Electronic Supplementary Information

Synthesis of Benzooxepane-Fused Cyclobutene Derivatives via Pd-Catalyzed Cascade Reactions of Haloarenes and Diynylic Ethers

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I. General Experimental Details

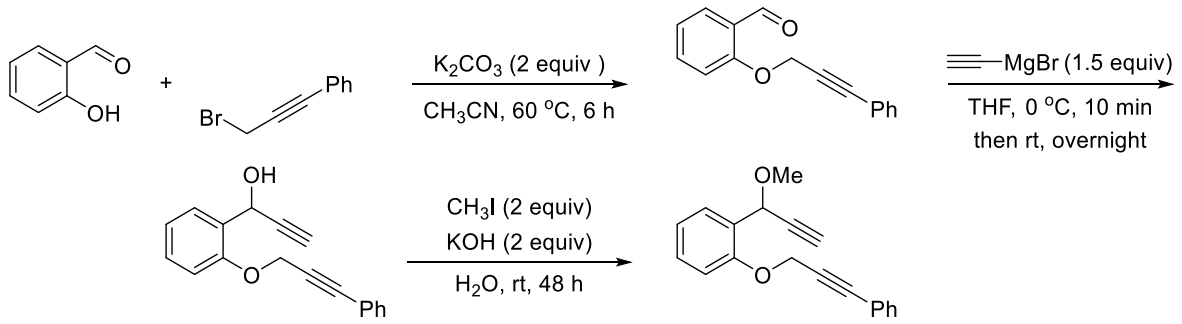
Unless otherwise noted, all reactions were performed in oven-dried glassware under nitrogen atmosphere. Reagents were used as purchased from Tansoole, Innochem, Bidepharm or Leyan unless otherwise noted. Anhydrous dichloromethane and methanol from Energy Chemical were used as purchased. Acetonitrile and triethylamine were distilled over calcium hydride (CaH_2) under nitrogen. Toluene and tetrahydrofuran were dried over sodium-benzophenone. All reactions were isolated from moisture and oxygen by a nitrogen atmosphere with a sealed 25 mL schlenk tube and heated in a heating module (heater + magnetic stirrer). All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using Huang Hai HSGF254 (0.25 mm) precoated plates. The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with silica gel (200–300 mesh). Nuclear magnetic resonance (NMR) spectra were recorded on Bruker BioSpin Avance III HD (400 MHz) spectrometers with tetramethylsilane as an internal standard. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ = 0.00 ppm) or residual peak of $CDCl_3$ (δ = 7.26 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to tetramethylsilane (δ = 0.00 ppm) or $CDCl_3$ (δ = 77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, m = multiplet, brs = broad signal), coupling constant (Hz), and integration. High resolution mass spectra (HRMS) were obtained from Bruker micrOTOF–QII with electrospray ionization (ESI).

II. Synthesis of Starting Materials

All starting materials were prepared according to literature reported procedures

(a) Typical reaction procedure A for the synthesis of 2 [1]



K_2CO_3 (180 mmol, 2.0 equiv) was suspended in acetonitrile (250 mL), followed by addition of Salicylaldehyde (90.0 mmol, 1.0 equiv). The suspension was stirred for 10 min, and then propargyl bromide (108 mmol, 1.2 equiv) was added via a syringe. The reaction mixture was stirred for 6 hours at 60 °C, whereupon a brown mixture was obtained. The crude product was collected by filtration, then purified by silica gel chromatography to give the o-(propargyloxy)-benzaldehyde (17.8 g, 84% yield).

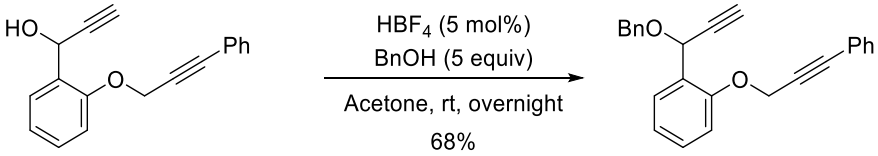
An oven dried round-bottom flask containing a magnetic stir bar was charged with the aldehyde derivative (20 mmol, 1.0 equiv) and dry THF (c = 1 M) and the resulting solution was cooled to 0 °C in an ice bath. Ethynylmagnesium bromide (0.5 M in THF), (30 mmol, 1.5 equiv) was added dropwise and the solution was stirred for 10 minutes before warming to room temperature. After 3 hours, the reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column silica gel chromatography to give the yellow oil (4.26 g, 81% yield).

To propargyl alcohol (15 mmol, 1.0 equiv) was added potassium hydroxide (KOH) (30 mmol, 2.0 equiv) in water (5 mL) and methyl iodide (30 mmol, 2.0 equiv). The two-phase mixture was

stirred rapidly for 48 h . The crude mixture was extracted with Et_2O, The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column silica gel chromatography to give the white solid (2.76 g, 54% yield).

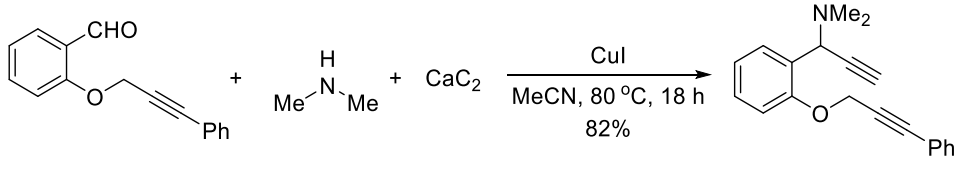
Other substrates **2a-2k, 2m** were synthesized according to the similar procedure above.

(b) Preparation of 1-(1-(benzyloxy)prop-2-yn-1-yl)-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (2l) [2]



To propargylic alcohol (2.5 mmol) in 5 mL of acetone was added benzyl alcohol (12.5 mmol, 5 equiv) and HBF_4 aqueous solution (40% wt.) (20 μL, 5 mol%) and the reaction mixture was stirred at room temperature for 18 hours. The resulting reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography to afford 1-(1-(benzyloxy)prop-2-yn-1-yl)-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (0.59 g, 68% yield).

(c) Preparation of N,N-dimethyl-1-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)prop-2-yn-1-amine (2n) [3]

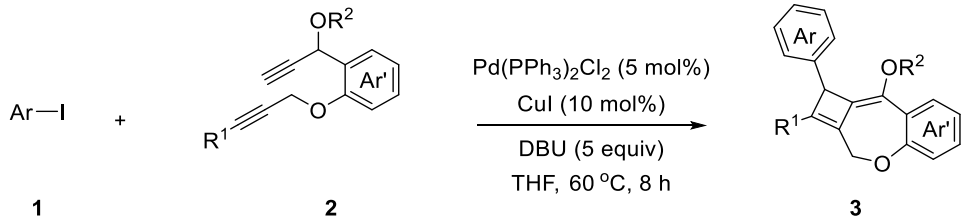


To a three-neck round bottomed flask fitted with reflux condenser and placed under the nitrogen was added the aldehyde (5.0 mmol) followed by addition of acetonitrile (10 mL). To the solution were added amine (6 mmol), calcium carbide (7.5 mmol) and CuI catalyst (0.6 mmol). The reaction mixture was stirred at 80 °C for 18 h. After the completion of the reaction, the mixture was passed

through celite pad and washed with Et_2O. The combined filtrate was concentrated under reduced pressure to obtain liquid which was purified by column chromatography over silica gel to afford N,N-dimethyl-1-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)prop-2-yn-1-amine (1.19 g, 82%).

III. General Procedures

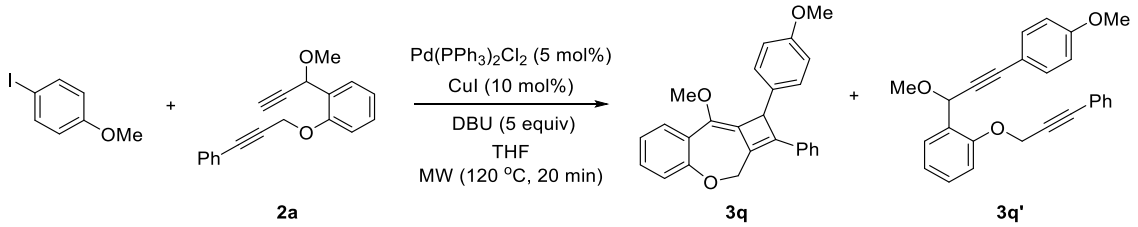
(a) General procedure B for Pd-catalyzed sequential reaction



1 **2** **3**

An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with $Pd(PPh_3)_2Cl_2$ (8.8 mg, 5 mol%), CuI (4.8 mg, 10 mol%) and **1** (0.25 mmol). The Schlenk tube was sealed and then evacuated and backfilled with N_2 (3 cycles). A solution of propargyl ethers **2** (0.30 mmol, 1.2 equiv) in 3 mL of THF, 0.2 mL of DBU (1.25 mmol, 5 equiv) were subsequently injected to the Schlenk tube. The reaction mixture was stirred at 60 °C for 8 hours. After the reaction was complete (monitored by TLC), the solvent was removed in vacuo. The residues were purified by silica gel column chromatography to afford the corresponding product.

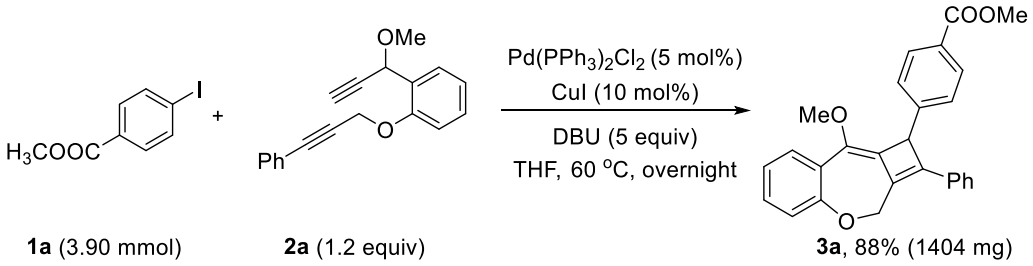
(b) Synthesis of 9-methoxy-1-(4-methoxyphenyl)-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepine (3q)



2a **3q** **3q'**

A solution of 4-Iodoanisole (58.5 mg, 0.25 mmol), propargyl ethers **2a** (82.9 mg, 0.30 mmol, 1.2 equiv), $Pd(PPh_3)_2Cl_2$ (8.8 mg, 5 mol%), CuI (4.8 mg, 10 mol%), DBU (0.2 mL, 1.25 mmol, 5 equiv) and 3 mL of THF under argon was magnetically stirred in a clean, dry microwave reaction tube at the microwave generated temperature in the microwave cavity. The reaction mixture was stirred at 120 °C for 20 minutes. After cooling to room temperature, the solvent was removed in vacuo. The residues were purified by silica gel column chromatography to afford the **3q** (12.5 mg, 13%, pale yellow foam) and **3q'** (81.3 mg, 85%, orange oil).

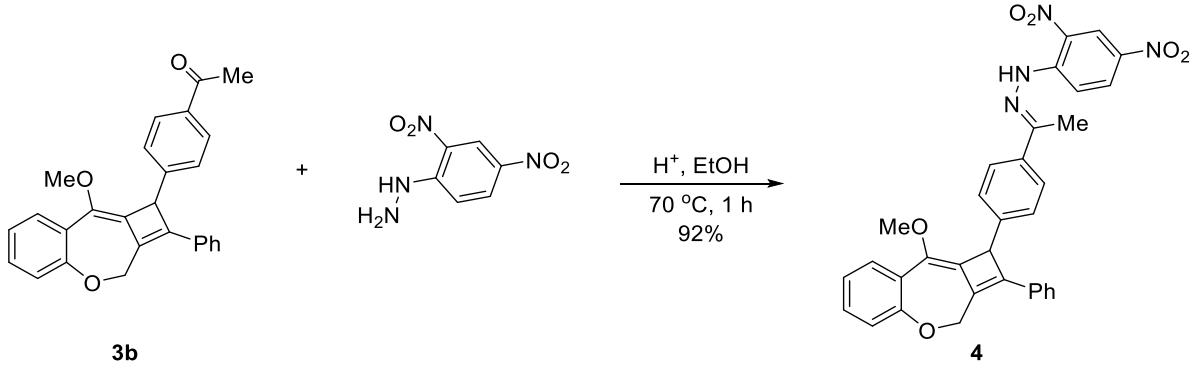
(c) Gram-scale synthesis of 3a



1a (3.90 mmol) **2a** (1.2 equiv) **3a**, 88% (1404 mg)

Following General procedure B, the reaction of $Pd(PPh_3)_2Cl_2$ (140 mg, 0.195 mmol), CuI (74 mg, 0.390 mmol), **1a** (1022 mg, 3.90 mmol), **2a** (1292 mg, 4.68 mmol) and DBU (2970 mg, 19.5 mmol) in THF (47 mL) afforded **3a** (1404 mg, 88%), pale yellow soild.

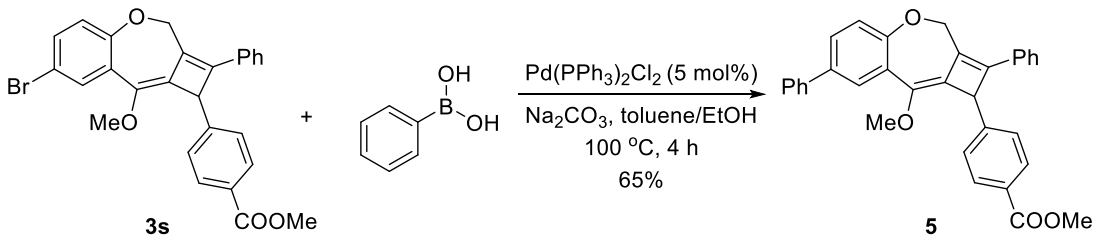
(d) Synthesis of (*E*)-1-(2,4-dinitrophenyl)-2-(1-(4-(9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)phenyl)ethylidene)hydrazine (4)



3b **4**

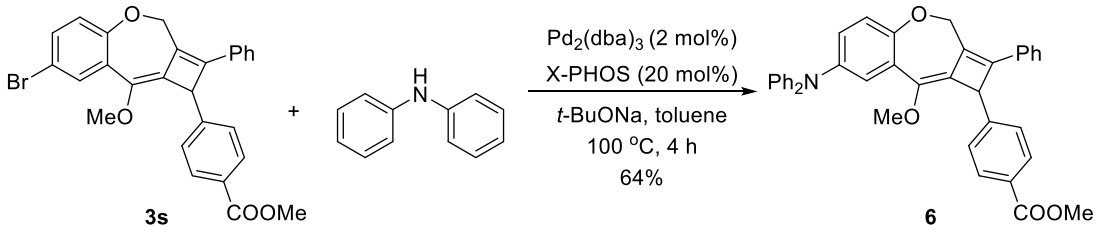
2,4-dinitrophenylhydrazine (92.0 mg, 0.46 mmol) was suspended in 60 mL anhydrous ethanol. Then concentrated sulfuric acid was added until the solution becomes clear, followed by addition of **3b** (173.7 mg, 0.44 mmol) in 60 mL of anhydrous ethanol dropwise. The reaction mixture was stirred at 70 °C for 1 hours, and then cooled to room temperatures, filter and wash the solid with cold water three times, and dry to obtain **4** (232.4 mg, 92%), red solid.

(e) Synthesis of methyl 4-(9-methoxy-2,7-diphenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (5)



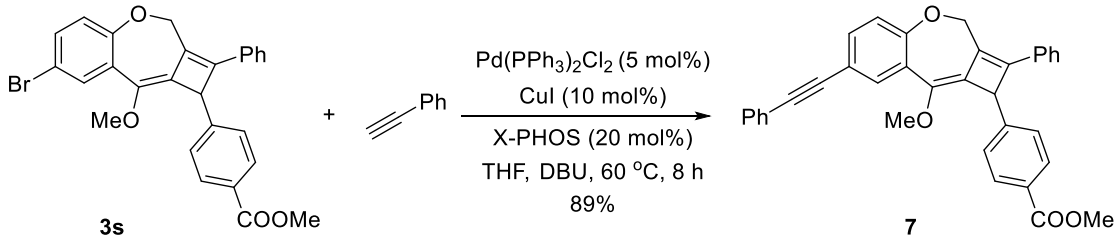
To an oven-dried Schlenk tube containing a Teflon-coated stir bar were added phenylboronic acid (13.4 mg, 0.11 mmol), toluene (2 mL), EtOH (1 mL), Na_2CO_3 (saturated aqueous solution) (0.5 mL), **3s** (48.9 mg, 0.1 mmol) and $Pd(PPh_3)_2Cl_2$ (3.6 mg, 0.005 mmol) under N_2. The reaction mixture was stirred at 100 °C for 4 hours, and then cooled to room temperatures. The reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with EtOAc. The combined extracts were washed with brine, and dried over Na_2SO_4. Then the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel column chromatography to afford **5** (33.3 mg, 65%), yellow foam.

(f) Synthesis of methyl 4-(7-(diphenylamino)-9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (6)



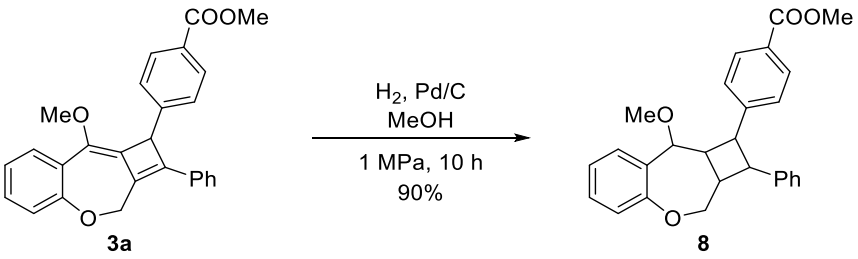
An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with $Pd_2(dba)_3$ (1.9 mg, 0.002 mmol), X-PHOS (9.5 mg, 0.02 mmol), Diphenylamine (25.4 mg, 0.15 mmol), **3s** (48.9 mg, 0.1 mmol) and *t*-BuONa (10.6 mg, 0.11 mmol). The Schlenk tube was sealed and then evacuated and backfilled with N_2 (3 cycles). 2 mL toluene was injected. Then the reaction mixture was stirred at 100 °C for 4 hours. After the reaction was complete (monitored by TLC), the solvent was removed in vacuo. The residues were purified by silica gel column chromatography to afford the **6** (36.8 mg, 64%), yellow foam.

(g) Synthesis of methyl 4-(9-methoxy-2-phenyl-7-(phenylethynyl)-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (7)



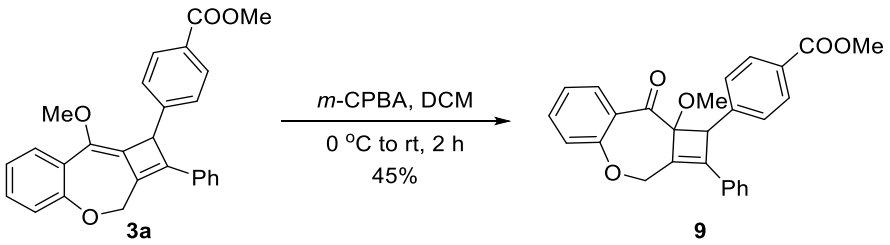
An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with $Pd(PPh_3)_2Cl_2$ (3.6 mg, 0.005 mmol), CuI (1.9 mg, 0.01 mmol), X-PHOS (9.5 mg, 0.02 mmol) and **3s** (48.9 mg, 0.1 mmol). The Schlenk tube was sealed and then evacuated and backfilled with N_2 (3 cycles). A solution of Phenylacetylene (22 uL, 0.2 mmol) in 2 mL of THF, 0.1 mL of DBU were subsequently injected to the Schlenk tube. The reaction mixture was stirred at 60 °C for 8 hours. After the reaction was complete (monitored by TLC), the solvent was removed in vacuo. The residues were purified by silica gel column chromatography to afford the **7** (45.5 mg, 89%), yellow foam.

(h) Synthesis of methyl 4-(9-methoxy-2-phenyl-1,2,2a,3,9,9a-hexahydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (8)



The product **3a** was dissolved in MeOH and then Pd/C (5 mol% Pd) was added under H_2 (1 Mpa) atmosphere. The mixture was stirred at room temperature for 10 hours and then filtered to remove Pd/C. The residue was concentrated under reduced pressure and then purified by rapid column chromatography to afford **8** (174.0 mg, 90%), white foam.

(i) Synthesis of methyl 4-(9a-methoxy-9-oxo-2-phenyl-1,3,9,9a-tetrahydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (9)

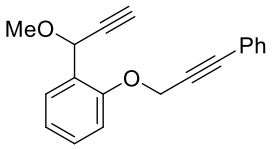


An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with **3a** (102.5 mg, 0.25 mmol). After the Schlenk tube was sealed and then evacuated and backfilled with N_2 (3 cycles), 2 mL DCM was injected. Then, *m*-CPBA (103.5 mg, 0.6 mmol) was dissolved in 2 mL of DCM was added at 0 ^{o}C. and the reaction mixture was stirred at rt for 2 hours. Upon the reaction completed, the mixture was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography to afford the methyl 4-(9a-methoxy-9-oxo-2-phenyl-1,3,9,9a-tetrahydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate **9** (47.9 mg, 45%), pale pink soild.

IV. Analytical data of New Compounds

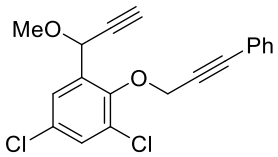
Substrates Characterization

1-(1-methoxyprop-2-yn-1-yl)-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (2a)



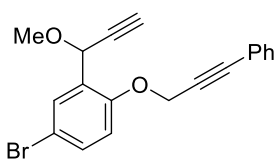
The title compound was obtained in 54% (2.76 g) yield according to procedure A, white solid, R_f = 0.33 (silica gel, petroleum ether:EtOAc 10:1); Mp 50.0–50.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 7.6 Hz, 1 H), 7.47–7.38 (m, 2 H), 7.36–7.24 (m, 4 H), 7.11 (d, *J* = 8.3 Hz, 1 H), 7.08–7.01 (m, 1 H), 5.53 (s, 1 H), 4.97 (t, *J* = 16.2 Hz, 2 H), 3.50–3.44 (m, 3 H), 2.60–2.54 (m, 1 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 155.0, 131.8, 129.8, 128.7, 128.6, 128.3, 127.2, 122.2, 121.7, 112.8, 87.2, 83.9, 81.7, 74.7, 66.7, 57.4, 56.4 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{19}H_{16}O_2Na^+$ 299.1043, found 299.1045.

1,5-dichloro-3-(1-methoxyprop-2-yn-1-yl)-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (2b)



The title compound was obtained in 57% (1.94 g) yield according to procedure A, white solid, R_f = 0.4 (silica gel, petroleum ether:EtOAc 7.5:1); Mp 67.5–68.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 2.6 Hz, 1 H), 7.46–7.38 (m, 3 H), 7.37–7.28 (m, 3 H), 5.58 (d, *J* = 2.1 Hz, 1 H), 5.03 (d, *J* = 15.4 Hz, 1 H), 4.97 (d, *J* = 15.3 Hz, 1 H), 3.46 (s, 3 H), 2.59 (d, *J* = 2.1 Hz, 1 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 150.3, 135.7, 131.8, 130.46, 130.45, 128.80, 128.77, 128.3, 127.3, 122.0, 88.2, 83.3, 80.6, 76.0, 67.3, 62.1, 56.7 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{19}H_{14}Cl_2O_2Na^+$ 367.0263, found 367.0267.

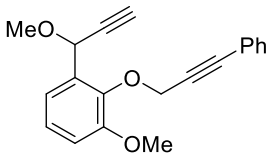
4-bromo-2-(1-methoxyprop-2-yn-1-yl)-1-((3-phenylprop-2-yn-1-yl)oxy)benzene (2c)



The title compound was obtained in 80% (1.41 g) yield according to procedure A, white solid, R_f = 0.47 (silica gel, petroleum ether:EtOAc 10:1);

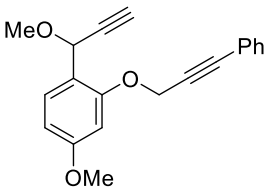
Mp 55.9–57.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 2.5 Hz, 1 H), 7.45–7.38 (m, 3 H), 7.35–7.24 (m, 3 H), 6.99 (d, *J* = 8.8 Hz, 1 H), 5.44 (d, *J* = 2.2 Hz, 1 H), 4.94 (s, 2 H), 3.47 (s, 3 H), 2.59 (d, *J* = 2.2 Hz, 1 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 153.9, 132.3, 131.7, 131.3, 129.5, 128.8, 128.3, 122.0, 114.6, 114.1, 87.7, 83.2, 81.0, 75.1, 66.3, 57.5, 56.5 ppm; **HRMS** (*m/z*): [M + Na]$^+$ calcd for $C_{19}H_{15}BrO_2Na^+$ 377.0148, found 377.0145.

1-methoxy-3-(1-methoxyprop-2-yn-1-yl)-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (2d)



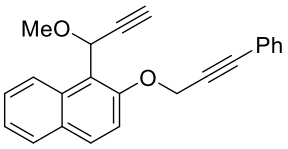
The title compound was obtained in 57% (1.94 g) yield according to procedure A, pale yellow oil, R_f = 0.4 (silica gel, petroleum ether:EtOAc 7.5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.46–7.38 (m, 2 H), 7.36–7.26 (m, 4 H), 7.19–7.09 (m, 1 H), 6.92 (dd, *J* = 8.2, 1.5 Hz, 1 H), 5.65 (d, *J* = 2.2 Hz, 1 H), 5.01 (d, *J* = 15.4 Hz, 1 H), 4.95 (d, *J* = 15.4 Hz, 1 H), 3.87 (s, 3 H), 3.45 (s, 3 H), 2.53 (d, *J* = 2.3 Hz, 1 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 152.4, 144.4, 133.0, 131.8, 128.4, 128.2, 124.9, 122.5, 119.8, 112.6, 87.2, 84.7, 81.9, 74.8, 67.3, 61.2, 56.5, 55.9 ppm; **HRMS** (*m/z*): [M + Na]$^+$ calcd for $C_{20}H_{18}O_3Na^+$ 329.1148, found 329.1147.

4-methoxy-1-(1-methoxyprop-2-yn-1-yl)-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (2e)



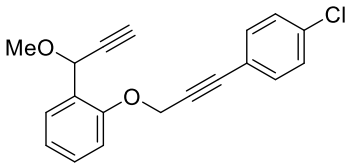
The title compound was obtained in 28% (0.651 g) yield according to procedure A, pale yellow oil, R_f = 0.56 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 8.5 Hz, 1 H), 7.50–7.39 (m, 2 H), 7.38–7.27 (m, 3 H), 6.68 (d, *J* = 2.4 Hz, 1 H), 6.58 (dd, *J* = 8.6, 2.4 Hz, 1 H), 5.47 (d, *J* = 2.2 Hz, 1 H), 5.01–4.87 (m, 2 H), 3.81 (s, 3 H), 3.44 (s, 3 H), 2.58 (d, *J* = 2.2 Hz, 1 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 161.0, 156.1, 131.8, 129.6, 128.7, 128.3, 122.2, 119.7, 105.8, 100.2, 87.4, 83.7, 81.9, 74.5, 66.5, 57.4, 56.1, 55.4 ppm; **HRMS** (*m/z*): [M + Na]$^+$ calcd for $C_{20}H_{18}O_3Na^+$ 329.1148, found 329.1147.

