl_3$



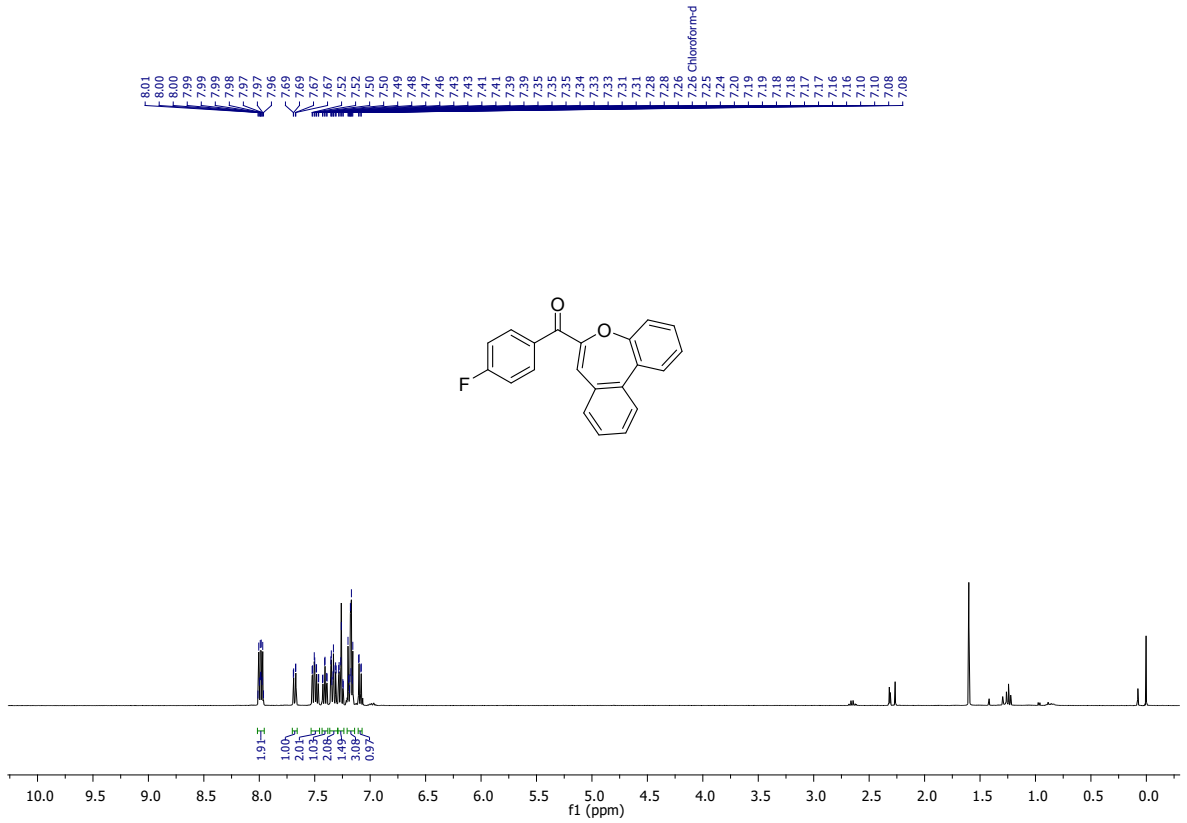
^{13}C{1H} NMR (100 MHz) spectrum of **5da** in $CDCl_3$



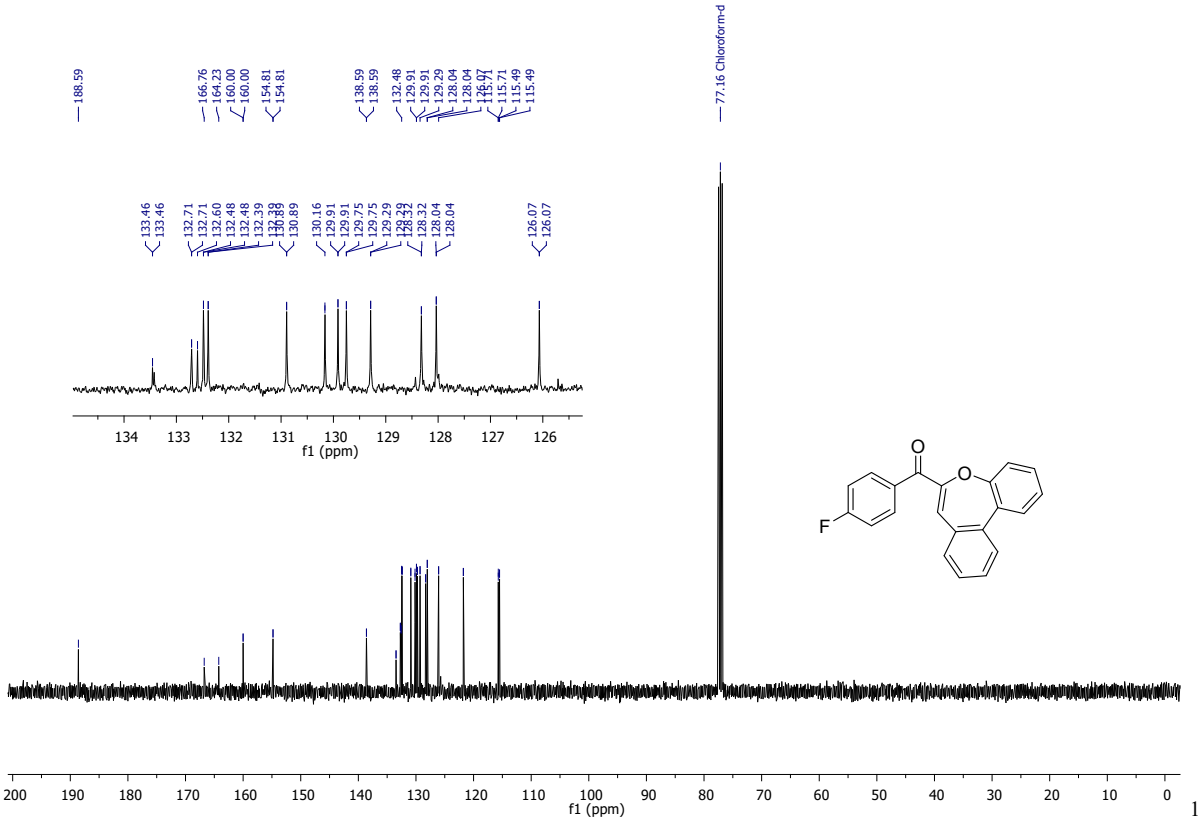
^{1}H NMR (400 MHz) spectrum of **5ea** in $CDCl_3$



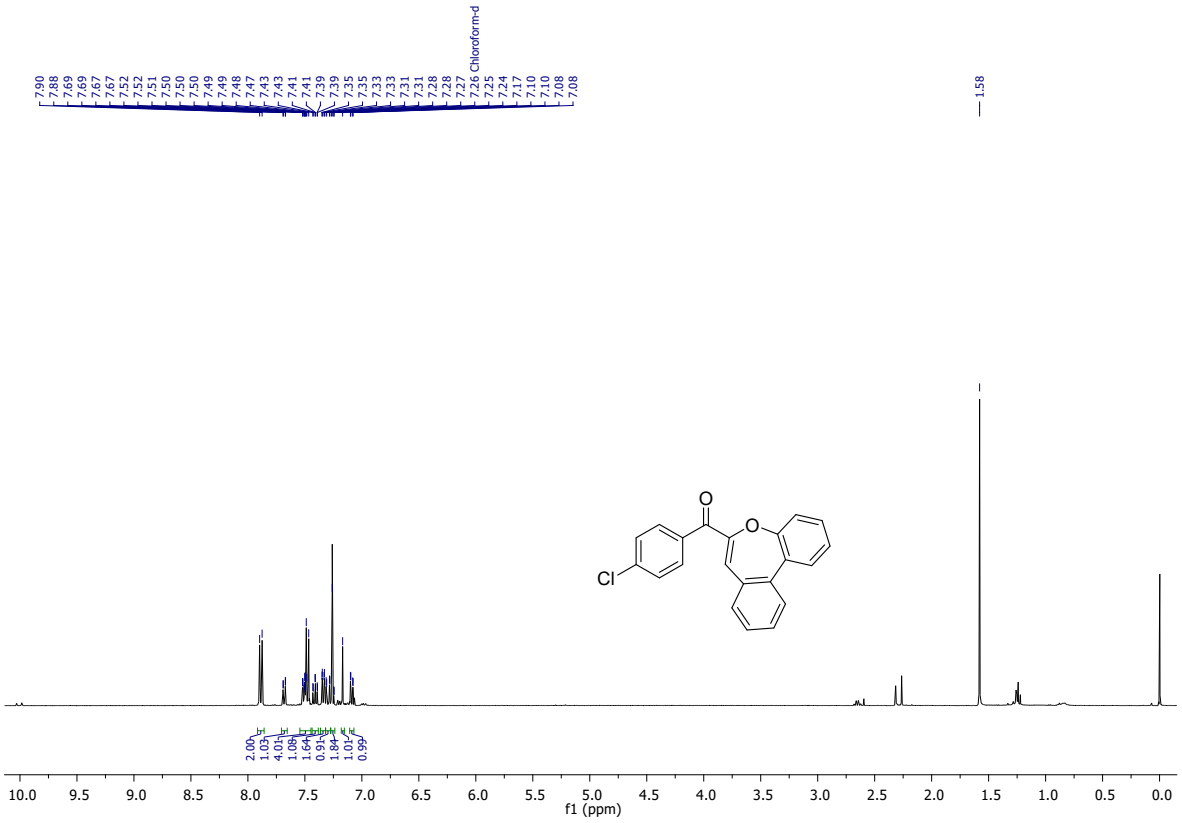
^{13}C{1H} NMR (100 MHz) spectrum of **5ea** in $CDCl_3$



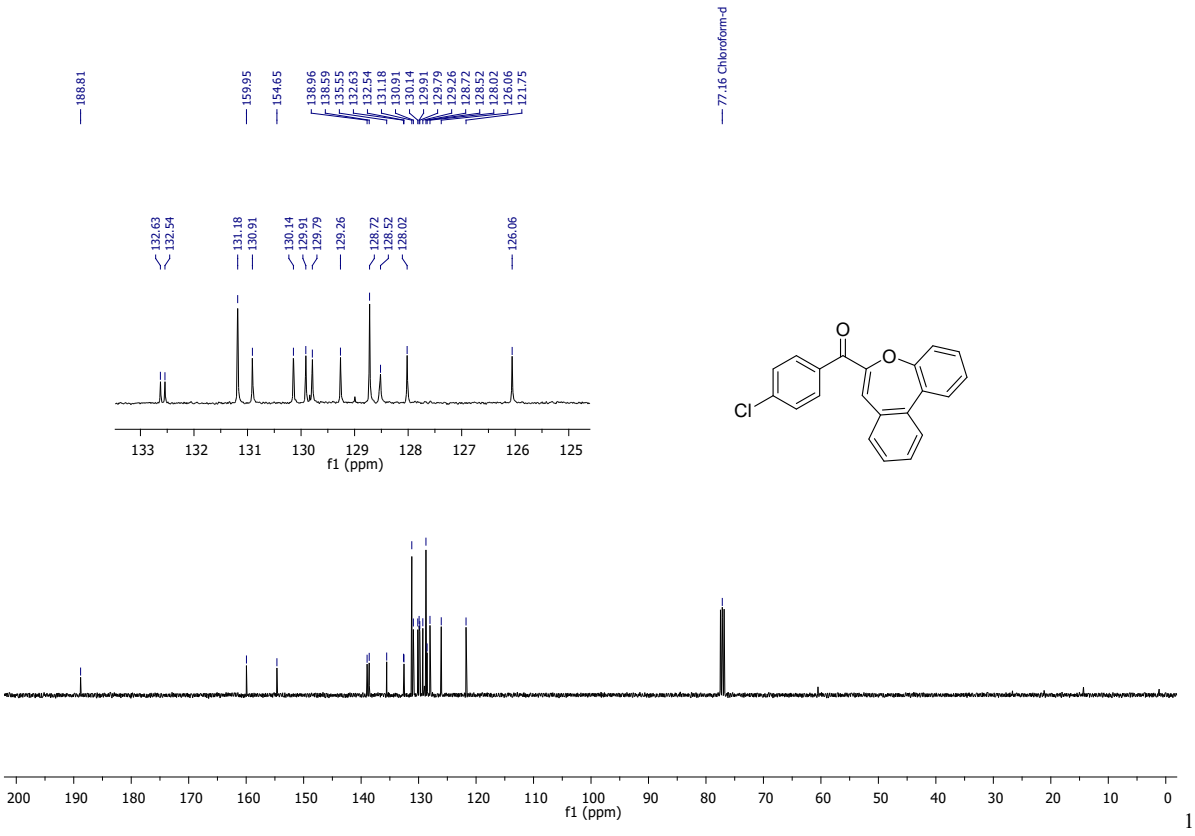
^{1}H NMR (400 MHz) spectrum of **5fa** in $CDCl_3$



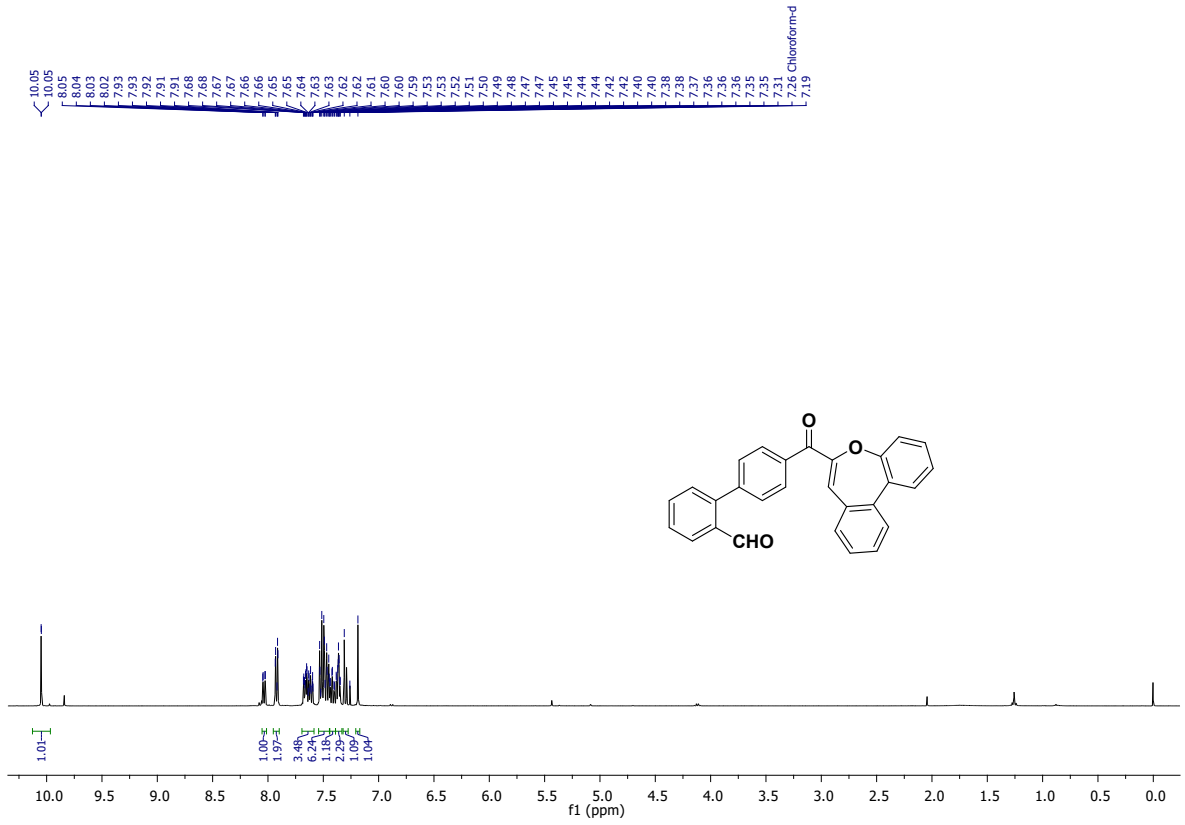
^{3}C{1H} NMR (100 MHz) spectrum of **5fa** in $CDCl_3$



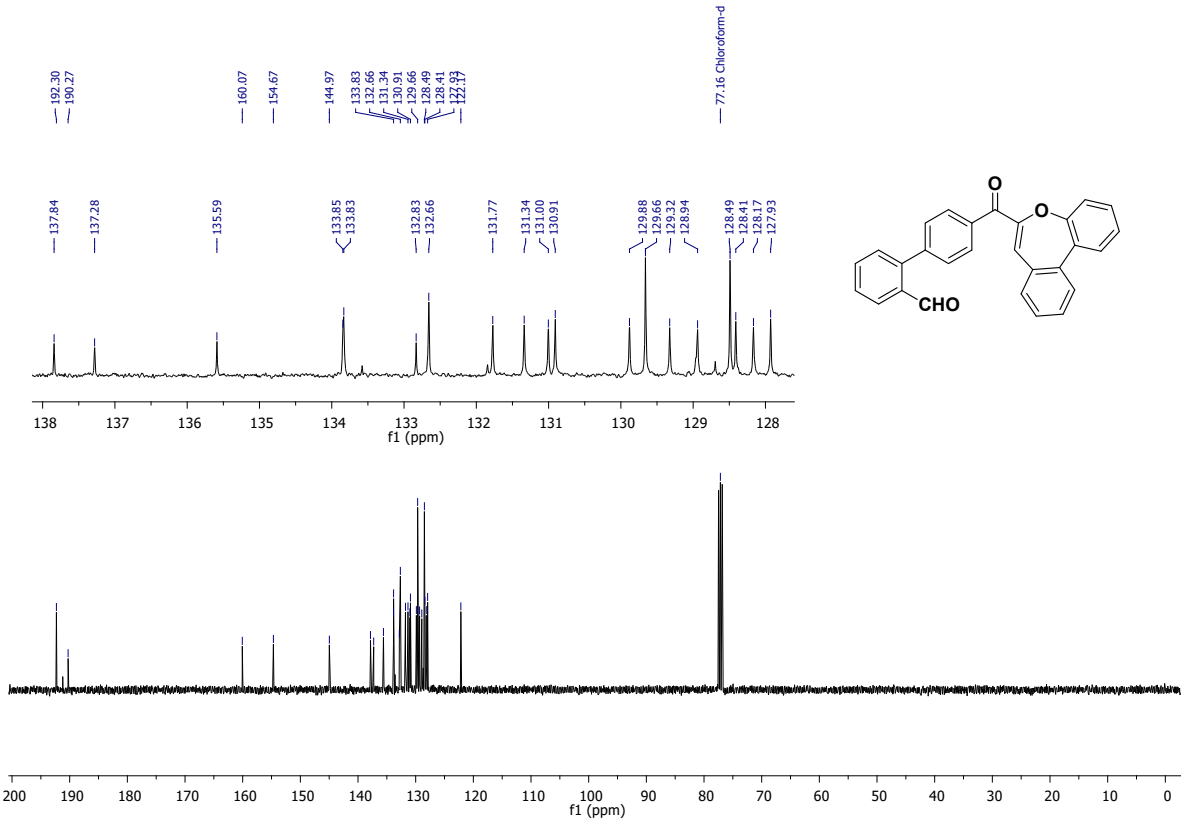
^{1}H NMR (400 MHz) spectrum of **5ga** in $CDCl_3$



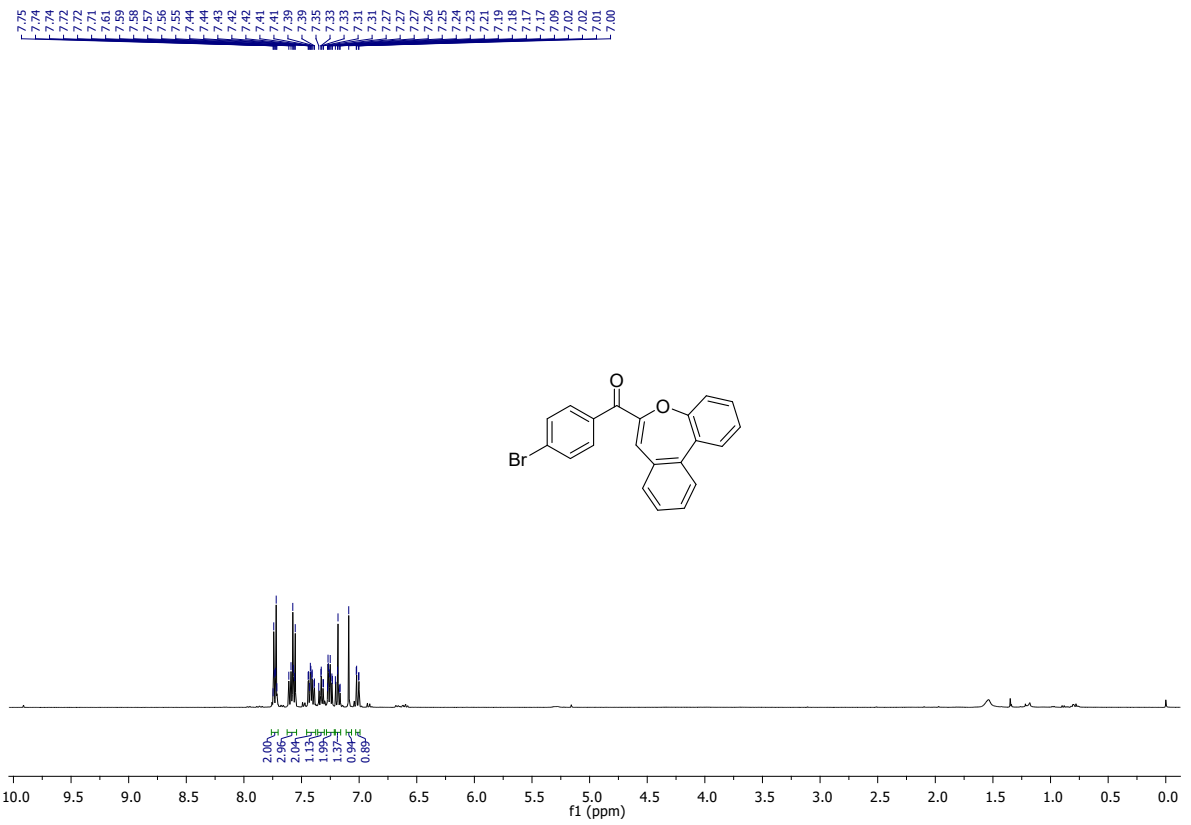
^{3}C{1H} NMR (100 MHz) spectrum of **5ga** in $CDCl_3$