1-(1-methoxyprop-2-yn-1-yl)-2-((3-phenylprop-2-yn-1-yl)oxy)naphthalene (2f)



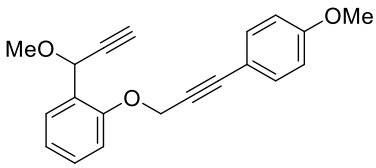
The title compound was obtained in 32% (1.03 g) yield according to procedure A, white solid, R_f = 0.36 (silica gel, petroleum ether:EtOAc 10:1); Mp 72.1–72.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 8.6 Hz, 1 H), 7.82 (d, *J* = 9.0 Hz, 1 H), 7.77 (d, *J* = 8.1 Hz, 1 H), 7.56–7.46 (m, 1 H), 7.44–7.34 (m, 4 H), 7.34–7.18 (m, 3 H), 6.17 (d, *J* = 2.4 Hz, 1 H), 5.04 (s, 2 H), 3.46 (s, 3 H), 2.55 (d, *J* = 2.4 Hz, 1 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 152.7, 131.9, 131.8, 130.9, 130.3, 128.7, 128.3, 126.4, 125.8, 124.3, 122.1, 120.4, 115.1, 87.5, 83.9, 82.4, 75.0, 65.1, 58.8, 56.7 ppm; **HRMS** (*m/z*): [M + Na]$^+$ calcd for $C_{23}H_{18}O_2Na^+$ 349.1199, found 349.1198.

1-((3-(4-chlorophenyl)prop-2-yn-1-yl)oxy)-2-(1-methoxyprop-2-yn-1-yl)benzene (2g)



The title compound was obtained in 58% (1.82 g) yield according to procedure A, pale yellow oil, R_f = 0.47 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 7.6, 1.7 Hz, 1 H), 7.37–7.24 (m, 5 H), 7.11–7.03 (m, 2 H), 5.53 (d, *J* = 2.2 Hz, 1 H), 4.95 (s, 2 H), 3.47 (s, 3 H), 2.58 (d, *J* = 2.2 Hz, 1 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 154.9, 134.8, 133.0, 129.8, 128.64, 128.62, 127.2, 121.8, 120.7, 112.8, 86.1, 84.9, 81.6, 74.7, 66.7, 57.3, 56.4 ppm; **HRMS** (*m/z*): [M + Na]$^+$ calcd for $C_{19}H_{15}ClO_2Na^+$ 333.0653, found 333.0651.

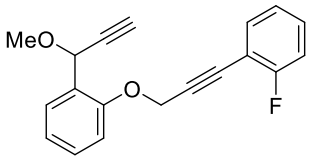
1-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)-2-(1-methoxyprop-2-yn-1-yl)benzene (2h)



The title compound was obtained in 55% (2.14 g) yield according to procedure A, white solid, R_f = 0.44 (silica gel, petroleum ether:EtOAc 5:1); Mp 48.1–49.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.71–7.65 (m, 1 H), 7.39–7.30 (m, 3 H), 7.13–7.02 (m, 2 H), 6.82 (d, *J* = 8.8 Hz, 2 H), 5.54 (d, *J* = 2.0 Hz, 1 H), 4.95 (s, 2 H), 3.79 (s, 3 H), 3.47 (s, 3 H), 2.57 (d, *J* = 2.2 Hz, 1 H) ppm; **^{13}C NMR**

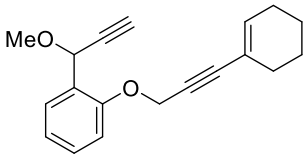
(100 MHz, $CDCl_3$): δ = 159.9, 155.0, 133.3, 129.7, 128.5, 127.2, 121.6, 114.3, 113.9, 112.9, 87.2, 82.5, 81.8, 74.6, 66.7, 57.5, 56.4, 55.3 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{20}H_{18}O_3Na^+$ 329.1148, found 329.1148.

1-fluoro-2-(3-(2-(1-methoxyprop-2-yn-1-yl)phenoxy)prop-1-yn-1-yl)benzene (2i)



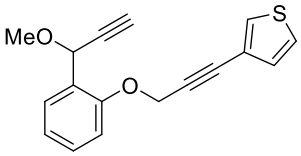
The title compound was obtained in 52% (1.51 g) yield according to procedure A, colorless oil, R_f = 0.46 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 7.7, 1.7 Hz, 1 H), 7.43–7.38 (m, 1 H), 7.36–7.26 (m, 2 H), 7.14–7.02 (m, 4 H), 5.53 (d, *J* = 2.2 Hz, 1 H), 5.05–4.94 (m, 2 H), 3.47 (s, 3 H), 2.58 (dd, *J* = 2.1, 0.6 Hz, 1 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 162.9 (d, *J* = 250.6 Hz), 154.9, 133.7 (d, *J* = 1.0 Hz), 130.5 (d, *J* = 8.0 Hz), 129.8, 128.6, 127.2, 123.9 (d, *J* = 3.7 Hz), 121.7, 115.5 (d, *J* = 20.6 Hz), 112.9, 110.8 (d, *J* = 15.5 Hz), 89.1 (d, *J* = 3.3 Hz), 81.7, 80.7, 74.7, 66.8, 57.3, 56.4 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -109.72–-109.89 (m, 1 F) ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{19}H_{15}FO_2Na^+$ 317.0948, found 317.0951.

1-((3-(cyclohex-1-en-1-yl)prop-2-yn-1-yl)oxy)-2-(1-methoxyprop-2-yn-1-yl)benzene (2j)



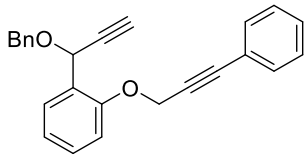
The title compound was obtained in 60% (1.82 g) yield according to procedure A, yellow oil, R_f = 0.60 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.69–7.62 (m, 1 H), 7.35–7.26 (m, *J* = 8.1, 1 H), 7.07–6.98 (m, 2 H), 6.15–6.08 (m, 1 H), 5.50 (d, *J* = 2.2 Hz, 1 H), 4.85 (s, 2 H), 3.46 (s, 3 H), 2.56 (d, *J* = 2.2 Hz, 1 H), 2.13–2.03 (m, 4 H), 1.67–1.51 (m, 4 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 155.0, 136.0, 129.7, 128.5, 127.2, 121.5, 119.9, 112.8, 89.2, 81.8, 81.1, 74.5, 66.7, 57.5, 56.4, 28.9, 25.6, 22.2, 21.4 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{19}H_{20}O_2Na^+$ 303.1356, found 303.1355.

3-(3-(2-(1-methoxyprop-2-yn-1-yl)phenoxy)prop-1-yn-1-yl)thiophene (2k)



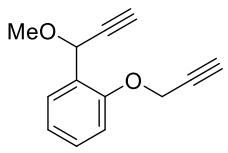
The title compound was obtained in 63% (2.15 g) yield according to procedure A, pale yellow oil, R_f = 0.37 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.5 Hz, 1 H), 7.45 (d, *J* = 3.0 Hz, 1 H), 7.32 (t, *J* = 7.8 Hz, 1 H), 7.26–7.22 (m, 1 H), 7.12–7.00 (m, 3 H), 5.53 (s, 1 H), 4.94 (s, 2 H), 3.47 (s, 3 H), 2.57 (d, *J* = 1.0 Hz, 1 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 155.0, 129.8, 129.7, 129.5, 128.6, 127.3, 125.4, 121.7, 121.3, 112.8, 83.5, 82.4, 81.7, 74.6, 66.7, 57.4, 56.4 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{17}H_{14}O_2SNa^+$ 305.0607, found 305.0609.

1-(1-(benzyloxy)prop-2-yn-1-yl)-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (2l)



The title compound was obtained in 68% (0.594 g) yield, colorless oil, R_f = 0.44 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 7.6 Hz, 1 H), 7.45–7.37 (m, 4 H), 7.35–7.21 (m, 7 H), 7.12–7.01 (m, 2 H), 5.67 (s, 1 H), 4.90 (s, 2 H), 4.77 (d, *J* = 11.5 Hz, 1 H), 4.65 (d, *J* = 11.6 Hz, 1 H), 2.59 (dd, *J* = 2.2, 0.9 Hz, 1 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 155.0, 137.7, 131.7, 129.7, 128.8, 128.7, 128.3, 128.24, 128.20, 127.6, 127.4, 122.2, 121.7, 112.7, 87.2, 83.9, 81.9, 74.7, 70.6, 64.6, 57.2 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{25}H_{20}O_2Na^+$ 375.1356, found 375.1355.

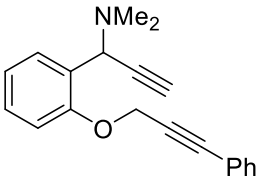
1-(1-methoxyprop-2-yn-1-yl)-2-(prop-2-yn-1-yloxy)benzene (2m)



The title compound was obtained in 57% (1.77 g) yield according to procedure A, pale yellow oil, R_f = 0.44 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.6 Hz, 1 H), 7.39–7.29 (m, 1 H), 7.15–6.98 (m, 2 H), 5.48 (d, *J* = 2.0 Hz, 1 H), 4.75 (d, *J* = 2.4 Hz, 2 H), 3.46 (s, 3 H), 2.58 (dd, *J* = 2.2, 1.0 Hz, 1 H), 2.51 (td, *J* =

2.4, 0.9 Hz, 1 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 154.7, 129.7, 128.6, 127.2, 121.8, 112.6, 81.6, 78.5, 75.7, 74.7, 66.7, 56.43, 56.38 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{13}H_{12}O_2Na^+$ 223.0730, found 223.0726.

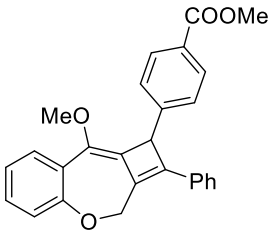
N,N-dimethyl-1-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)prop-2-yn-1-amine (2n)



The title compound was obtained in 82% (1.19 g) yield. R_f = 0.25 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.5 Hz, 1 H), 7.41 (d, *J* = 7.0 Hz, 2 H), 7.34–7.23 (m, 4 H), 7.08 (d, *J* = 8.2 Hz, 1 H), 7.04–6.97 (m, 1 H), 5.10 (s, 1 H), 5.01 (d, *J* = 15.7 Hz, 1 H), 4.93 (d, *J* = 15.8 Hz, 1 H), 2.45 (s, 1 H), 2.31 (s, 6 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 155.5, 131.8, 130.1, 129.1, 128.7, 128.4, 127.3, 122.4, 121.1, 113.3, 87.2, 84.2, 79.8, 74.9, 57.6, 55.0, 41.5 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{20}H_{20}NO^+$ 290.1539, found 290.1537.

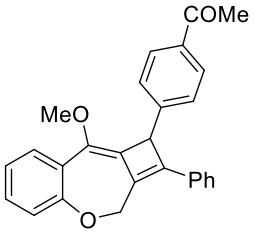
Products Characterization

Methyl 4-(9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (3a)



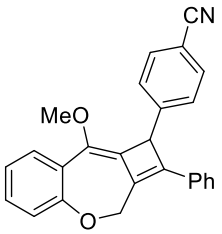
Following the general procedure B, the title compound was obtained in 96% (97.6 mg) yield when Methyl 4-Iodobenzoate reacted with **2a**, the Methyl 4-Bromobenzoate with **2a** gave the title compound in 30% (30.8 mg) yield, pale yellow solid. R_f = 0.50 (silica gel, petroleum ether:EtOAc 5:1); Mp 180.3–180.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 7.9 Hz, 2 H), 7.61 (d, *J* = 7.5 Hz, 1 H), 7.53 (d, *J* = 7.9 Hz, 2 H), 7.32–7.02 (m, 9 H), 5.12 (d, *J* = 15.2 Hz, 1 H), 5.01 (s, 1 H), 4.90 (d, *J* = 15.1 Hz, 1 H), 3.88 (s, 3 H), 3.48 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.1, 156.3, 146.2, 141.6, 139.5, 139.4, 133.1, 130.2, 130.1, 129.1, 128.84, 128.82, 128.0, 127.8, 127.0, 126.7, 126.6, 124.6, 123.1, 68.6, 59.1, 52.8, 52.2 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{27}H_{23}O_4^+$ 411.1591, found 411.1583.

1-(4-(9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)phenyl)ethan-1-one (3b)



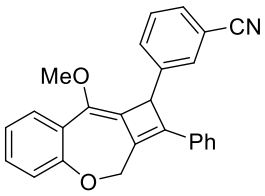
Following the general procedure B, the title compound was obtained in 88% (87.0 mg) yield when 4-Iodoacetophenone reacted with **2a**, and the 4-Acetylphenyl Trifluoromethanesulfonate with **2a** gave 46% (45.7 mg) in yield, yellow foam. R_f = 0.30 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.2 Hz, 2 H), 7.64–7.60 (m, 1 H), 7.54 (d, *J* = 8.3 Hz, 2 H), 7.29–7.12 (m, 6 H), 7.12–7.06 (m, 2 H), 5.10 (dd, *J* = 15.2, 1.6 Hz, 1 H), 5.00 (brs, 1 H), 4.89 (dd, *J* = 15.2, 2.9 Hz, 1 H), 3.50 (s, 3 H), 2.55 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 197.6, 156.1, 146.3, 141.5, 139.34, 139.26, 136.0, 132.9, 129.9, 128.9, 128.7, 128.0, 127.6, 126.9, 126.5, 126.4, 124.4, 123.0, 68.4, 59.0, 52.6, 26.5 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{27}H_{22}O_3Na^+$ 417.1461, found 417.1462.

4-(9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzonitrile (3c)



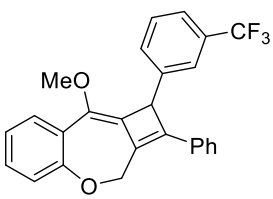
Following the general procedure B, the title compound was obtained as a orange foam (69.2 mg, 74%). R_f = 0.41 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.63–7.54 (m, 5 H), 7.31–7.13 (m, 7 H), 7.10–7.05 (m, 2 H), 5.10 (dd, *J* = 15.2, 1.6 Hz, 1 H), 5.02–4.97 (m, 1 H), 4.89 (dd, *J* = 15.2, 3.0 Hz, 1 H), 3.49 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 156.1, 146.3, 141.8, 139.5, 139.1, 132.7, 132.6, 129.6, 128.9, 128.8, 128.6, 127.9, 126.8, 126.6, 126.4, 124.5, 123.1, 118.9, 110.8, 68.4, 59.1, 52.3 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{26}H_{19}NO_2Na^+$ 400.1308, found 400.1303.

3-(9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzonitrile (3d)



Following the general procedure B, the title compound was obtained as a orange foam (68.6 mg, 73%). R_f = 0.44 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.77–7.66 (m, 2 H), 7.64–7.56 (m, 1 H), 7.54–7.47 (m, 1 H), 7.42–7.37 (m, 1 H), 7.32–7.13 (m, 6 H), 7.07 (d, *J* = 7.2 Hz, 2 H), 5.09 (dd, *J* = 15.1, 1.6 Hz, 1 H), 4.97 (s, 1 H), 4.90 (dd, *J* = 15.2, 2.9 Hz, 1 H), 3.49 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 156.1, 142.2, 141.8, 139.5, 139.0, 132.6, 132.3, 131.4, 130.8, 129.64, 129.55, 128.9, 128.8, 127.8, 126.8, 126.6, 126.4, 124.5, 123.1, 118.9, 112.7, 68.4, 59.1, 51.8 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{26}H_{20}NO_2^+$ 378.1489, found 378.1485.

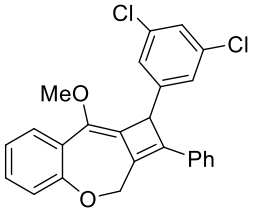
9-methoxy-2-phenyl-1-(3-(trifluoromethyl)phenyl)-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepine (3e)



Following the general procedure B, the title compound was obtained as a pale yellow foam (88.9 mg, 85%). R_f = 0.49 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.71 (s, 1 H), 7.66–7.57 (m , 2 H), 7.48 (d, *J* = 7.4 Hz, 1 H), 7.44–7.35 (m, 1 H), 7.30–7.06 (m, 8 H), 5.11 (dd, *J* = 15.3, 1.4 Hz, 1 H), 5.00 (s, 1 H), 4.88 (dd, *J* = 15.2, 2.9 Hz, 1 H), 3.47 (s, 3 H) ppm; **^{13}C NMR** (100 MHz,

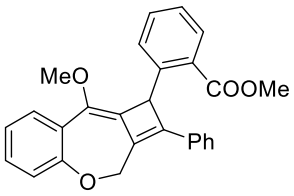
$CDCl_3$): δ = 156.2, 141.61, 141.58, 139.3, 139.2, 132.9, 131.1, 131.0 (q, *J* = 31.8 Hz), 129.9, 129.2, 128.8, 128.7, 127.7, 127.1, 126.9, 126.5, 124.7 (q, *J* = 3.8 Hz), 124.5, 124.2 (q, *J* = 270.7 Hz), 123.9 (q, *J* = 3.8 Hz), 123.1, 68.5, 59.1, 52.3 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.33 (s, 3 F) ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{26}H_{19}F_3O_2Na^+$ 443.1229, found 443.1230.

1-(3,5-dichlorophenyl)-9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepine (3f)



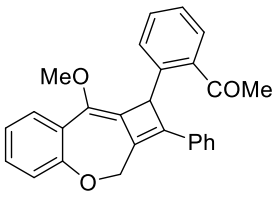
Following the general procedure B, the title compound was obtained as a colorless oil (71.1 mg, 68%). R_f = 0.51 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.65–7.58 (m, 1 H), 7.35–7.14 (m, 9 H), 7.10 (d, *J* = 7.3 Hz, 2 H), 5.14–5.04 (m, 1 H), 4.95–4.86 (m, 2 H), 3.54 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 156.1, 144.2, 141.8, 139.4, 138.9, 135.2, 132.7, 129.7, 128.83, 128.80, 127.8, 127.3, 126.9, 126.5, 126.23, 126.17, 124.5, 123.0, 68.4, 59.1, 51.8 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{25}H_{18}Cl_2O_2Na^+$ 443.0576, found 443.0581.

Methyl 2-(9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (3g)



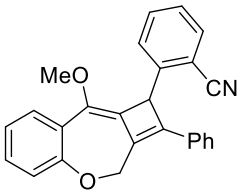
Following the general procedure B, the title compound was obtained as a white foam (94.3 mg, 92%). R_f = 0.56 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.65–7.51 (m, 2 H), 7.39–7.30 (m, 1 H), 7.29–7.06 (m, 9 H), 6.16 (s, 1 H), 5.10 (dd, *J* = 15.2, 1.8 Hz, 1 H), 4.92 (dd, *J* = 15.1, 3.0 Hz, 1 H), 3.99 (s, 3 H), 3.48 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.6, 156.1, 141.6, 141.2, 140.5, 138.8, 133.1, 132.3, 130.2, 130.1, 130.0, 128.6, 128.5, 128.4, 127.4, 127.3, 126.9, 126.7, 126.6, 124.3, 122.9, 68.5, 58.6, 52.3, 47.6 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{27}H_{22}O_4Na^+$ 433.1410, found 433.1410.

1-(2-(9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)phenyl)ethan-1-one (3h)



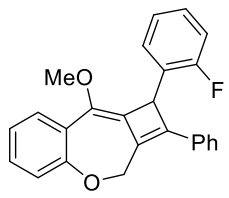
Following the general procedure B, the title compound was obtained as a pale yellow foam (83.4 mg, 85%). R_f = 0.58 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.71–7.64 (m, 1 H), 7.63–7.53 (m, 2 H), 7.36–7.09 (m, 10 H), 5.95 (s, 1 H), 5.08 (dd, *J* = 15.2, 1.8 Hz, 1 H), 4.91 (dd, *J* = 15.1, 3.0 Hz, 1 H), 3.47 (s, 3 H), 2.71 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 202.8, 156.1, 141.1, 140.8, 139.8, 138.6, 138.2, 133.1, 131.8, 130.0, 128.71, 128.69, 128.6, 128.4, 128.1, 127.5, 126.82, 126.76, 126.5, 124.3, 123.0, 68.5, 58.6, 47.0, 30.3 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{27}H_{22}O_3Na^+$ 417.1461, found 417.1465.

2-(9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzonitrile (3i)



Following the general procedure B, the title compound was obtained as a yellow solid (59.8 mg, 64%). R_f = 0.48 (silica gel, petroleum ether:EtOAc 5:1); Mp 82.1–83.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.2 Hz, 1 H), 7.66–7.57 (m, 1 H), 7.52 (d, *J* = 7.5 Hz, 1 H), 7.49–7.41 (m, 1 H), 7.37–7.07 (m, 9 H), 5.48 (s, 1 H), 5.07 (dd, *J* = 15.3, 1.8 Hz, 1 H), 4.97 (dd, *J* = 15.3, 2.8 Hz, 1 H), 3.60 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 156.1, 144.5, 142.2, 139.6, 139.0, 133.3, 132.8, 132.5, 129.7, 128.9, 128.0, 127.8, 127.5, 127.0, 126.4, 126.0, 124.5, 123.0, 118.1, 112.2, 68.4, 58.9, 49.8 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{26}H_{20}NO_2^+$ 378.1489, found 378.1485.

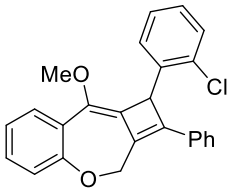
1-(2-fluorophenyl)-9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepine (3j)



Following the general procedure B, the title compound was obtained as a white foam (85.2 mg, 92%). R_f = 0.52 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.68–7.61 (m, 1 H), 7.38 (td, *J* = 7.6, 1.5 Hz, 1 H), 7.33–7.04 (m, 10 H), 7.03–6.96 (m, 1 H), 5.41 (s, 1 H), 5.05 (dd, *J* = 15.2, 1.3 Hz, 1 H), 4.90 (dd, *J*

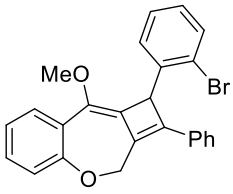
= 15.2, 2.8 Hz, 1 H), 3.59 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 160.5 (d, *J* = 242.7 Hz), 156.1, 141.4, 139.2, 138.9, 132.9, 130.1, 128.9 (d, *J* = 4.0 Hz), 128.7, 128.6, 128.4 (d, *J* = 8.2 Hz), 127.5, 127.1 (d, *J* = 14.3 Hz), 127.0, 126.4, 125.2, 124.6 (d, *J* = 3.6 Hz), 124.3, 122.9, 115.4 (d, *J* = 22.4 Hz), 68.5, 58.4, 44.2 (d, *J* = 3.2 Hz) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -119.91 (s, 1 F) ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{20}FO_2^+$ 371.1442, found 371.1433.

1-(2-chlorophenyl)-9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepine (3k)



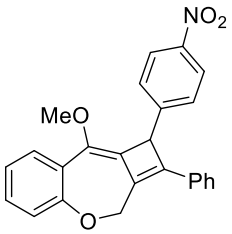
Following the general procedure B, the title compound was obtained as a yellow foam (70.5 mg, 73%). R_f = 0.66 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.71–7.56 (m, 2 H), 7.42 (d, *J* = 7.8 Hz, 1 H), 7.30–7.11 (m, 9 H), 7.08–7.01 (m, 1 H), 5.59 (s, 1 H), 5.09 (dd, *J* = 15.2, 1.7 Hz, 1 H), 4.92 (dd, *J* = 15.2, 2.9 Hz, 1 H), 3.58 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 156.2, 141.8, 140.2, 139.6, 139.1, 133.0, 130.3, 129.2, 128.9, 128.8, 128.6, 128.2, 127.6, 127.2, 126.8, 125.7, 124.5, 123.0, 68.7, 58.5, 51.2 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{20}ClO_2^+$ 387.1146, found 387.1143.

1-(2-bromophenyl)-9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepine (3l)



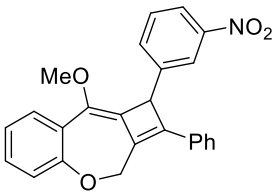
Following the general procedure B, the title compound was obtained as a yellow foam (86.0 mg, 80%). R_f = 0.47 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.69–7.60 (m, 1 H), 7.47–7.35 (m, 2 H), 7.30–7.06 (m, 10 H), 5.61 (s, 1 H), 5.12–5.05 (m, 1 H), 4.95–4.87 (m, 1 H), 3.58 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 156.2, 141.8, 140.0, 139.1, 137.9, 133.6, 133.0, 130.3, 129.7, 129.0, 128.9, 128.7, 128.3, 127.63, 127.55, 127.2, 126.7, 125.6, 124.5, 123.0, 68.7, 58.4, 48.3 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{20}BrO_2^+$ 431.0641, found 431.0641.

9-methoxy-1-(4-nitrophenyl)-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepine (3m)



Following the general procedure B, the title compound was obtained as a golden foam (68.8 mg, 70%). R_f = 0.42 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.24–8.15 (m, 2 H), 7.70–7.58 (m, 3 H), 7.30–7.14 (m, 6 H), 7.11–7.05 (m, 2 H), 5.11 (dd, *J* = 15.2, 1.6 Hz, 1 H), 5.05 (brs, 1 H), 4.92 (dd, *J* = 15.2, 2.9 Hz, 1 H), 3.50 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 156.1, 148.5, 147.0, 141.9, 139.7, 139.1, 132.6, 129.6, 128.9, 128.8, 128.6, 127.9, 126.9, 126.5, 126.4, 124.5, 124.1, 123.1, 68.4, 59.1, 52.0 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{25}H_{19}NO_4Na^+$ 420.1206, found 420.1205.

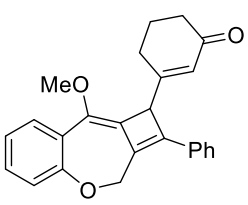
9-methoxy-1-(3-nitrophenyl)-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepine (3n)



Following the general procedure B, the title compound was obtained as a golden foam (101 mg, 97%). R_f = 0.63 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.30 (s, 1 H), 8.12–8.04 (m, 1 H), 7.78 (d, *J* = 7.8 Hz, 1 H), 7.63–7.56 (m, 1 H), 7.51–7.42 (m, 1 H), 7.31–7.13 (m, 6 H), 7.09 (d, *J* = 7.4 Hz, 2 H), 5.15–5.03 (m, 2 H), 4.94 (dd, *J* = 15.1, 2.7 Hz, 1 H), 3.52 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 156.1, 148.6, 142.8, 141.9, 139.6, 139.0, 133.9, 132.6, 129.7, 129.6, 128.9, 128.8, 127.9, 126.9, 126.5, 126.4, 124.5, 123.1, 122.7, 122.2, 68.4, 59.2, 51.8 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{25}H_{19}NO_4Na^+$ 420.1206, found 420.1207.

58.6, 47.0, 30.3 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{27}H_{22}O_3Na^+$ 417.1461, found 417.1465.

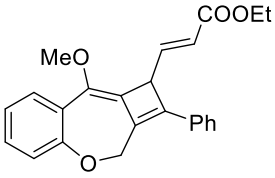
3-(9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)cyclohex-2-en-1-one (3o)



Following the general procedure B, the title compound was obtained as a yellow foam (43.2 mg, 47%). R_f = 0.26 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.67 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.38–7.32 (m,

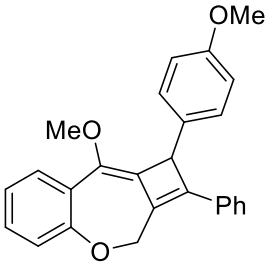
2 H), 7.29–7.22 (m, 3 H), 7.21–7.12 (m, 4 H), 6.32 (s, 1 H), 5.02 (dd, *J* = 15.3, 1.6 Hz, 1 H), 4.86 (dd, *J* = 15.3, 2.9 Hz, 1 H), 4.67 (brs, 1 H), 3.78 (s, 3 H), 2.51–2.32 (m, 3 H), 2.29–2.20 (m, 1 H), 1.96–1.88 (m, 2 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 200.2, 165.6, 156.3, 141.9, 140.9, 136.0, 133.4, 129.8, 129.2, 129.1, 128.4, 128.1, 127.2, 126.2, 124.6, 123.1, 122.0, 68.4, 59.6, 55.0, 38.0, 24.6, 22.9 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{23}O_3^+$ 371.1642, found 371.1641.

Ethyl (*E*)-3-(9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)acrylate (3p)



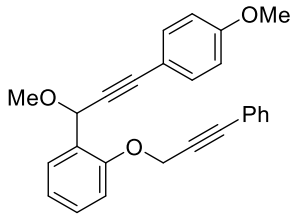
Following the general procedure B, the title compound was obtained as a yellow oil (61.1 mg, 65%). R_f = 0.35 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.67 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.37–7.31 (m, 2 H), 7.28–7.09 (m, 7 H), 6.19 (d, *J* = 15.6 Hz, 1 H), 4.97–4.82 (m, 2 H), 4.62 (dt, *J* = 9.5, 2.2 Hz, 1 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 3.82 (s, 3 H), 1.27 (t, *J* = 7.1 Hz, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.3, 156.0, 148.9, 140.9, 140.6, 136.7, 133.3, 129.9, 128.9, 128.8, 127.7, 127.0, 126.4, 124.4, 123.0, 122.7, 122.3, 68.4, 60.5, 59.4, 50.2, 14.2 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{23}O_4^+$ 375.1591, found 375.1595.

9-methoxy-1-(4-methoxyphenyl)-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepine (3q)



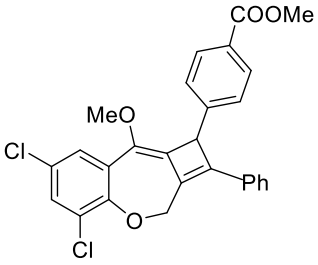
The title compound was obtained as a pale yellow foam (12.5 mg, 13%). R_f = 0.65 (silica gel, petroleum ether:EtOAc 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 7.9 Hz, 1 H), 7.36 (d, *J* = 8.3 Hz, 2 H), 7.29–7.10 (m, 8 H), 6.84 (d, *J* = 8.2 Hz, 2 H), 5.10 (d, *J* = 15.1 Hz, 1 H), 4.97–4.84 (m, 2 H), 3.78 (s, 3 H), 3.54 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 158.5, 156.1, 140.9, 139.9, 138.7, 133.4, 132.4, 130.3, 128.8, 128.6, 128.4, 127.5, 127.4, 126.9, 126.6, 124.3, 122.9, 114.1, 68.6, 59.0, 55.2, 52.3 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{26}H_{23}O_3^+$ 383.1642, found 383.1643.

1-(1-methoxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (3q')



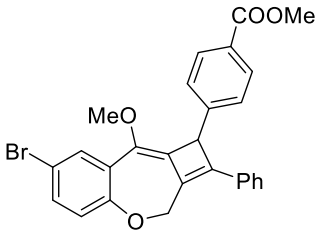
Following the general procedure B, the title compound was obtained as a orange oil (91.1 mg, 95%). R_f = 0.58 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.75 (dd, *J* = 7.6, 1.7 Hz, 1 H), 7.45–7.37 (m, 4 H), 7.36–7.22 (m, 4 H), 7.14–7.01 (m, 2 H), 6.80 (d, *J* = 8.8 Hz, 2 H), 5.74 (s, 1 H), 5.04–4.90 (m, 2 H), 3.76 (s, 3 H), 3.51 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 159.6, 155.1, 133.2, 131.7, 129.6, 128.9, 128.6, 128.3, 128.0, 122.2, 121.7, 114.8, 113.8, 112.9, 87.2, 86.6, 85.7, 84.0, 67.5, 57.4, 56.3, 55.2 ppm; **HRMS** (*m/z*): [M + Na]$^+$ calcd for $C_{26}H_{22}O_3Na^+$ 405.1461, found 405.1461.

Methyl 4-(5,7-dichloro-9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (3r)



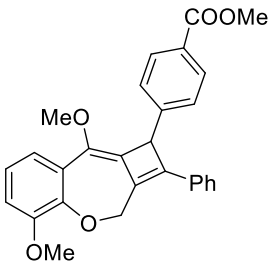
Following the general procedure B, the title compound was obtained as a yellow foam (56.2 mg, 48%). R_f = 0.48 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.2 Hz, 2 H), 7.55–7.45 (m, 3 H), 7.32 (d, *J* = 2.6 Hz, 1 H), 7.29–7.18 (m, 3 H), 7.13–7.06 (m, 2 H), 5.19 (dd, *J* = 15.2, 1.6 Hz, 1 H), 5.01 (s, 1 H), 4.90 (dd, *J* = 15.2, 3.0 Hz, 1 H), 3.89 (s, 3 H), 3.47 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.8, 150.0, 145.4, 140.7, 140.2, 137.6, 133.2, 132.4, 130.2, 129.6, 129.2, 129.1, 128.8, 128.3, 128.2, 127.8, 126.7, 125.2, 68.7, 59.1, 52.7, 52.1 ppm; **HRMS** (*m/z*): [M + Na]$^+$ calcd for $C_{27}H_{20}Cl_2O_4Na^+$ 501.0631, found 501.0629.

Methyl 4-(7-bromo-9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (3s)



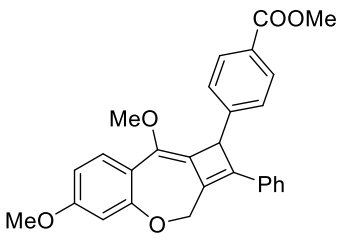
Following the general procedure B, the title compound was obtained as a yellow foam (117 mg, 96%). R_f = 0.43 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.3 Hz, 2 H), 7.73 (d, *J* = 2.6 Hz, 1 H), 7.51 (d, *J* = 8.3 Hz, 2 H), 7.35–7.12 (m, 4 H), 7.11–7.04 (m, 2 H), 7.00 (d, *J* = 8.5 Hz, 1 H), 5.08 (dd, *J* = 15.1, 1.5 Hz, 1 H), 4.99 (s, 1 H), 4.85 (dd, *J* = 15.2, 3.0 Hz, 1 H), 3.87 (s, 3 H), 3.48 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.8, 155.1, 145.7, 140.8, 140.1, 138.0, 132.7, 131.9, 131.2, 130.1, 129.6, 129.0, 128.7, 127.9, 127.8, 126.9, 126.6, 124.7, 117.5, 68.5, 58.9, 52.7, 52.0 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{27}H_{21}BrO_4Na^+$ 511.0515, found 511.0509.

Methyl 4-(5,9-dimethoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (3t)



Following the general procedure B, the title compound was obtained as a yellow foam (107 mg, 97%). R_f = 0.30 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.3 Hz, 2 H), 7.53 (d, *J* = 8.3 Hz, 2 H), 7.31–7.13 (m, 4 H), 7.12–7.04 (m, 3 H), 6.88 (dd, *J* = 8.1, 1.6 Hz, 1 H), 5.14 (dd, *J* = 15.2, 1.6 Hz, 1 H), 5.00 (s, 1 H), 4.92 (dd, *J* = 15.2, 3.0 Hz, 1 H), 3.89 (s, 3 H), 3.87 (s, 3 H), 3.47 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.9, 152.7, 146.1, 145.3, 141.7, 139.4, 139.2, 132.9, 131.4, 130.1, 128.9, 128.7, 127.9, 127.6, 127.1, 126.5, 124.1, 118.6, 111.6, 68.7, 59.0, 56.3, 52.5, 52.0 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{28}H_{24}O_5Na^+$ 463.1516, found 463.1514.

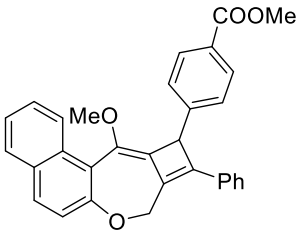
Methyl 4-(6,9-dimethoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (3u)



Following the general procedure B, the title compound was obtained as a pale yellow foam (94.7 mg, 86%). R_f = 0.43 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.3 Hz, 2 H), 7.57–7.49 (m, 3 H), 7.28–7.19 (m, 2 H), 7.19–7.12 (m, 1 H), 7.12–7.04 (m, 2 H), 6.76–6.68 (m,

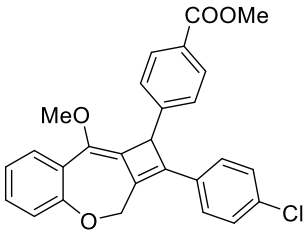
2 H), 5.11 (dd, *J* = 15.1, 1.4 Hz, 1 H), 4.99 (s, 1 H), 4.88 (dd, *J* = 15.1, 2.9 Hz, 1 H), 3.88 (s, 3 H), 3.81 (s, 3 H), 3.48 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.9, 159.9, 157.2, 146.3, 141.5, 139.3, 138.8, 133.1, 130.1, 128.8, 128.6, 127.9, 127.4, 126.3, 124.3, 122.5, 110.3, 108.3, 68.4, 58.8, 55.4, 52.7, 52.0 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{28}H_{24}O_5Na^+$ 463.1516, found 463.1517.

Methyl 4-(11-methoxy-9-phenyl-8,10-dihydrocyclobuta[*e*]naphtho[2,1-*b*]oxepin-10-yl)benzoate (3v)



Following the general procedure B, the title compound was obtained as a yellow foam (102 mg, 89%). R_f = 0.55 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 9.2 Hz, 1 H), 8.01 (d, *J* = 8.2 Hz, 2 H), 7.81–7.75 (m, 1 H), 7.71 (d, *J* = 8.8 Hz, 1 H), 7.59 (d, *J* = 8.3 Hz, 2 H), 7.45–7.37 (m, 2 H), 7.34–7.22 (m, 4 H), 7.22–7.16 (m, 1 H), 7.15–7.08 (m, 2 H), 5.10 (s, 1 H), 4.96 (brs, 2 H), 3.88 (s, 3 H), 3.31 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.0, 155.8, 146.0, 141.1, 140.1, 140.0, 132.8, 131.9, 131.8, 130.0, 129.7, 128.8, 128.7, 128.1, 127.9, 127.8, 126.8, 126.6, 126.1, 124.9, 123.9, 122.9, 69.4, 58.4, 52.5, 52.0 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{31}H_{24}O_4Na^+$ 483.1567, found 483.1565.

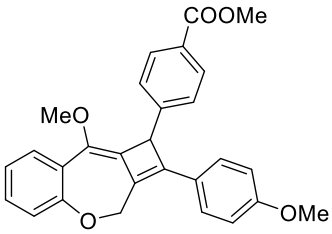
Methyl 4-(2-(4-chlorophenyl)-9-methoxy-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (3w)



Following the general procedure B, the title compound was obtained as a yellow foam (108 mg, 97%). R_f = 0.55 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.3 Hz, 2 H), 7.65–7.58 (m, 1 H), 7.50 (d, *J* = 8.3 Hz, 2 H), 7.27–7.10 (m, 5 H), 6.99 (d, *J* = 8.6 Hz, 2 H), 5.08 (dd, *J* = 15.2, 1.6 Hz, 1 H), 4.98 (s, 1 H), 4.86 (dd, *J* = 15.2, 3.0 Hz, 1 H), 3.88 (s, 3 H), 3.49 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.8, 156.0, 145.7, 142.0, 139.6, 138.1, 133.3, 131.4, 130.2,

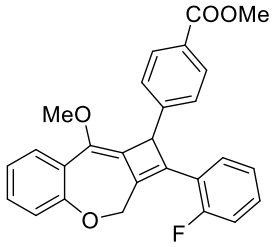
129.8, 129.0, 128.9, 128.8, 127.8, 127.5, 127.0, 125.9, 124.5, 122.9, 68.3, 58.9, 52.6, 52.1 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{27}H_{21}ClO_4Na^+$ 467.1021, found 467.1018.

Methyl 4-(9-methoxy-2-(4-methoxyphenyl)-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (3x)



Following the general procedure B, the title compound was obtained as a pale yellow foam (105 mg, 95%). R_f = 0.40 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.4 Hz, 2 H), 7.62–7.57 (m, 1 H), 7.53 (d, *J* = 8.3 Hz, 2 H), 7.27–7.09 (m, 3 H), 7.04 (d, *J* = 8.8 Hz, 2 H), 6.78 (d, *J* = 8.8 Hz, 2 H), 5.09 (dd, *J* = 15.1, 1.5 Hz, 1 H), 4.95 (s, 1 H), 4.85 (dd, *J* = 15.1, 3.0 Hz, 1 H), 3.87 (s, 3 H), 3.74 (s, 3 H), 3.45 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.0, 159.2, 156.1, 146.2, 139.2, 138.8, 138.3, 130.1, 128.8, 128.4, 128.0, 127.9, 127.3, 126.7, 125.9, 124.4, 123.0, 114.3, 68.5, 59.0, 55.2, 52.5, 52.0 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{28}H_{24}O_5Na^+$ 463.1516 found 463.1515.

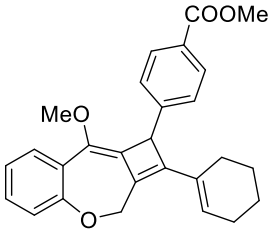
Methyl 4-(2-(2-fluorophenyl)-9-methoxy-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (3y)



Following the general procedure B, the title compound was obtained as a pale yellow foam (101 mg, 94%). R_f = 0.54 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.3 Hz, 2 H), 7.62–7.57 (m, 1 H), 7.53 (d, *J* = 8.3 Hz, 2 H), 7.25–7.20 (m, 1 H), 7.19–7.11 (m, 3 H), 7.03–6.92 (m, 3 H), 5.13 (dt, *J* = 15.7, 1.9 Hz, 1 H), 5.01 (s, 1 H), 4.89 (dt, *J* = 15.7, 2.3 Hz, 1 H), 3.88 (s, 3 H), 3.48 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.9, 159.2 (d, *J* = 248.0 Hz), 156.2, 145.9, 143.9 (d, *J* = 2.0 Hz), 139.7, 133.4, 130.1, 129.7, 129.3 (d, *J* = 8.3 Hz), 128.9, 128.8, 127.95 (d, *J* = 4.2 Hz), 127.86, 127.2, 126.8, 124.34, 124.27 (d, *J* = 3.4 Hz), 123.0, 120.7 (d, *J* = 15.9 Hz), 115.7 (d, *J* = 21.7

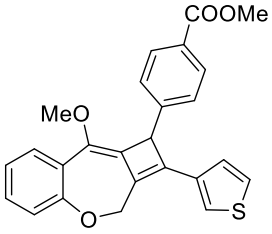
Hz), 69.8 (d, *J* = 15.4 Hz), 59.0, 52.6, 52.0 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -113.45–-113.66 (m, 1 F) ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{27}H_{21}FO_4Na^+$ 451.1316, found 451.1317.

Methyl 4-(2-(cyclohex-1-en-1-yl)-9-methoxy-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (3z)



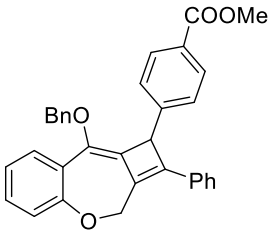
Following the general procedure B, the title compound was obtained as a yellow foam (96.0 mg, 93%). R_f = 0.61 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.2 Hz, 2 H), 7.55 (dd, *J* = 7.7, 1.7 Hz, 1 H), 7.45 (d, *J* = 8.2 Hz, 2 H), 7.21–7.06 (m, 3 H), 5.59 (s, 1 H), 4.97 (d, *J* = 3.6 Hz, 1 H), 4.77–4.66 (m, 2 H), 3.89 (s, 3 H), 3.37 (s, 3 H), 2.25–2.11 (m, 2 H), 2.00 (q, *J* = 19.6, 17.4 Hz, 2 H), 1.67–1.59 (m, 2 H), 1.56–1.47 (m, 2 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.1, 156.3, 146.7, 141.9, 138.5, 138.2, 131.3, 130.0, 129.9, 129.3, 128.7, 128.2, 128.0, 127.8, 126.6, 124.2, 122.9, 69.1, 59.1, 52.0, 26.3, 25.7, 22.3, 21.8 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{27}H_{27}O_4^+$ 415.1904 found 415.1907.

Methyl 4-(9-methoxy-2-(thiophen-3-yl)-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (3za)



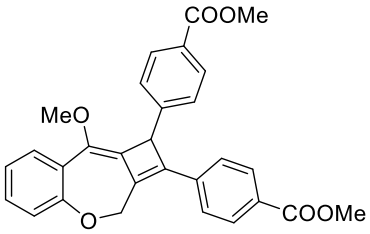
Following the general procedure B, the title compound was obtained as a white solid (116 mg, 97%). R_f = 0.43 (silica gel, petroleum ether:EtOAc 5:1); Mp 225.3–225.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 7.8 Hz, 2 H), 7.62 (d, *J* = 7.6 Hz, 1 H), 7.52 (d, *J* = 7.9 Hz, 2 H), 7.32–7.10 (m, 4 H), 7.00–6.86 (m, 2 H), 5.03 (d, *J* = 15.0 Hz, 1 H), 4.95 (s, 1 H), 4.80 (d, *J* = 14.9 Hz, 1 H), 3.89 (s, 3 H), 3.48 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.9, 156.1, 146.0, 139.04, 138.96, 135.2, 134.7, 130.1, 129.9, 129.0, 128.6, 127.9, 126.9, 126.4, 126.3, 125.7, 124.4, 123.0, 122.2, 68.3, 58.8, 53.3, 52.0 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{21}O_4S^+$ 417.1155, found 417.1145.

Methyl 4-(9-(benzyloxy)-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (3zb)



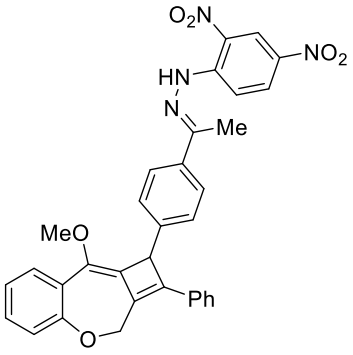
Following the general procedure B, the title compound was obtained as a pale yellow foam (113 mg, 93%). R_f = 0.43 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.3 Hz, 2 H), 7.67 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.51 (d, *J* = 8.3 Hz, 2 H), 7.37–7.21 (m, 6 H), 7.20–7.13 (m, 5 H), 7.11–7.05 (m, 2 H), 5.12 (dd, *J* = 15.2, 1.7 Hz, 1 H), 4.94 (dd, *J* = 15.3, 3.0 Hz, 1 H), 4.83 (s, 1 H), 4.65–4.54 (m, 2 H), 3.88 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.9, 156.2, 145.8, 141.3, 139.6, 138.0, 137.0, 132.9, 130.1, 129.9, 129.1, 128.9, 128.69, 128.67, 128.4, 127.94, 127.91, 127.85, 127.8, 126.9, 126.6, 124.5, 123.1, 73.2, 68.5, 52.3, 52.0 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{33}H_{26}O_4Na^+$ 509.1723, found 509.1725.

Dimethyl 4,4'-(9-methoxy-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepine-1,2-diyl)dibenzoate (3zc)



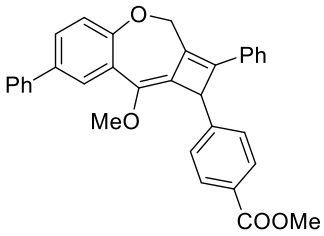
Following the general procedure B, the title compound was obtained as a yellow foam (89.3 mg, 77%). R_f = 0.30 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.3 Hz, 2 H), 7.90 (d, *J* = 8.5 Hz, 2 H), 7.67–7.60 (m, 1 H), 7.52 (d, *J* = 8.3 Hz, 2 H), 7.28–7.22 (m, 1 H), 7.19–7.14 (m, 2 H), 7.11 (d, *J* = 8.5 Hz, 2 H), 5.13 (dd, *J* = 15.4, 1.6 Hz, 1 H), 5.04 (s, 1 H), 4.92 (dd, *J* = 15.4, 2.9 Hz, 1 H), 3.88 (s, 3 H), 3.86 (s, 3 H), 3.52 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.8, 166.5, 156.0, 145.6, 144.5, 140.6, 138.2, 137.1, 130.2, 129.9, 129.7, 129.1, 128.4, 127.8, 127.1, 126.0, 125.5, 124.5, 122.9, 68.3, 58.8, 52.8, 52.12, 52.07 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{29}H_{24}O_6Na^+$ 491.1465, found 491.1460.

(*E*)-1-(2,4-dinitrophenyl)-2-(1-(4-(9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)phenyl)ethylidene)hydrazine (4)



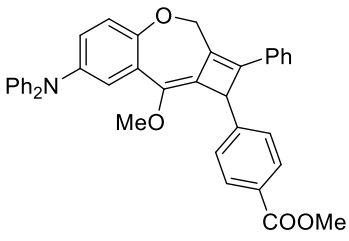
The title compound was obtained as a red soild (247.6 mg, 92%). R_f = 0.58 (silica gel, petroleum ether:EtOAc 5:1); Mp 237.7–238.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 11.33 (s, 1 H), 9.15 (d, *J* = 2.6 Hz, 1 H), 8.34 (dd, *J* = 9.5, 2.6 Hz, 1 H), 8.10 (d, *J* = 9.5 Hz, 1 H), 7.81 (d, *J* = 8.2 Hz, 2 H), 7.67–7.60 (m, 1 H), 7.55 (d, *J* = 8.3 Hz, 2 H), 7.33–7.10 (m, 8 H), 5.13 (dd, *J* = 15.1, 1.6 Hz, 1 H), 5.03 (s, 1 H), 4.93 (dd, *J* = 15.1, 2.9 Hz, 1 H), 3.56 (s, 3 H), 2.43 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 156.2, 152.2, 145.0, 143.1, 141.5, 139.5, 139.2, 138.2, 136.0, 133.1, 130.1, 130.0, 129.7, 128.72, 128.70, 128.2, 127.6, 127.0, 126.9, 126.8, 126.6, 124.4, 123.5, 123.0, 116.8, 68.5, 59.1, 52.6, 13.6 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{33}H_{27}N_4O_6^+$ 575.1925, found 575.1911.

Methyl 4-(9-methoxy-2,7-diphenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (5)



The title compound was obtained as a yellow foam (33.3 mg, 65%). R_f = 0.26 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.2 Hz, 2 H), 7.84 (d, *J* = 2.1 Hz, 1 H), 7.61–7.53 (m, 4 H), 7.47–7.40 (m, 3 H), 7.35–7.16 (m, 5 H), 7.11 (d, *J* = 8.2 Hz, 2 H), 5.15 (d, *J* = 15.1 Hz, 1 H), 5.04 (s, 1 H), 4.95 (dd, *J* = 15.2, 2.5 Hz, 1 H), 3.89 (s, 3 H), 3.52 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.1, 155.7, 146.1, 141.5, 140.8, 139.8, 139.3, 137.6, 133.1, 130.3, 130.2, 129.1, 128.9, 128.0, 127.9, 127.4, 127.3, 127.2, 127.1, 126.7, 126.5, 125.7, 123.6, 68.7, 59.2, 52.8, 52.2 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{33}H_{27}O_4^+$ 487.1904, found 487.1896.

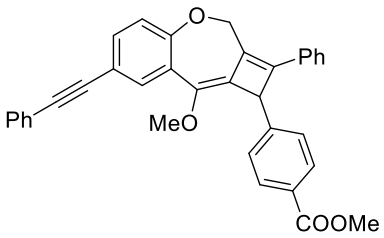
Methyl 4-(7-(diphenylamino)-9-methoxy-2-phenyl-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (6)



The title compound was obtained as a yellow foam (36.8 mg, 64%). R_f = 0.27 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz,

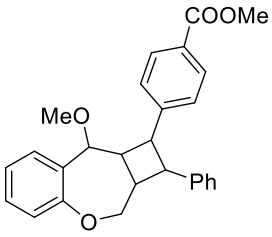
$CDCl_3$): δ = 7.97 (d, *J* = 8.1 Hz, 2 H), 7.51 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 2.5 Hz, 1 H), 7.27–7.15 (m, 7 H), 7.10–7.03 (m, 7 H), 6.99–6.92 (m, 3 H), 5.13 (d, *J* = 15.2 Hz, 1 H), 4.96 (s, 1 H), 4.88 (dd, *J* = 15.2, 3.0 Hz, 1 H), 3.87 (s, 3 H), 3.33 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.1, 152.1, 148.0, 146.1, 144.3, 141.6, 139.6, 133.1, 130.8, 130.2, 129.5, 129.3, 128.8, 128.0, 127.8, 127.4, 126.7, 125.3, 124.3, 124.0, 123.7, 123.4, 122.5, 68.7, 59.0, 52.7, 52.2 ppm; **HRMS** (*m/z*): [M + H]$^+$ calcd for $C_{39}H_{32}NO_4^+$ 578.2326, found 578.2310.

Methyl 4-(9-methoxy-2-phenyl-7-(phenylethynyl)-1,3-dihydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (7)



The title compound was obtained as a yellow foam (45.5 mg, 89%). R_f = 0.28 (silica gel, petroleum ether:EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.05–7.96 (m, 2 H), 7.81 (s, 1 H), 7.56–7.50 (m, 3 H), 7.40–7.08 (m, 11 H), 5.13 (d, *J* = 15.0 Hz, 1 H), 5.02 (s, 1 H), 4.89 (d, *J* = 15.2 Hz, 1 H), 3.88 (s, 3 H), 3.50 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.0, 156.2, 146.0, 141.2, 140.0, 138.7, 133.0, 131.8, 131.67, 130.6, 130.29, 130.26, 129.1, 128.9, 128.5, 128.3, 128.0, 127.9, 127.0, 126.7, 123.4, 119.6, 89.18, 89.16, 68.7, 59.1, 52.9, 52.2 ppm; **HRMS** (*m/z*): [M + H]$^+$ calcd for $C_{35}H_{27}O_4^+$ 511.1904 found 511.1895.

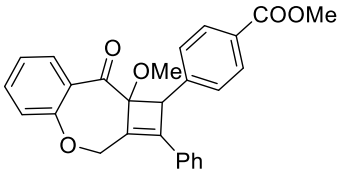
Methyl 4-(9-methoxy-2-phenyl-1,2,2a,3,9,9a-hexahydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (8)



The title compound was obtained as a white foam (174.0 mg, 90%). R_f = 0.62 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.0 Hz, 2 H), 7.37–7.29 (m, 2 H), 7.21–7.13 (m, 4 H), 7.09 (d, *J* = 7.3 Hz, 1 H), 7.02 (d, *J* = 8.4 Hz, 2 H), 6.88–6.78 (m, 2 H), 5.02–4.89 (m, 1 H), 4.73 (t, *J* = 10.6 Hz, 1 H), 4.67 (d, *J* = 3.5 Hz, 1 H), 4.40 (t, *J* = 10.4 Hz, 1 H), 3.89 (s, 3 H), 3.72–3.54 (m, 3 H), 2.99

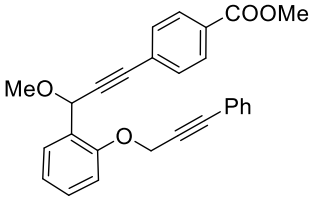
(s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.5, 159.0, 146.8, 137.9, 133.5, 131.5, 129.7, 128.6, 127.8, 127.3, 126.8, 126.2, 120.3, 119.8, 84.1, 70.2, 55.0, 52.0, 45.1, 44.2, 42.3, 39.4 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{27}H_{27}O_4^+$ 415.1904, found 415.1904.

Methyl 4-(9a-methoxy-9-oxo-2-phenyl-1,3,9,9a-tetrahydrobenzo[*b*]cyclobuta[*e*]oxepin-1-yl)benzoate (9)



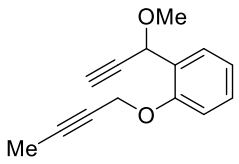
The title compound was obtained as a pale pink soild (47.9 mg, 45%). R_f = 0.47 (silica gel, petroleum ether:EtOAc 5:1); Mp 136.7–138.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.4 Hz, 2 H), 7.25–7.11 (m, 5 H), 7.05–6.98 (m, 2 H), 6.77–6.69 (m, 1 H), 6.51 (d, *J* = 8.3 Hz, 2 H), 6.21 (dd, *J* = 7.8, 1.6 Hz, 1 H), 5.34 (dd, *J* = 10.4, 2.3 Hz, 1 H), 5.11–4.97 (m, 2 H), 3.86 (s, 3 H), 3.52 (s, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 203.6, 166.9, 155.4, 153.3, 138.93, 138.89, 133.4, 131.8, 131.2, 130.2, 129.4, 129.2, 129.0, 128.5, 128.1, 127.9, 124.2, 122.5, 94.7, 66.7, 56.3, 53.8, 52.0 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{27}H_{23}O_5^+$ 427.1540, found 427.1531.