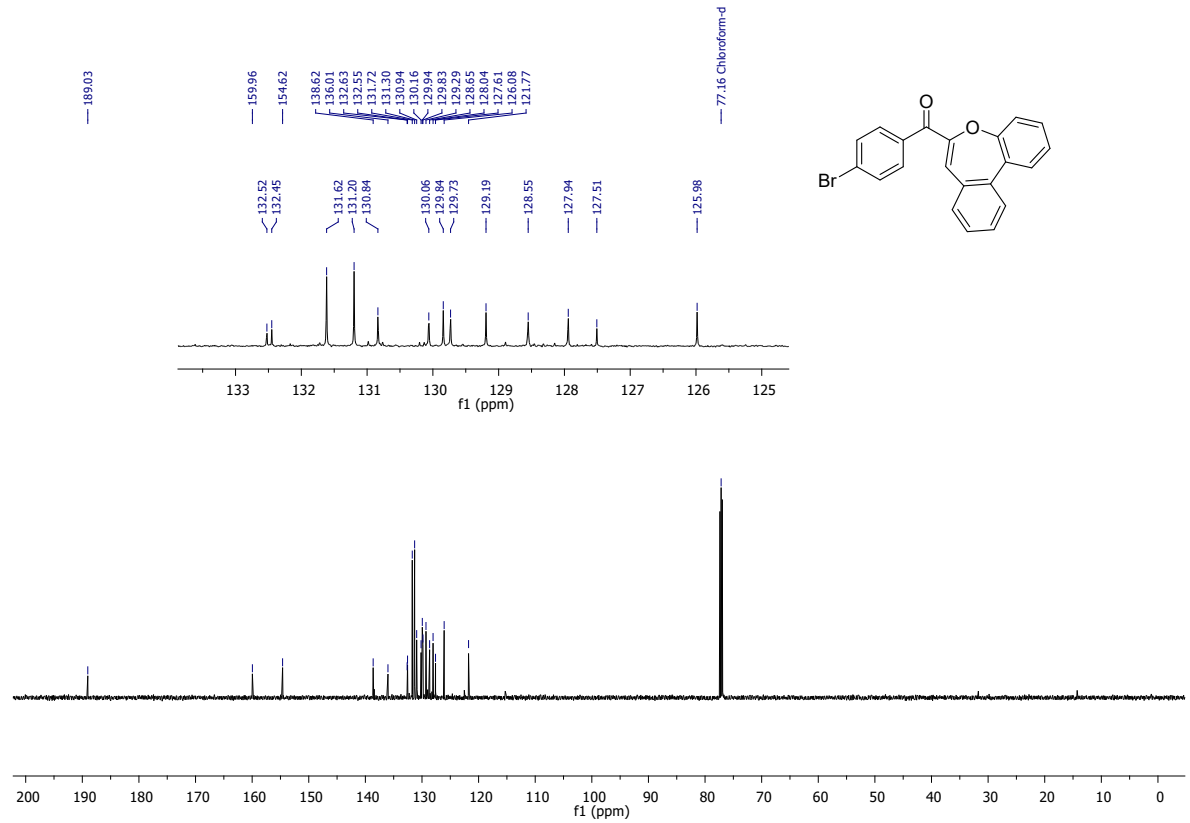
^{1}H NMR (400 MHz) spectrum of **5ha** in $CDCl_3$



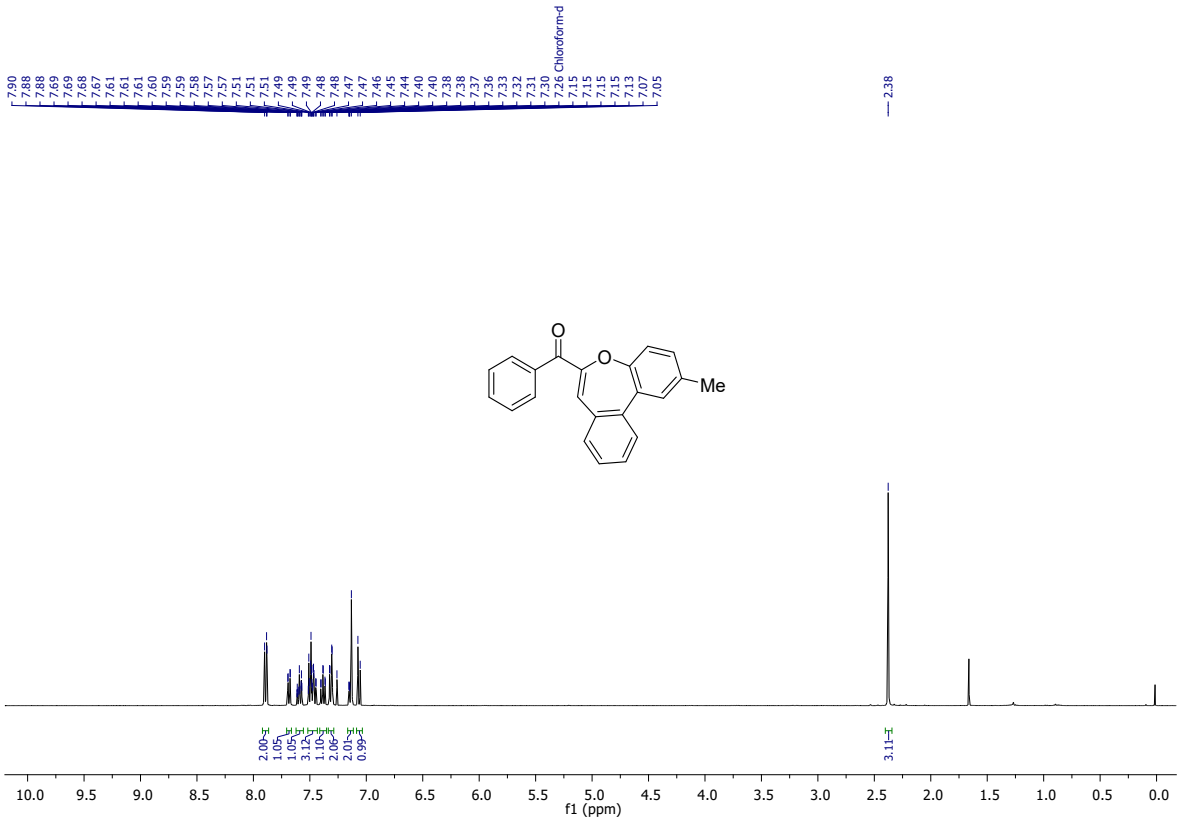
^{13}C{1H} NMR (100 MHz) spectrum of **5ha** in $CDCl_3$



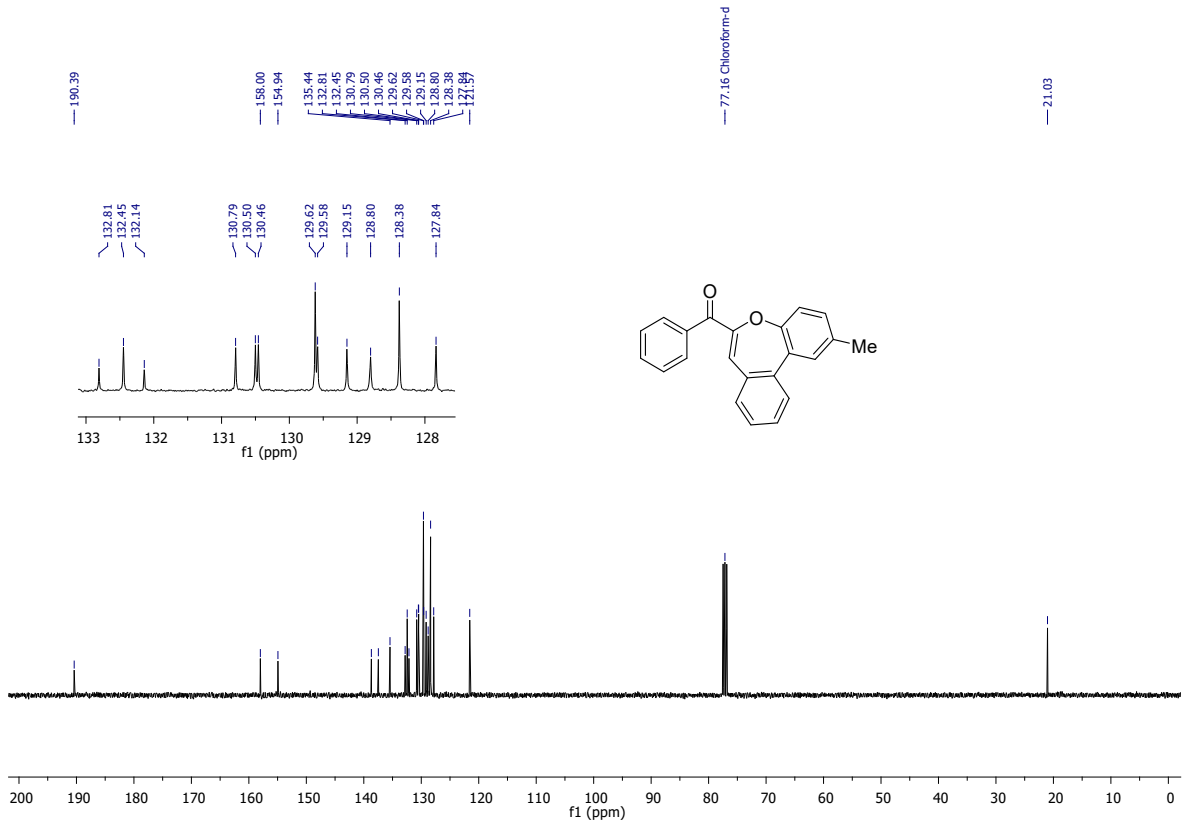
^{1}H NMR (400 MHz) spectrum of **5ia** in $CDCl_3$



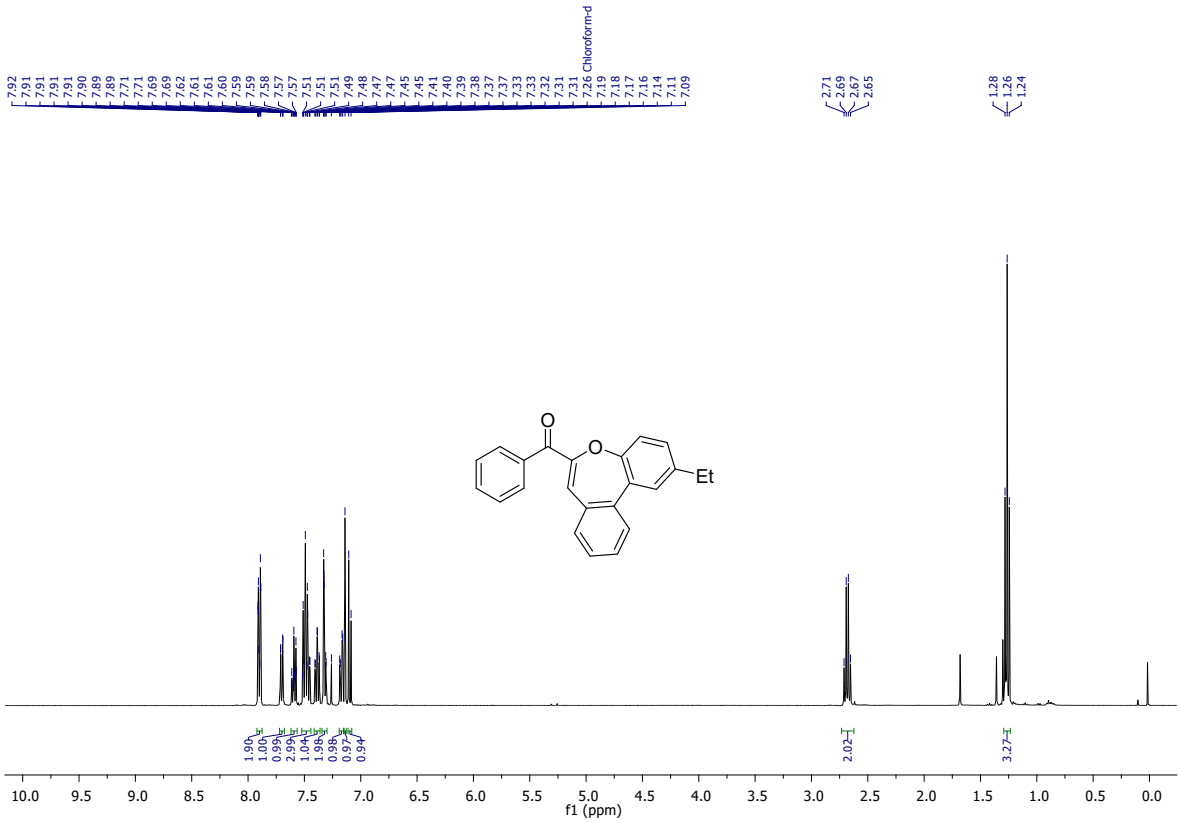
^{13}C{1H} NMR (100 MHz) spectrum of **5ia** in $CDCl_3$



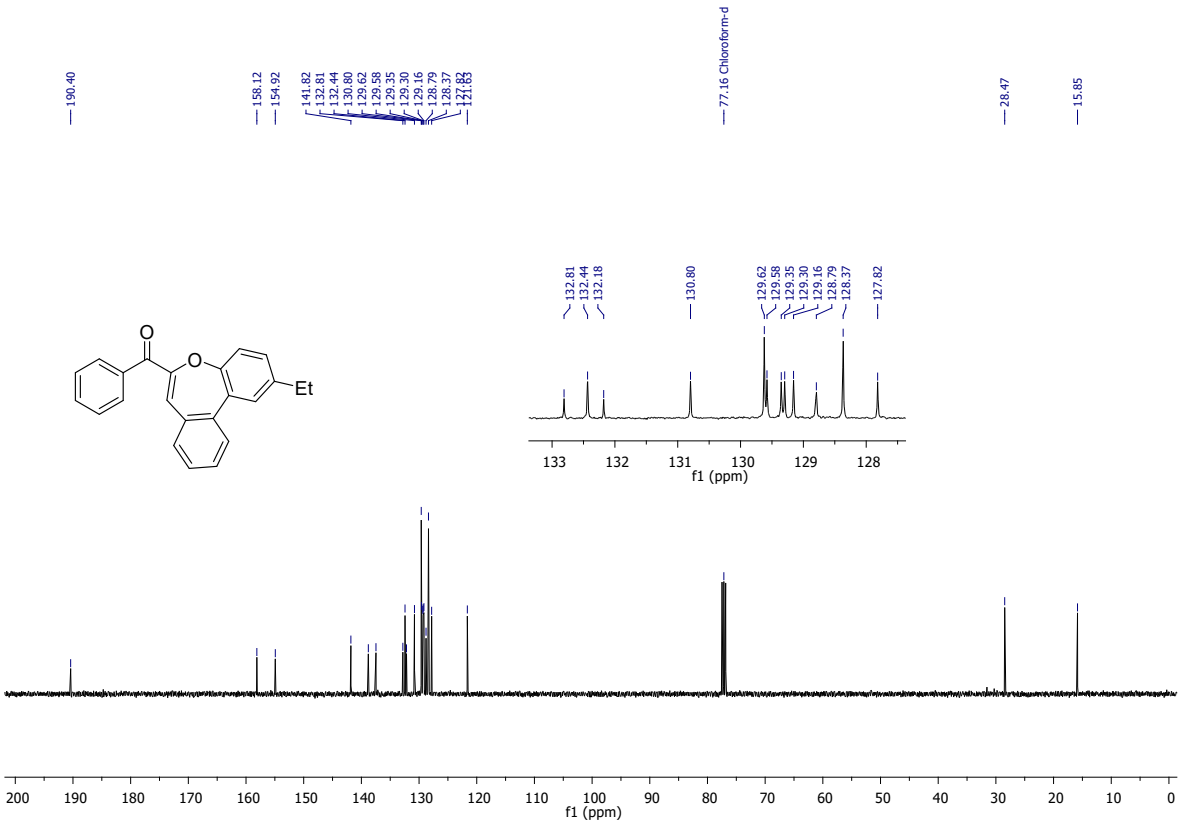
^{1}H NMR (400 MHz) spectrum of **5ja** in $CDCl_3$



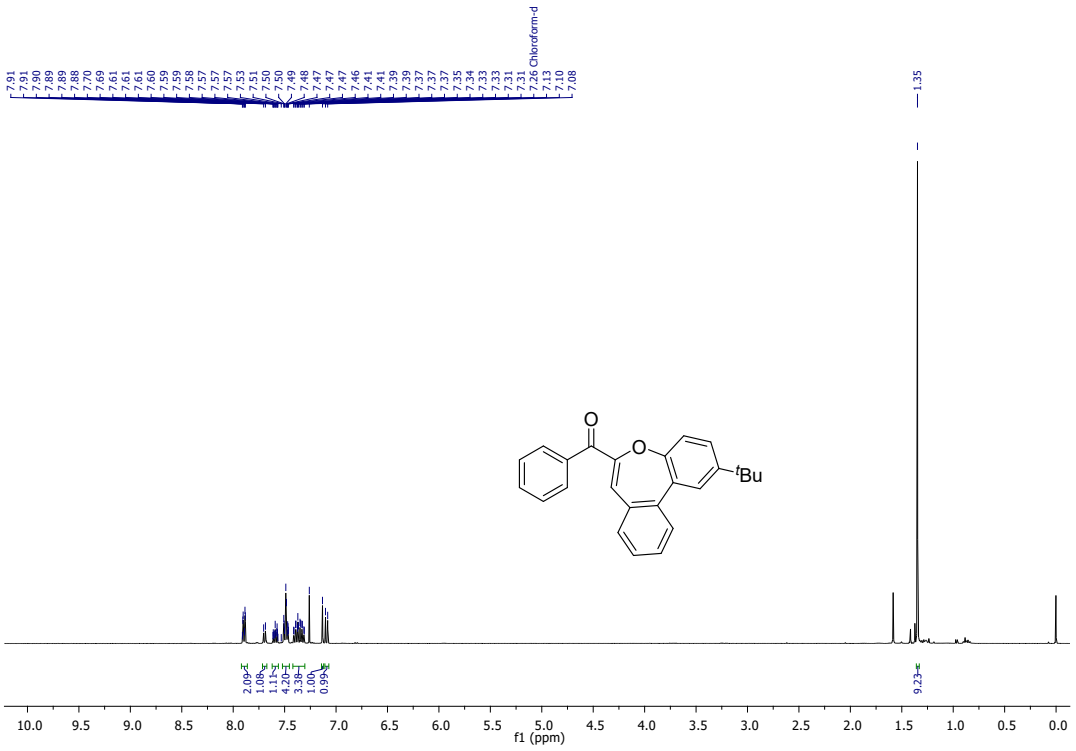
^{13}C{1H} NMR (100 MHz) spectrum of **5ja** in $CDCl_3$



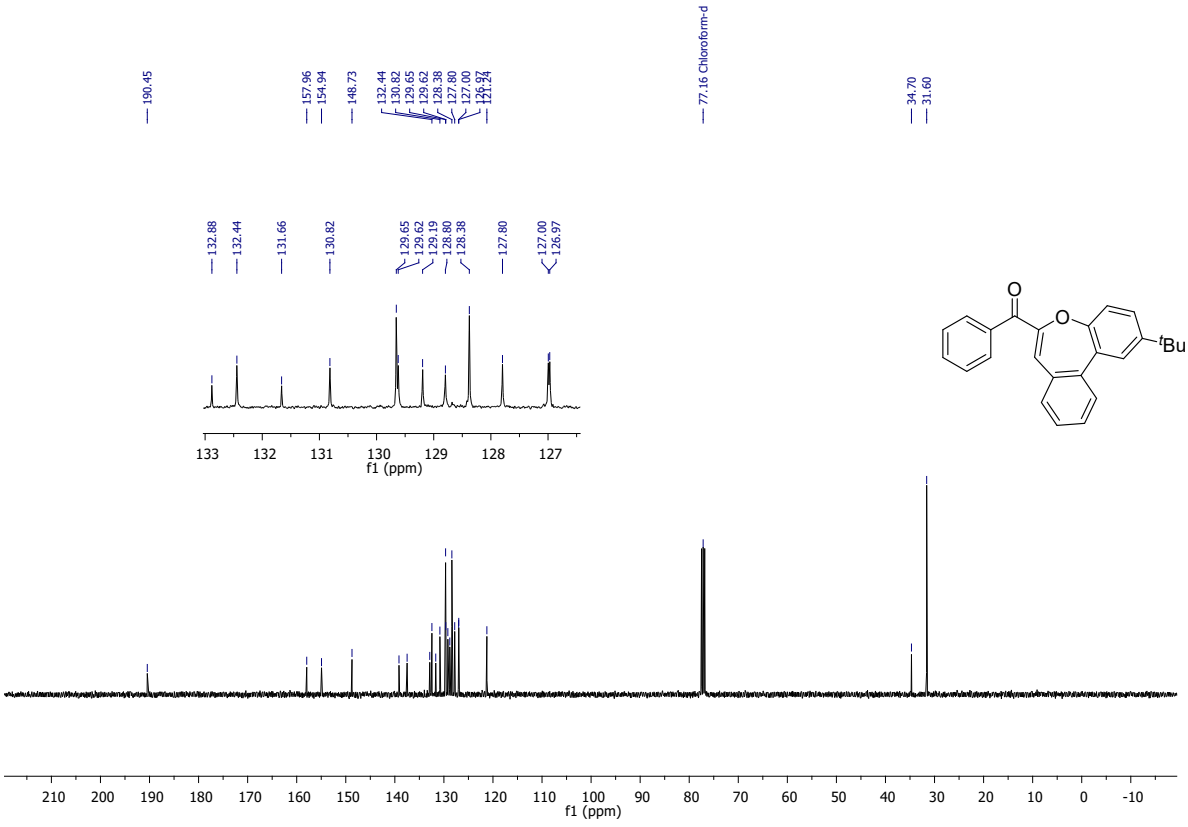
^{1}H NMR (400 MHz) spectrum of **5ka** in $CDCl_3$