Methyl 4-(3-methoxy-3-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)prop-1-yn-1-yl)benzoate (10)



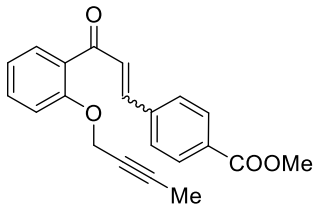
The title compound was obtained as a yellow soild (402.0 mg, 98%). R_f = 0.36 (silica gel, petroleum ether:EtOAc 5:1); Mp 80.0–80.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.4 Hz, 2 H), 7.76–7.69 (m, 1 H), 7.56–7.48 (m, 2 H), 7.45–7.39 (m, 2 H), 7.38–7.26 (m, 4 H), 7.17–7.04 (m, 2 H), 5.76 (d, *J* = 1.8 Hz, 1 H), 5.00 (t, *J* = 16.6 Hz, 2 H), 3.90 (s, 3 H), 3.53 (d, *J* = 1.4 Hz, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.5, 155.1, 131.8, 131.7, 129.8, 129.6, 129.4, 128.72, 128.70, 128.3, 127.53, 127.50, 122.2, 121.8, 113.0, 90.4, 87.3, 85.7, 83.9, 67.5, 57.5, 56.6, 52.2 ppm; **HRMS** (*m/z*): $[M + Na]^+$ calcd for $C_{27}H_{22}O_4Na^+$ 433.1410, found 433.1413.

1-(but-2-yn-1-yloxy)-2-(1-methoxyprop-2-yn-1-yl)benzene (11)



The title compound was obtained in 58% (1.78 g) yield according to procedure A, pale yellow oil, R_f = 0.62 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.72–7.64 (m, 1 H), 7.35–7.27 (m, 1 H), 7.07–6.99 (m, 2 H), 5.51 (d, *J* = 2.0 Hz, 1 H), 4.69 (q, *J* = 2.4 Hz, 2 H), 3.46 (s, 3 H), 2.60 (d, *J* = 2.2 Hz, 1 H), 1.83 (t, J = 2.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl3): δ = 154.8, 129.6, 128.4, 126.9, 121.3, 112.5, 83.7, 81.6, 74.6, 74.0, 66.6, 56.9, 56.1, 3.5 ppm; **HRMS** (m/z): $[M + H]^+$ calcd for $C_{14}H_{15}O_2^+$ 215.1067, found 215.1065.

Methyl 4-(3-(2-(but-2-yn-1-yloxy)phenyl)-3-oxoprop-1-en-1-yl)benzoate (12)



The title compound was obtained as a plae yellow soild (37.5 mg, 45%). R_f = 0.46 (silica gel, petroleum ether:EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.98 (dd, *J* = 56.6, 8.0 Hz, 2 H), 7.75–7.31 (m, 5 H), 7.13–6.76 (m, 3 H), 4.80–4.67 (m, 2 H), 3.91 (d, *J* = 16.7 Hz, 3 H), 1.84 (d, *J* = 6.0 Hz, 3 H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 193.4, 191.8, 166.7, 166.5, 157.0, 156.7, 141.0, 140.2, 139.7, 137.1, 133.6, 133.2, 132.0, 131.1, 130.84, 130.78, 130.0, 129.6, 129.4, 129.3, 129.2, 128.2, 121.6, 121.3, 113.5, 113.4, 84.39, 84.38, 73.57, 73.55, 57.2, 57.0, 52.3, 52.1, 3.7 ppm; **HRMS** (*m/z*): $[M + H]^+$ calcd for $C_{21}H_{19}O_4^+$ 335.1278, found 335.1277.

V. Complete reference for Gaussian 16

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

VI. Complete reference for Gaussian 16

All DFT calculations were carried out using Gaussian 16 program. All the geometry optimizations and frequency calculations in this paper were performed with M06[4] functional in implicit THF, at 6-31G(d) basis set by using the Solvation Model based on Density[5] (SMD) with keyword in the Gaussian code route section "SCRF = (SMD, Solvent = THF)". The vibrational frequencies were computed at the same level of theory as for the geometry optimizations to confirm whether each optimized structure is an energy minimum or a transition state, and to evaluate the zero-point vibrational energy (ZPVE) and thermal corrections. Single-point energy calculations were also performed on an optimized geometry using a higher level basis set 6-311+G(d,p). The Gibbs free energies presented in this paper are the M06 calculated single-point energy in THF solvent with M06 calculated thermodynamic corrections in THF solvent.

VII. M06 calculated absolute energies, enthalpies, and free energies of all structures.

Geometry	$E_{(elec\text{-}M06)}$[1]	$H_{(corr\text{-}M06)}$[2]	$G_{(corr\text{-}M06)}$[3]	$G_{(solv\text{-}M06)}$[4]	IF[5]
10	-1342.312282	0.448241	0.360053	-1341.952229	
DBU	-461.874099	0.256328	0.210738	-461.663361	
15	-1804.20096	0.706857	0.594813	-1803.606147	
TS_1	-1804.175487	0.701129	0.590255	-1803.585232	972.23*i*
16	-1804.186414	0.70598	0.591263	-1803.595151	
TS_2	-1804.17589	0.701064	0.590098	-1803.585792	1059.58*i*
13-17	-1342.321595	0.447889	0.359794	-1341.961801	
TS_3	-1342.284489	0.446084	0.357386	-1341.927103	375.14*i*
18_{oss}	-1342.306431	0.446417	0.356594	-1341.949837	
TS_{5oss}	-1342.282091	0.445887	0.36189	-1341.920201	219.53*i*
TS_{4oss}	-1342.303756	0.445667	0.357127	-1341.946629	186.91*i*
3a	-1342.38359	0.450297	0.364232	-1342.019358	

19	-1342.313292	0.449331	0.365316	-1341.947976

[1]The electronic energy calculated by M06 in THF solvent. [2]The thermal correction to enthalpy calculated by M06 in THF solvent. [3]The thermal correction to Gibbs free energy calculated by M06 in THF solvent. [4]The Gibbs free energy calculated by M06 in THF solvent. [5]The M06 calculated imaginary frequencies for the transition states

VIII. M06 calculated absolute energies, enthalpies, and free energies of all structures.

10

C	4.47046000	-0.17850000	0.13610800
C	3.97797100	1.11538000	-0.11280200
C	4.72719200	2.02592500	-0.85706400
C	5.97542100	1.65635400	-1.35332300
C	6.48388600	0.39066200	-1.09696700
C	5.73166400	-0.51073100	-0.34564900
H	4.35383500	3.03179600	-1.03570000
H	6.55216500	2.37593100	-1.93249400
H	7.46441400	0.10197500	-1.47094300
H	6.13118200	-1.49702900	-0.11799400
C	3.68805500	-1.16219000	1.00251200
O	4.33869600	-2.41178100	1.10441400
C	2.27931900	-1.30553400	0.60873300
C	1.10171300	-1.42574900	0.34859300
C	-0.29489600	-1.46723500	0.06612400
C	-1.19326600	-2.00525800	1.00083500
C	-0.79019300	-0.90773600	-1.12195600
C	-2.55635400	-1.95476500	0.76140200
H	-0.80833000	-2.44207000	1.92051600
C	-2.15511800	-0.85954500	-1.35564800
H	-0.09091500	-0.48943400	-1.84419200
C	-3.04759500	-1.37286500	-0.40987100
H	-3.26368500	-2.34939900	1.48838900
H	-2.53503200	-0.40604500	-2.26817600
C	4.12316100	-3.29168000	0.02098700
H	4.85774400	-4.09803900	0.12113600
H	3.11288100	-3.72701800	0.04696100
H	4.26615200	-2.80229800	-0.95509000
H	3.69003500	-0.76556100	2.03294800
O	2.77127800	1.41011300	0.43508100
C	2.05769700	2.52906500	-0.07319600
H	2.45648300	3.46271600	0.35663600
H	2.18341800	2.59517500	-1.16641300
C	0.64750800	2.36782300	0.24291900
C	-0.53516500	2.22036600	0.46380900
C	-1.92733300	2.01416600	0.70709400
C	-2.35775500	1.43601900	1.91045300
C	-2.87433000	2.34776700	-0.27298000
C	-3.70914200	1.19681700	2.12453400
H	-1.61965600	1.16777800	2.66512100
C	-4.22450100	2.10903800	-0.04913200
H	-2.53707200	2.78751400	-1.21071000
C	-4.64492200	1.53335000	1.14847900
H	-4.03488800	0.74001000	3.05776600
H	-4.95220200	2.36667100	-0.81764500
H	-5.70287000	1.34141900	1.32135200
C	-4.51843200	-1.30000900	-0.58390000
O	-5.32496800	-1.72006100	0.21976100
O	-4.86753600	-0.71684300	-1.73936700
C	-6.26854100	-0.57942400	-1.95650200
H	-6.73199500	0.00973900	-1.15660100
H	-6.37629900	-0.06352800	-2.91344000
H	-6.75413700	-1.56079300	-2.00207500

DBU

C	0.28438400	-0.76541200	-0.37960200
C	1.36632600	1.35038500	0.11151200
C	2.66008100	0.57314200	-0.01585800
C	2.45302800	-0.81870800	0.55856100
H	1.44072900	2.33761900	-0.36503100
H	2.92982600	0.50418900	-1.08038300
H	2.43404000	-0.76420100	1.66121700
N	1.23729200	-1.48059000	0.11089800
N	0.30059000	0.60763200	-0.54357200
C	-0.98556400	-1.46238600	-0.79848900
H	-1.21716100	-1.20303000	-1.84107100
H	-0.76431500	-2.53513300	-0.78499100
C	-2.19922500	-1.15452400	0.11596400
H	-3.08974800	-0.97469900	-0.50603200
H	-2.42156200	-2.04829200	0.71429900
C	-2.01125800	0.02075400	1.07380100
H	-1.11620100	-0.16187900	1.69102700
H	-2.85500200	0.05008800	1.77789900
C	-1.88476700	1.37607100	0.38406700
H	-2.86989200	1.71438300	0.02631500
H	-1.54200900	2.12712300	1.11216800
C	-0.93454300	1.33023000	-0.81097000
H	-1.43813800	0.87099000	-1.67170600
H	-0.66003200	2.34576300	-1.12728500
H	1.12709900	1.51876300	1.17936100
H	3.47695600	1.09554100	0.49923500
H	3.30945900	-1.46383000	0.30977700

15

C	2.98960900	2.20898500	0.31339400
C	2.67000700	1.32599300	1.36125200
C	3.37107600	1.37206100	2.56588500
C	4.41395500	2.28157900	2.72909000
C	4.76257700	3.13756500	1.69356500
C	4.05145300	3.08920800	0.49556100
H	3.13064700	0.68204300	3.37205300

H	4.95882200	2.30386700	3.67166700
H	5.58504400	3.84097300	1.81002300
H	4.32774300	3.74303900	-0.32927700
C	2.27312200	2.13141700	-1.03111500
O	2.71822900	3.13220900	-1.92568100
C	0.80834300	2.10242100	-0.92116200
C	-0.40008000	2.01105000	-0.87670400
C	-1.80721500	1.81237200	-0.76875200
C	-2.56422100	1.43324800	-1.88898200
C	-2.43892100	1.93334700	0.47896300
C	-3.91454200	1.15811600	-1.75263900
H	-2.07391700	1.34048500	-2.85664300
C	-3.78868700	1.64838900	0.61116700
H	-1.84913600	2.22815800	1.34558900
C	-4.53353000	1.24978500	-0.50273800
H	-4.50714100	0.84319000	-2.60956400
H	-4.26605000	1.71959400	1.58565700
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H	2.71525400	5.10951700	-2.34100600
H	1.08680900	4.41942700	-2.09904100
H	2.14354500	4.72798900	-0.69323900
H	2.55407000	1.16725000	-1.50256500
O	1.68160400	0.42696600	1.10540000
C	1.10919500	-0.27728800	2.19570800
H	1.79061100	-1.07554600	2.54015300
H	0.95042100	0.40320100	3.04891700
C	-0.16913900	-0.82625000	1.76986100
C	-1.26019500	-1.22960100	1.42725300
C	-2.56478400	-1.64879800	1.02345700
C	-2.83141200	-1.94494500	-0.32131500
C	-3.60727600	-1.71127000	1.96114400
C	-4.11499600	-2.30153200	-0.71574500
H	-2.02822500	-1.86972300	-1.05423900
C	-4.88791100	-2.06693000	1.55771200
H	-3.40129900	-1.47044800	3.00313700
C	-5.14467500	-2.36491500	0.22056300
H	-4.31541300	-2.52052400	-1.76354900
H	-5.69336200	-2.10514900	2.29005500
H	-6.14970400	-2.64167400	-0.09475100
C	-5.96163900	0.86328400	-0.40663900
O	-6.64265100	0.51663800	-1.34966500
O	-6.42547400	0.93215100	0.84901900
C	-7.78317000	0.53933900	1.02312600
H	-7.93993700	-0.48955600	0.67915500
H	-7.98311300	0.61190700	2.09472400
H	-8.45565600	1.20498100	0.46998700
C	3.26387400	-1.77592000	-1.55738600
C	1.79808800	-3.38237300	-0.49180400
C	0.77074000	-2.95223200	-1.51834900
C	0.92545000	-1.46081700	-1.77321100
H	1.77606200	-4.46850200	-0.32848200
H	0.93708100	-3.51812100	-2.44728900
H	0.50167000	-0.89074900	-0.92775700
N	2.29950900	-1.02195600	-1.95957900
N	3.12362100	-3.01760500	-0.96534700
C	4.67463500	-1.26281700	-1.68854700
H	5.29949100	-2.01485700	-2.18937100
H	4.63696000	-0.39507300	-2.35713200
C	5.29775100	-0.86153800	-0.32934400
H	6.37348000	-1.09522900	-0.34003000
H	5.22097900	0.23128300	-0.21825500
C	4.64360800	-1.48828500	0.90077100
H	3.58997600	-1.16488200	0.92669900
H	5.10706000	-1.06398100	1.80364600
C	4.69774500	-3.00974900	0.97428100
H	5.71776800	-3.34982200	1.21187700
H	4.05525800	-3.34894500	1.80250500
C	4.26015000	-3.67093100	-0.33282300
H	5.09801800	-3.69198700	-1.04087600
H	3.98261400	-4.72006400	-0.16300800
H	1.57999800	-2.89851600	0.48180600
H	-0.24208800	-3.18904700	-1.16311200
H	0.34175700	-1.15980700	-2.65812300

TS_1

C	-2.97618900	-2.00010300	0.50788300
C	-2.59720200	-1.13179100	1.56295800
C	-3.36353800	-1.01938500	2.71811900
C	-4.55040200	-1.74570600	2.84821900
C	-4.96607900	-2.56905300	1.81096100
C	-4.18858100	-2.68280500	0.65841300
H	-3.05504700	-0.35091300	3.51961000
H	-5.14222700	-1.64992400	3.75727800
H	-5.89622700	-3.13049100	1.89183300
H	-4.52511500	-3.31535900	-0.16141600
C	-2.19809800	-2.07024700	-0.74888200
O	-2.83430400	-2.80513500	-1.77897700
C	-0.79003800	-2.19901900	-0.69045300
C	0.43607400	-2.18613600	-0.67215700
C	1.83061100	-1.97932900	-0.59667700
C	2.64275000	-1.94138100	-1.75012400
C	2.43469600	-1.73876300	0.65593300
C	3.98654700	-1.63095000	-1.65090500
H	2.19080400	-2.13271400	-2.72257000
C	3.77991600	-1.43221400	0.74657800
H	1.81598800	-1.77050000	1.55207300
C	4.57132400	-1.36133300	-0.40694800
H	4.60727000	-1.57076800	-2.54351100

H	4.22246400	-1.22526700	1.71873200
C	-2.50966500	-4.17575800	-1.80091100
H	-3.17524800	-4.66147300	-2.52555300
H	-1.46641700	-4.34252200	-2.11614000
H	-2.64789200	-4.65200700	-0.81563200
H	-2.24476300	-0.67692400	-1.27280500
O	-1.45928700	-0.41125600	1.34295200
C	-1.00191400	0.47425500	2.34516200
H	-1.73798400	1.27938400	2.52384100
H	-0.86783800	-0.05506000	3.30434800
C	0.27216200	1.01769400	1.89491800
C	1.34443100	1.40364400	1.48041600
C	2.62449500	1.78409400	0.97346000
C	2.85010500	1.80628000	-0.41107800
C	3.68543900	2.06402600	1.84767600
C	4.11499500	2.09402900	-0.90729600
H	2.03196500	1.56538000	-1.08998400
C	4.94682200	2.35343800	1.34250700
H	3.51111300	2.03814800	2.92236600
C	5.16531900	2.36781400	-0.03368200
H	4.28647300	2.08986000	-1.98281400
H	5.76788000	2.56012000	2.02775800
H	6.15644800	2.58840700	-0.42819700
C	5.98450800	-0.94188900	-0.37504100
O	6.68056000	-0.77547500	-1.35795600
O	6.43552200	-0.74914200	0.87710700
C	7.77729900	-0.29120200	0.98012100
H	7.91462600	0.65200800	0.43805600
H	7.96471600	-0.14058800	2.04630800
H	8.47750600	-1.03347100	0.57919100
C	-3.23536000	1.25926700	-1.49415100
C	-1.86062500	3.19592500	-1.07934300
C	-0.79916800	2.52092300	-1.92239800
C	-0.82414300	1.02875200	-1.65436400
H	-1.92133500	4.27032800	-1.28849100
H	-0.99803100	2.72660500	-2.98375400
H	-0.35211100	0.79693600	-0.68693100
N	-2.18282800	0.49869600	-1.62513600
N	-3.16332500	2.60371700	-1.37458300
C	-4.58652600	0.60435500	-1.44633100
H	-5.18578900	1.00577300	-2.27538600
H	-4.44096600	-0.46080600	-1.66595100
C	-5.33119300	0.78367000	-0.09841900
H	-6.37078900	1.08317700	-0.29840600
H	-5.37917700	-0.19565200	0.39673000
C	-4.69936000	1.77876800	0.87264300
H	-3.64676500	1.49015000	1.04165800
H	-5.18926900	1.68362200	1.85184800
C	-4.76652400	3.23045700	0.40913600
H	-5.78992200	3.61976600	0.51941200
H	-4.12214600	3.85352700	1.04752300
C	-4.35773100	3.38006800	-1.05272700
H	-5.17144000	3.05990300	-1.71505600
H	-4.14726600	4.42693700	-1.30424200
H	-1.63124700	3.07358100	-0.00410900
H	0.19059900	2.93150300	-1.68264400
H	-0.26064000	0.47811200	-2.42122800

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C	3.19020500	1.93416500	0.78477300
C	2.77201100	0.91732500	1.69367400
C	3.62733100	0.43954600	2.68032600
C	4.93829000	0.91497200	2.78917200
C	5.38630900	1.87091400	1.88590100
C	4.52916900	2.36056500	0.90616100
H	3.28582700	-0.32193700	3.37795700
H	5.59019600	0.52794400	3.57061600
H	6.40753700	2.24738500	1.94241800
H	4.88729600	3.10378400	0.19624000
C	2.35434400	2.46879300	-0.26769300
O	3.02738500	3.22009500	-1.24663600
C	0.98152600	2.47388800	-0.29756400
C	-0.25736500	2.47834200	-0.35635300
C	-1.63608100	2.27949700	-0.37055000
C	-2.44965300	2.59244600	-1.49271800
C	-2.27451300	1.69916200	0.76068700
C	-3.79573000	2.29290500	-1.49183200
H	-1.98824200	3.05080900	-2.36703600
C	-3.62022500	1.40594300	0.74700400
H	-1.66588700	1.46140900	1.63309600
C	-4.40917600	1.68364200	-0.38401600
H	-4.40620100	2.50949200	-2.36779500
H	-4.07702100	0.93129800	1.61450700
C	2.84519100	4.60955200	-1.10033000
H	3.47198200	5.10797100	-1.85055600
H	1.79530700	4.90206600	-1.26750100
H	3.14314300	4.95695900	-0.09632600
H	2.03778100	0.63729400	-1.28642700
O	1.50334400	0.43104200	1.51400900
C	1.12841300	-0.70083600	2.27232200
H	1.86807600	-1.51338800	2.14674100
H	1.10523200	-0.46142200	3.34938800
C	-0.18659100	-1.15296700	1.84228100
C	-1.28219600	-1.53993600	1.49376700
C	-2.59130900	-1.94919200	1.09403000
C	-3.07574800	-1.63386500	-0.18540900
C	-3.42713500	-2.62104300	1.99802600
C	-4.37053900	-1.98328200	-0.54690900

H	-2.44000300	-1.08179000	-0.87887800
C	-4.72040800	-2.96741500	1.62765500
H	-3.05390000	-2.85793000	2.99327400
C	-5.19533700	-2.64897700	0.35725400
H	-4.74335000	-1.71938700	-1.53614400
H	-5.36350100	-3.48480200	2.33775500
H	-6.21194100	-2.91662700	0.07265000
C	-5.81666700	1.29657300	-0.48536900
O	-6.52677500	1.47396700	-1.46040300
O	-6.26735900	0.68293300	0.63051000
C	-7.60419900	0.21257900	0.56698300
H	-7.74932800	-0.45182100	-0.29362900
H	-7.77846800	-0.33583100	1.49686200
H	-8.31389200	1.04548700	0.48858900
C	2.84492000	-1.16689800	-1.67325800
C	1.30633900	-3.01050900	-1.53805000
C	0.26952100	-2.10961600	-2.17744400
C	0.41730000	-0.70070800	-1.64021600
H	1.26312800	-4.02750400	-1.94163000
H	0.40428000	-2.12387900	-3.26763800
H	-0.01927000	-0.60341400	-0.63660200
N	1.82901200	-0.33682500	-1.55437100
N	2.64634900	-2.47891600	-1.80282500
C	4.23652600	-0.61449500	-1.63841200
H	4.70287100	-0.85047900	-2.60526400
H	4.16285300	0.47995200	-1.59764300
C	5.10488400	-1.13987600	-0.46675600
H	6.07750100	-1.46547700	-0.86305100
H	5.30758600	-0.29675400	0.20733800
C	4.48846100	-2.27107900	0.35152500
H	3.49579600	-1.94893000	0.71199400
H	5.09041300	-2.42606000	1.25738300
C	4.35648000	-3.59107200	-0.40209300
H	5.33948800	-4.07424700	-0.50278200
H	3.72083200	-4.28252000	0.17054600
C	3.78705500	-3.39712900	-1.80242700
H	4.54976000	-2.99989100	-2.48288300
H	3.44349500	-4.34349800	-2.23470200
H	1.15014600	-3.06805900	-0.44596600
H	-0.73861700	-2.48376600	-1.96037700
H	-0.07960900	0.03196800	-2.28884500

TS_2

C	-3.77849100	-1.97654200	-0.24371000
C	-3.30261800	-1.96865900	1.09230200
C	-4.14510100	-2.27786200	2.15680200
C	-5.48074900	-2.61336100	1.93148500
C	-5.96773100	-2.64153500	0.63210300
C	-5.12419000	-2.32977400	-0.42918300
H	-3.76339700	-2.27829700	3.17535500
H	-6.12427600	-2.85457400	2.77609900
H	-7.00680600	-2.90352000	0.43659600
H	-5.50584900	-2.33925000	-1.44801800
C	-2.95918000	-1.65328700	-1.41241700
O	-3.57345700	-1.91415100	-2.64722400
C	-1.72214800	-1.13893900	-1.45378600
C	-0.61202400	-0.51048900	-1.62773100
C	0.75562200	-0.99595300	-1.52656400
C	1.78295100	-0.42564900	-2.30284300
C	1.12190700	-1.94712900	-0.55509900
C	3.11099400	-0.74156600	-2.07647800
H	1.51800500	0.29527700	-3.07761400
C	2.45098600	-2.25431700	-0.31643900
H	0.33305200	-2.40023700	0.04523000
C	3.46471100	-1.63747700	-1.06049400
H	3.90250300	-0.27626300	-2.66218000
H	2.71290700	-2.96217200	0.46831400
C	-3.30605200	-3.21530400	-3.11548200
H	-3.86108700	-3.35153400	-4.05194200
H	-2.23100000	-3.35648700	-3.31532900
H	-3.62945100	-3.98698300	-2.39644300
H	-0.66694300	1.06414600	-1.74812800
O	-1.98539800	-1.66100200	1.26165100
C	-1.52353700	-1.40765200	2.57861900
H	-2.20805500	-0.71089200	3.09446200
H	-1.49936200	-2.33745700	3.17110800
C	-0.19704300	-0.82394300	2.46906300
C	0.89459200	-0.32954200	2.28947100
C	2.16457200	0.24286800	1.98156200
C	2.25842900	1.17427700	0.93593500
C	3.32719800	-0.15558000	2.65502100
C	3.49474300	1.68803200	0.56833400
H	1.34937100	1.45417400	0.39836000
C	4.55994300	0.36810600	2.28469300
H	3.25374500	-0.88465500	3.46064100
C	4.64812100	1.28604200	1.23997700
H	3.56200000	2.39953500	-0.25475600
H	5.45912900	0.05363500	2.81221600
H	5.61755900	1.68392700	0.94427600
C	4.89876200	-1.84698200	-0.78831700
O	5.80461300	-1.29980800	-1.38708500
O	5.11414300	-2.71623800	0.21526400
C	6.48032800	-2.93934500	0.54217000
H	6.97294900	-2.00276100	0.82897700
H	6.48031500	-3.63573600	1.38430500
H	7.02024300	-3.37758200	-0.30526600
C	-1.45365900	2.85442300	-0.92634000
C	-0.01670300	4.79207400	-0.77903300

C	0.50020300	4.37837800	-2.14164900
C	0.61655100	2.86884100	-2.20079300
H	-0.18486700	5.87395800	-0.72809800
H	-0.19745200	4.73279900	-2.91352200
H	1.48356300	2.51874700	-1.61691700
N	-0.58888500	2.23095800	-1.68761900
N	-1.29166300	4.12549300	-0.51693700
C	-2.63625300	2.09150000	-0.41537800
H	-3.53705100	2.70573500	-0.53074900
H	-2.78202700	1.19922700	-1.03563000
C	-2.42511200	1.67842100	1.05482200
H	-3.40886500	1.56381700	1.53453000
H	-1.95587300	0.68459200	1.04481300
C	-1.53172800	2.61044700	1.87136600
H	-0.49992100	2.53578500	1.48574100
H	-1.47841800	2.23572200	2.90372900
C	-1.93772100	4.08145100	1.90026000
H	-2.85976400	4.21331300	2.48579300
H	-1.15281400	4.64759900	2.42304300
C	-2.17156900	4.68618200	0.51107600
H	-3.21155200	4.54655000	0.19526200
H	-1.99931700	5.76857100	0.52185000
H	0.70729400	4.52672800	0.01251500
H	1.47380900	4.84349300	-2.33495900
H	0.76830500	2.52457100	-3.23255500