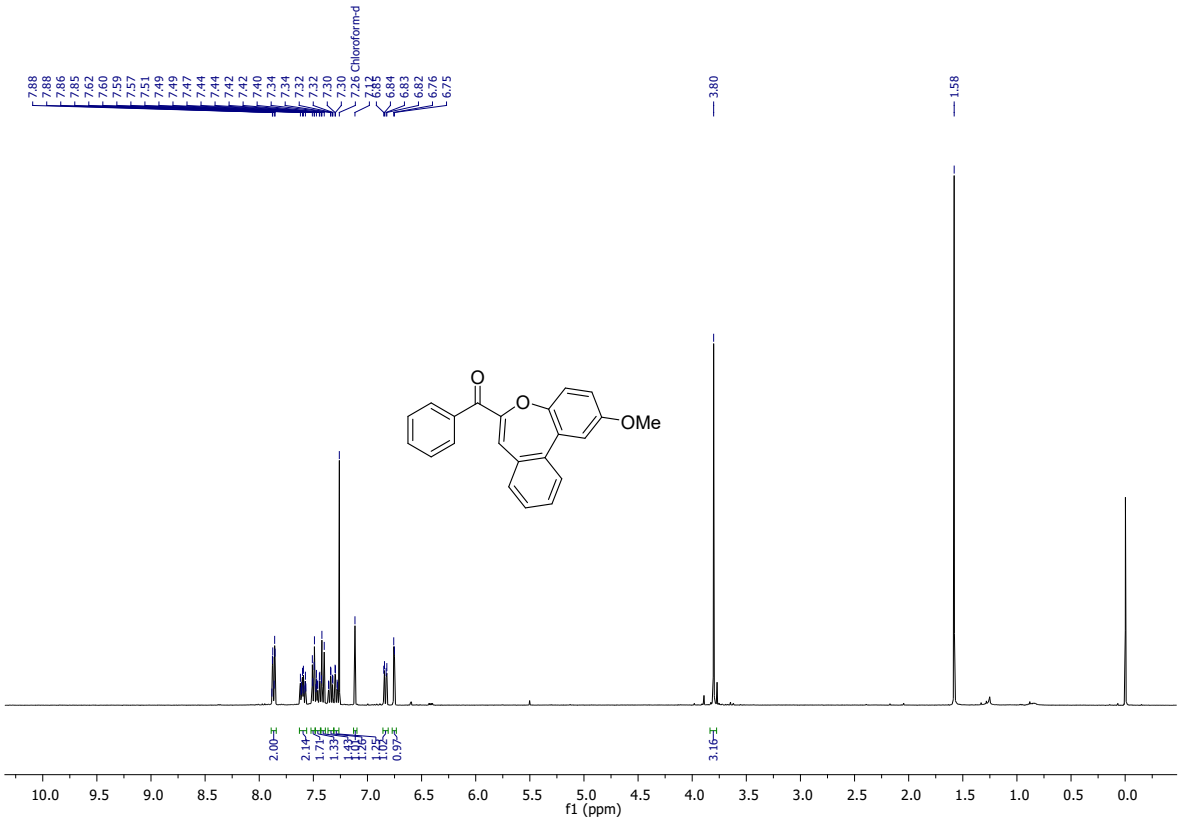
^{13}C{1H} NMR (100 MHz) spectrum of **5ka** in $CDCl_3$



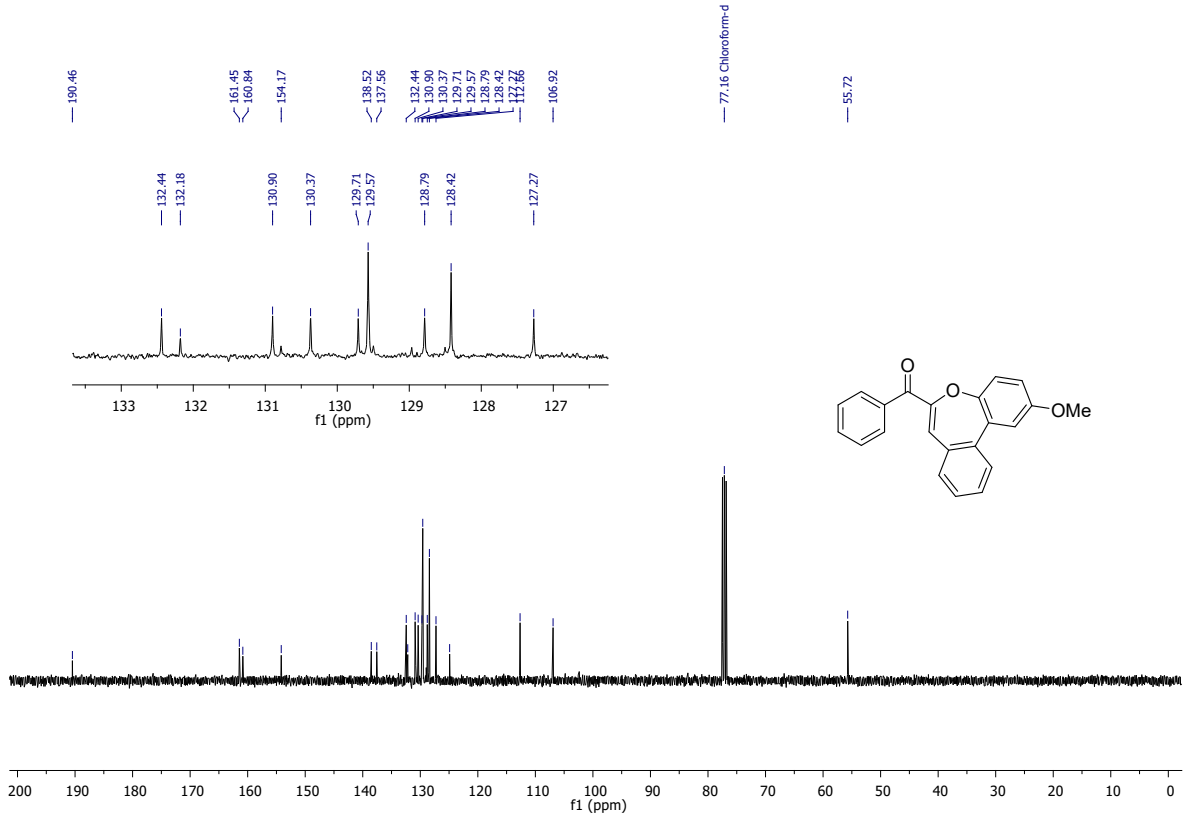
H NMR (400 MHz) spectrum of **5op** in $CDCl_3$



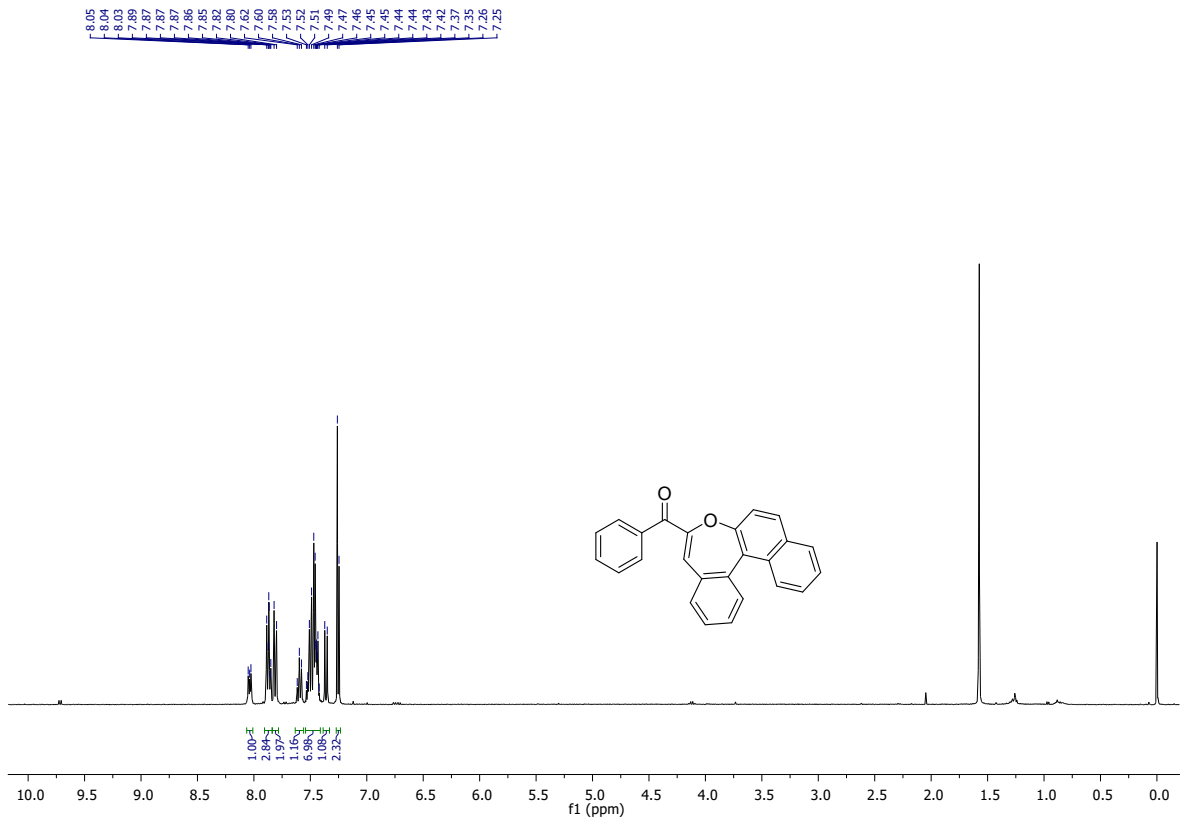
$^{13}C\{1H\}$ NMR (100 MHz) spectrum of **5la** in $CDCl_3$



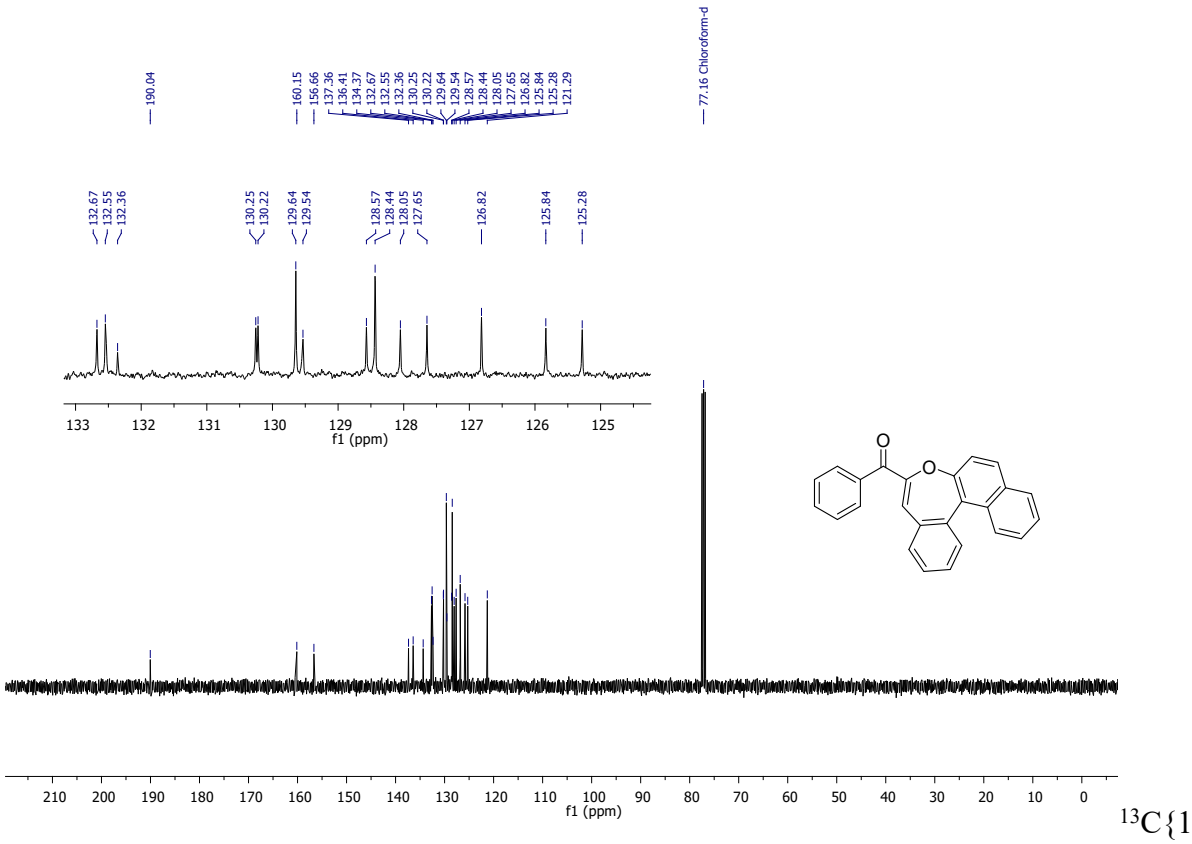
^{1}H NMR (400 MHz) spectrum of **5ma** in $CDCl_3$



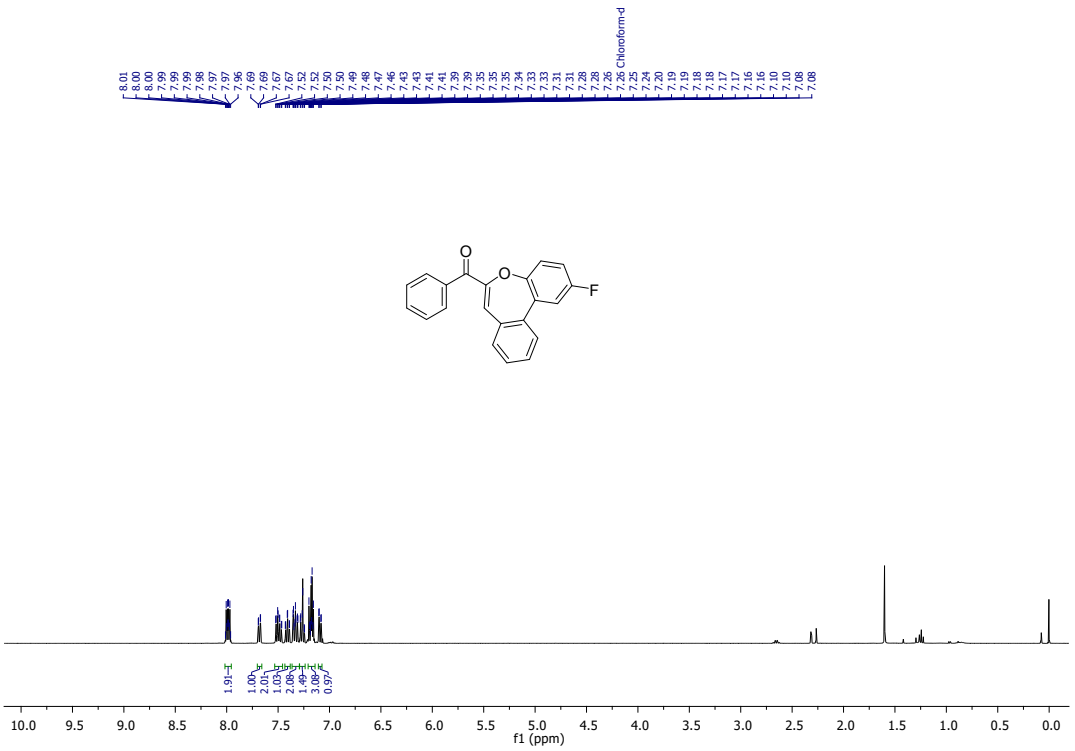
^{13}C{1H} NMR (100 MHz) spectrum of **5ma** in $CDCl_3$



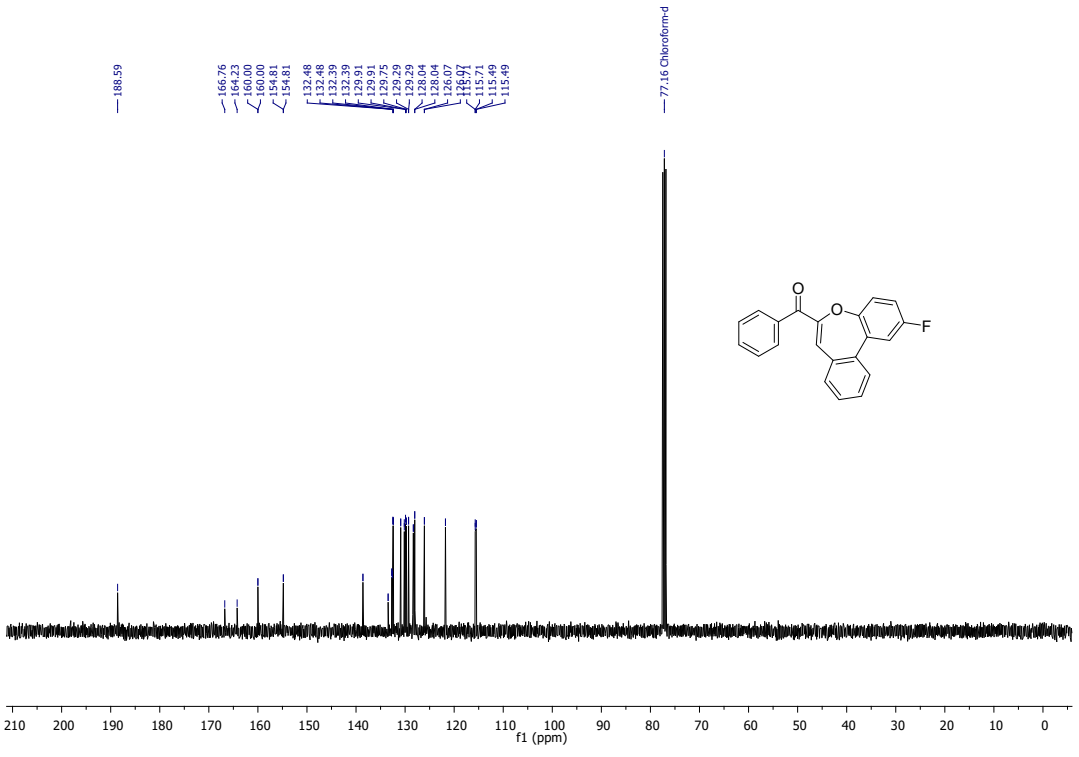
^{1}H NMR (400 MHz) spectrum of **5na** in $CDCl_3$



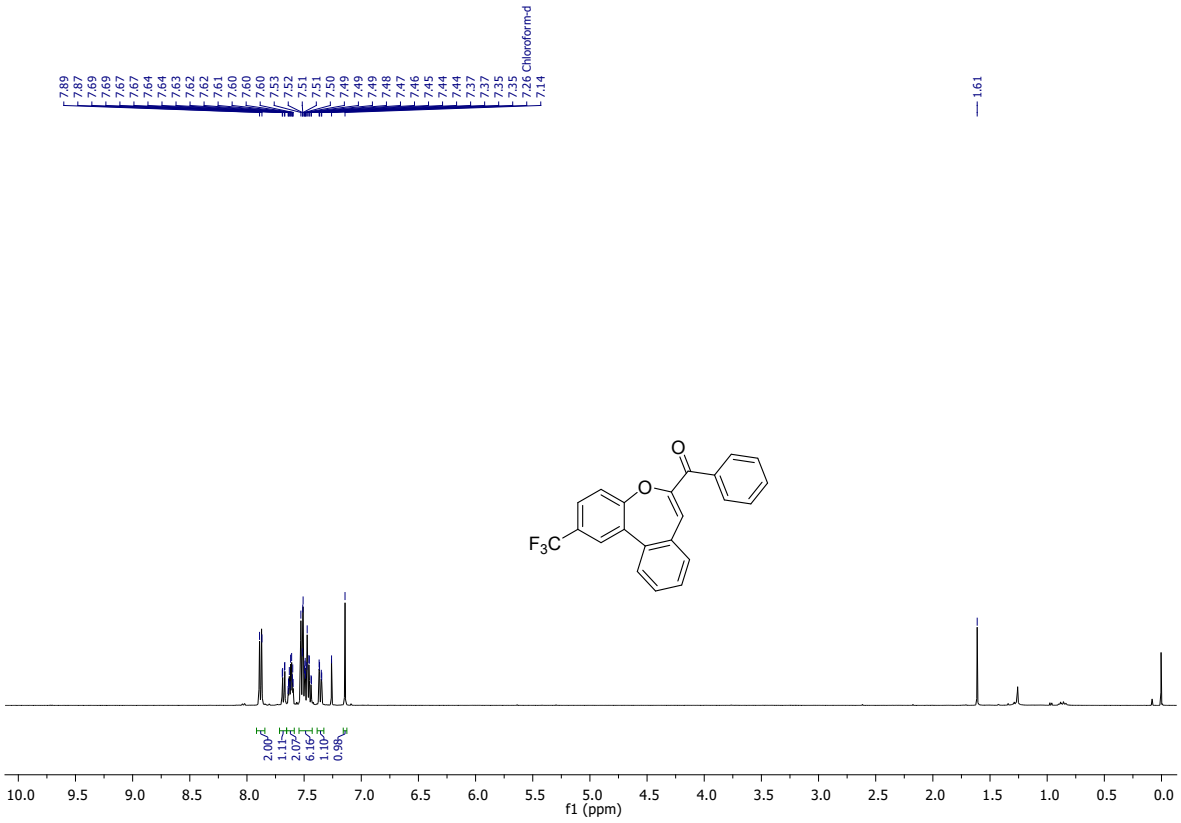
^{13}C{1H} NMR (100 MHz) spectrum of **5na** in $CDCl_3$



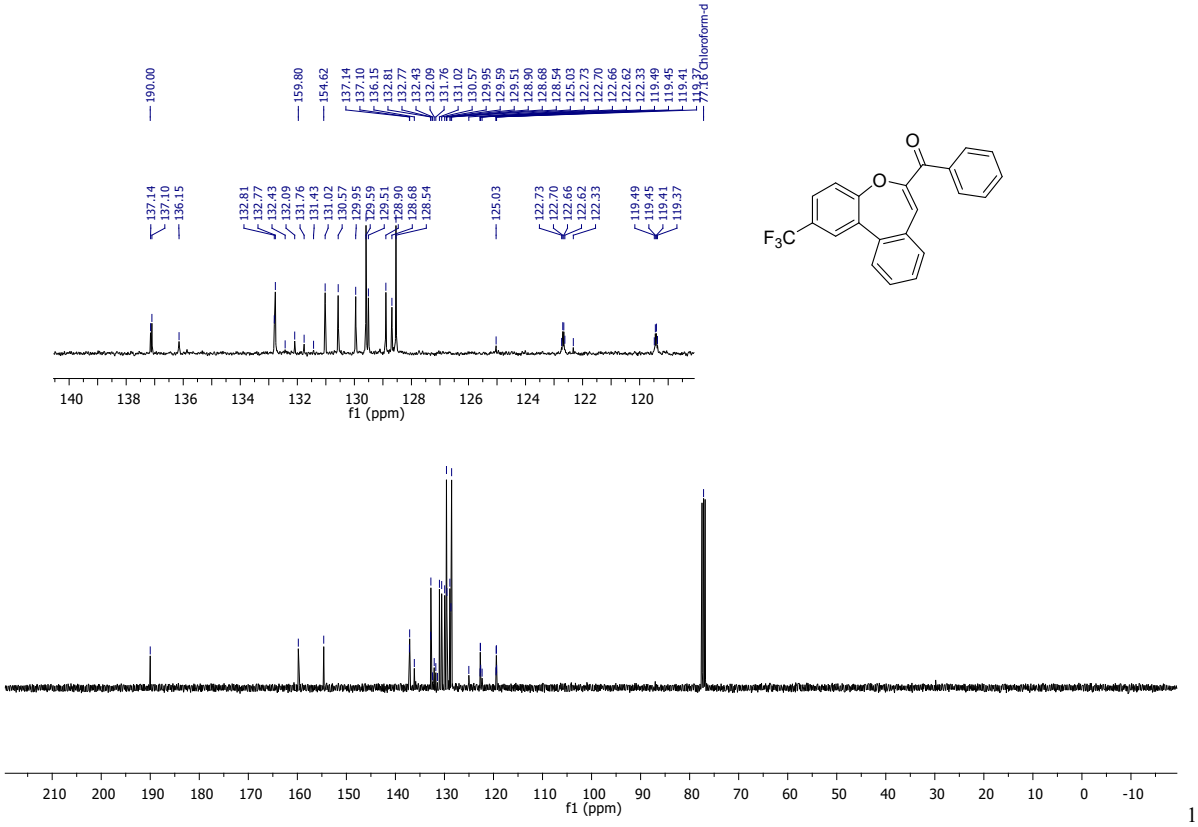
H NMR (400 MHz) spectrum of **5oa** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of **5oa** in $CDCl_3$

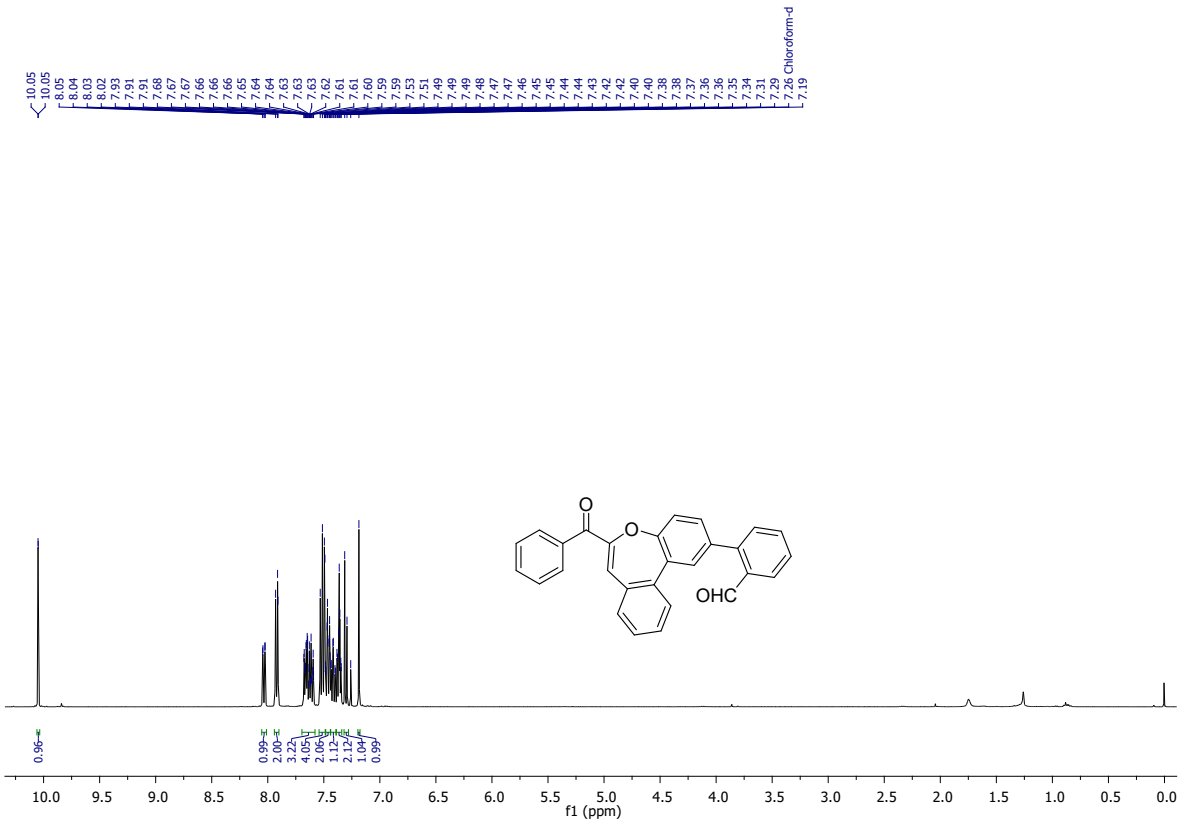


^{1}H NMR (400 MHz) spectrum of **5pa** in $CDCl_3$

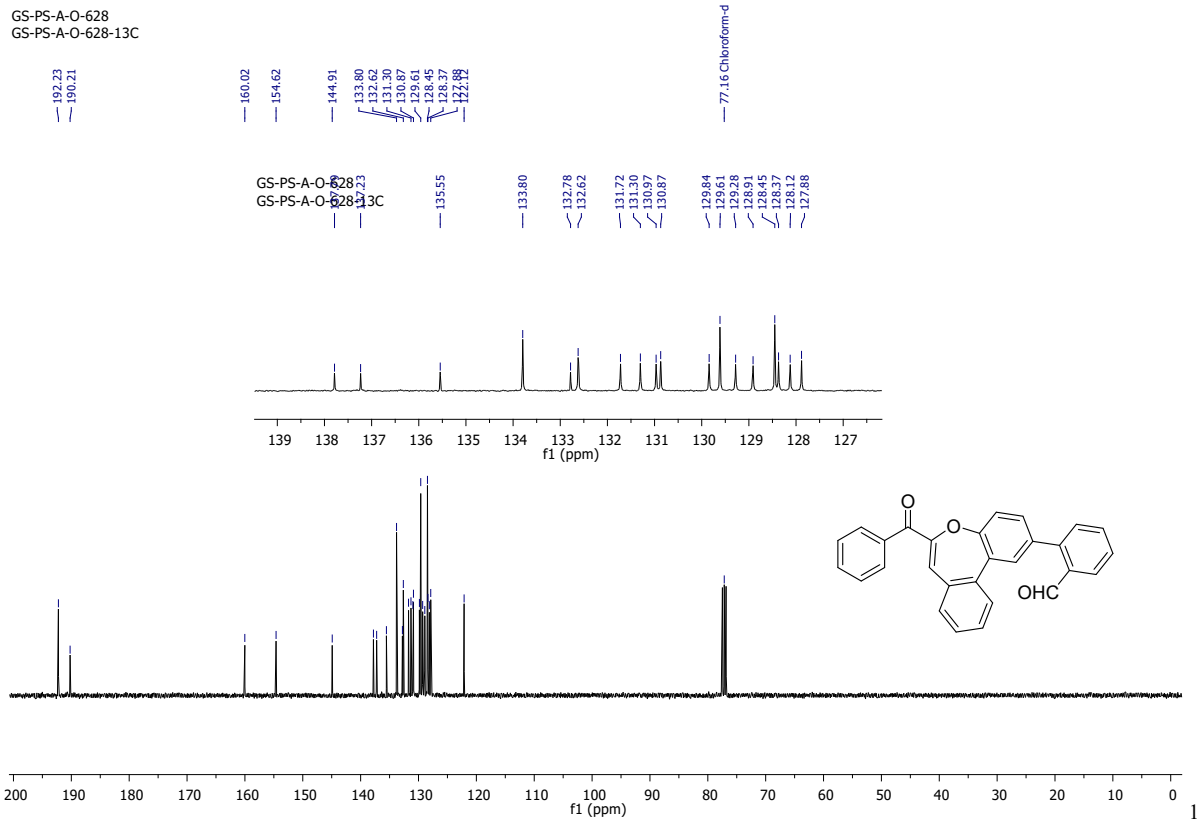


1

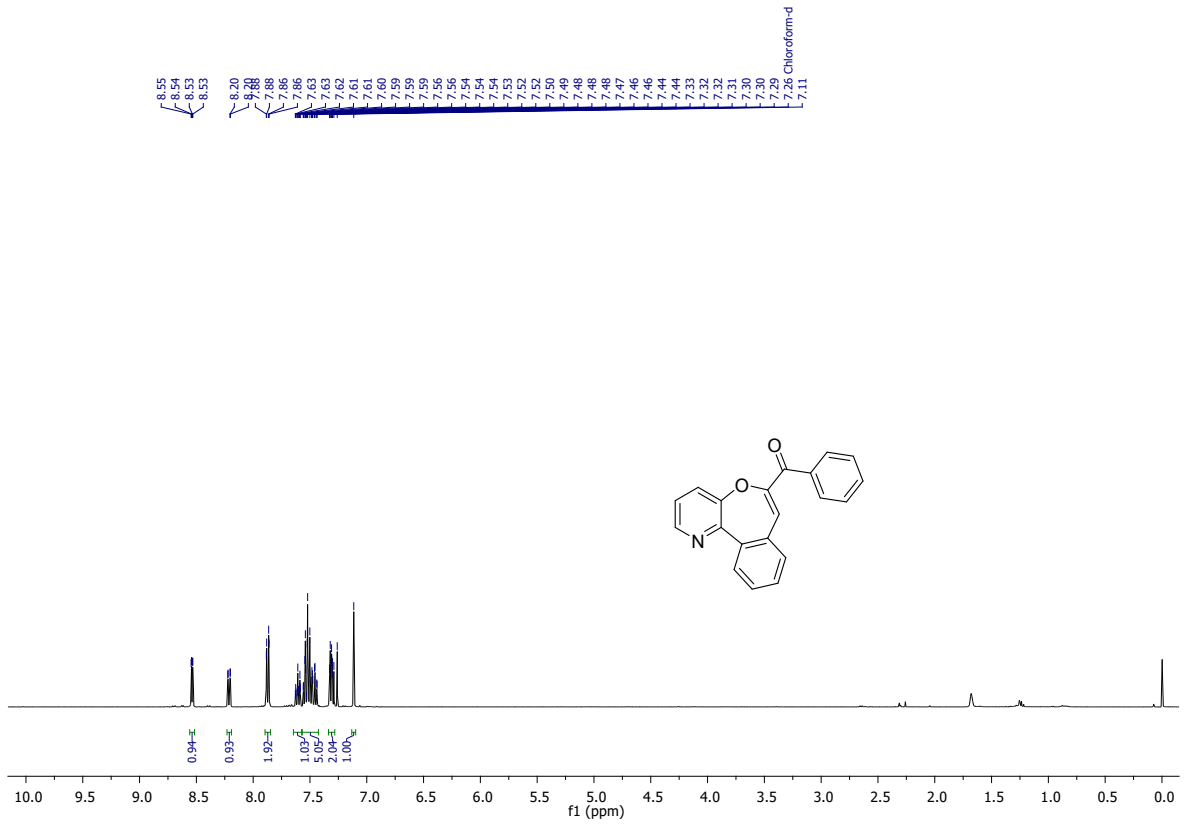
$^{3}C\{1H\}$ NMR (100 MHz) spectrum of **5pa** in $CDCl_3$



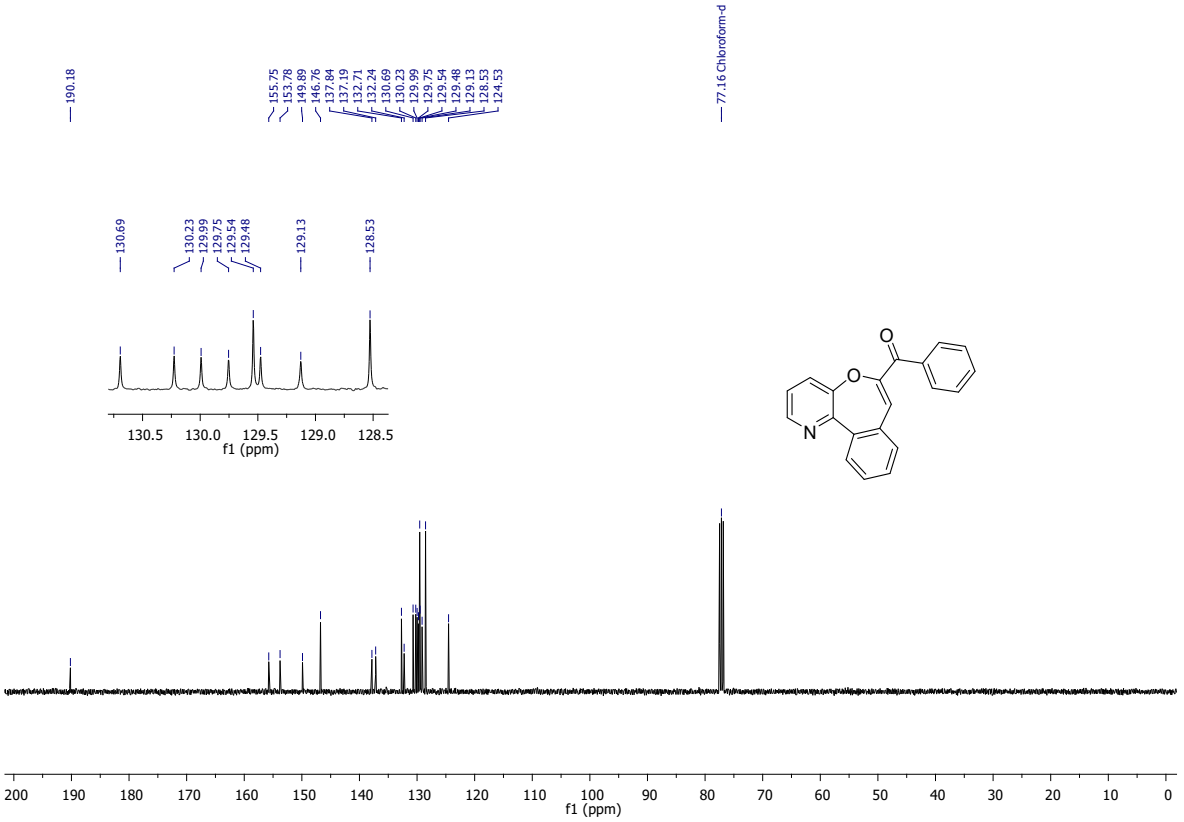
^{1}H NMR (400 MHz) spectrum of **5qa** in $CDCl_3$



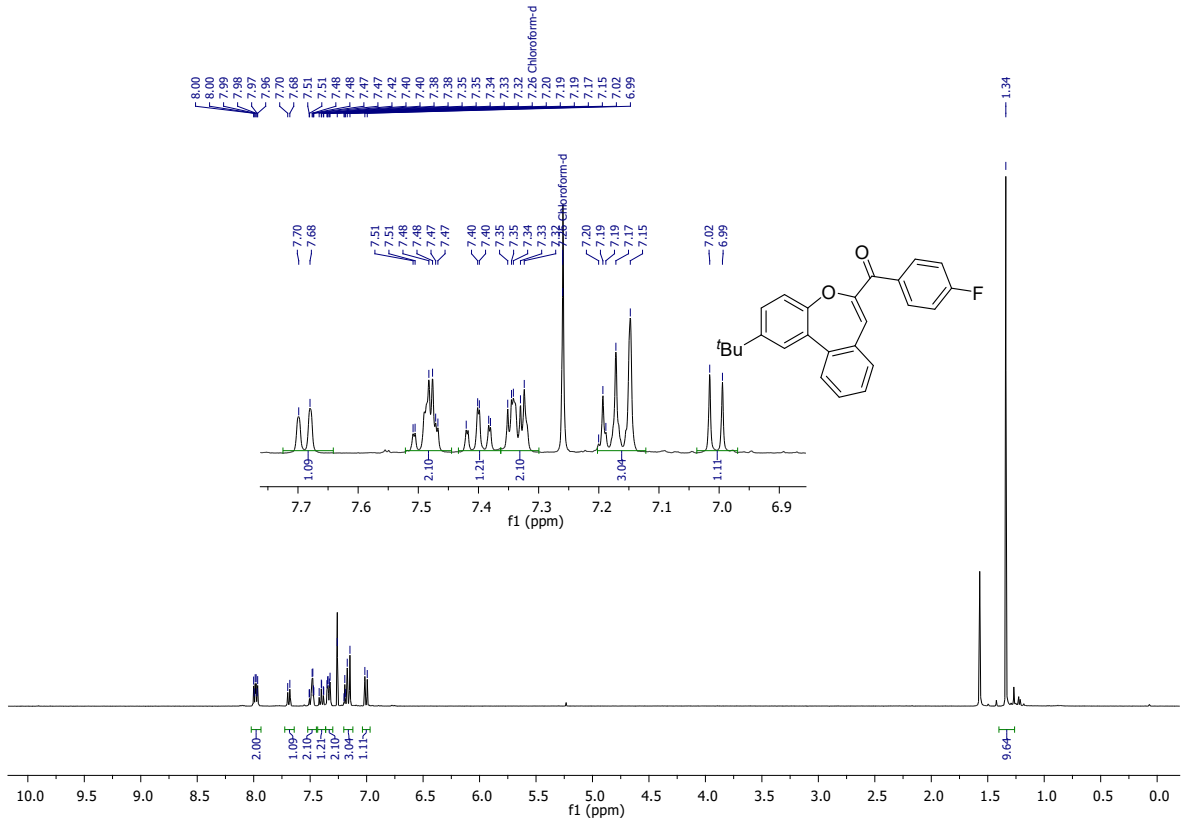
^{3}C{1H} NMR (100 MHz) spectrum of **5qa** in $CDCl_3$



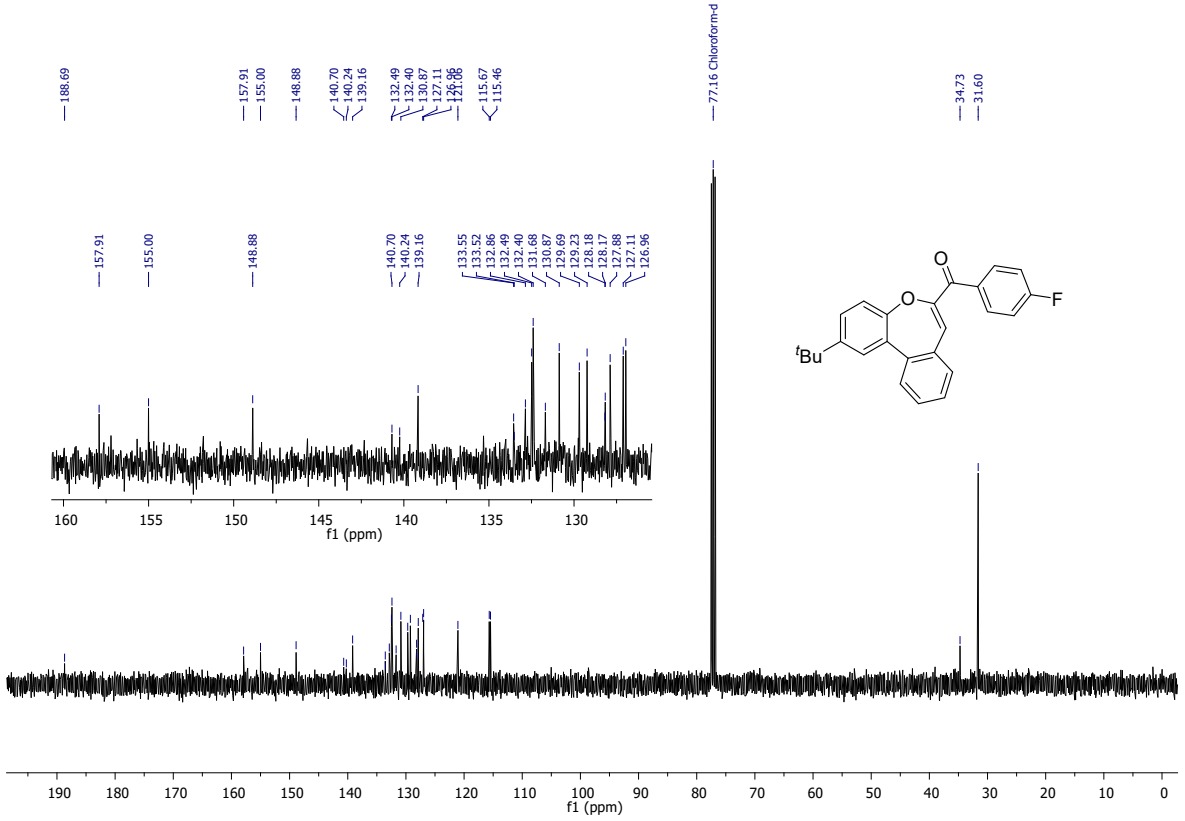
^{1}H NMR (400 MHz) spectrum of **5ra** in $CDCl_3$



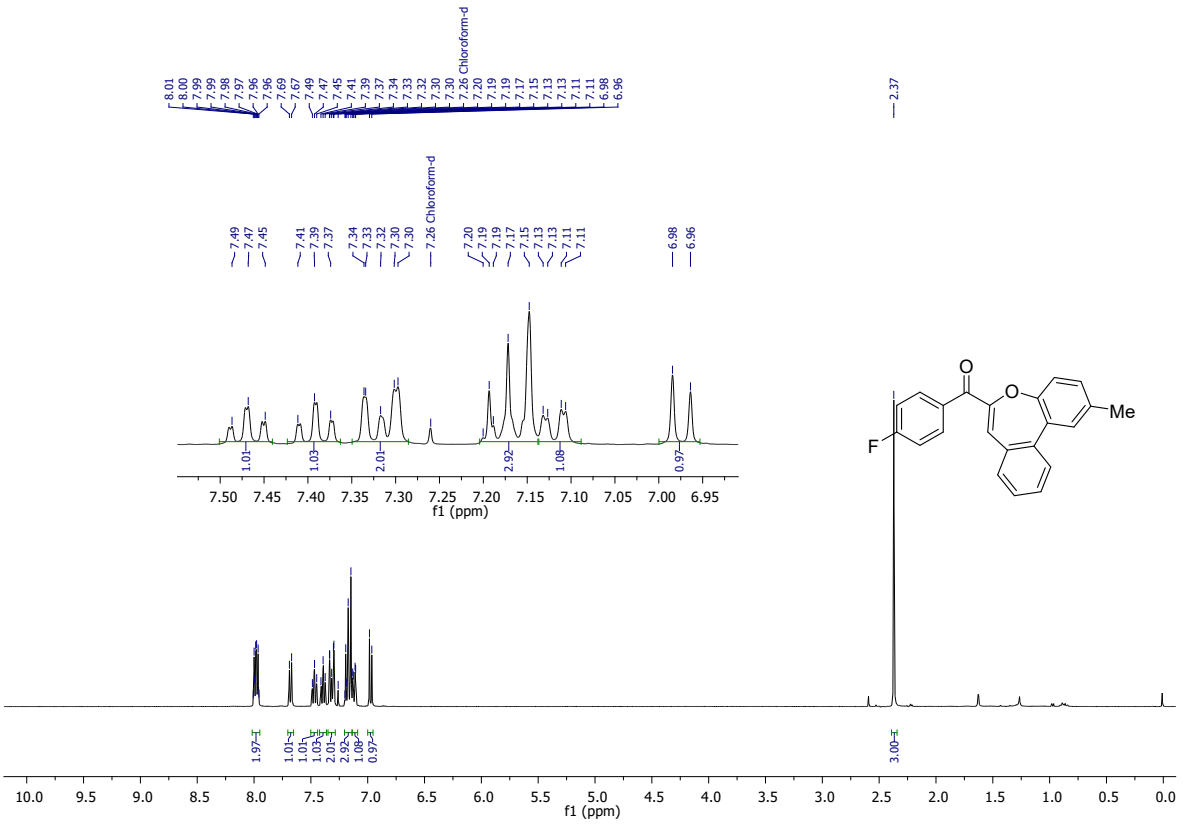
^{13}C{1H} NMR (100 MHz) spectrum of **5ra** in $CDCl_3$