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C	-4.32553900	-0.22609500	-0.02959700
C	-3.80543700	1.07544500	0.14243200
C	-4.64472800	2.11898300	0.53297200
C	-5.99705500	1.87912900	0.76655400
C	-6.52125000	0.60170600	0.61701700
C	-5.68389200	-0.43536400	0.22184500
H	-4.25498300	3.12621800	0.65668000
H	-6.63764300	2.70619900	1.06872000
H	-7.57656400	0.41039500	0.80156400
H	-6.07911700	-1.44121100	0.09309500
C	-3.49605100	-1.36702400	-0.45896000
O	-4.03794900	-2.61918500	-0.22445700
C	-2.33723500	-1.32134900	-1.08518600
C	-1.20407100	-1.37966200	-1.74366800
C	0.13501400	-1.38716700	-1.14525400
C	1.24930200	-1.58550100	-1.97020100
C	0.33673600	-1.19963500	0.22991900
C	2.52832100	-1.61176200	-1.43625300
H	1.09990400	-1.72509900	-3.04094800
C	1.61421700	-1.21859500	0.76416600
H	-0.52587100	-1.02341700	0.87330000
C	2.72256800	-1.43069300	-0.06571800
H	3.39675400	-1.76703300	-2.07386800
H	1.76129200	-1.06280500	1.83090500
C	-3.80230100	-3.07761900	1.09541500
H	-4.30867000	-4.04312500	1.19527200
H	-2.72430900	-3.21376600	1.27542500
H	-4.20386700	-2.38128500	1.84792300
H	-1.23226500	-1.43016900	-2.83787000
O	-2.47898800	1.22355900	-0.08217800
C	-1.89702200	2.49815400	0.16196100
H	-2.31933100	3.24522600	-0.52984700
H	-2.12877100	2.83208400	1.18688400
C	-0.46023200	2.38699500	-0.01056800
C	0.74075500	2.28363400	-0.13336900
C	2.15590100	2.13801200	-0.24993100
C	2.75607000	1.97381500	-1.50696500
C	2.95546000	2.12237800	0.90247300
C	4.13025200	1.79652500	-1.60491400
H	2.13115600	1.97735900	-2.39898200
C	4.32916400	1.94766600	0.79623300
H	2.48475900	2.24120600	1.87755800
C	4.91864600	1.78254100	-0.45561300
H	4.58944400	1.66375200	-2.58314100
H	4.94257100	1.93806200	1.69630900
H	5.99493700	1.63656400	-0.53598700
C	4.11315700	-1.45630000	0.44345000
O	5.08968000	-1.68660600	-0.24022500
O	4.18422600	-1.20622800	1.75995400
C	5.49839800	-1.20442900	2.30761900
H	6.13503500	-0.47309700	1.79575500
H	5.38682400	-0.93539600	3.36067100
H	5.95808600	-2.19570100	2.22067600

TS_3

C	0.73565500	2.99144100	0.34978700
C	1.34967900	3.35806800	-0.86475300
C	1.06204100	4.59023800	-1.44926200
C	0.21147300	5.48748600	-0.81911300
C	-0.34958600	5.16765000	0.41841900
C	-0.08679600	3.93510800	0.99230600
H	1.54989000	4.83577700	-2.39094000
H	0.00574200	6.45057000	-1.28320600
H	-1.00239600	5.87522000	0.92596500
H	-0.54649200	3.66131300	1.94029800
C	0.82631300	1.64214200	0.89320700
O	0.75775100	1.58245300	2.23797700
C	1.04897700	0.54590400	0.10177100
C	0.39330300	-0.49077000	-0.41546600
C	-1.04930700	-0.74017900	-0.35776400
C	-1.53171200	-1.94980000	-0.87902400

C	-1.97102100	0.16626100	0.18914500
C	-2.88316600	-2.25222700	-0.84227600
H	-0.82589400	-2.65830500	-1.31267800
C	-3.32310600	-0.13152500	0.22315500
H	-1.62422400	1.12313700	0.58010700
C	-3.79100000	-1.34641500	-0.28998000
H	-3.25504500	-3.19330800	-1.24257800
H	-4.02526500	0.58252200	0.64695700
C	0.71036100	0.28999100	2.82732900
H	0.70421700	0.45171400	3.90807600
H	-0.19721800	-0.25171000	2.53048000
H	1.59377200	-0.30066400	2.54513600
O	2.24726300	2.57389900	-1.52037500
C	3.22877100	1.88796700	-0.75687200
H	4.15947500	1.95146100	-1.33294500
H	3.38448700	2.41546800	0.19764300
C	2.91843300	0.46257400	-0.49148200
C	3.43278100	-0.67555000	-0.46163000
C	3.67627200	-2.04495100	-0.21854400
C	3.52285500	-3.00524900	-1.24098500
C	4.09849300	-2.48201200	1.05468900
C	3.76659700	-4.34680500	-0.98883400
H	3.20510700	-2.67693300	-2.23041200
C	4.34798900	-3.82657300	1.29075900
H	4.22935700	-1.74743600	1.84886500
C	4.18184400	-4.76712600	0.27521100
H	3.63610200	-5.07472100	-1.78868800
H	4.67284500	-4.14540300	2.28051400
H	4.37677700	-5.82103800	0.46611200
C	-5.22544800	-1.71791900	-0.27824700
O	-5.66610300	-2.76082400	-0.71534500
O	-5.99467800	-0.76919800	0.27325900
C	-7.38971100	-1.06095500	0.31626500
H	-7.86287800	-0.19898500	0.79186900
H	-7.78886500	-1.19950300	-0.69469400
H	-7.57958700	-1.96634600	0.90343500
H	0.97031900	-1.24411800	-0.96031000

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C	-2.16923200	-2.57777600	0.03508200
C	-3.47585000	-2.23485600	-0.39541200
C	-4.34517000	-3.20595100	-0.89176600
C	-3.97492000	-4.53988400	-0.95104400
C	-2.71510700	-4.91714600	-0.48624900
C	-1.84359200	-3.95583600	-0.00994000
H	-5.33124800	-2.87541200	-1.21327800
H	-4.67165000	-5.28118600	-1.33842500
H	-2.40646100	-5.96062800	-0.50830600
H	-0.85067400	-4.25361300	0.31395700
C	-1.10315300	-1.65840000	0.42969400
O	0.06383800	-2.29851000	0.75450600
C	-1.07024300	-0.25752900	0.47488700
C	0.11756700	0.48691100	0.68838500
C	1.49135200	0.21969900	0.36446700
C	1.92077000	-0.71898400	-0.60134600
C	2.48059600	1.01220600	0.98994800
C	3.26230300	-0.87119200	-0.88995800
H	1.18519700	-1.30852500	-1.14144000
C	3.82453100	0.85060300	0.70898300
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C	4.23229300	-0.10088200	-0.23383700
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C	0.29333400	-2.43412700	2.14690400
H	0.28465500	-1.45803100	2.65345100
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C	-2.35373000	3.19034100	-0.04103600
C	-2.15537600	4.12490500	1.02075300
C	-2.58662900	3.70363500	-1.35243000
C	-2.19116400	5.48331500	0.77255700
H	-1.97605300	3.74502000	2.02598700
C	-2.61732000	5.06685200	-1.57332300
H	-2.73673000	3.00129500	-2.17077700
C	-2.42156800	5.96784200	-0.52021000
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H	-2.79530600	5.44132200	-2.58052100
H	-2.44709600	7.04003400	-0.70597700
C	5.65077100	-0.32096900	-0.58562800
O	6.04045600	-1.14296700	-1.39052500
O	6.47892100	0.49342800	0.08730500
C	7.86392300	0.33365900	-0.20628800
H	8.06317200	0.53329000	-1.26523000
H	8.38986900	1.06014400	0.41741800
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H	-0.04466800	1.47686600	1.12413800

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C	-4.85230100	-3.70473600	-1.04284000

C	-3.86589000	-4.36429600	-0.31394200
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C	2.55226400	0.44145100	1.34414600
C	2.93473500	-1.11526100	-0.92843500
H	0.79960400	-1.23513700	-1.05737000
C	3.83599300	0.17186000	0.91277800
H	2.39332800	1.05270600	2.23284300
C	4.04332300	-0.61379900	-0.23022300
H	3.10809100	-1.71712100	-1.81862000
H	4.68918800	0.56712000	1.45927000
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H	0.05523300	-1.73439600	2.80487100
H	-1.30713900	-2.89740500	2.81656600
H	0.36173100	-3.47037000	2.51663400
O	-3.68747000	-0.27941400	-1.00189500
C	-3.49848900	0.61794200	0.09013100
H	-3.98234500	1.55939200	-0.19374200
H	-4.00636700	0.22105700	0.98417300
C	-2.03934700	0.81941200	0.33899500
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C	-1.27918100	3.88009400	-1.25804800
C	-1.37693400	5.65337500	0.89781900
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H	-1.23798700	3.17865800	-2.09017500
C	-1.27728200	6.13935400	-0.40782700
H	-1.41499300	6.34856500	1.73527200
H	-1.15255500	5.62291300	-2.49903600
H	-1.23493000	7.21199900	-0.58893400
C	5.39113800	-0.93808200	-0.74103500
O	5.60932300	-1.61405400	-1.72651200
O	6.36712800	-0.40088400	0.00819200
C	7.69469200	-0.67899800	-0.42769000
H	7.86171500	-0.29378300	-1.43985200
H	8.35638900	-0.17362800	0.27960900
H	7.88976700	-1.75735800	-0.41965100
H	0.06380300	0.90163200	2.00923400

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C	-3.52495700	-1.44135200	0.14637500
C	-4.00571000	-0.69903600	-0.95444200
C	-5.28864100	-0.92026800	-1.45159000
C	-6.12354100	-1.87392100	-0.88589600
C	-5.67064200	-2.61319100	0.20280300
C	-4.39373000	-2.39796200	0.69951400
H	-5.60519100	-0.32607300	-2.30719300
H	-7.12158100	-2.03339400	-1.29059200
H	-6.30978000	-3.36323000	0.66555900
H	-4.04156600	-2.98542700	1.54330400
C	-2.17073000	-1.30766300	0.72313900
O	-1.83336400	-2.42059200	1.41819700
C	-1.42371100	-0.18406900	0.60485300
C	-0.09432000	0.42175900	1.11015000
C	1.19495700	-0.15591300	0.58916700
C	1.35245500	-0.45952400	-0.76789000
C	2.26644000	-0.38186100	1.45699300
C	2.54724800	-0.97906400	-1.23825400
H	0.52492400	-0.29158800	-1.45731900
C	3.46776600	-0.90109300	0.99071100
H	2.15085700	-0.14938800	2.51690500
C	3.61567200	-1.20479900	-0.36400300
H	2.67219400	-1.21980100	-2.29232900
H	4.29181700	-1.07319900	1.67928700
C	-0.57296700	-2.47592900	2.04815100
H	0.23964900	-2.42000000	1.31181000
H	-0.45478500	-1.67483000	2.79196200
H	-0.52720200	-3.44289900	2.55767600
O	-3.25617100	0.22030800	-1.63489800
C	-2.88271600	1.38708700	-0.90487300
H	-2.64148200	2.15036000	-1.65562800
H	-3.74333200	1.75375900	-0.31946900
C	-1.72164000	1.07366000	-0.04462100
C	-0.58764600	1.68381700	0.40009700
C	-0.00043200	2.99998100	0.30052800
C	1.29530600	3.23553500	0.78764800
C	-0.70378200	4.07486600	-0.27147600
C	1.87385800	4.49459000	0.68915200
H	1.85402500	2.41668600	1.24110900
C	-0.12054500	5.33007000	-0.37197500
H	-1.72470400	3.92532900	-0.62313500
C	1.17154400	5.54633500	0.10566500
H	2.88127800	4.65562500	1.07042000
H	-0.68094600	6.15010300	-0.81886600
H	1.62522300	6.53315200	0.02921800
C	4.86784400	-1.76334000	-0.92461500
O	5.03292100	-2.03667700	-2.09553700

O	5.81392400	-1.93842500	0.00950200
C	7.04820000	-2.47306800	-0.46238000
H	7.50038100	-1.80919500	-1.20769100
H	7.69671900	-2.55056000	0.41320200
H	6.89861100	-3.46255400	-0.90874600
H	-0.03707300	0.52632100	2.20480800

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C	-3.17474800	-1.23268000	-0.04407800
C	-4.33908700	-0.47801900	-0.33959000
C	-5.41410000	-1.07738900	-1.01265000
C	-5.39552900	-2.40898300	-1.37446900
C	-4.28156900	-3.18676800	-1.05503200
C	-3.21200800	-2.60127600	-0.40848900
H	-6.27678100	-0.44635400	-1.21904300
H	-6.25004300	-2.84346100	-1.89057500
H	-4.24329400	-4.24128100	-1.32089100
H	-2.33415200	-3.20197200	-0.18965000
C	-1.89289800	-0.76059800	0.52161600
O	-1.03887400	-1.78116900	0.85155800
C	-1.45216100	0.51640300	0.73112200
C	-0.13625800	0.77650100	1.27363500
C	1.08673100	0.18239900	0.79411300
C	1.23982500	-0.26179800	-0.53293100
C	2.19894700	0.10654800	1.65333300
C	2.44606700	-0.77795700	-0.96816700
H	0.39715800	-0.19001900	-1.21981500
C	3.40557600	-0.41267400	1.21896900
H	2.09821200	0.46496700	2.67888800
C	3.54101800	-0.86292600	-0.09973600
H	2.56377900	-1.12237200	-1.99390500
H	4.25110300	-0.47132400	1.90052300
C	-1.17075500	-2.24117000	2.18405600
H	-0.90796400	-1.44808200	2.90203900
H	-2.19531200	-2.58727400	2.39143700
H	-0.47599800	-3.07815500	2.30366500
O	-4.57922000	0.81340300	-0.03852000
C	-3.80504800	1.46803400	0.95928000
H	-4.30744700	2.42907700	1.10839400
H	-3.85717900	0.88735700	1.89369500
C	-2.38949600	1.67407500	0.52626100
C	-1.92900400	2.75034600	-0.10526300
C	-0.59446000	3.02054600	-0.35597100
C	0.29865300	3.05282000	0.76482000
C	-0.03770900	3.08564800	-1.66801300
C	1.68695100	3.21770200	0.55583300
H	-0.11879900	3.24692200	1.74901900
C	1.31953200	3.13565700	-1.83715700
H	-0.71112200	3.04842700	-2.52299800
C	2.19485400	3.20367600	-0.71858800
H	2.35015300	3.32146600	1.41359000
H	1.74071900	3.13415900	-2.84153000
H	3.26763800	3.28728800	-0.88561200
C	4.80438100	-1.42174900	-0.62568800
O	4.96166400	-1.81448900	-1.76413400
O	5.77663700	-1.45212900	0.29934800
C	7.02276400	-1.98407400	-0.14163300
H	7.43031300	-1.38958300	-0.96706300
H	7.69221100	-1.93740500	0.72042200
H	6.90820700	-3.02254100	-0.47240300
H	-0.10586700	1.14145300	2.30229800

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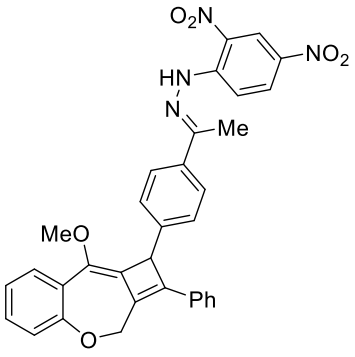
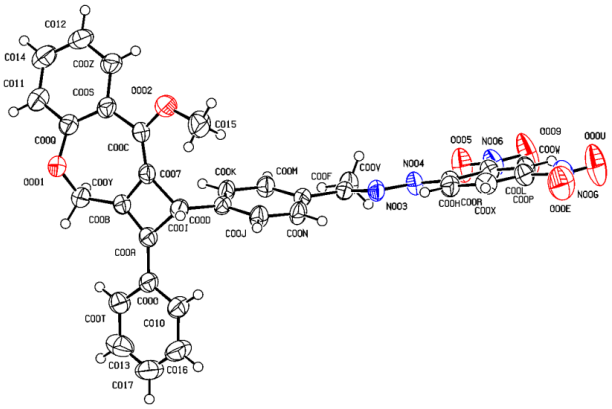
C	-3.15551700	-1.14422400	0.16367300
C	-4.03423500	-0.67035000	-0.84079400
C	-5.01025500	-1.51341900	-1.38235700
C	-5.15703000	-2.82070300	-0.95481400
C	-4.31624300	-3.30801100	0.04426900
C	-3.34368100	-2.48175000	0.57701800
H	-5.65523000	-1.09309100	-2.15204900
H	-5.92753500	-3.45266300	-1.39331300
H	-4.40743600	-4.33359300	0.39691100
H	-2.66189000	-2.88188000	1.32220900
C	-1.99761400	-0.43227500	0.74013800
O	-1.33042700	-1.14020500	1.71520100
C	-1.45495000	0.76385700	0.38882700
C	-0.14035800	1.20210700	1.02901500
C	1.03400700	0.37579000	0.55256200
C	1.16866600	-0.00977000	-0.78451200
C	2.02307400	-0.00912800	1.46199100
C	2.27071400	-0.74224500	-1.20072200
H	0.39888000	0.26122900	-1.50702700
C	3.12605900	-0.74534200	1.05426400
H	1.91909100	0.27075000	2.51157200
C	3.25918600	-1.11466300	-0.28695300
H	2.37786000	-1.04103300	-2.24176900
H	3.88388500	-1.04032700	1.77646400
C	-1.87066200	-0.96707000	3.01455300
H	-1.85395400	0.09197500	3.31610700
H	-2.90764800	-1.33047700	3.07756100
H	-1.24537200	-1.54756400	3.70042900
O	-4.02591900	0.56561700	-1.39355200
C	-3.60084300	1.67164500	-0.60357000
H	-3.98208700	2.55755000	-1.12135700
H	-4.07238800	1.60949000	0.39037200
C	-2.11622800	1.72797700	-0.48874300
C	-1.33089700	2.67143100	-1.03399000
C	-0.09063400	3.01534100	-0.62782500

C	0.11584300	2.75909000	0.85300000
C	1.02875500	3.36946700	-1.44762800
C	1.43954800	3.19921800	1.37460300
H	-0.67790000	3.23977200	1.44311500
C	2.23809200	3.62174700	-0.88481300
H	0.88221700	3.43461900	-2.52514200
C	2.43129900	3.58027600	0.54910800
H	1.57559900	3.22654800	2.45663000
H	3.08531400	3.88554800	-1.51617700
H	3.39322700	3.89457100	0.95153000
C	4.41008300	-1.90048500	-0.78795300
O	4.56128500	-2.23689900	-1.94437200
O	5.28348300	-2.20678300	0.18319200
C	6.41719800	-2.96421800	-0.23144100
H	7.00162200	-2.41412400	-0.97758500
H	7.01567300	-3.12731400	0.66776600
H	6.10874100	-3.92562900	-0.65713300
H	-0.21829600	1.05604500	2.11569800

IX. X-Ray Crystallographic Data





Single crystal preparation: Compound **4** (1 mg) was dissolved in acetonitrile (4 mL), n-hexane (5 mL) was added. Then the cap of the sample vial was closed, followed by slow evaporation of the solvent at room temperature until crystals formed.

X-ray structure of **4** (CCDC 2192133)

Table 1 Crystal data and structure refinement for 4.

Identification code	HWL_7_5
Empirical formula	$C_{33}H_{26}N_4O_6$
Formula weight	574.58
Temperature/K	243.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.5972(12)
b/Å	10.0613(8)
c/Å	21.8687(17)
α/°	90
β/°	90.553(7)
γ/°	90
Volume/Å^3	2771.6(4)
Z	4
ρ_{calc} g/cm^3	1.377
μ/mm^{-1}	0.097
F(000)	1200.0
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.726 to 62.182
Index ranges	$-16 \le h \le 17$, $-13 \le k \le 11$, $-27 \le l \le 28$
Reflections collected	25602
Independent reflections	6910 [R_{int} = 0.0742, R_{sigma} = 0.0733]
Data/restraints/parameters	6910/0/390
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0608, wR_2 = 0.1611
Final R indexes [all data]	R_1 = 0.1193, wR_2 = 0.1859

Largest diff. peak/hole / e $Å^{-3}$	0.34/-0.29

X. References

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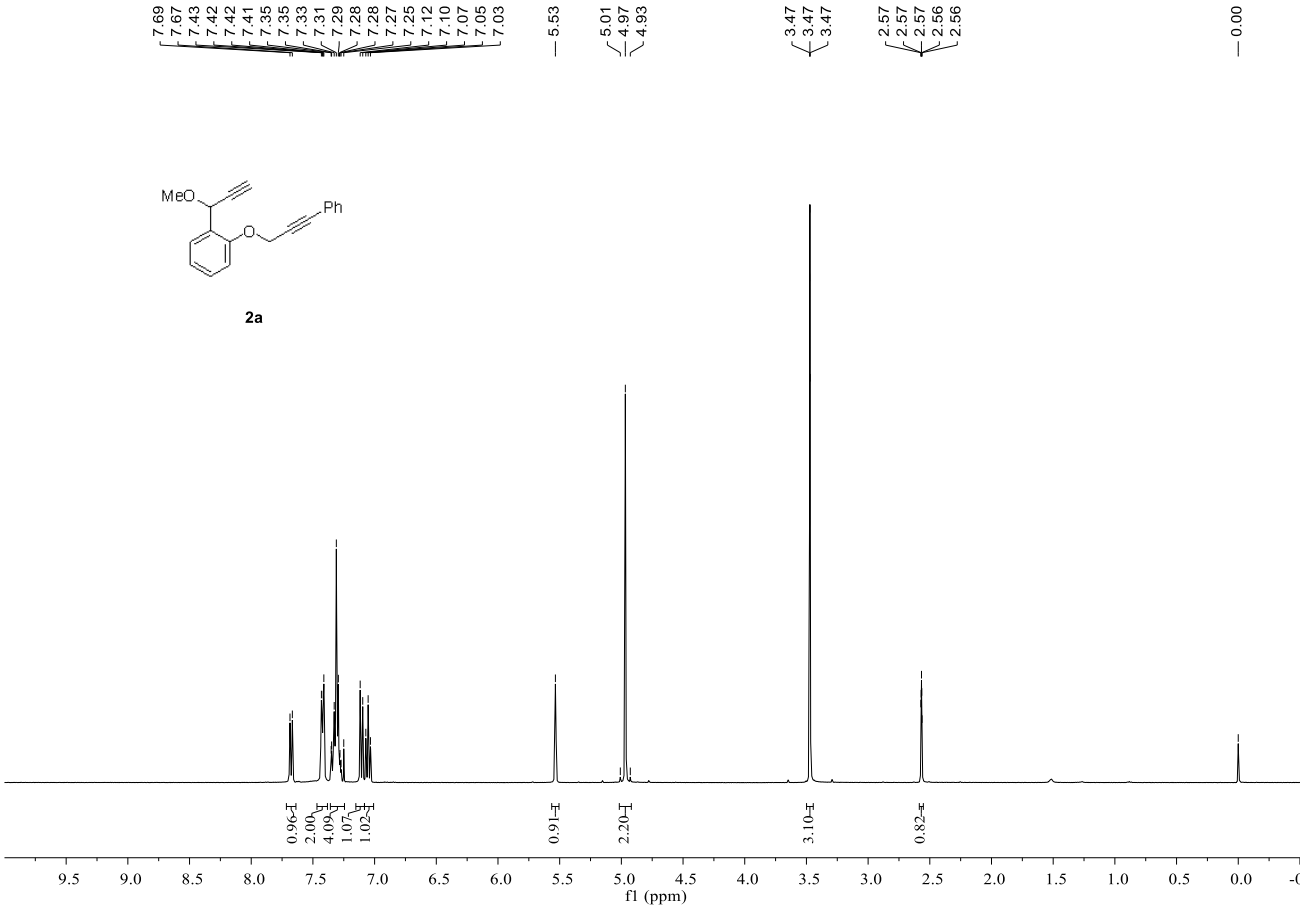
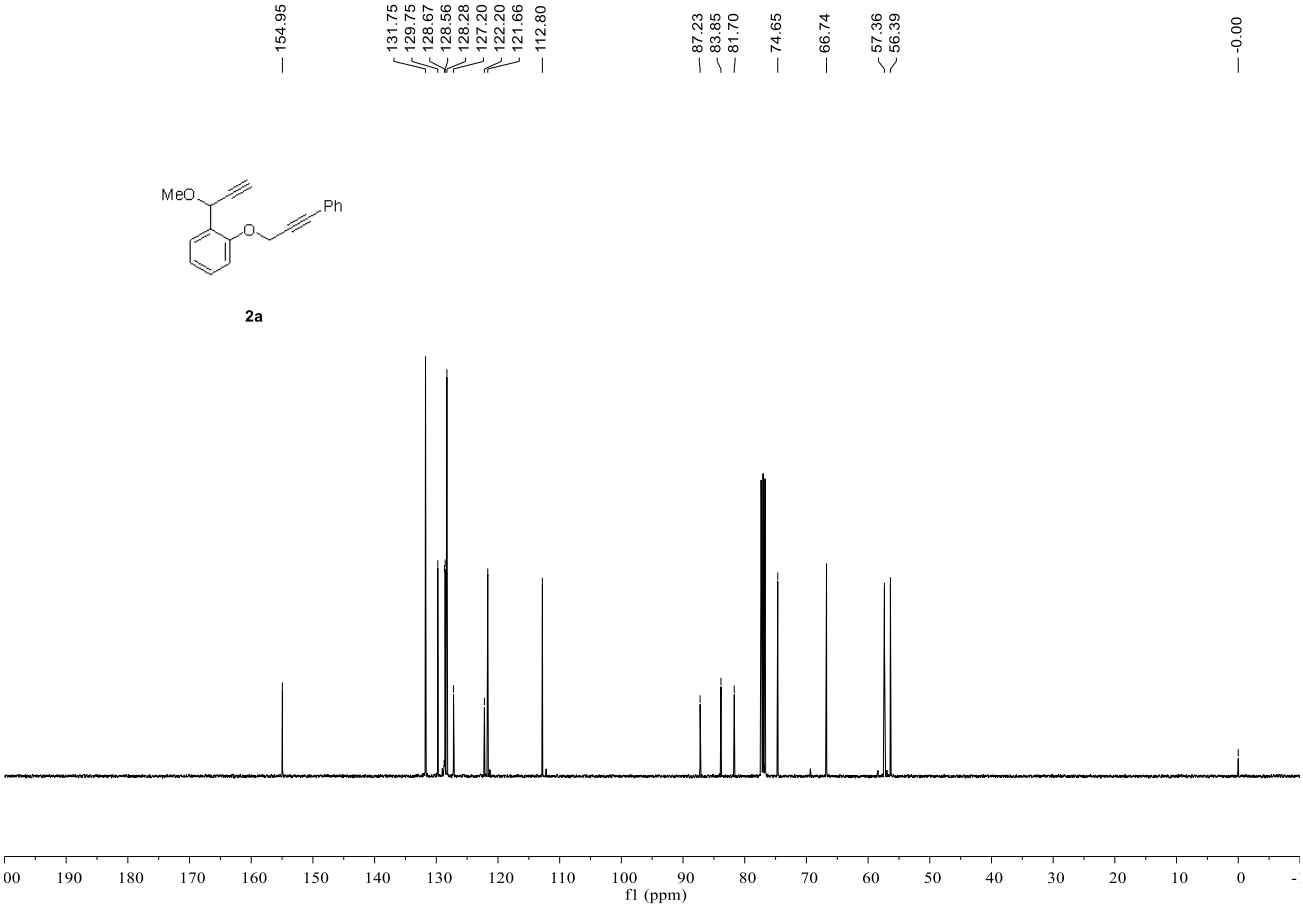
XI. NMR Spectra

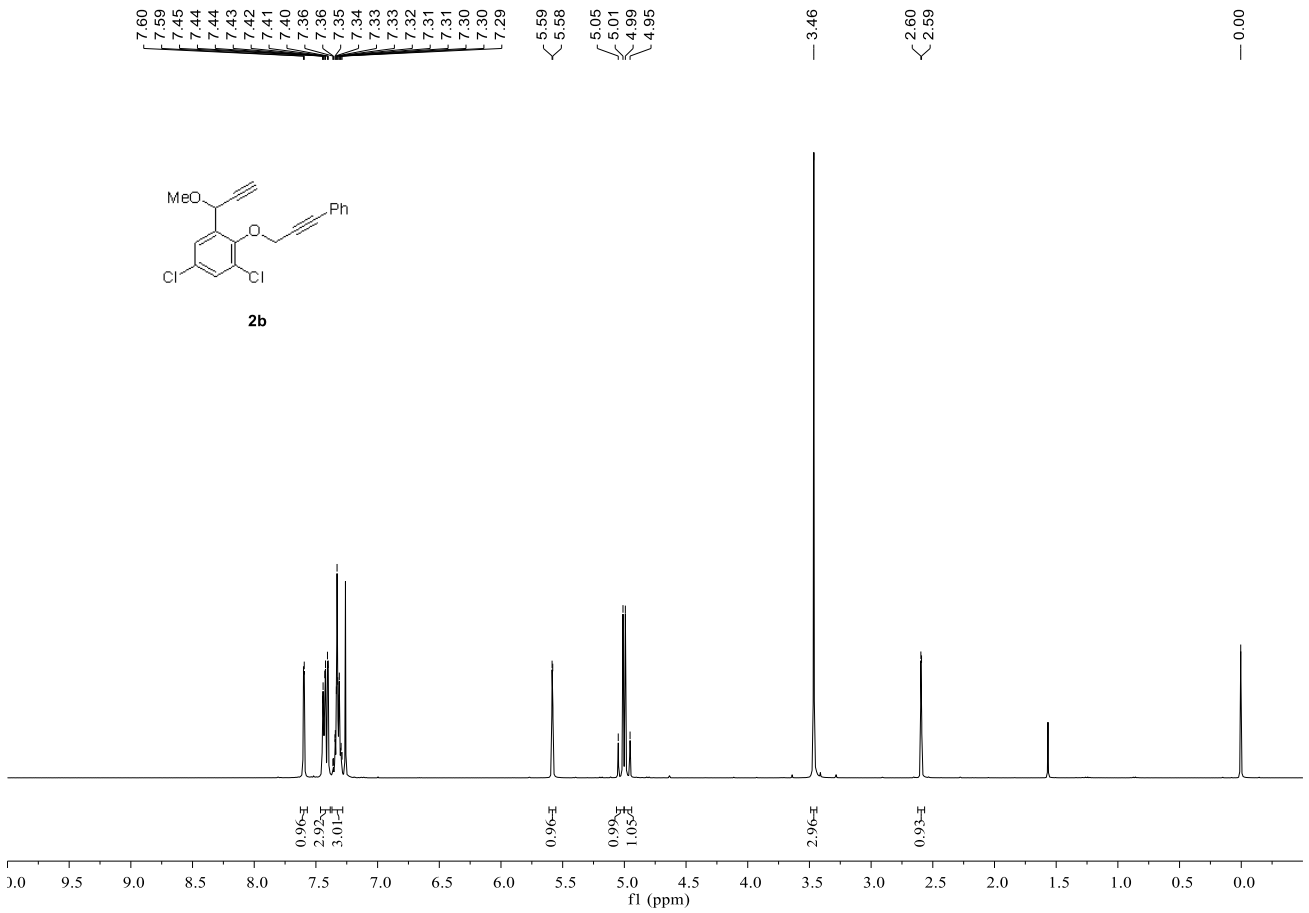
^{1}H NMR (400 MHz) of **2a** in $CDCl_3$



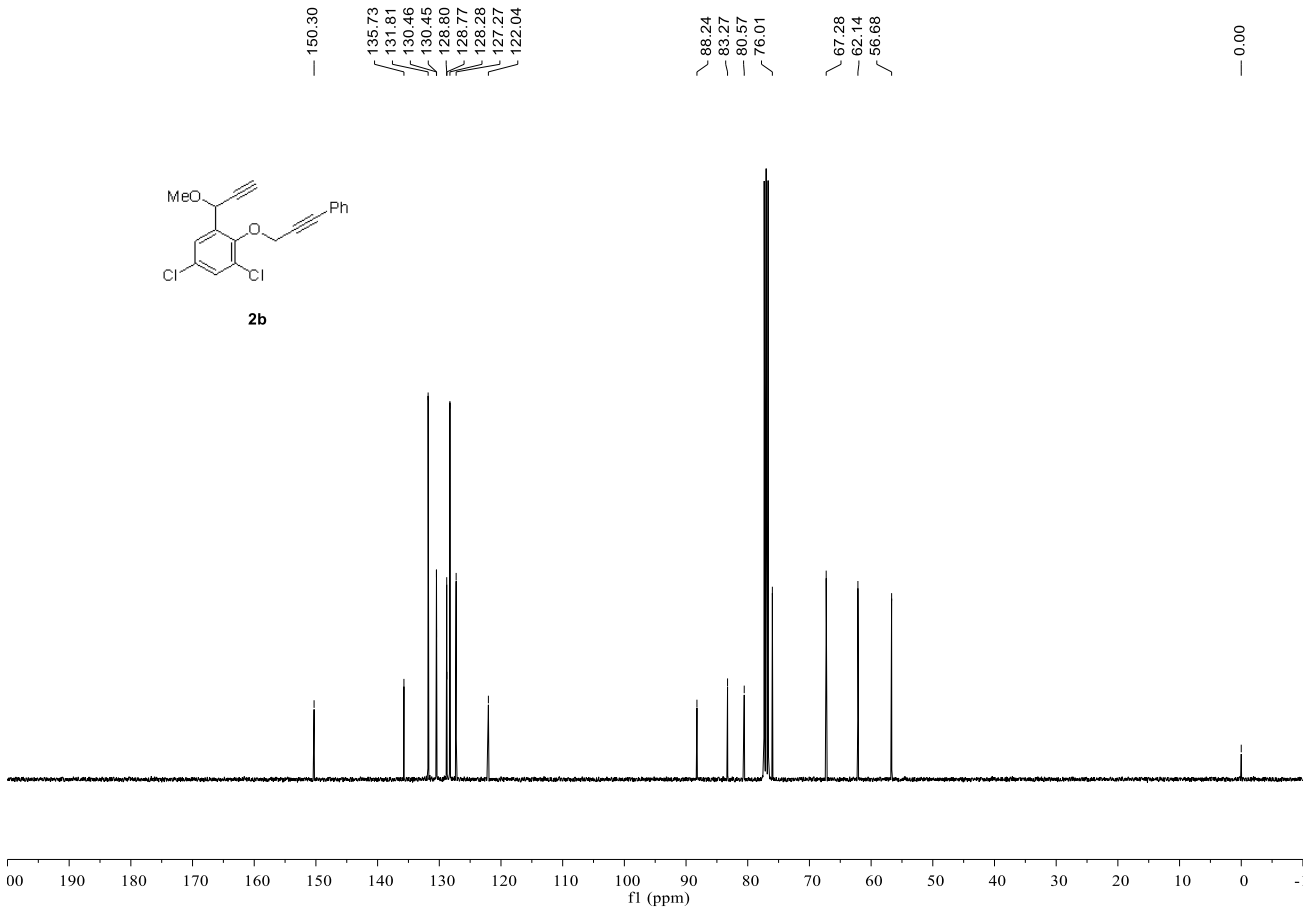
^{13}C NMR (100 MHz) of **2a** in $CDCl_3$



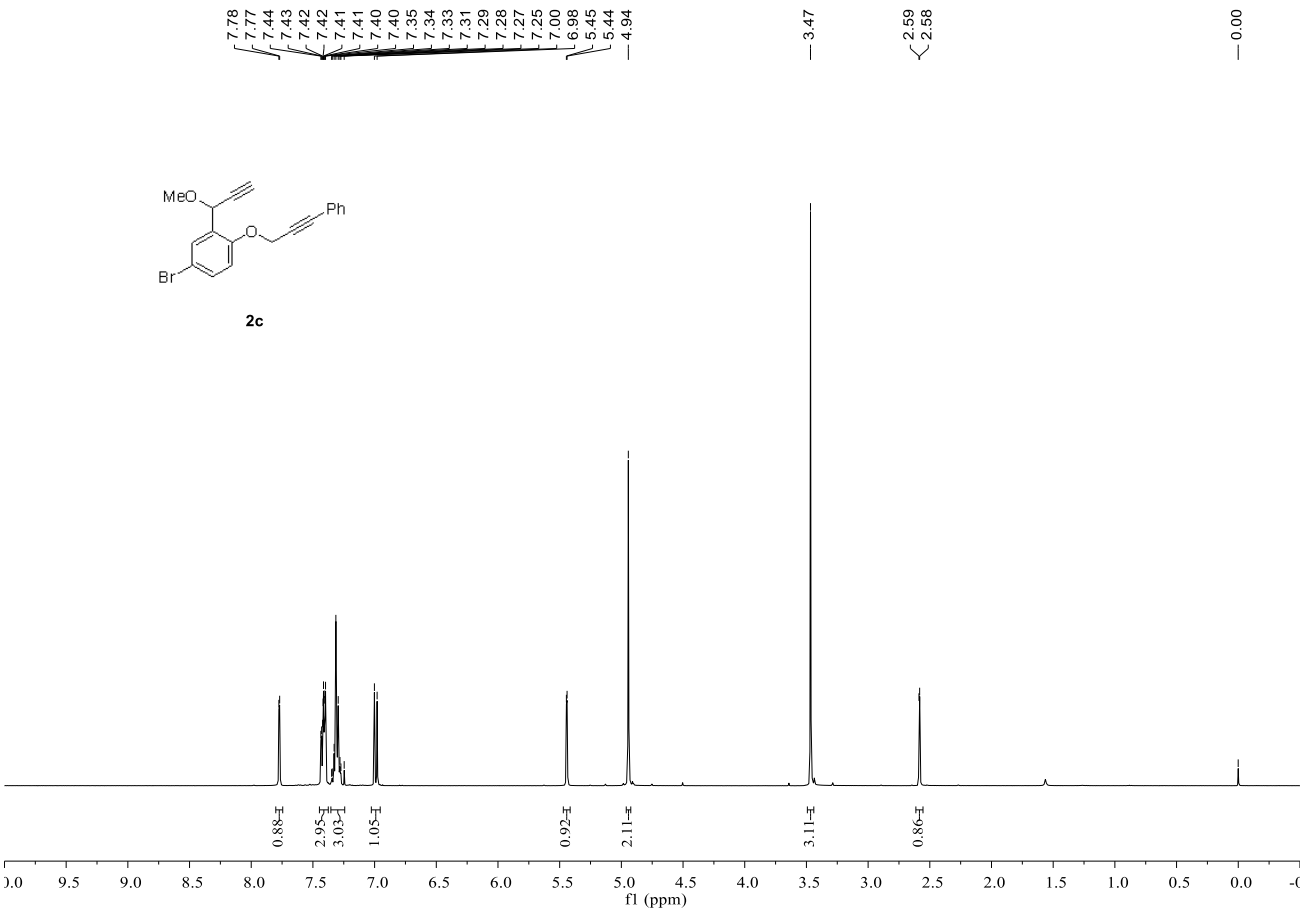
^{1}H NMR (400 MHz) of **2b** in $CDCl_3$



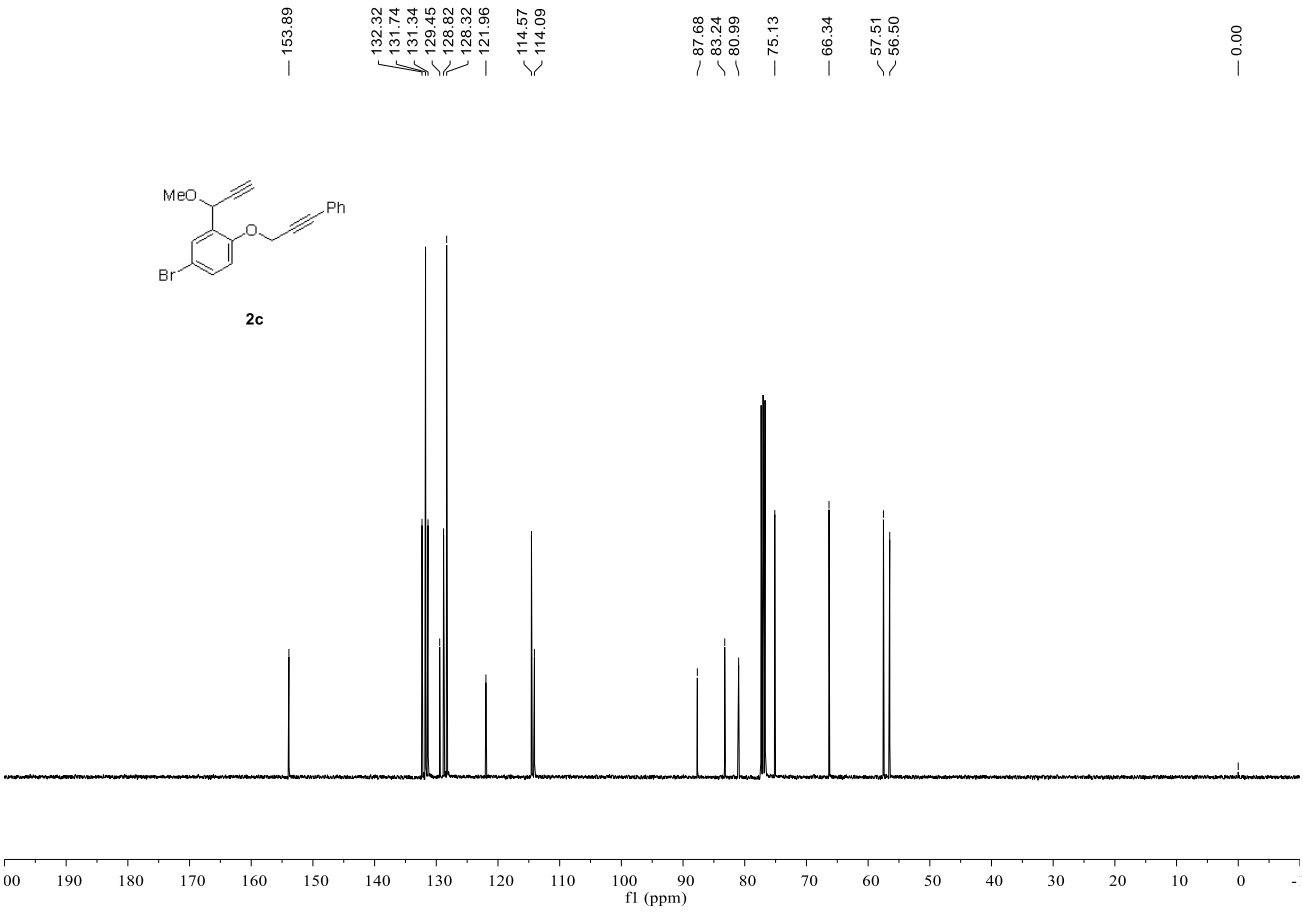
^{13}C NMR (100 MHz) of **2b** in $CDCl_3$



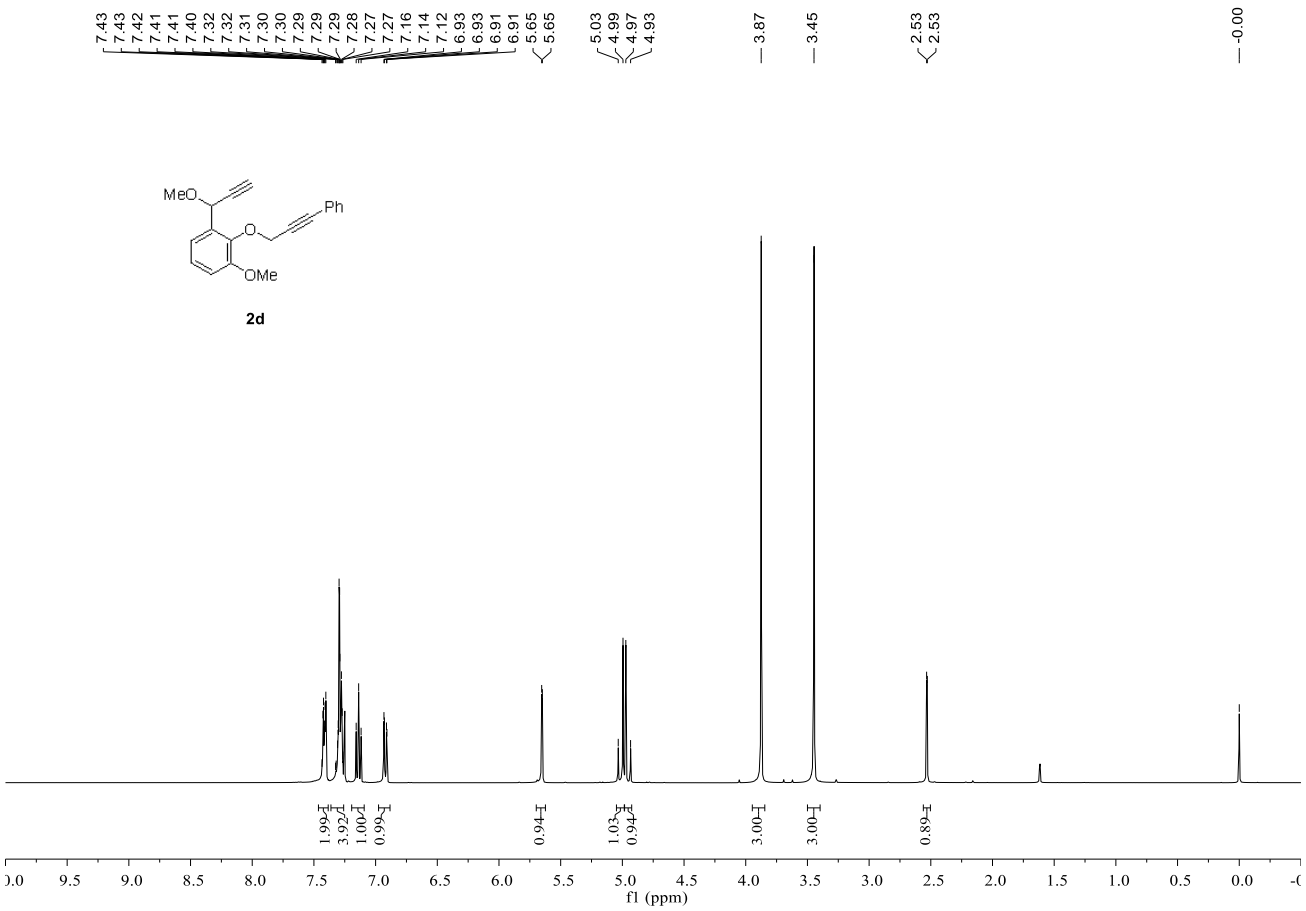
^{1}H NMR (400 MHz) of **2c** in $CDCl_3$



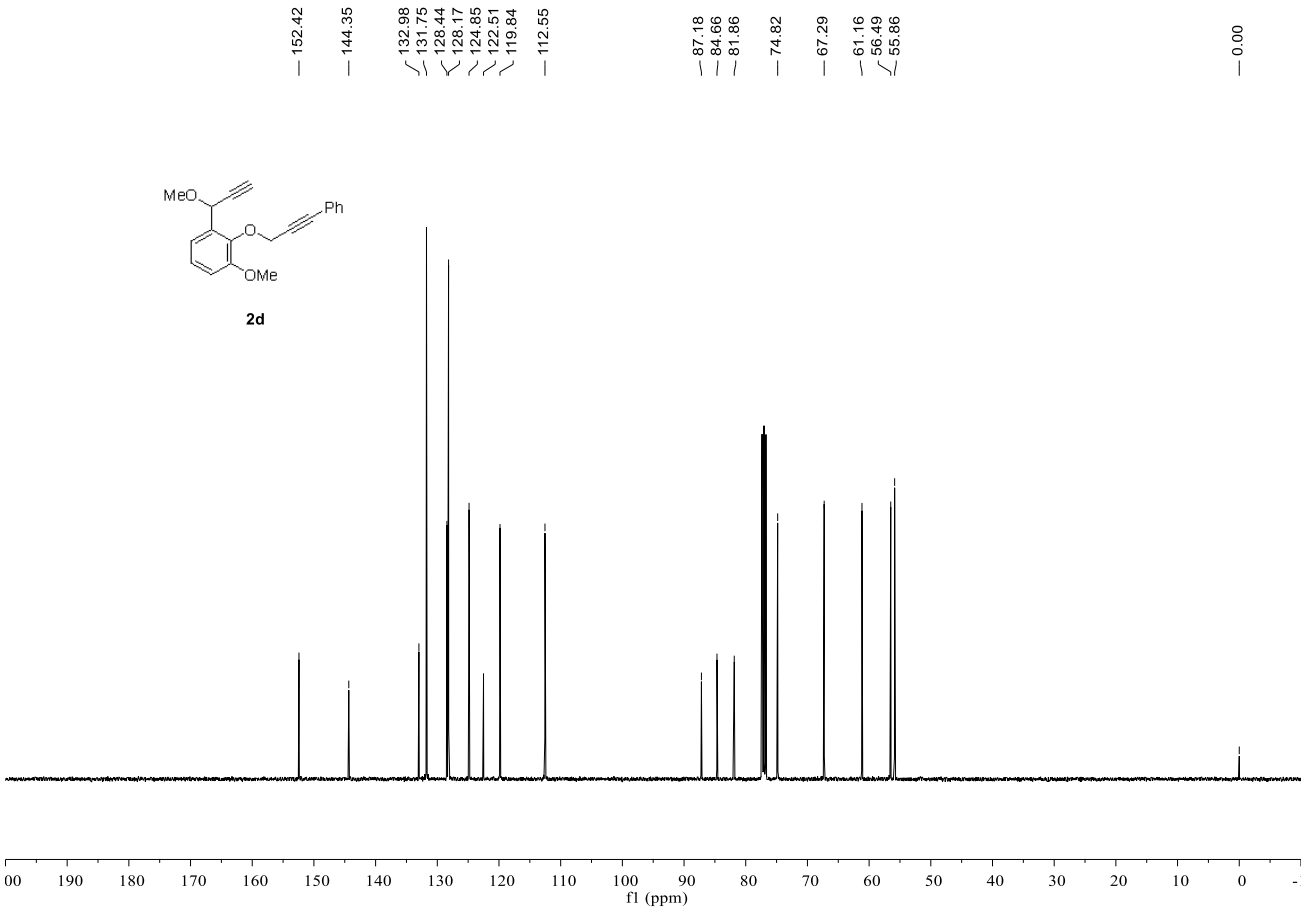
^{13}C NMR (100 MHz) of **2c** in $CDCl_3$



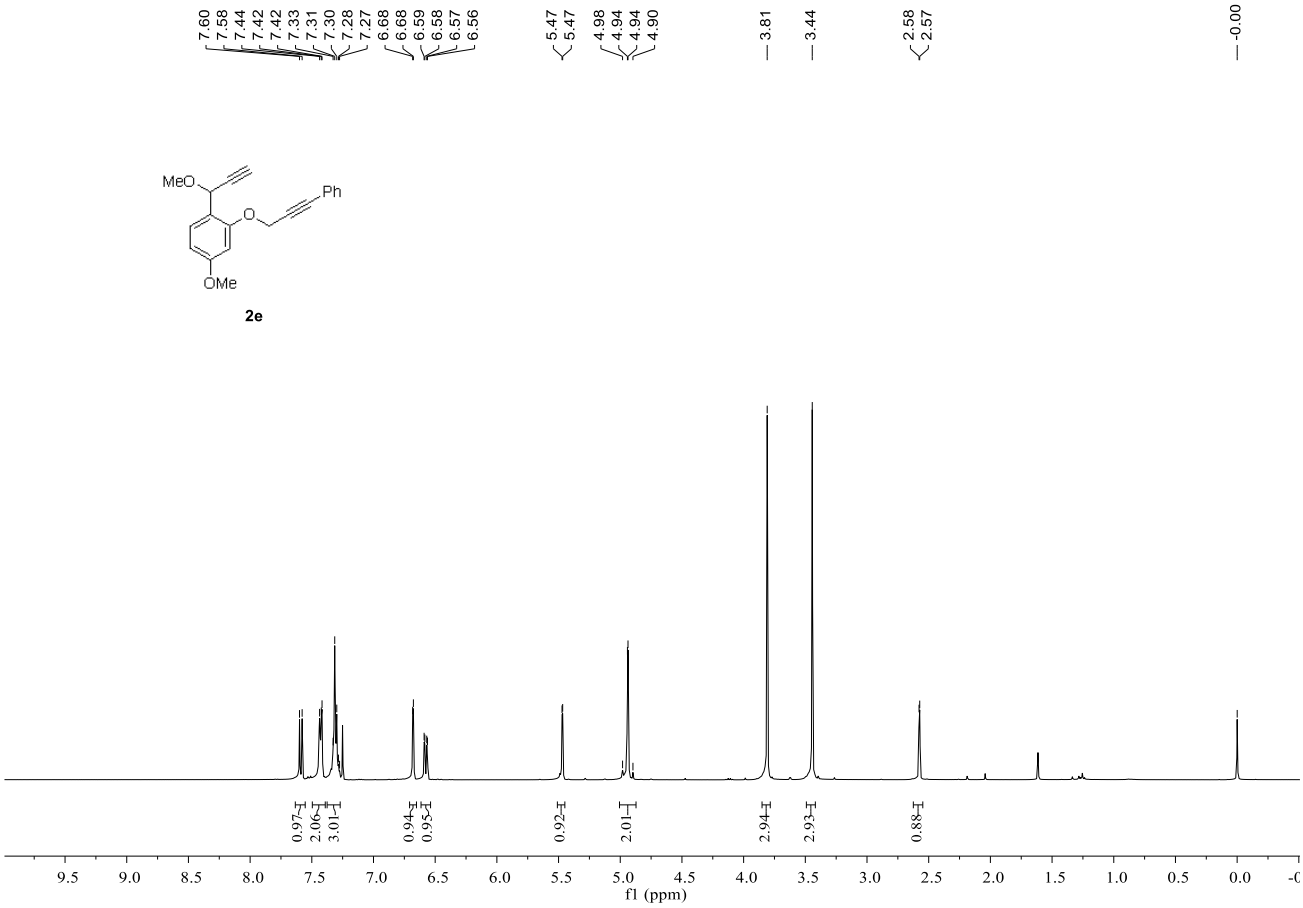
^{1}H NMR (400 MHz) of **2d** in $CDCl_3$