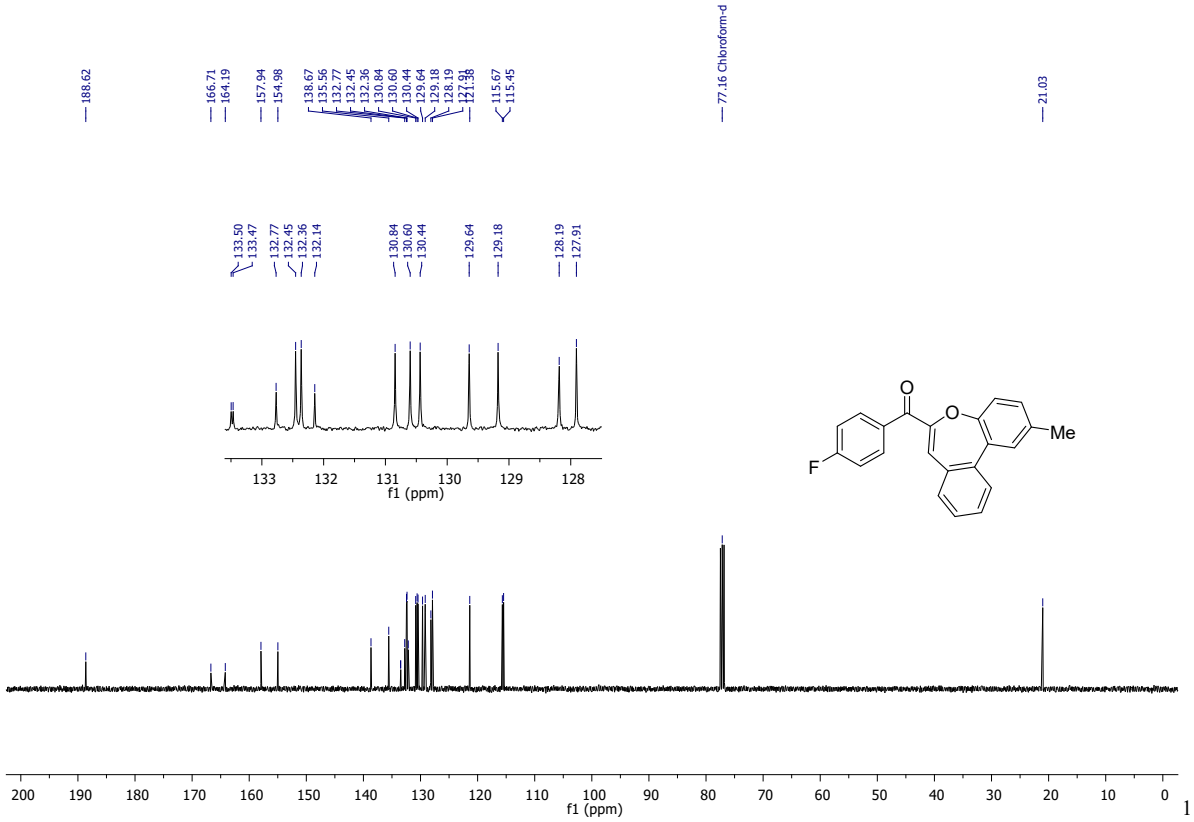
^{1}H NMR (400 MHz) spectrum of **5ta** in $CDCl_3$



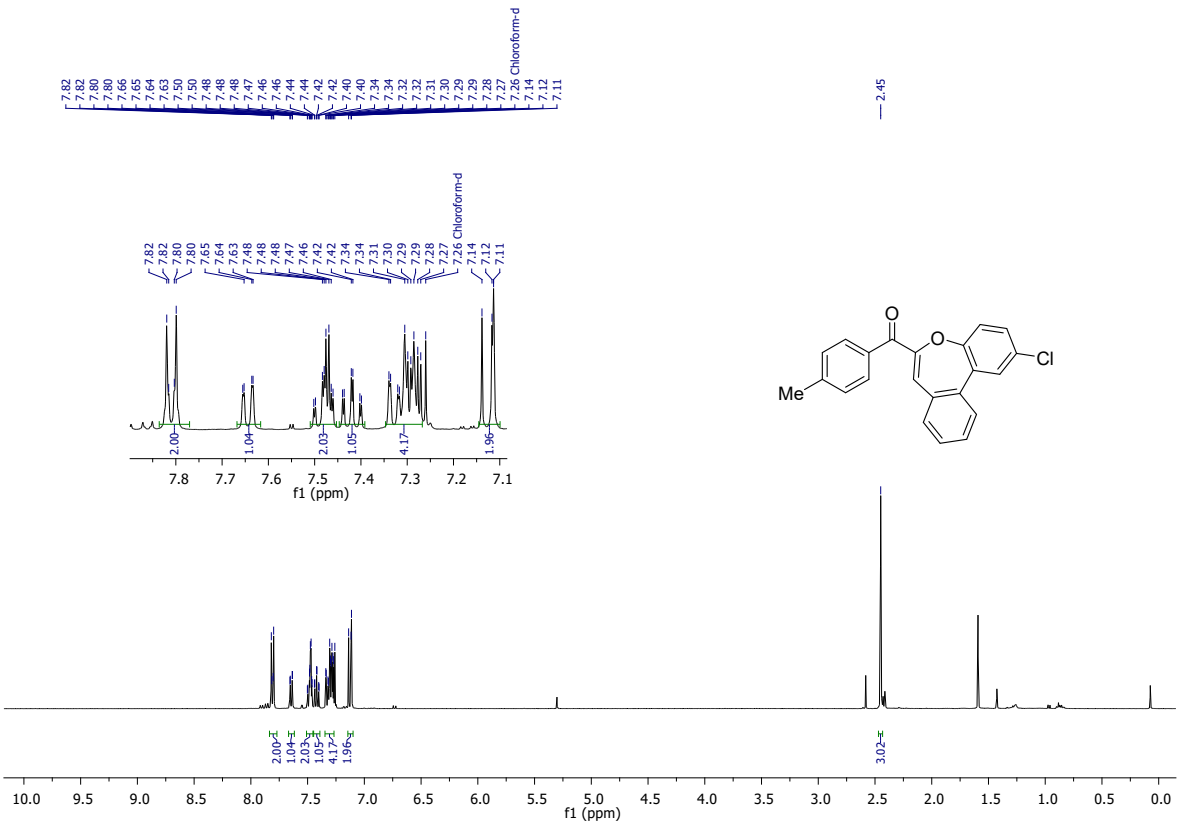
^{13}C{1H} NMR (100 MHz) spectrum of **5ta** in $CDCl_3$



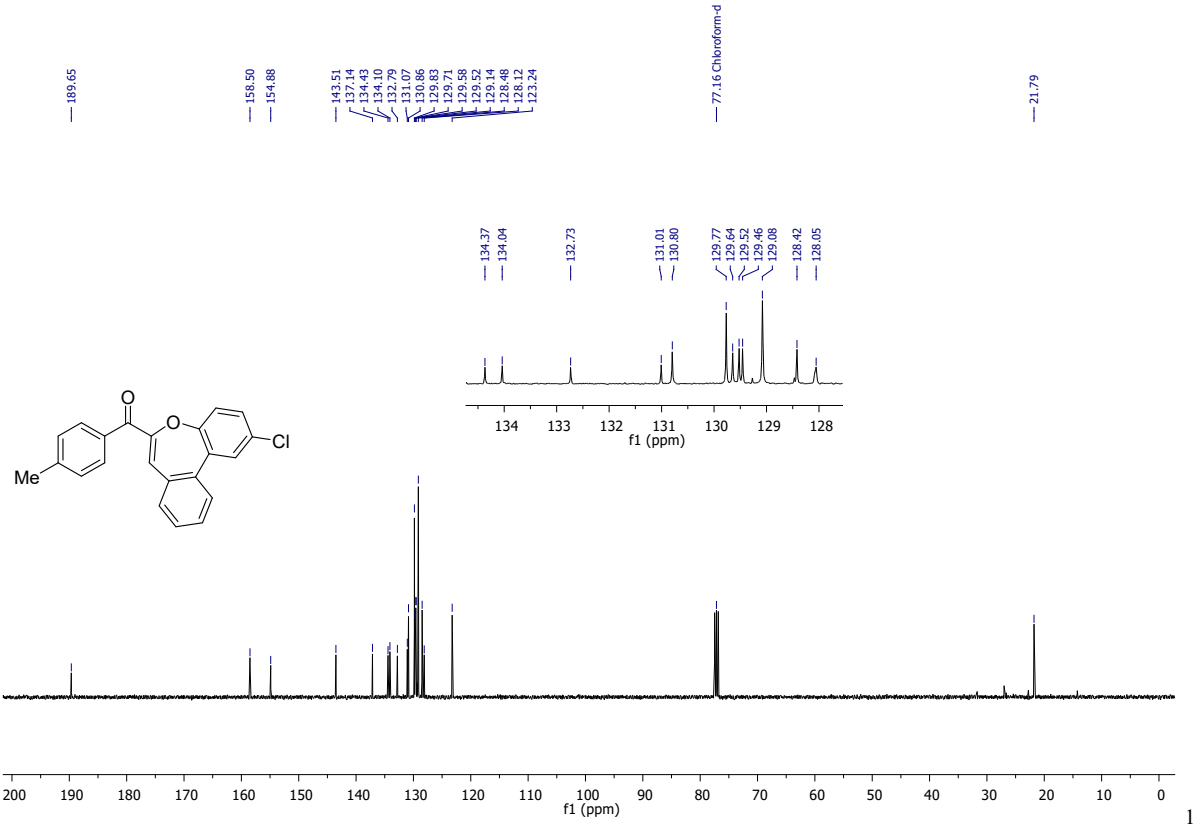
^{1}H NMR (400 MHz) spectrum of **5ua** in $CDCl_3$



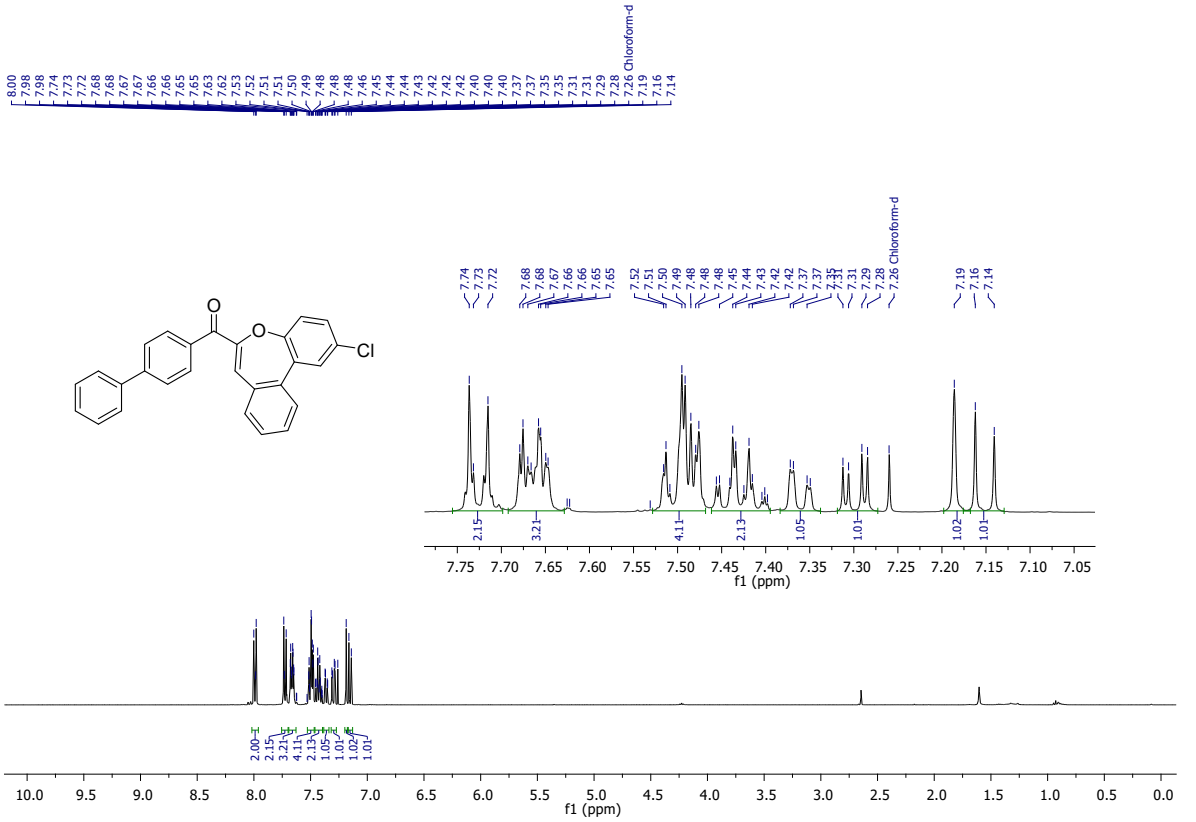
^{3}C{1H} NMR (100 MHz) spectrum of **5ua** in $CDCl_3$



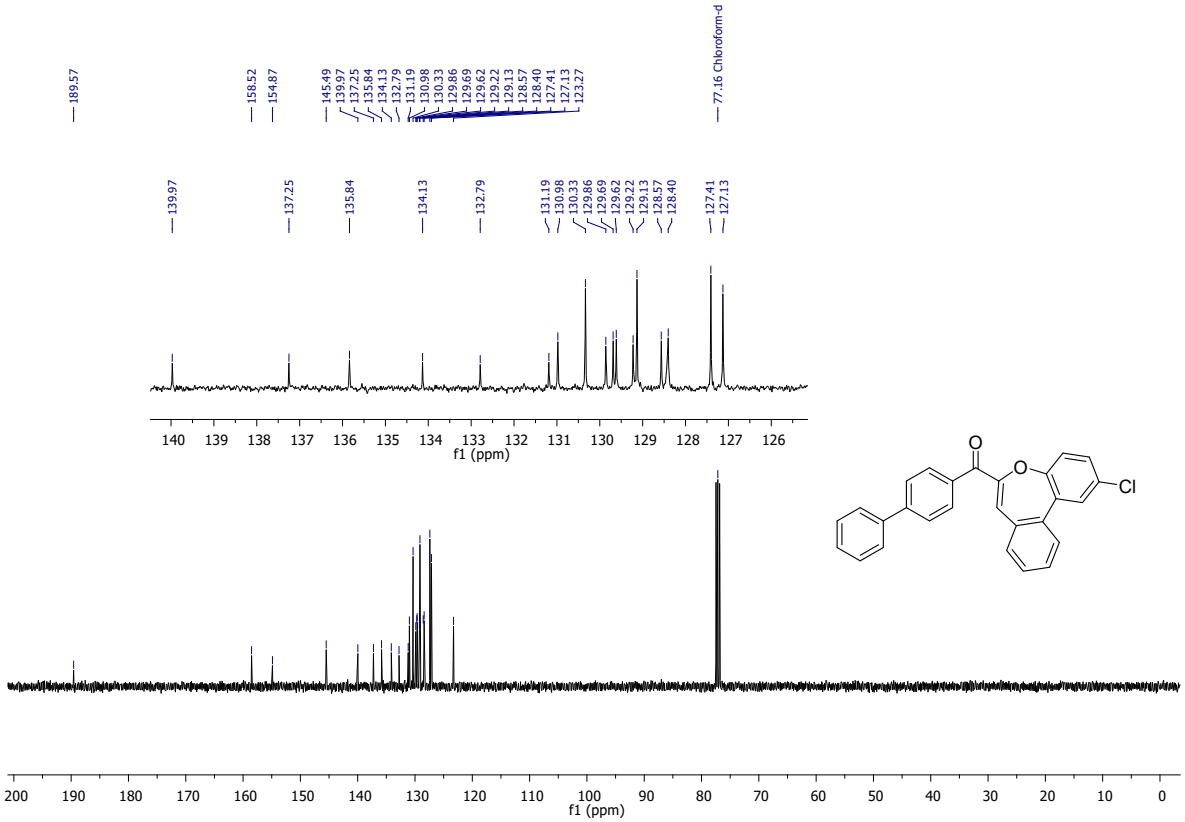
^{1}H NMR (400 MHz) spectrum of **5va** in $CDCl_3$



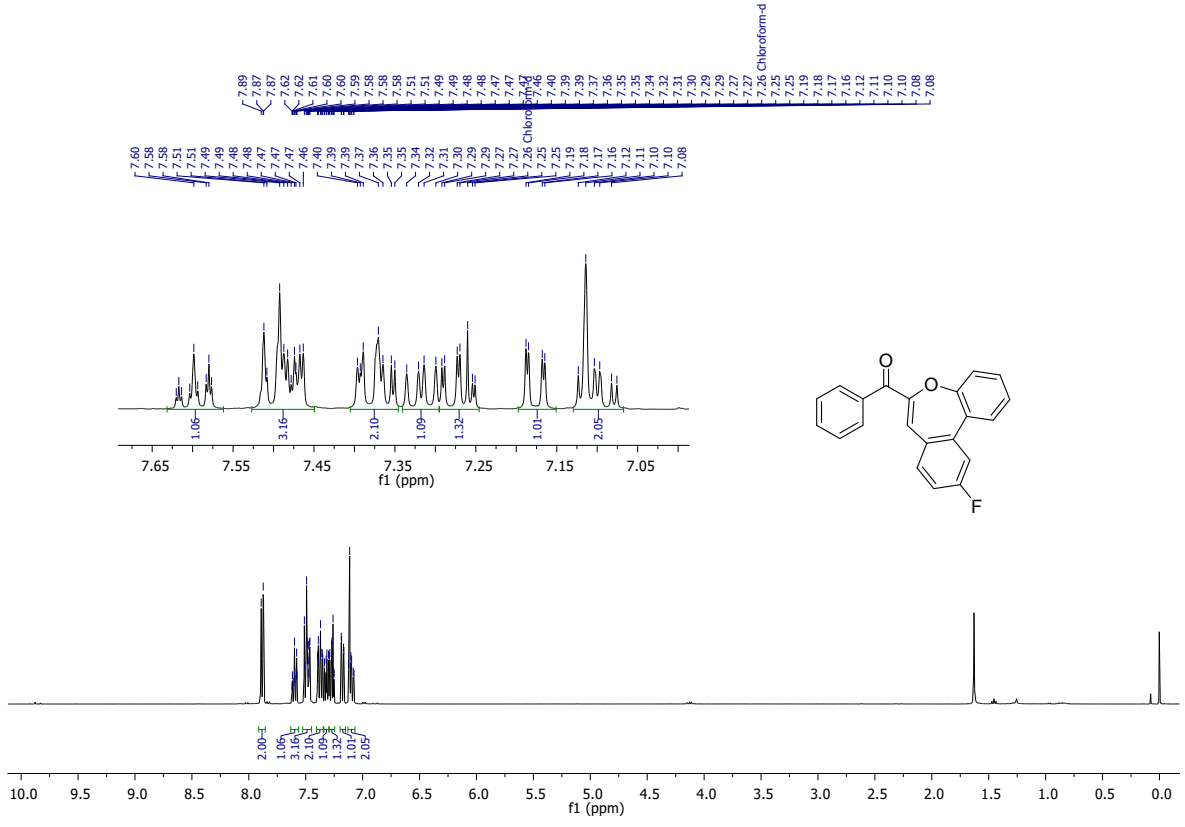
^{3}C{1H} NMR (100 MHz) spectrum of **5va** in $CDCl_3$



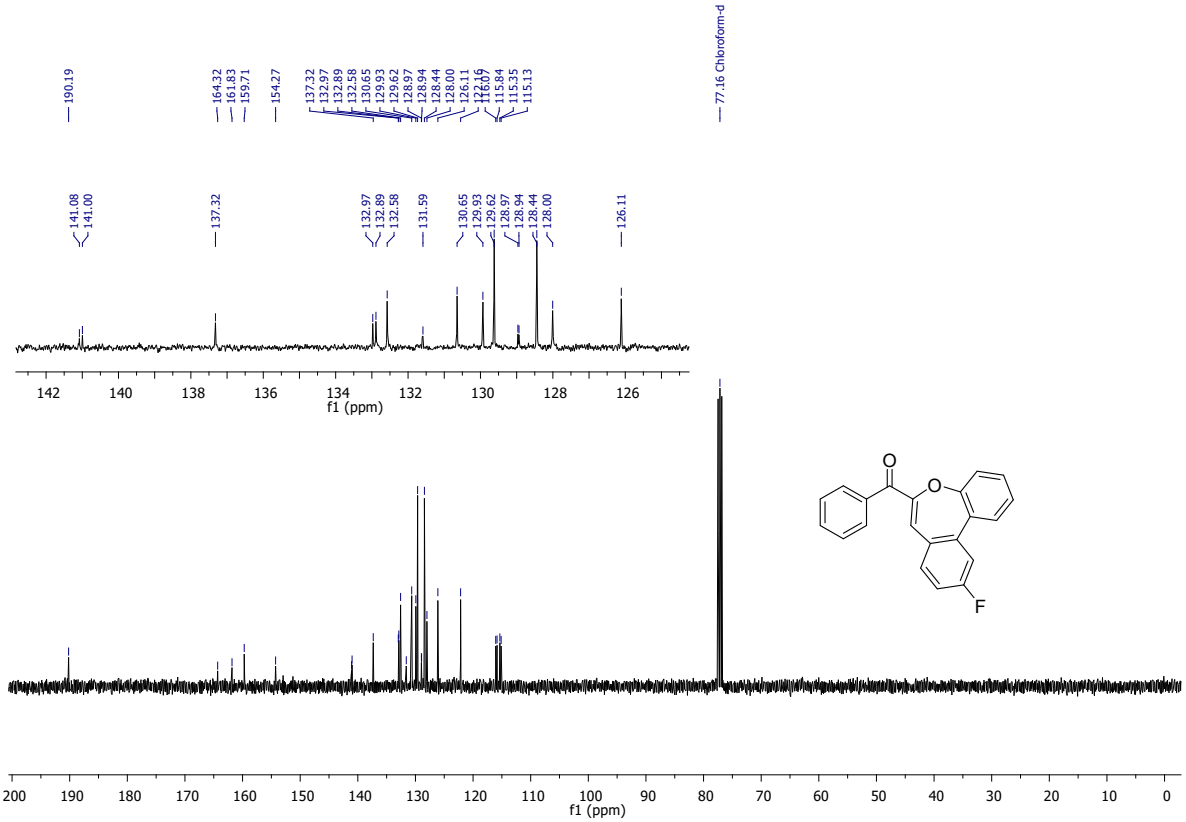
^{1}H NMR (400 MHz) spectrum of **5sa** in $CDCl_3$