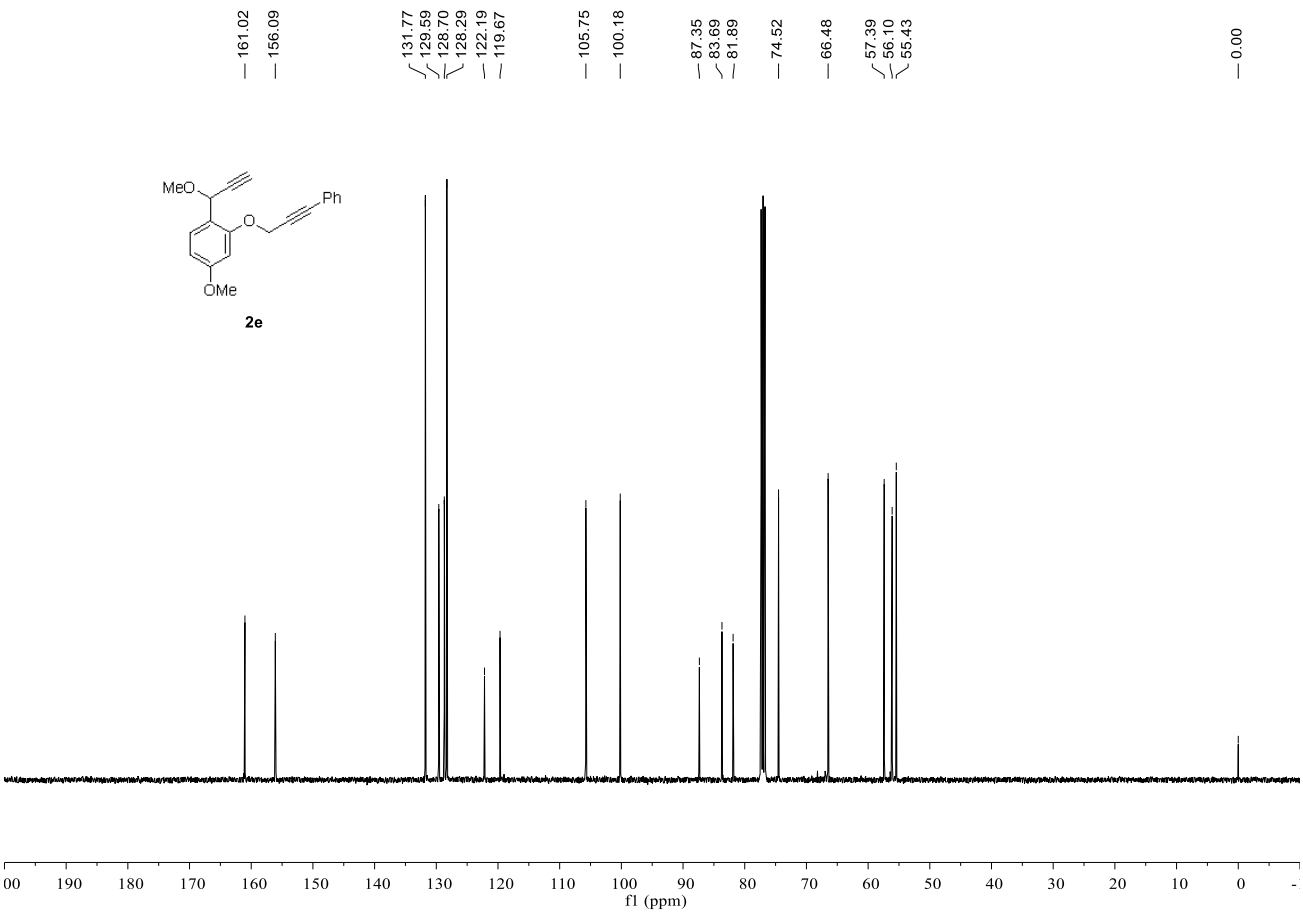
^{13}C NMR (100 MHz) of **2d** in $CDCl_3$



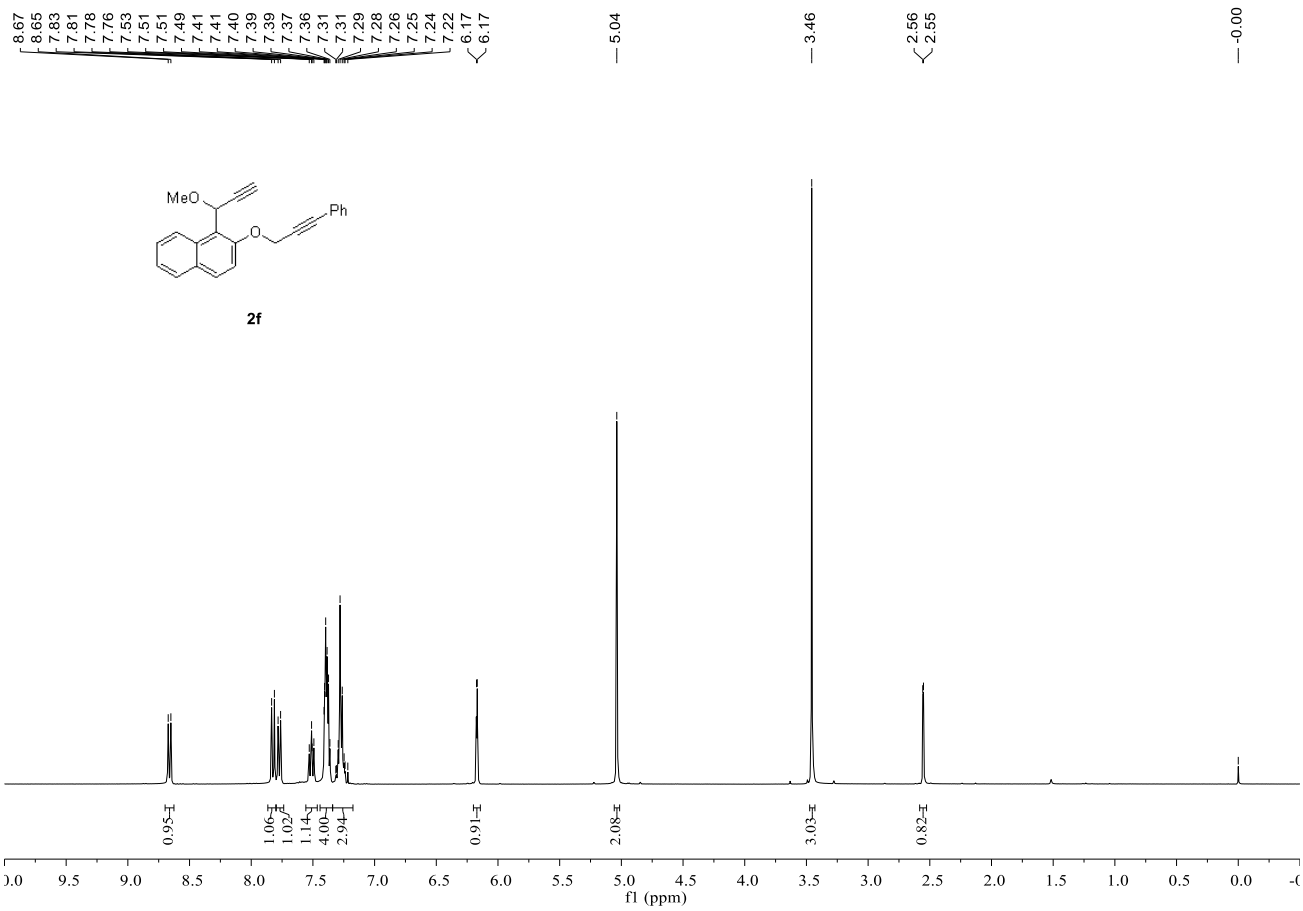
^{1}H NMR (400 MHz) of **2e** in $CDCl_3$



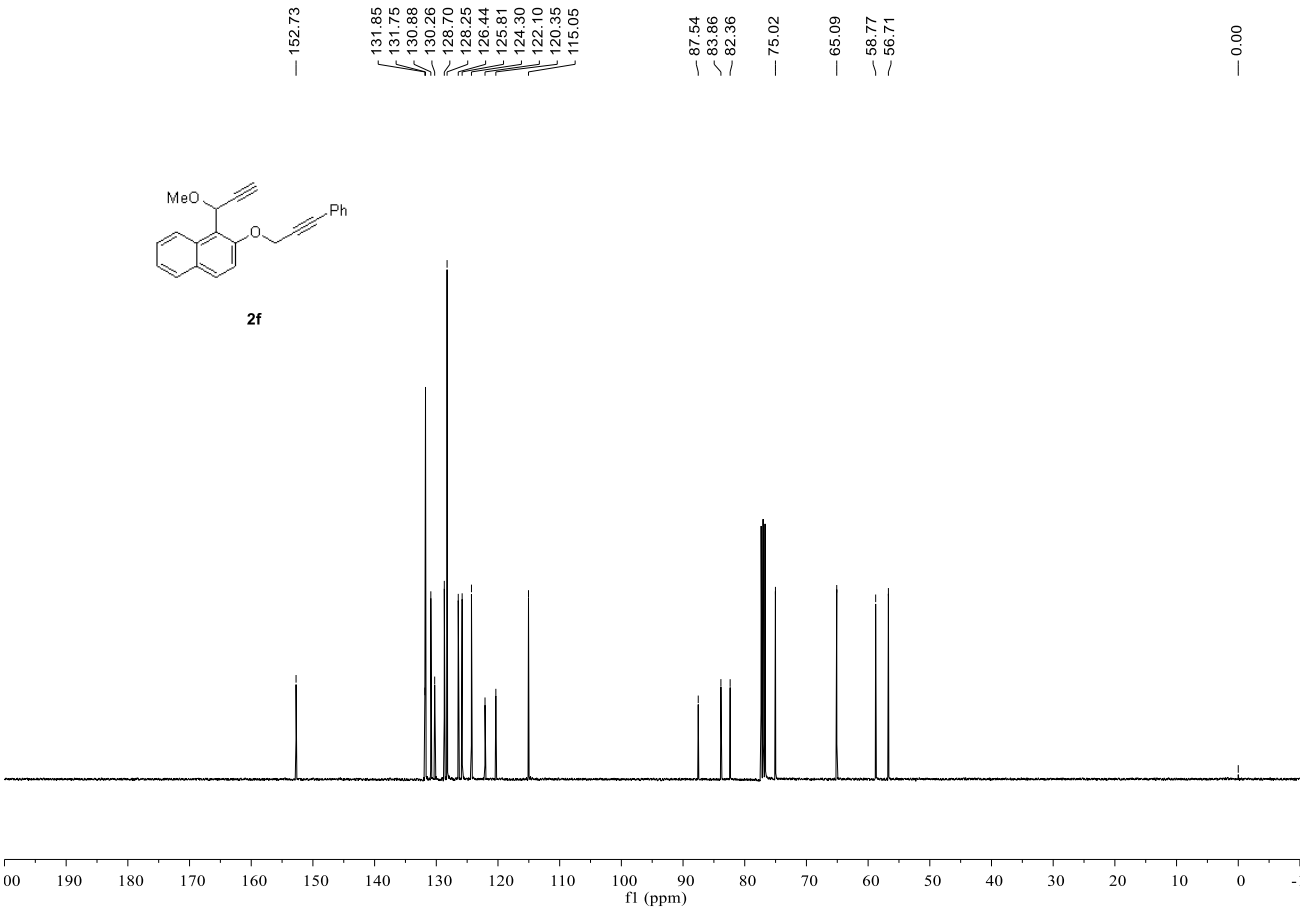
^{13}C NMR (100 MHz) of **2e** in $CDCl_3$



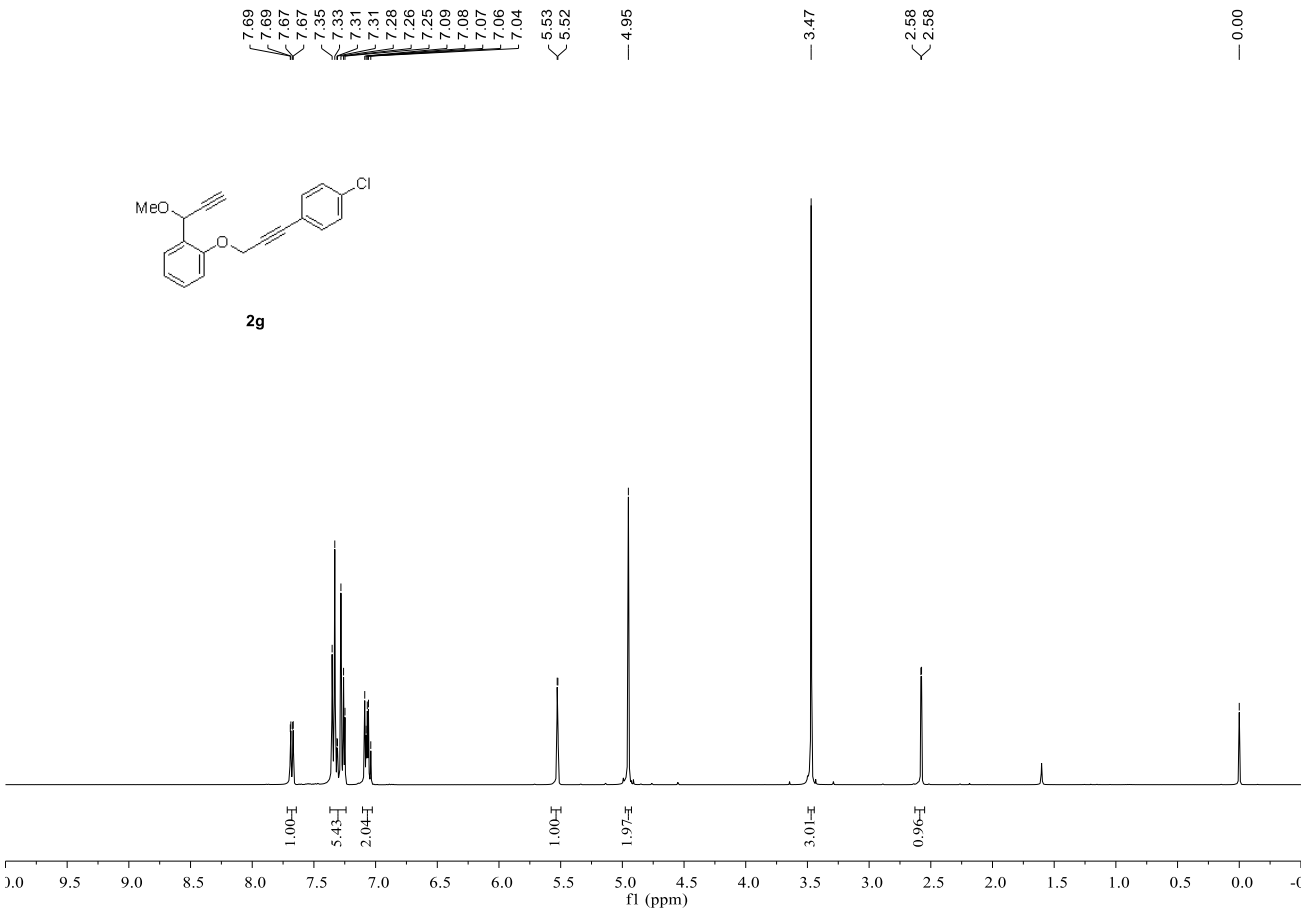
^{1}H NMR (400 MHz) of **2f** in $CDCl_3$



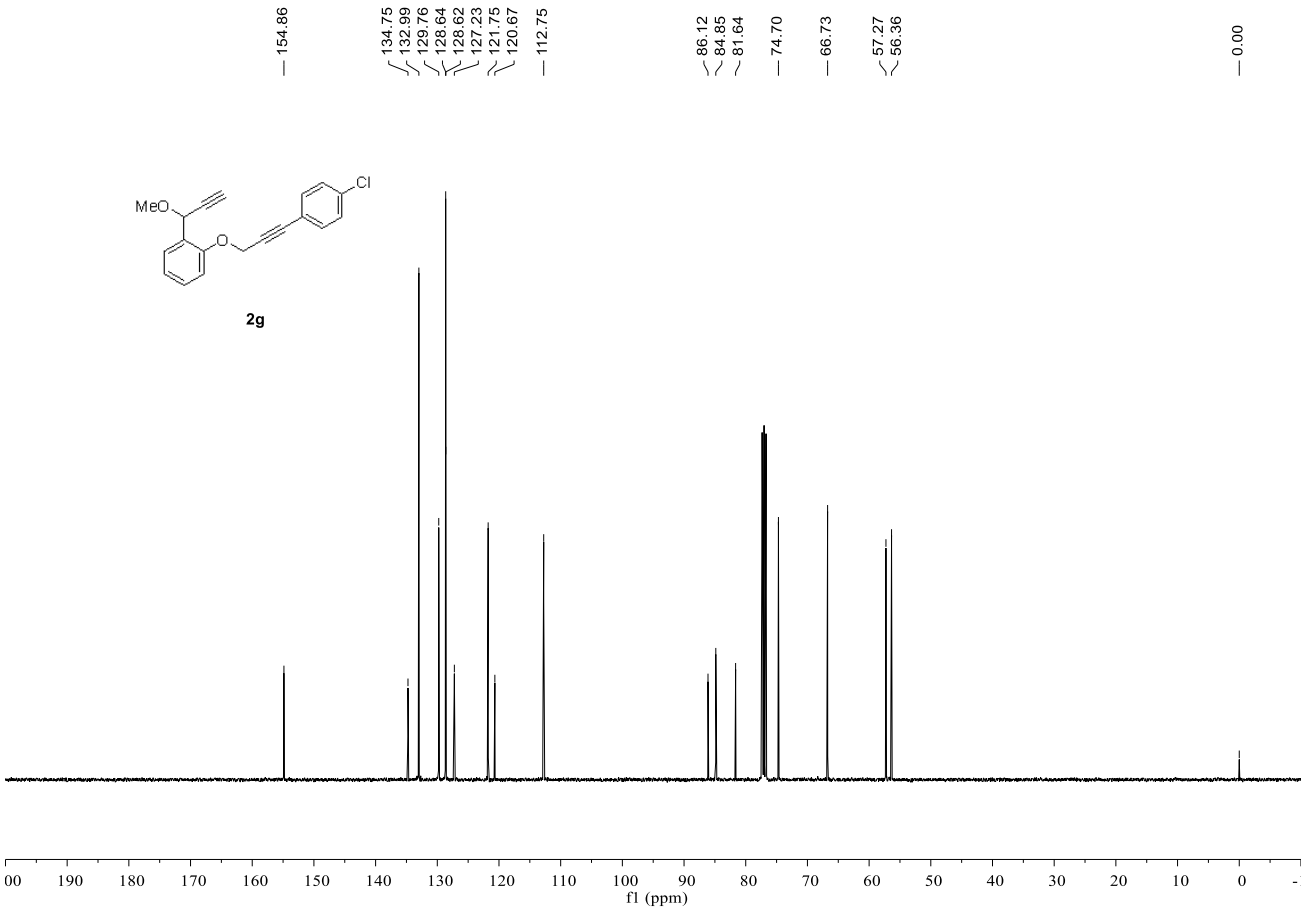
^{13}C NMR (100 MHz) of **2f** in $CDCl_3$



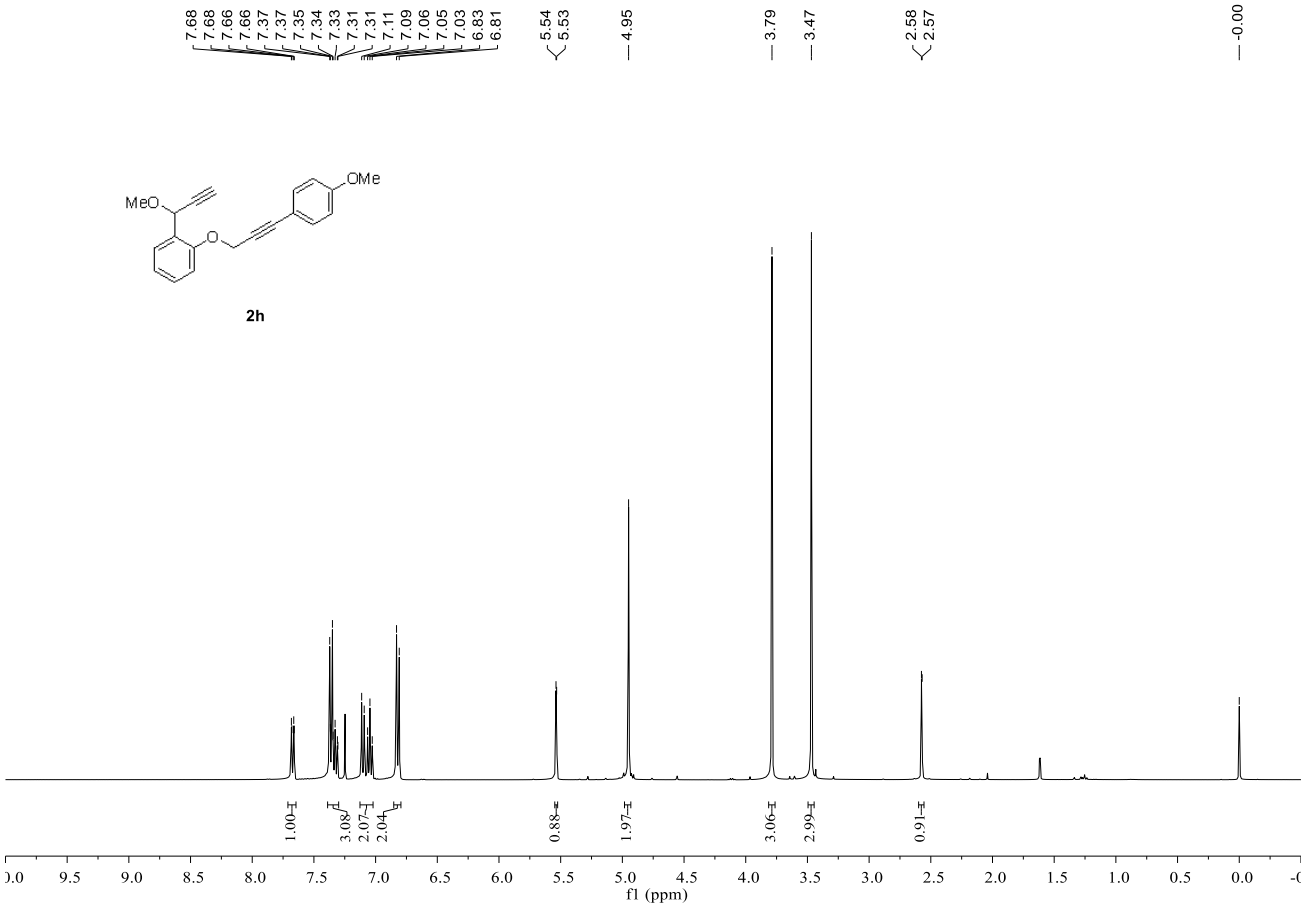
^{1}H NMR (400 MHz) of **2g** in $CDCl_3$



^{13}C NMR (100 MHz) of **2g** in $CDCl_3$



^{1}H NMR (400 MHz) of **2h** in $CDCl_3$



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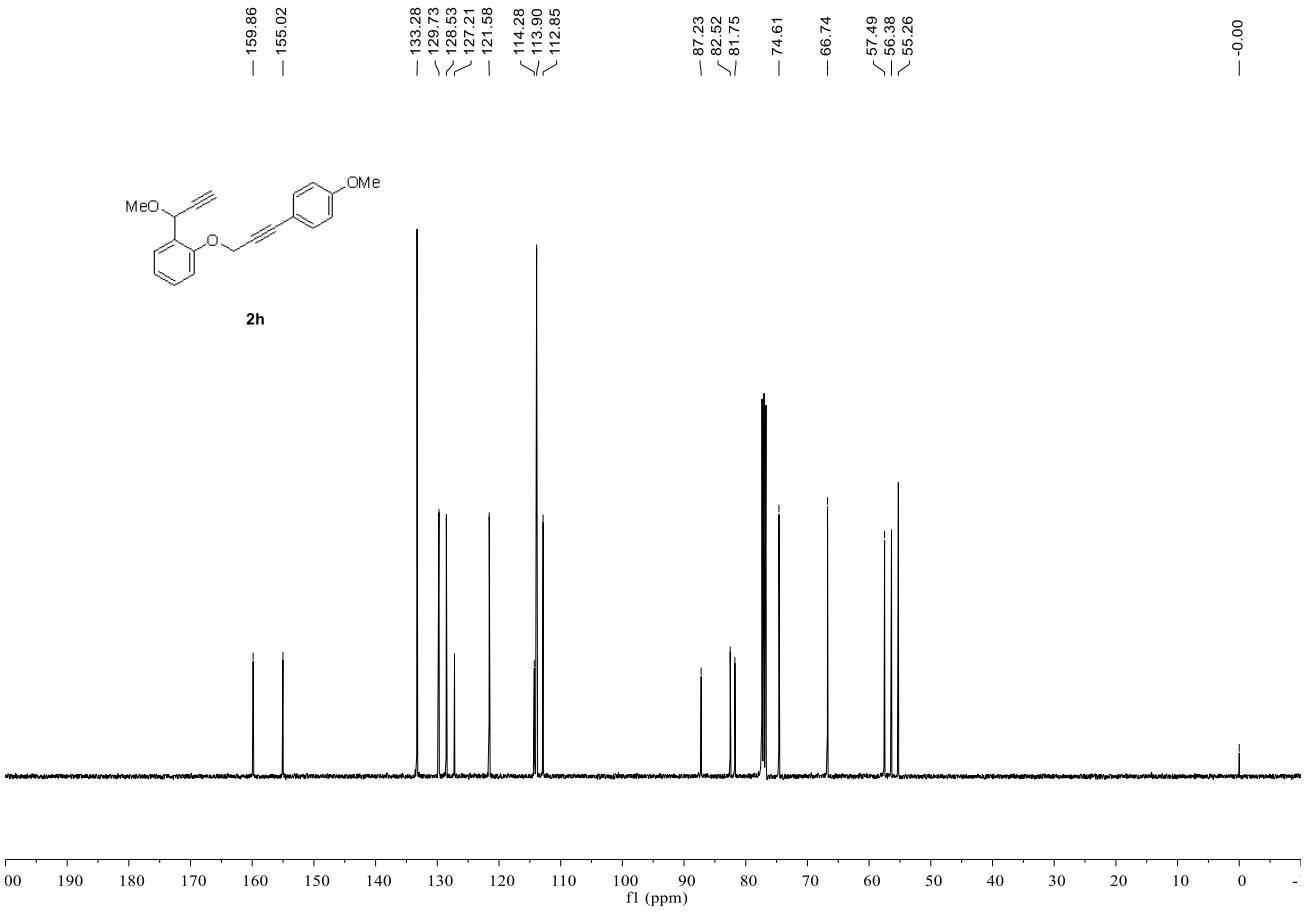
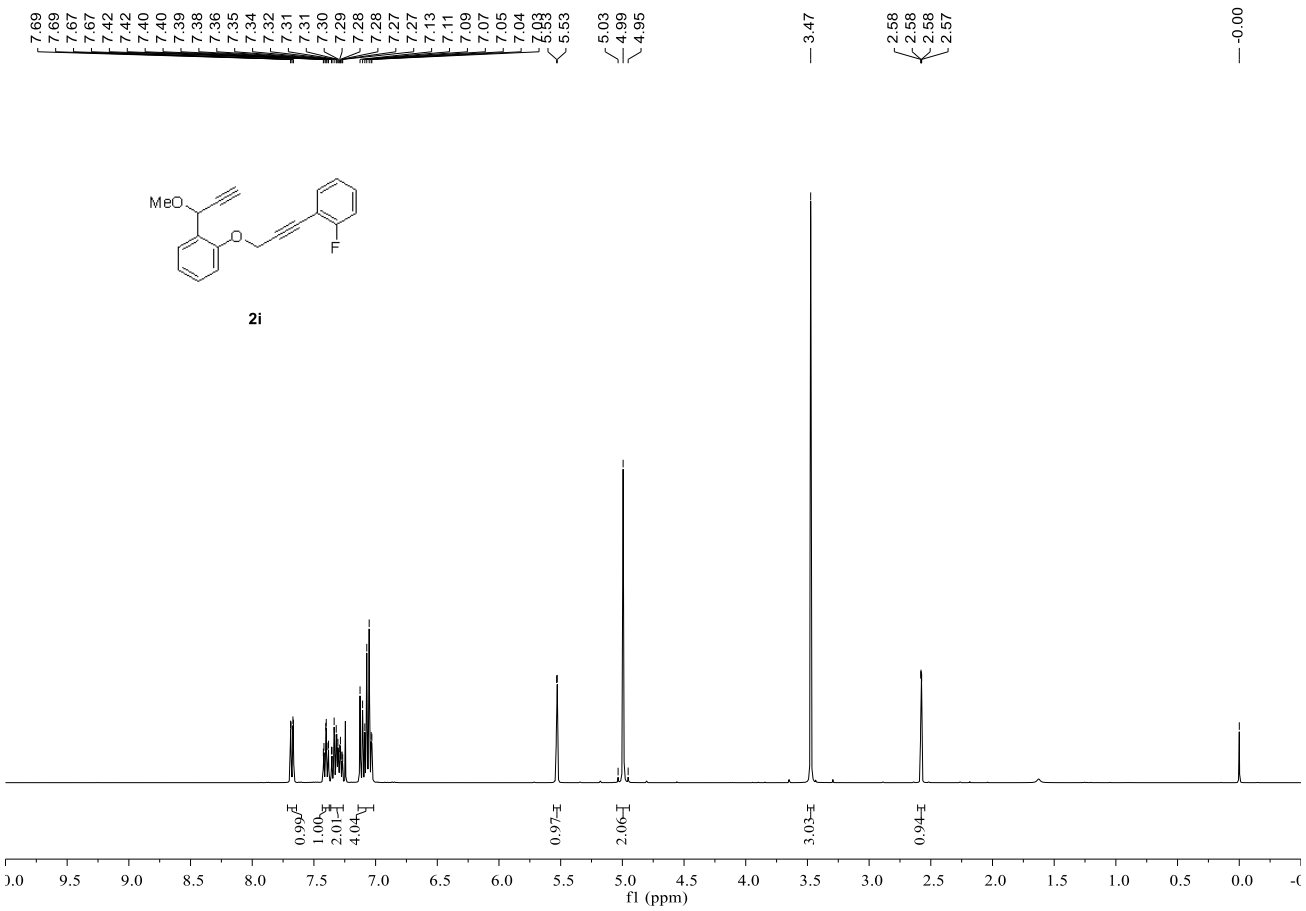
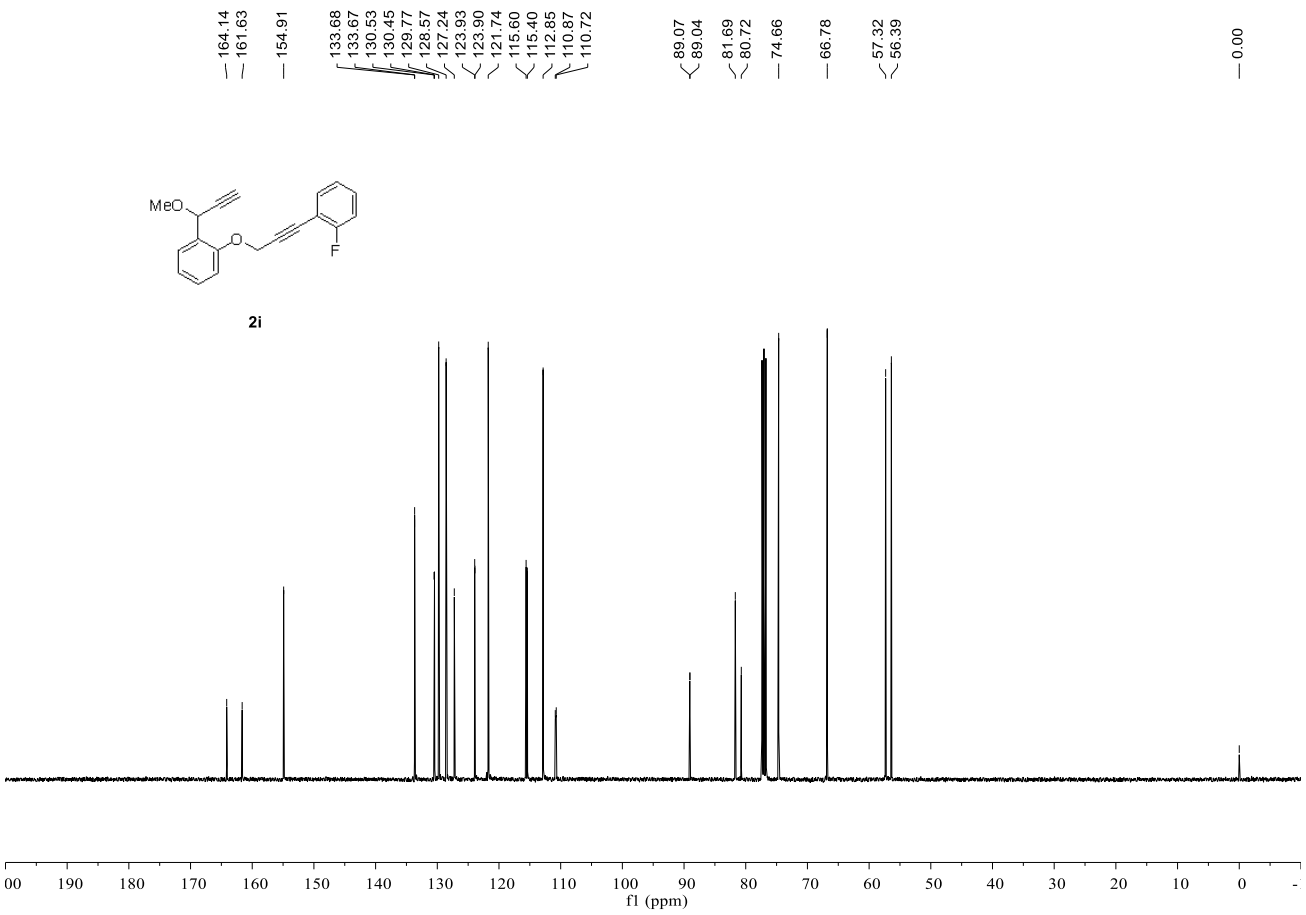