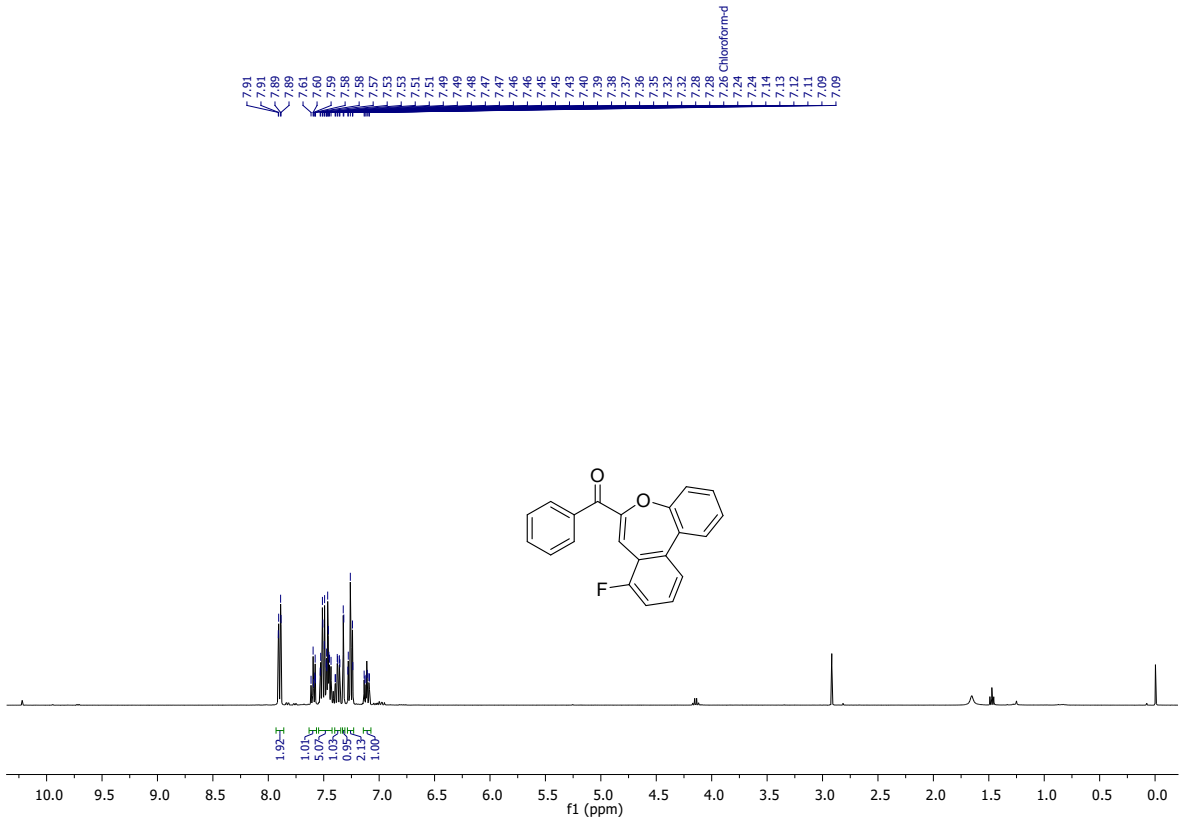
^{13}C{1H} NMR (100 MHz) spectrum of **5sa** in $CDCl_3$



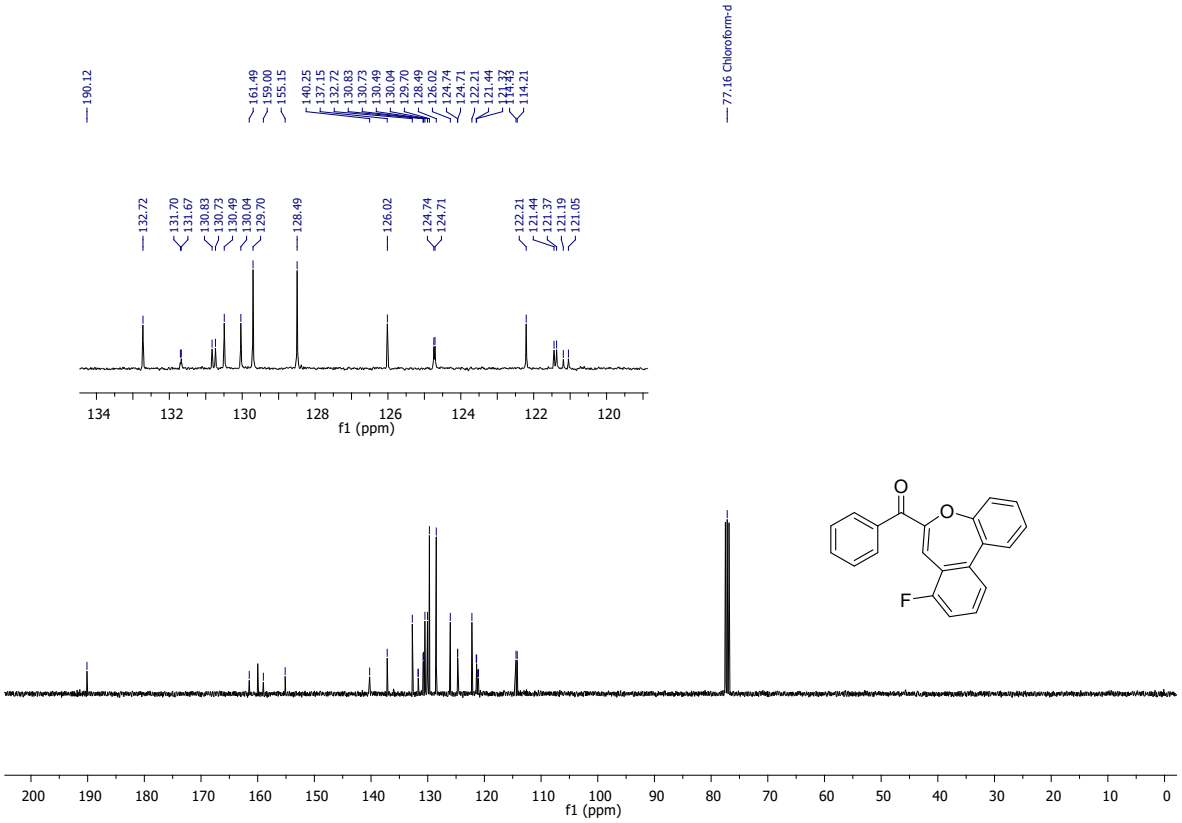
^{1}H NMR (400 MHz) spectrum of **5ac** in $CDCl_3$



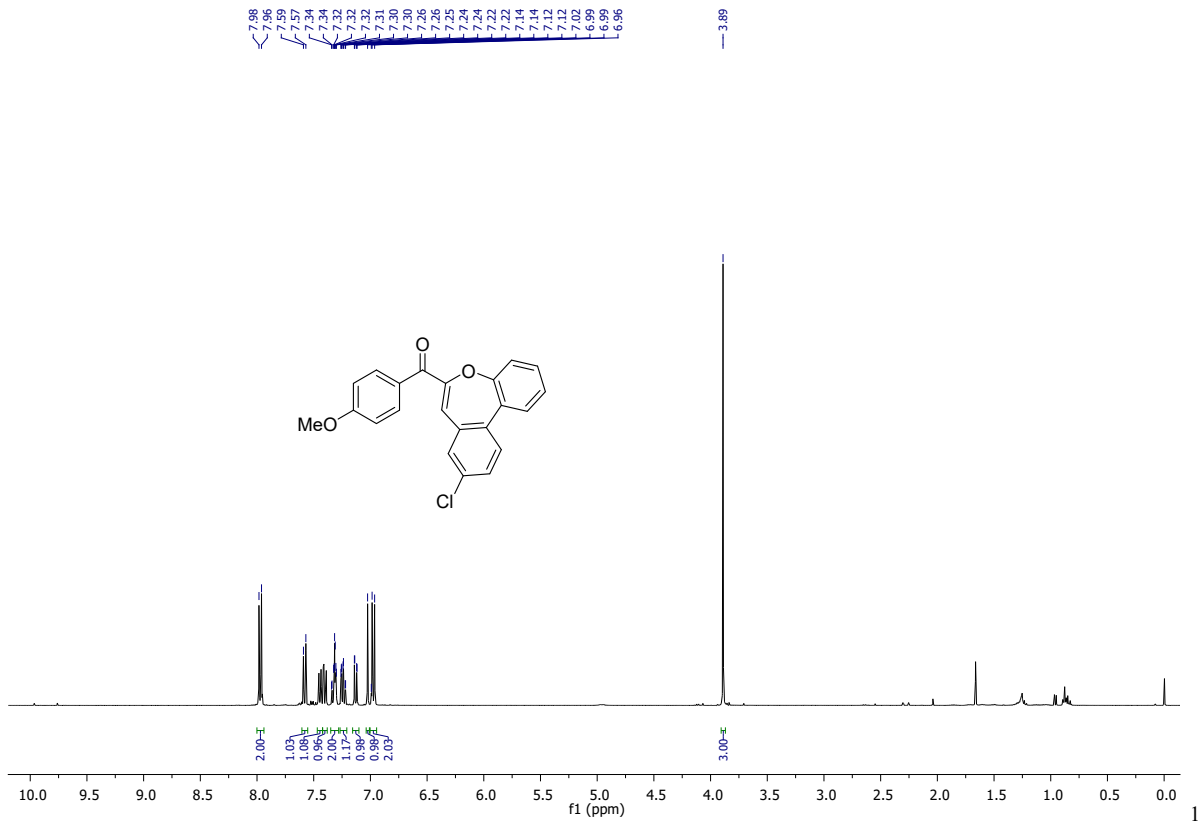
^{13}C{1H} NMR (100 MHz) spectrum of **5ac** in $CDCl_3$



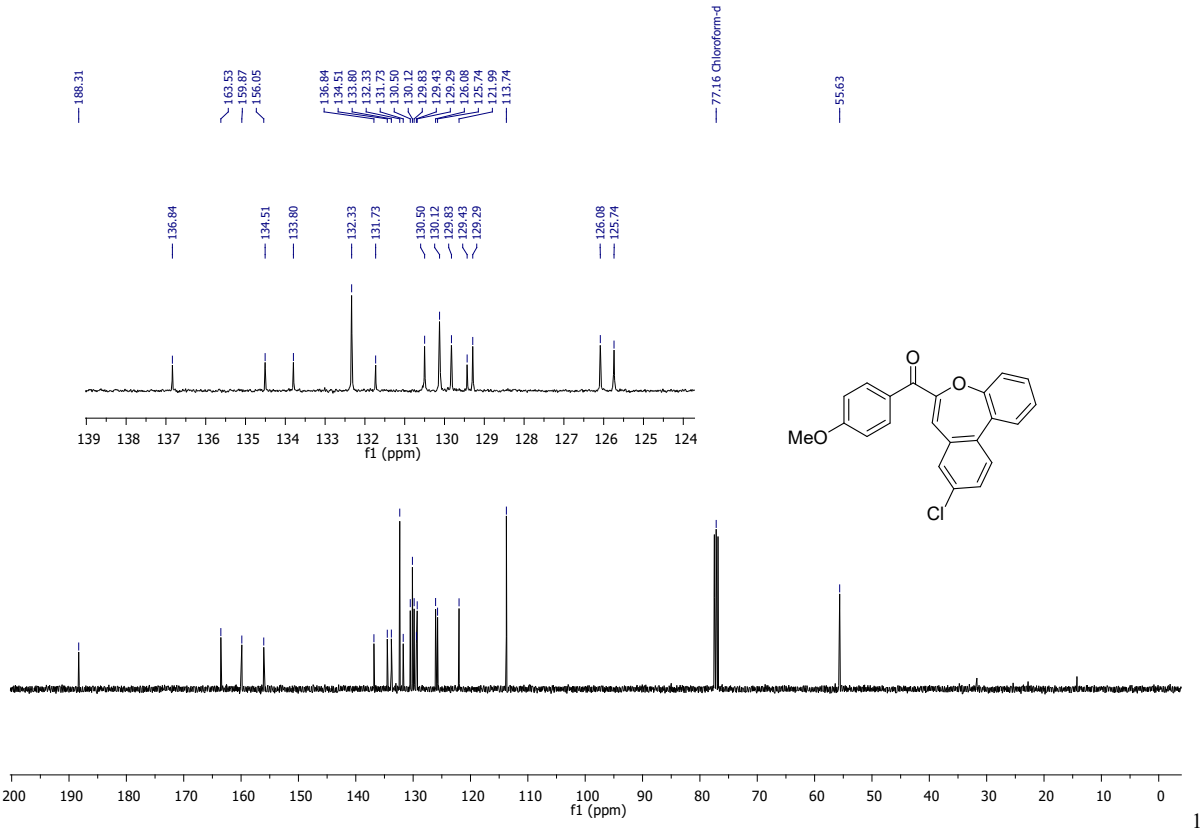
^{1}H NMR (400 MHz) spectrum of **5ab** in $CDCl_3$



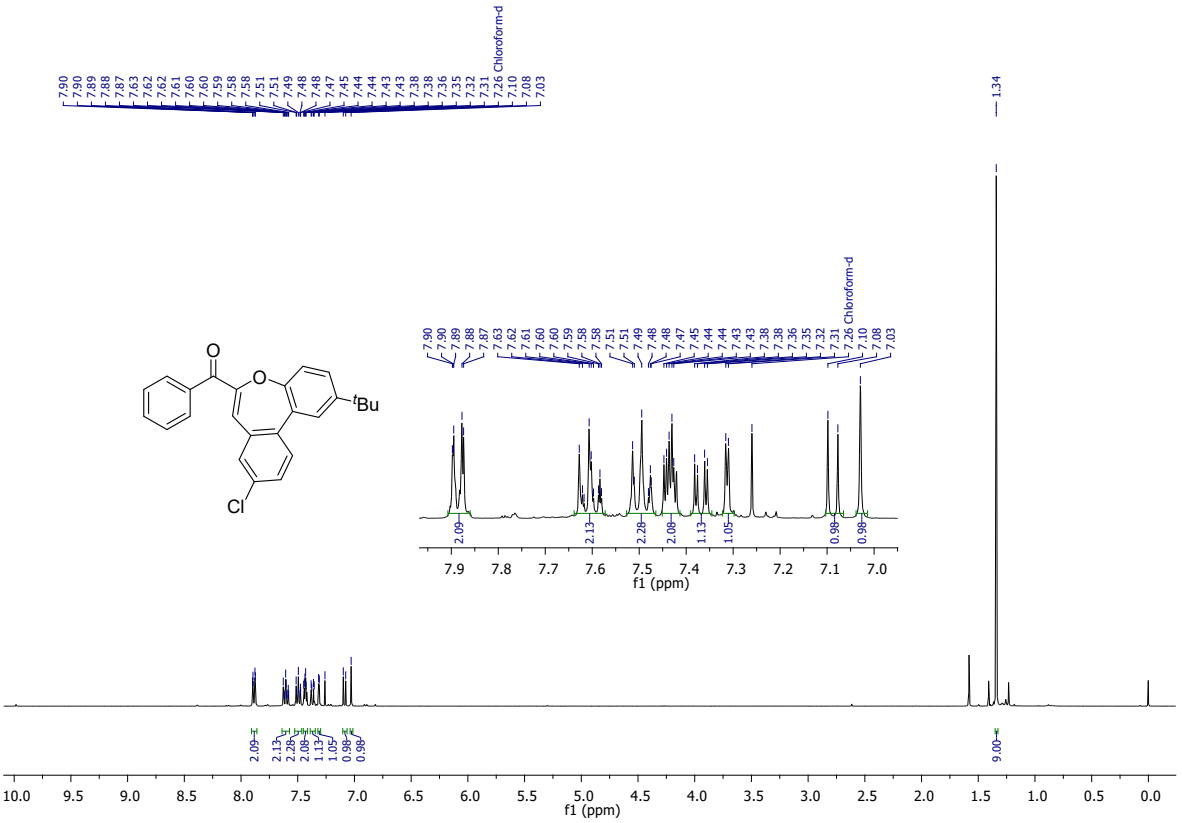
^{13}C{1H} NMR (100 MHz) spectrum of **5ab** in $CDCl_3$



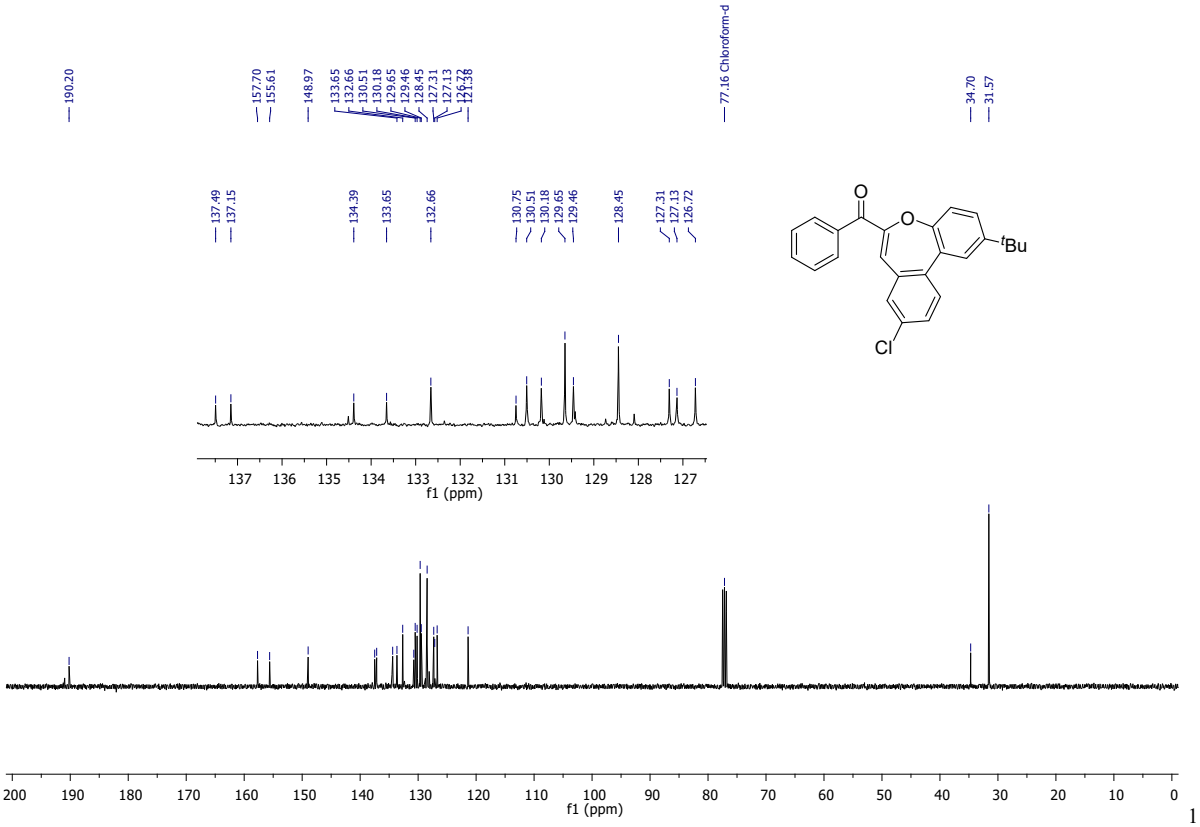
H NMR (400 MHz) spectrum of **5cd** in $CDCl_3$



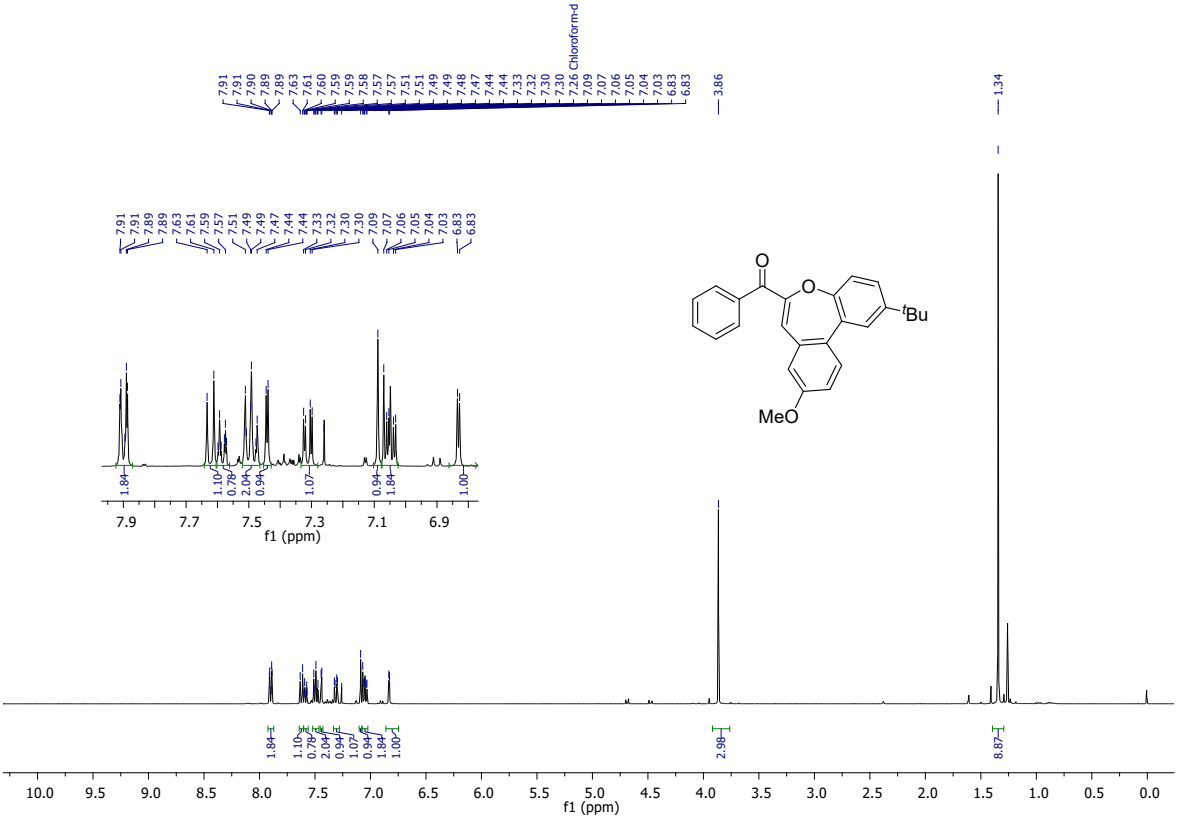
$^{3}C\{1H\}$ NMR (100 MHz) spectrum of **5cd** in $CDCl_3$



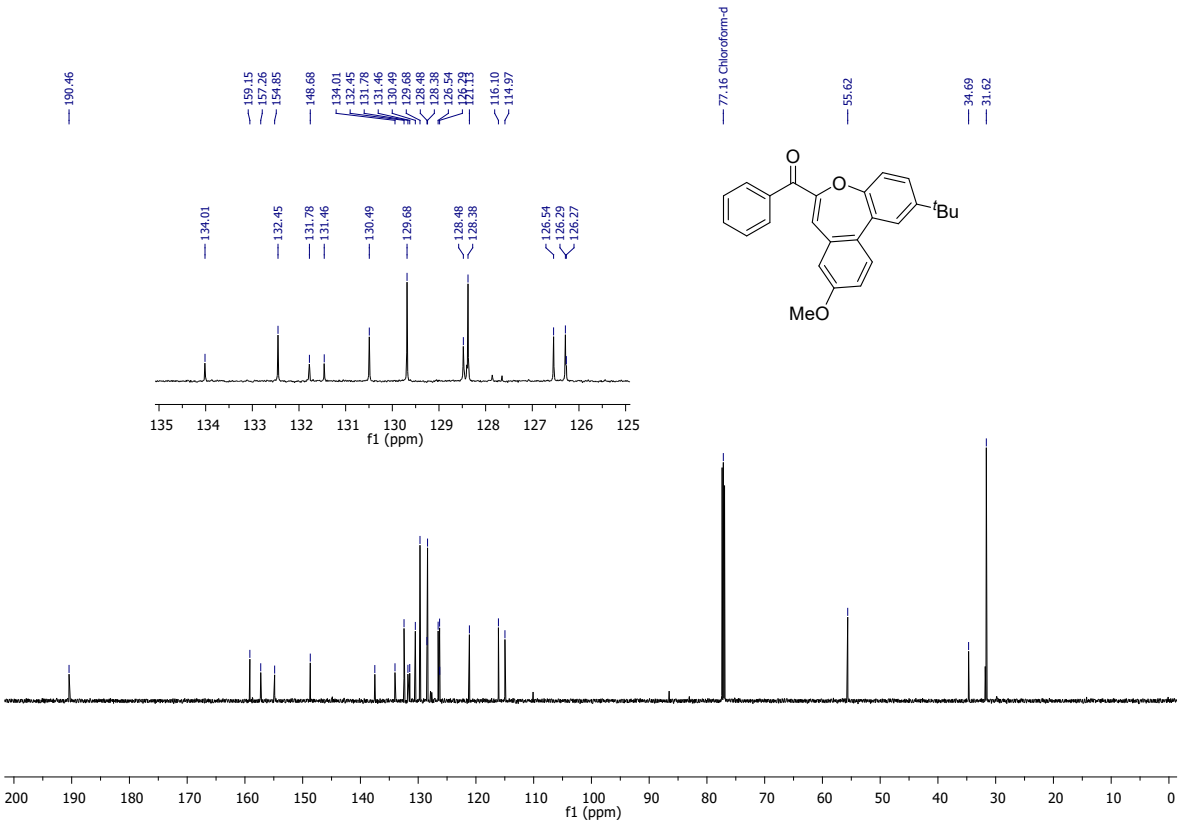
^{1}H NMR (400 MHz) spectrum of **5ld** in $CDCl_3$



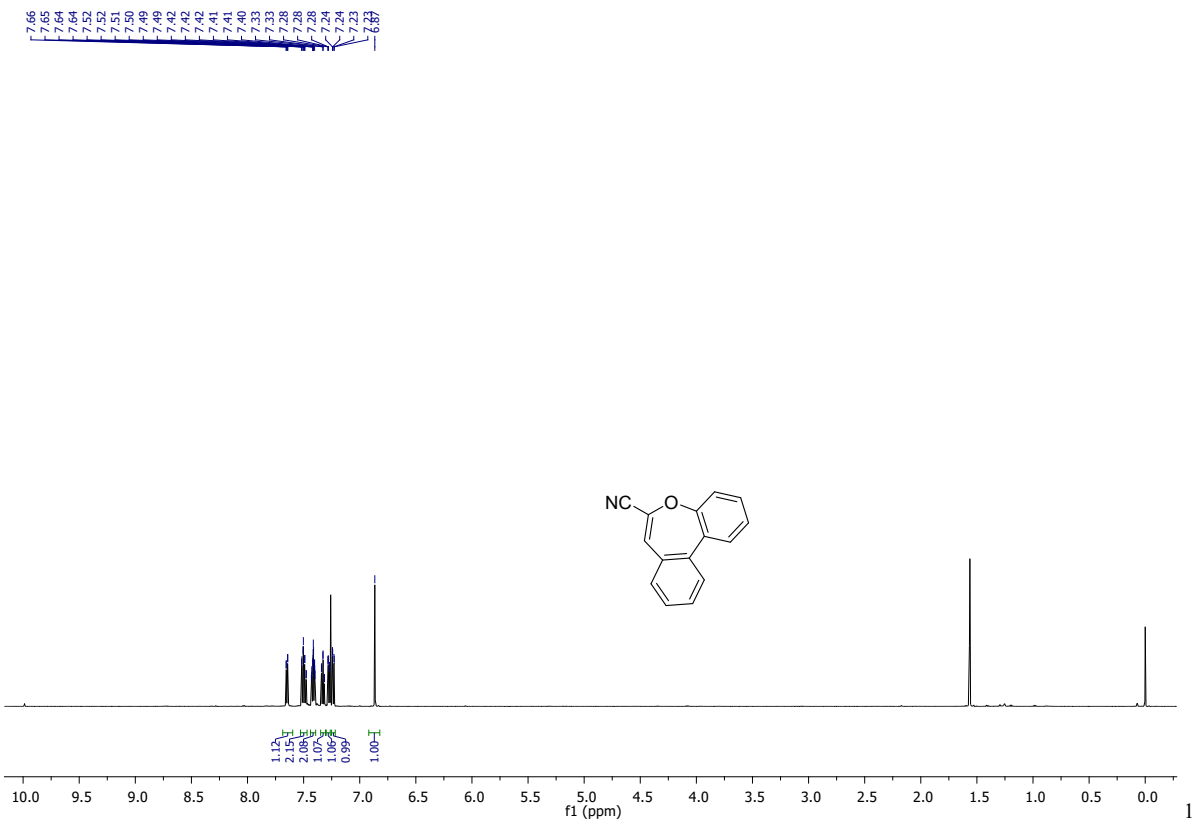
^{3}C{1H} NMR (100 MHz) spectrum of **5ld** in $CDCl_3$



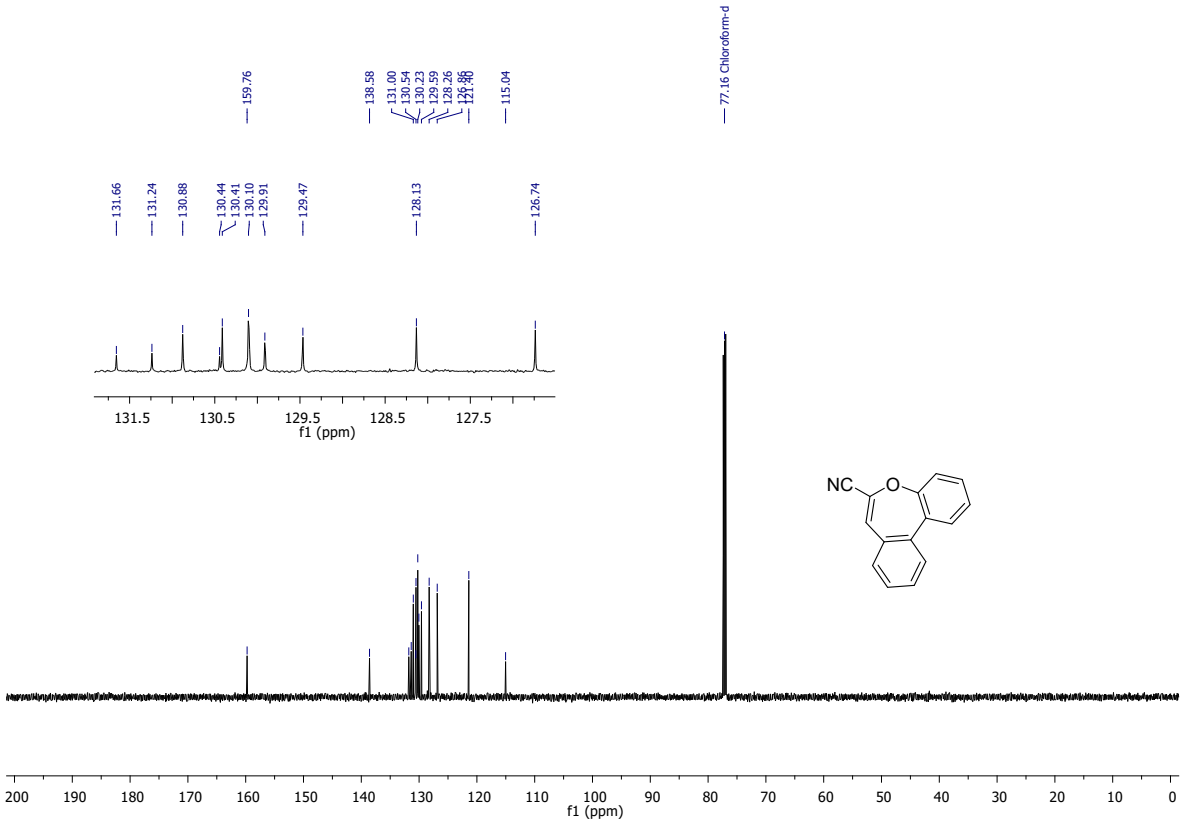
^{1}H NMR (400 MHz) spectrum of **5le** in $CDCl_3$



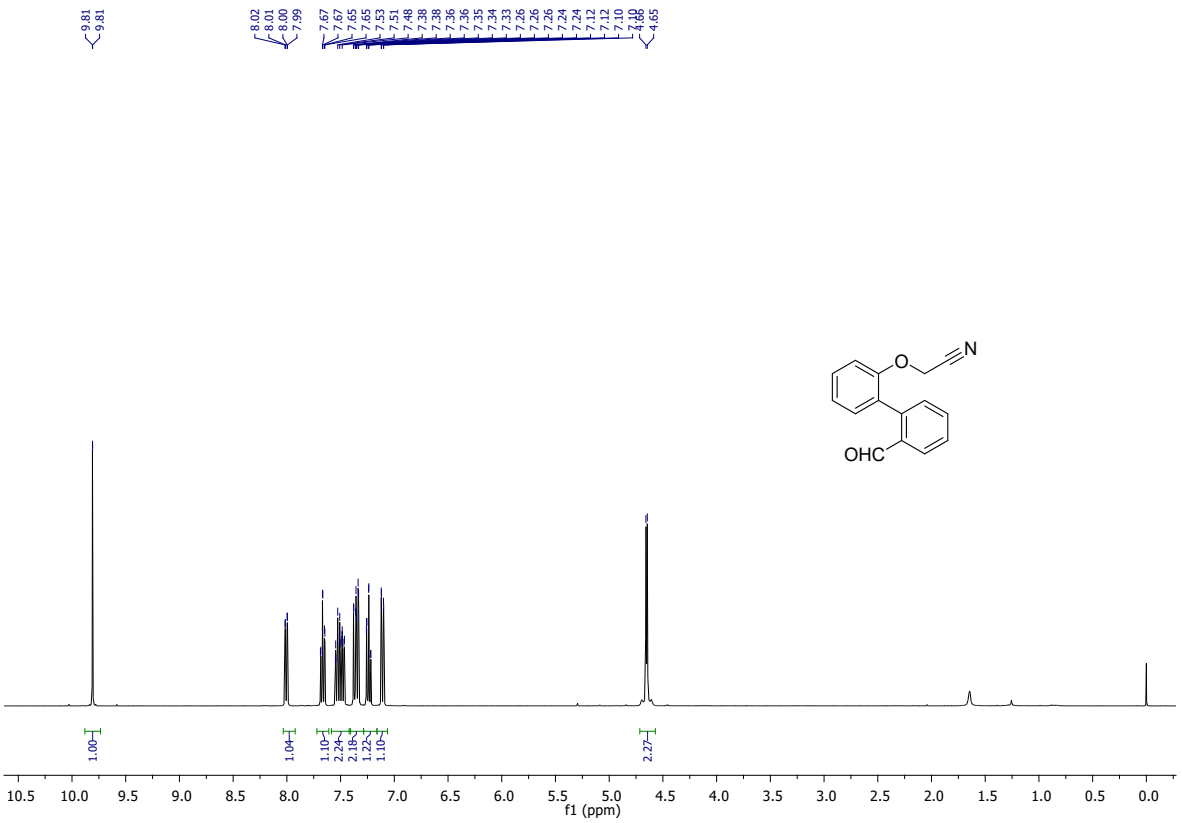
^{13}C{1H} NMR (100 MHz) spectrum of **5le** in $CDCl_3$



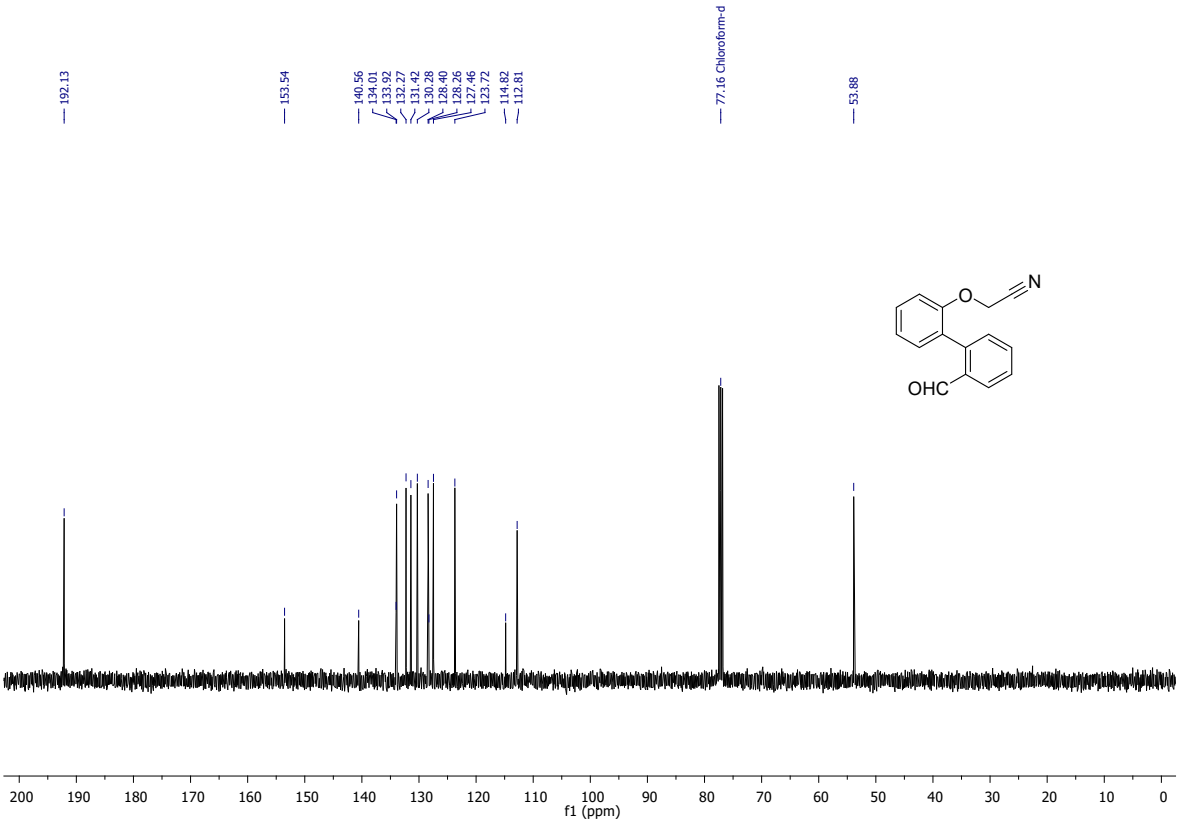
H NMR (400 MHz) spectrum of **5xa** in $CDCl_3$



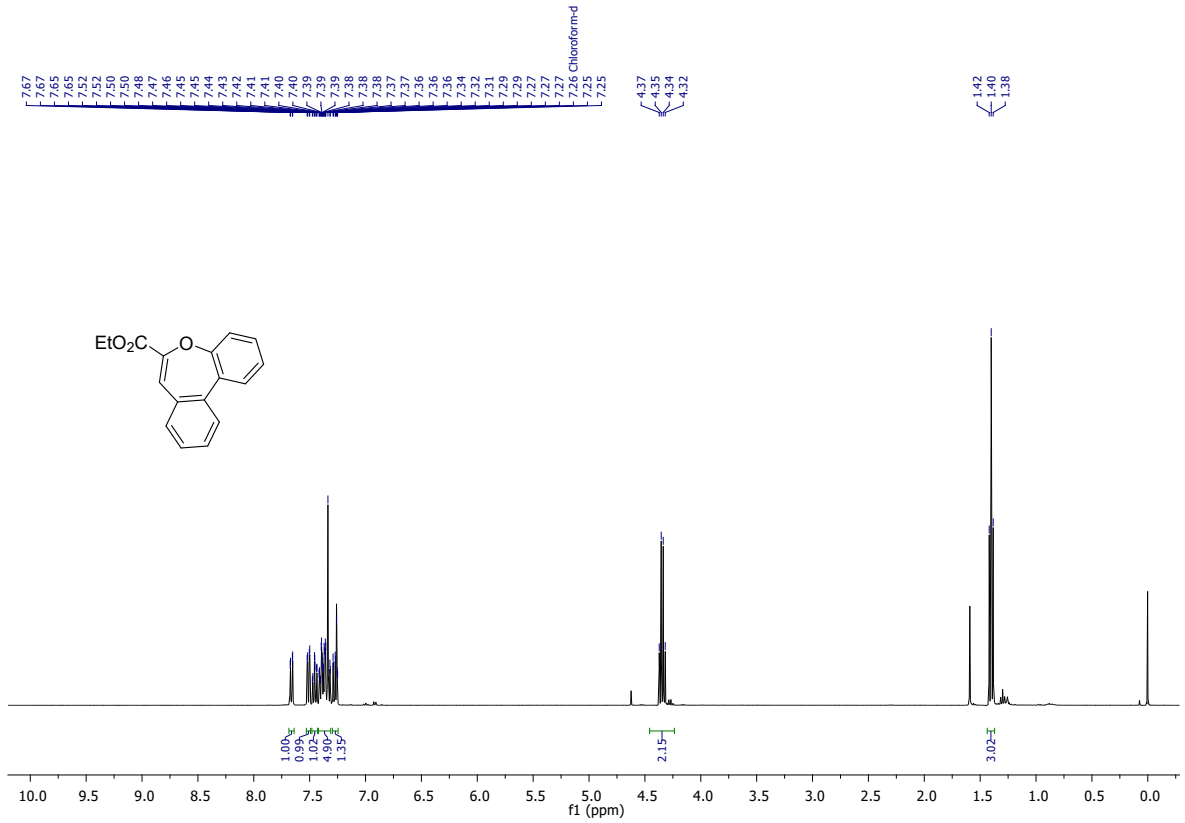
$^{13}C\{1H\}$ NMR (100 MHz) spectrum of **5xa** in $CDCl_3$



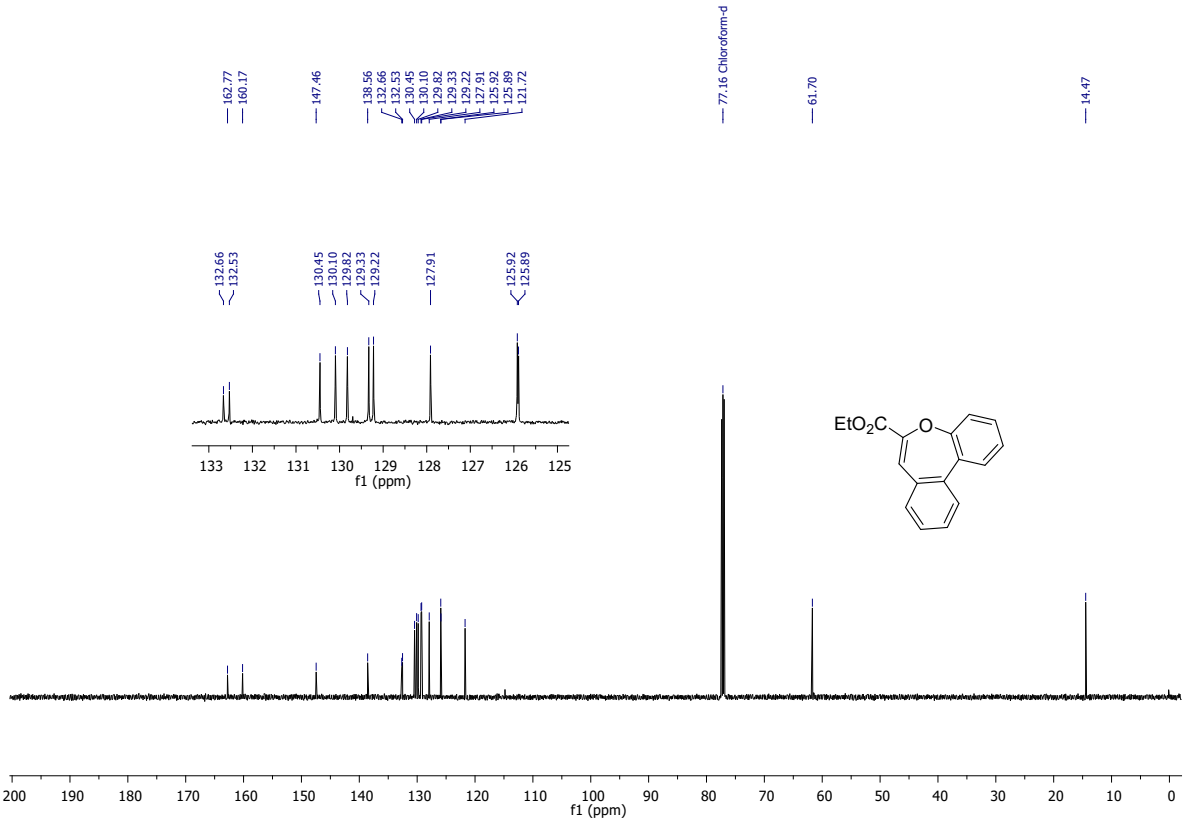
^{1}H NMR (600 MHz) spectrum of **6aa** in $CDCl_3$



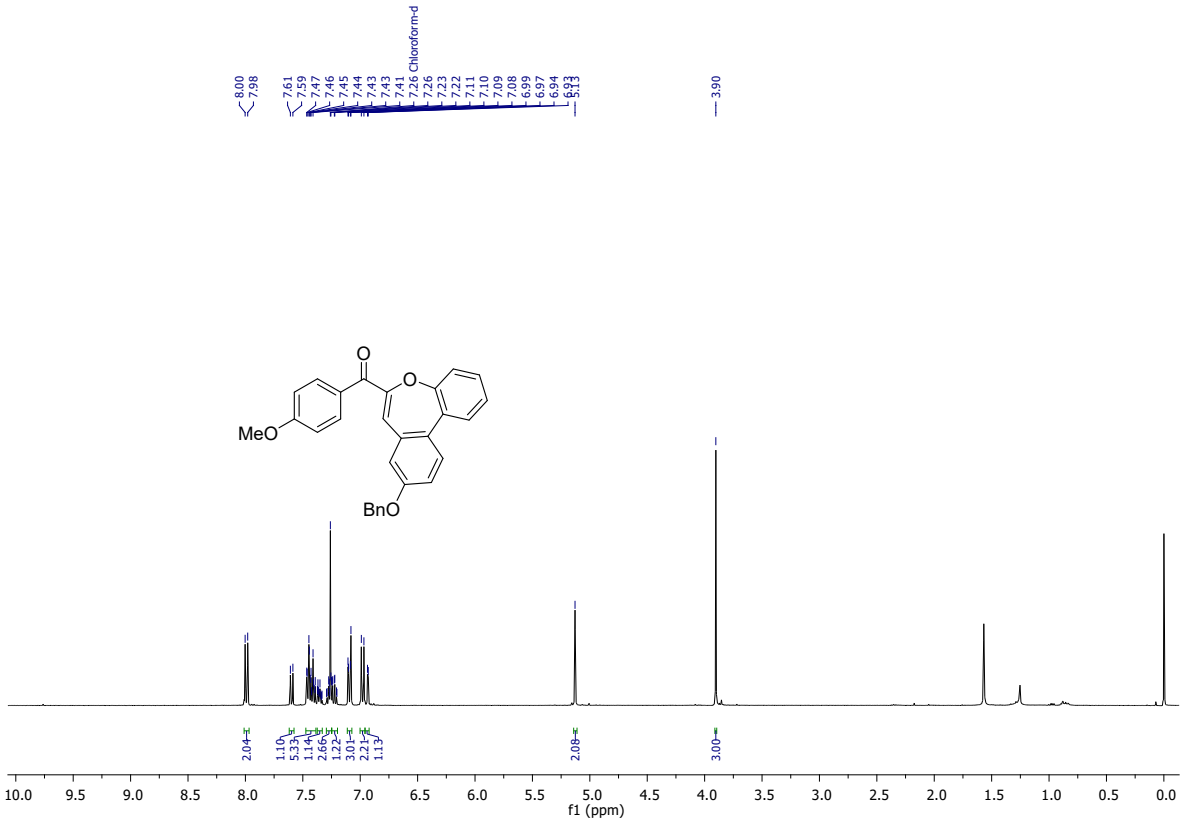
^{13}C{1H} NMR (100 MHz) spectrum of **6aa** in $CDCl_3$



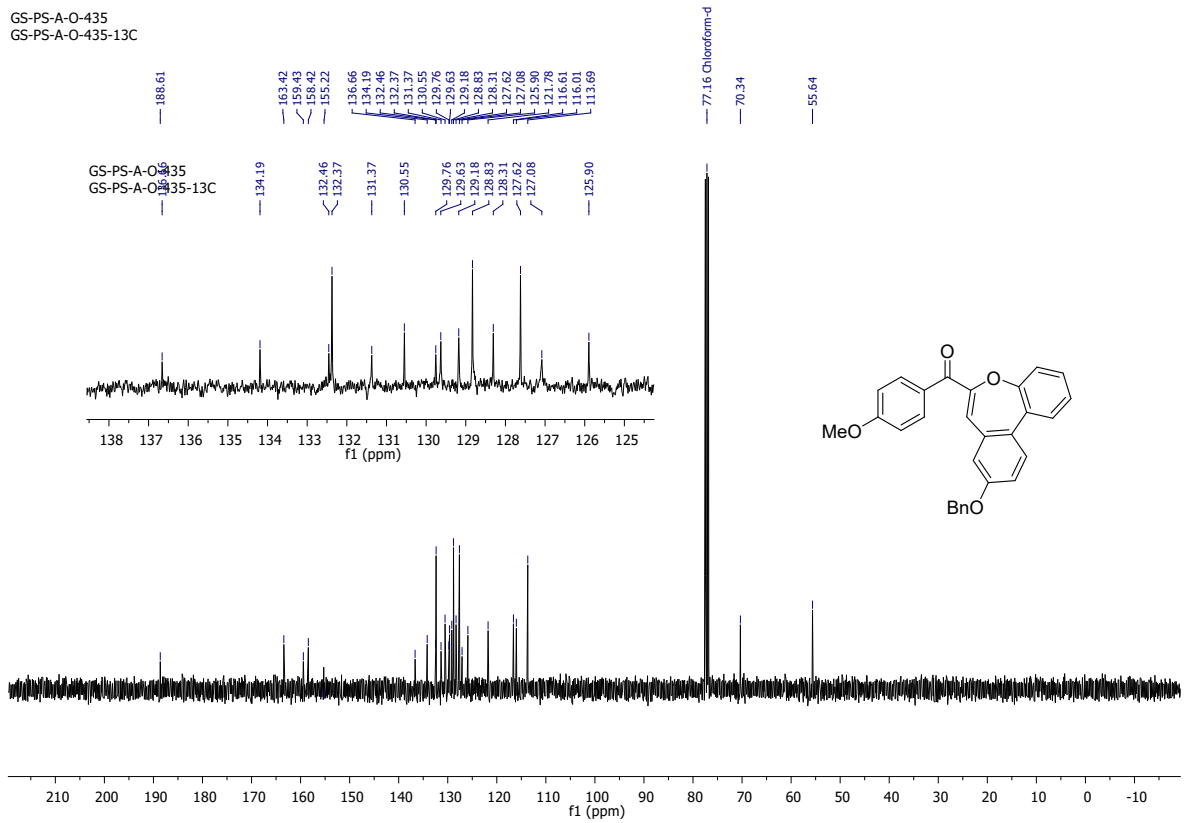
^{1}H NMR (400 MHz) spectrum of **5aa** in $CDCl_3$



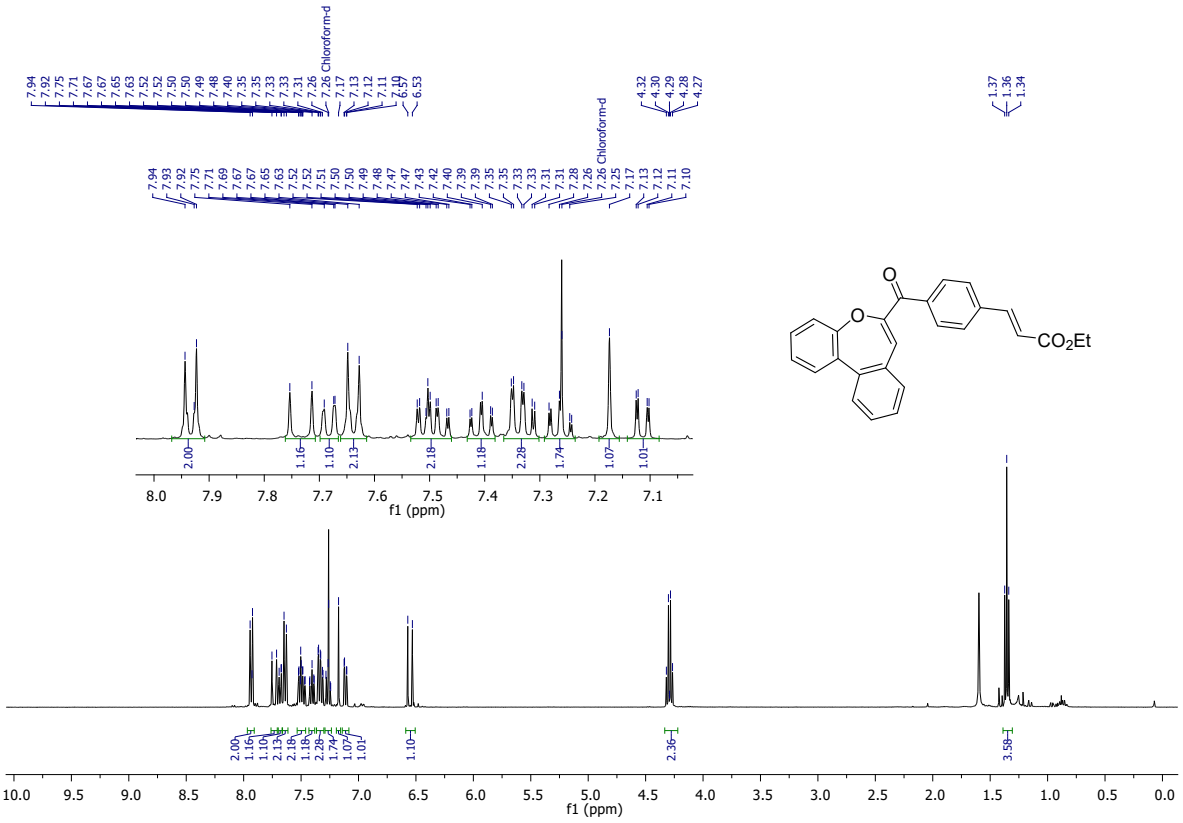
^{13}C{1H} NMR (100 MHz) spectrum of **5ya** in $CDCl_3$



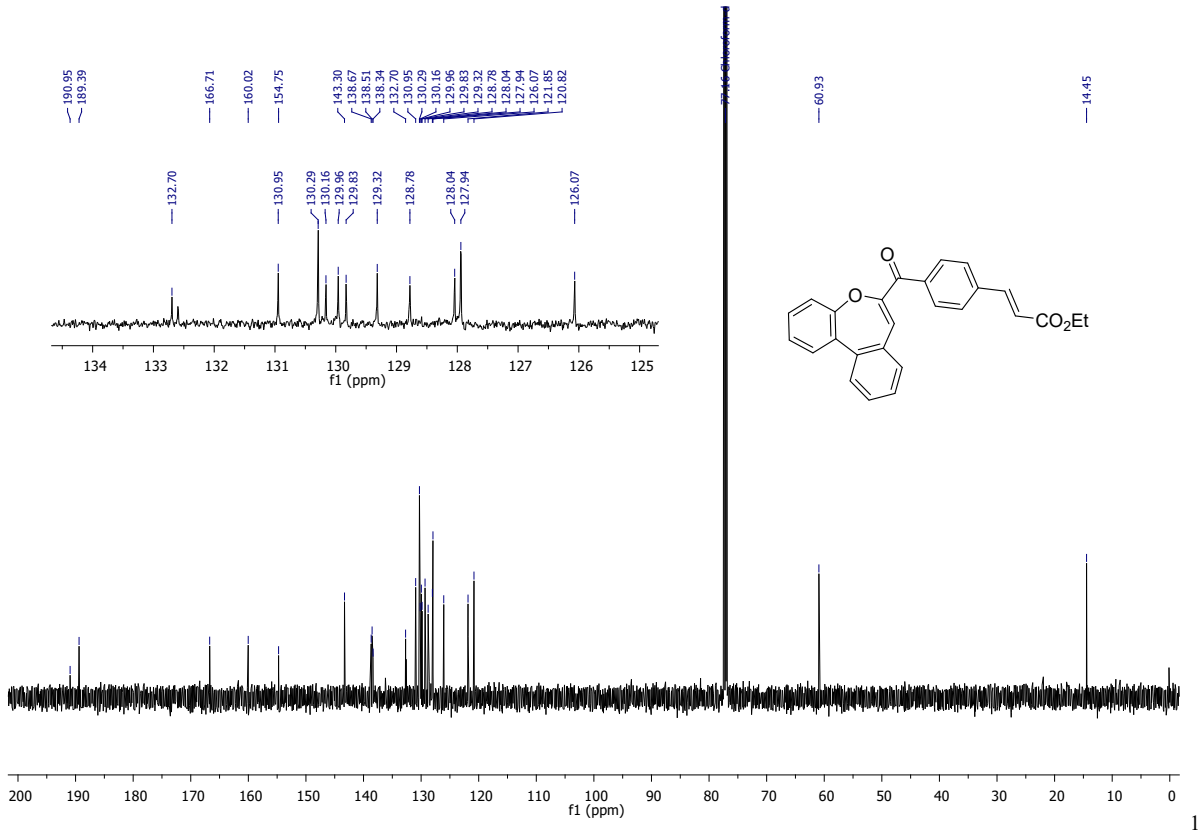
^{1}H NMR (400 MHz) spectrum of **5aa** in $CDCl_3$



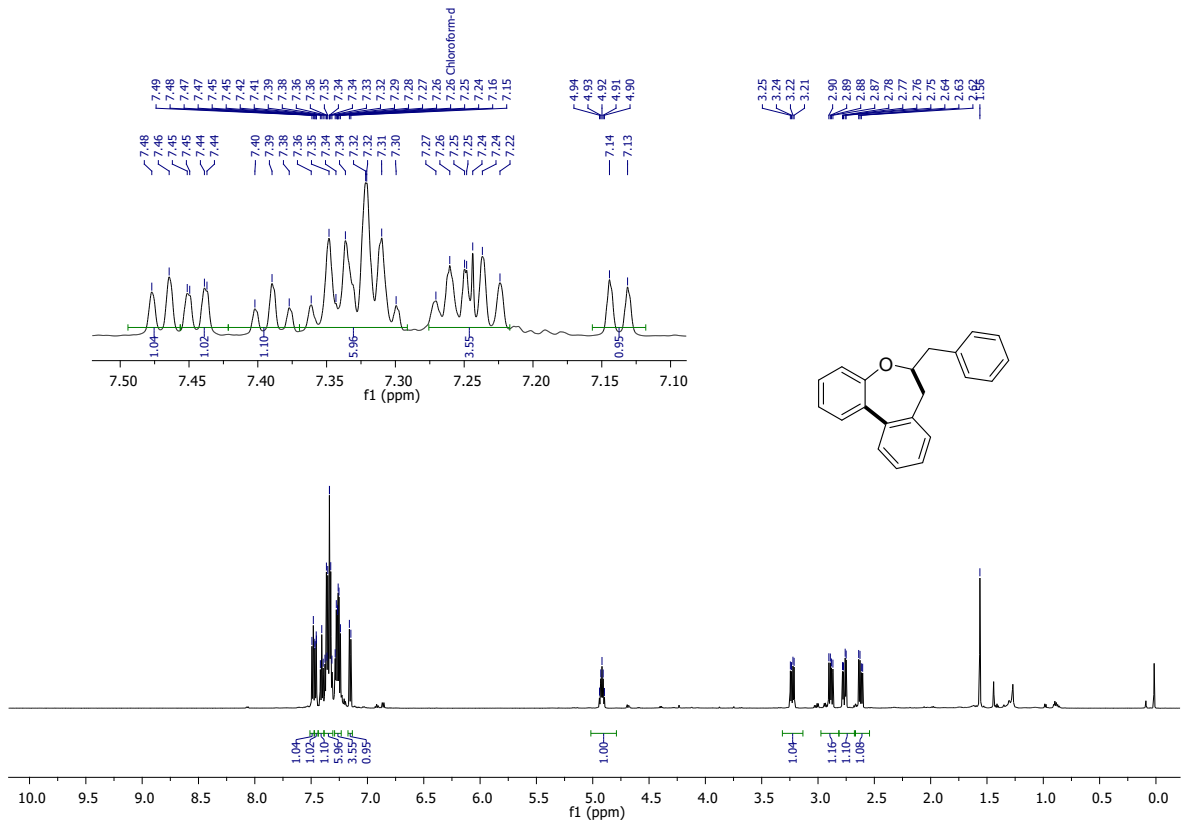
^{13}C{1H} NMR (100 MHz) spectrum of **7ca** in $CDCl_3$



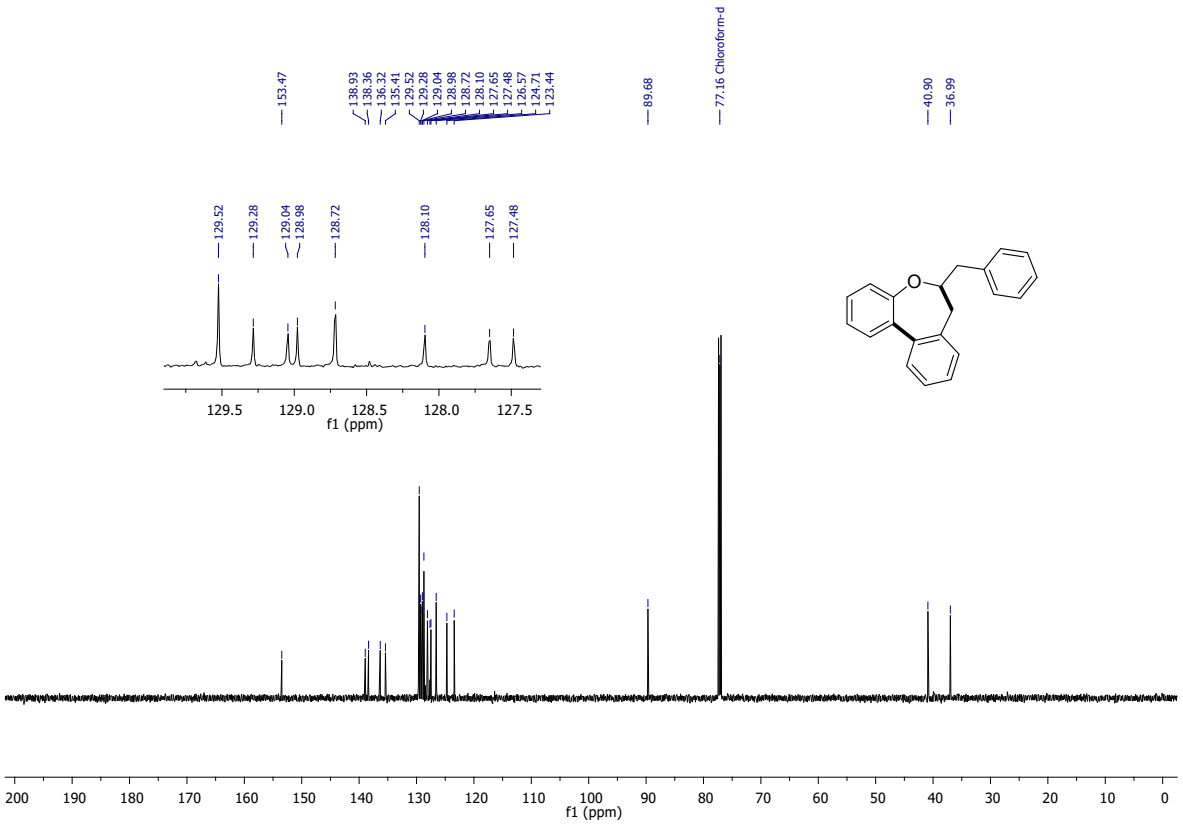
^{1}H NMR (400 MHz) spectrum of **8iaa** in $CDCl_3$



^{3}C{1H} NMR (100 MHz) spectrum of **8iaa** in $CDCl_3$



^{1}H NMR (600 MHz) spectrum of **9aa** in $CDCl_3$



^{13}C{1H} NMR (100 MHz) spectrum of **9aa** in $CDCl_3$

X-ray Diffraction Analysis of Compound:

Crystal of compound **5aa** was obtained by dissolving the product in a mixture of CH_2Cl_2 and hexane in a 3:1 ratio, allowing the solvent to evaporate slowly at room temperature. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC No. 2350807 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk

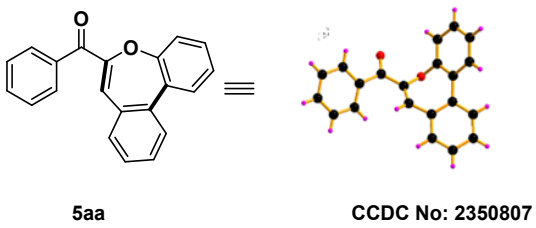


Figure S1. X-ray structure of the product **5aa** with the ellipsoids drawn at the ~~50%~~ probability level

mo_GS_PS_A_O_284_0m

Table 1 Crystal data and structure refinement for mo_GS_PS_A_O_284_0m.

Identification code	mo_GS_PS_A_O_284_0m
Empirical formula	$C_{21}H_{14}O_2$
Formula weight	298.32
Temperature/K	273.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	11.0954(7)
b/Å	15.8197(9)
c/Å	17.3494(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3045.3(3)

Z	8
ρ_{calc}g/cm^3	1.301
μ/mm^{-1}	0.083
F(000)	1248.0
Crystal size/mm^3	0.27 × 0.21 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.062 to 54.276
Index ranges	-14 ≤ h ≤ 12, -19 ≤ k ≤ 20, -22 ≤ l ≤ 16
Reflections collected	27887
Independent reflections	3365 [R_{int} = 0.0682, R_{sigma} = 0.0422]
Data/restraints/parameters	3365/0/208
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0425, wR_2 = 0.0933
Final R indexes [all data]	R_1 = 0.0898, wR_2 = 0.1111
Largest diff. peak/hole / e Å^{-3}	0.12/-0.15