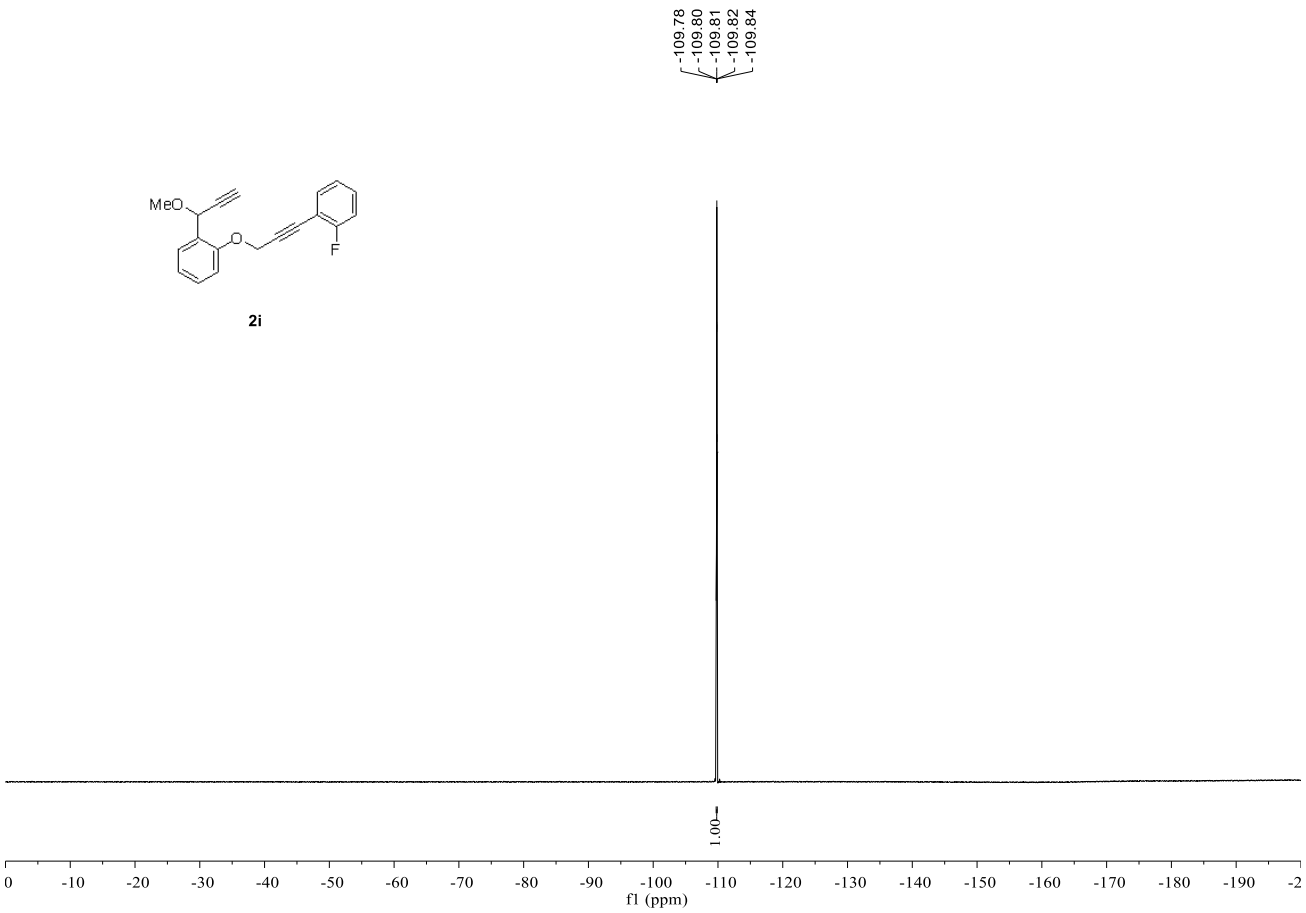
^{1}H NMR (400 MHz) of **2i** in $CDCl_3$



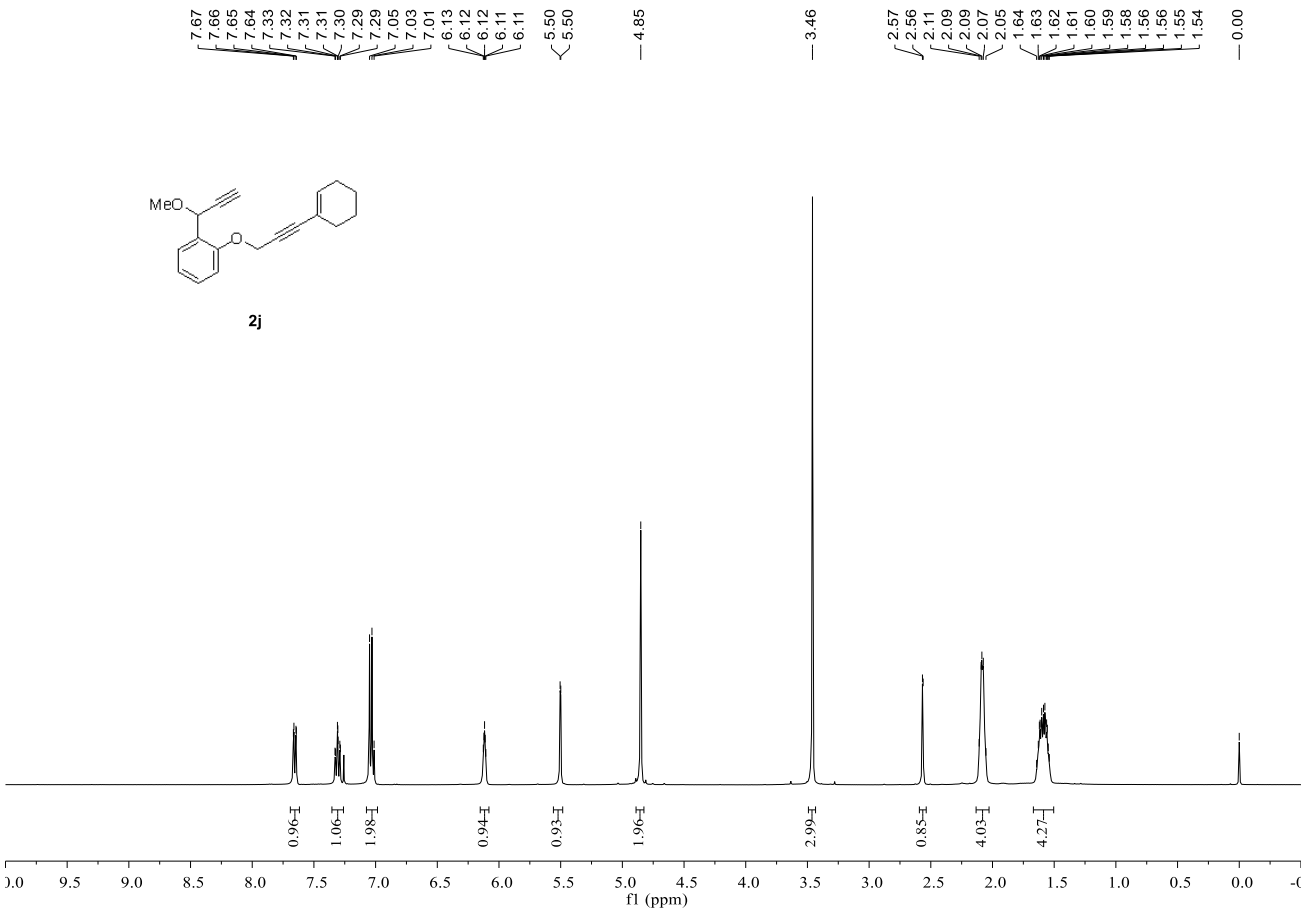
^{13}C NMR (100 MHz) of **2i** in $CDCl_3$



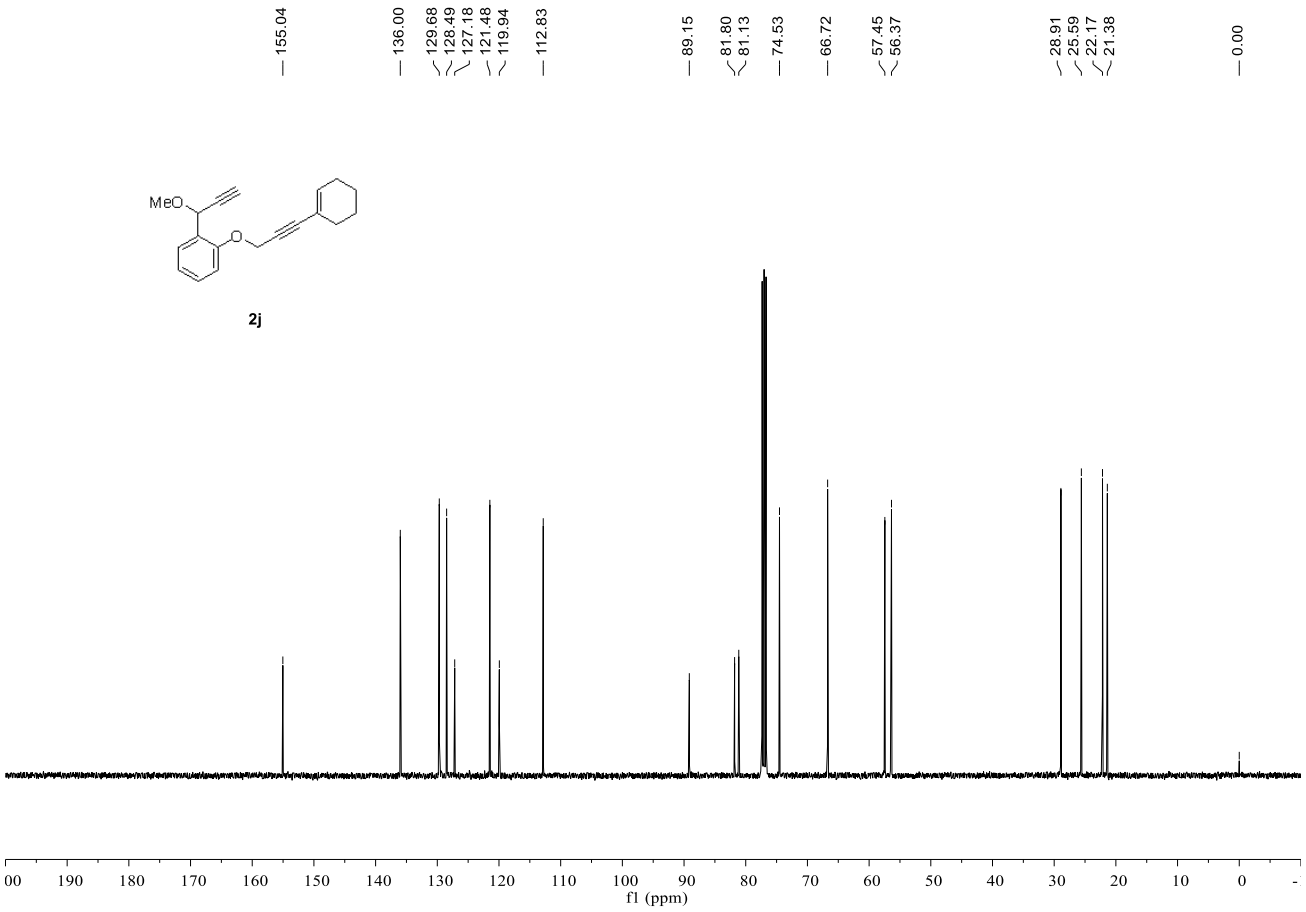
^{19}F NMR (376 MHz) of **2i** in $CDCl_3$



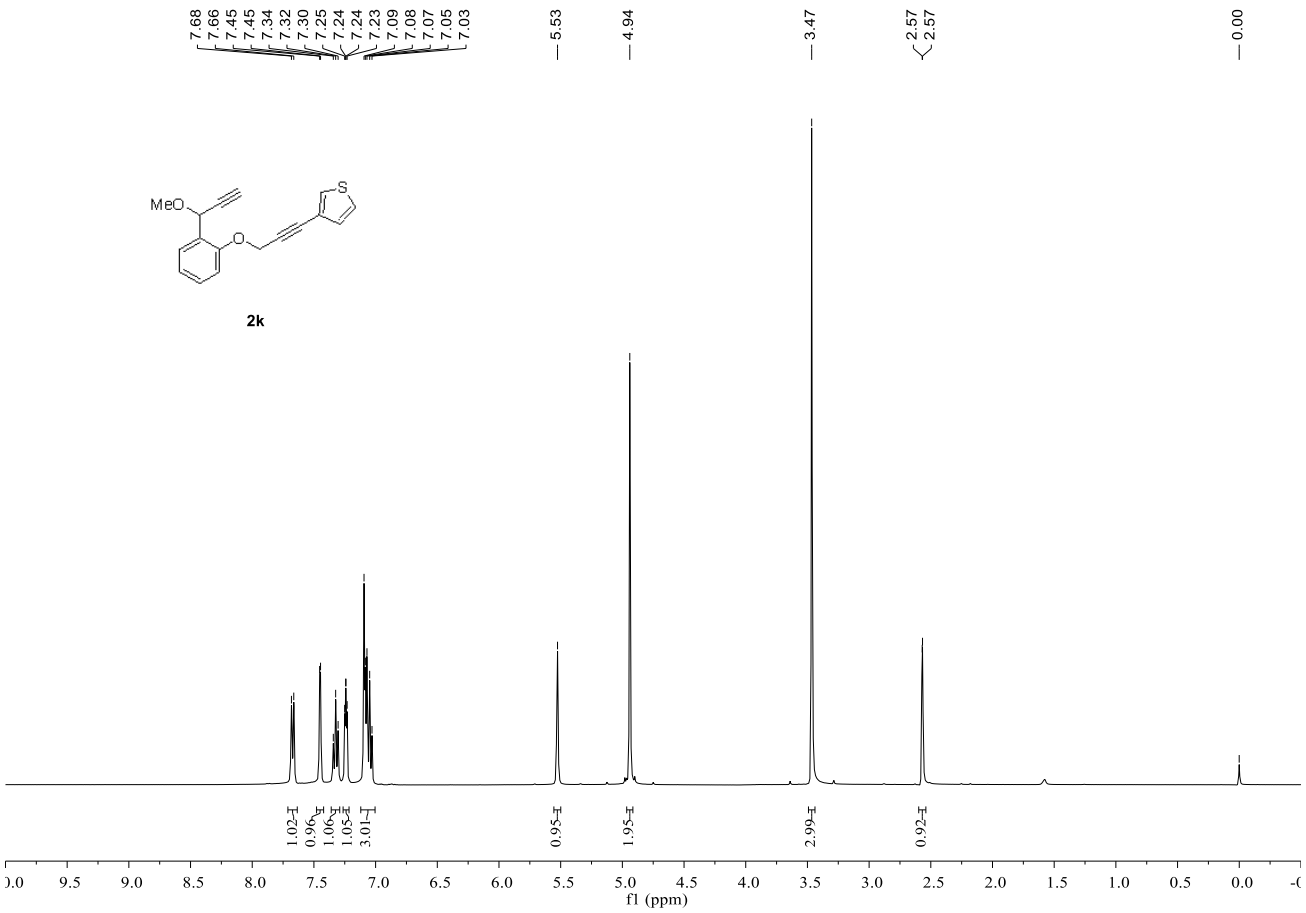
^{1}H NMR (400 MHz) of **2j** in $CDCl_3$



^{13}C NMR (100 MHz) of **2j** in $CDCl_3$



^{1}H NMR (400 MHz) of **2k** in $CDCl_3$



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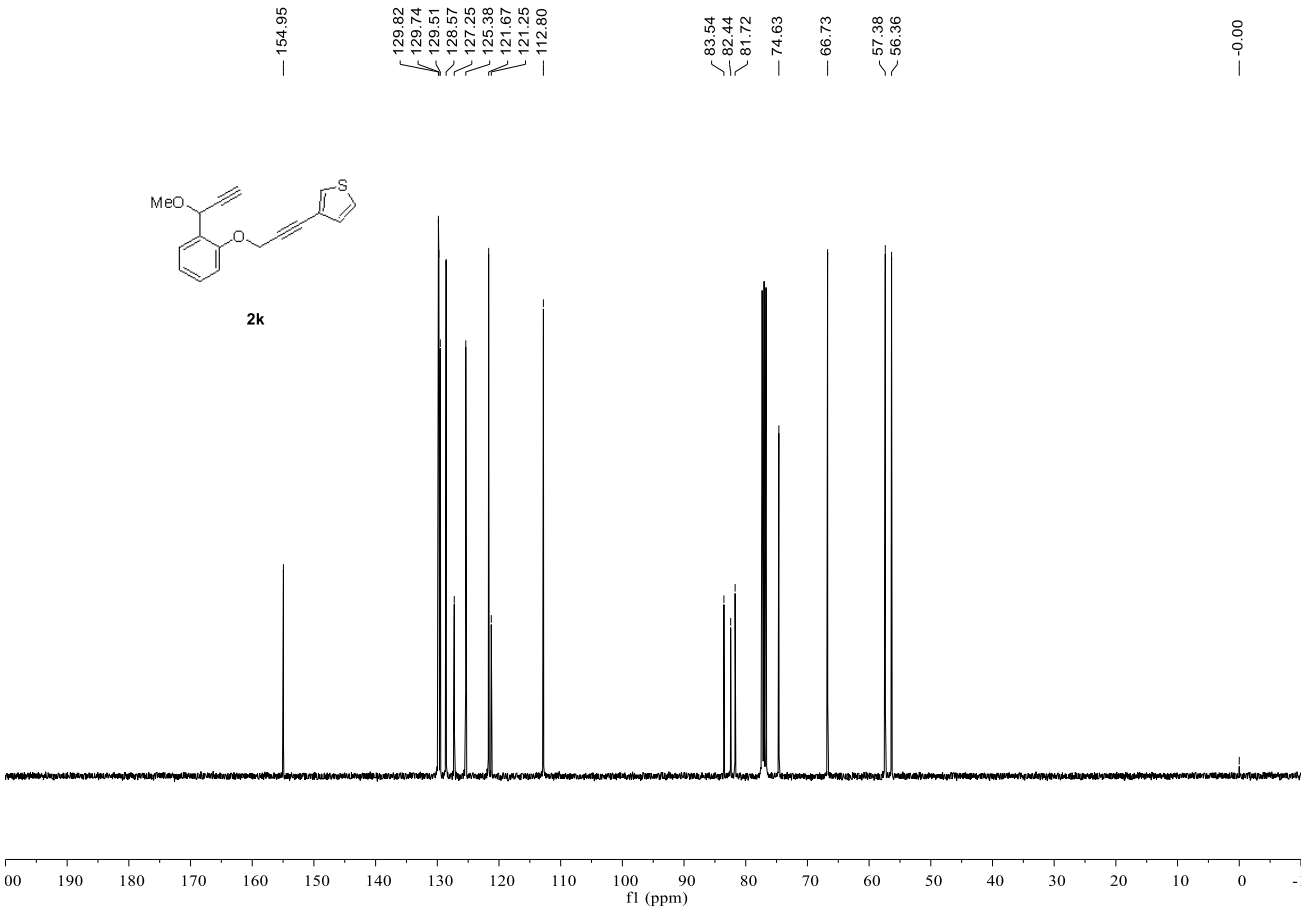
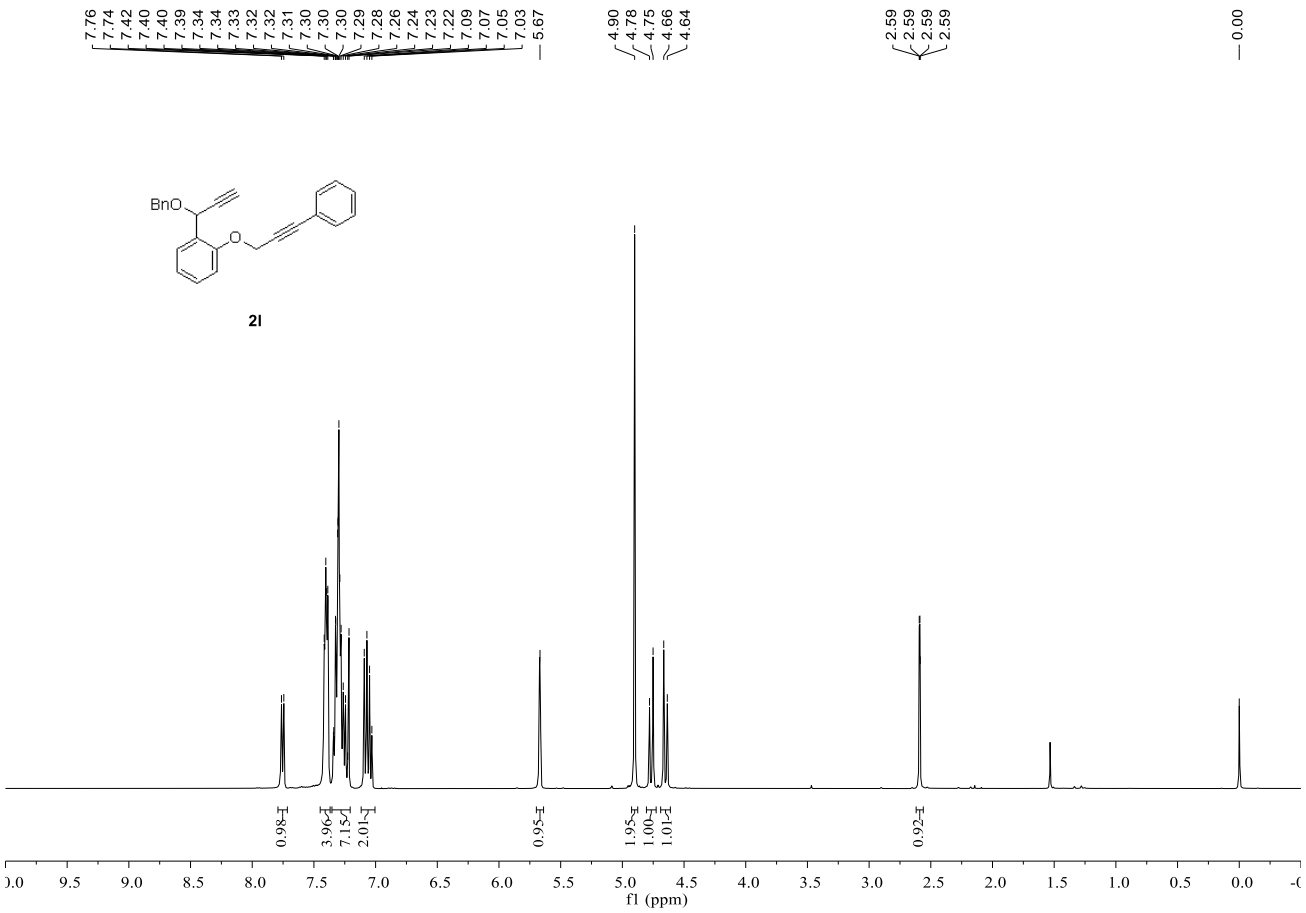


^{1}H NMR (400 MHz) of **2l** in $CDCl_3$



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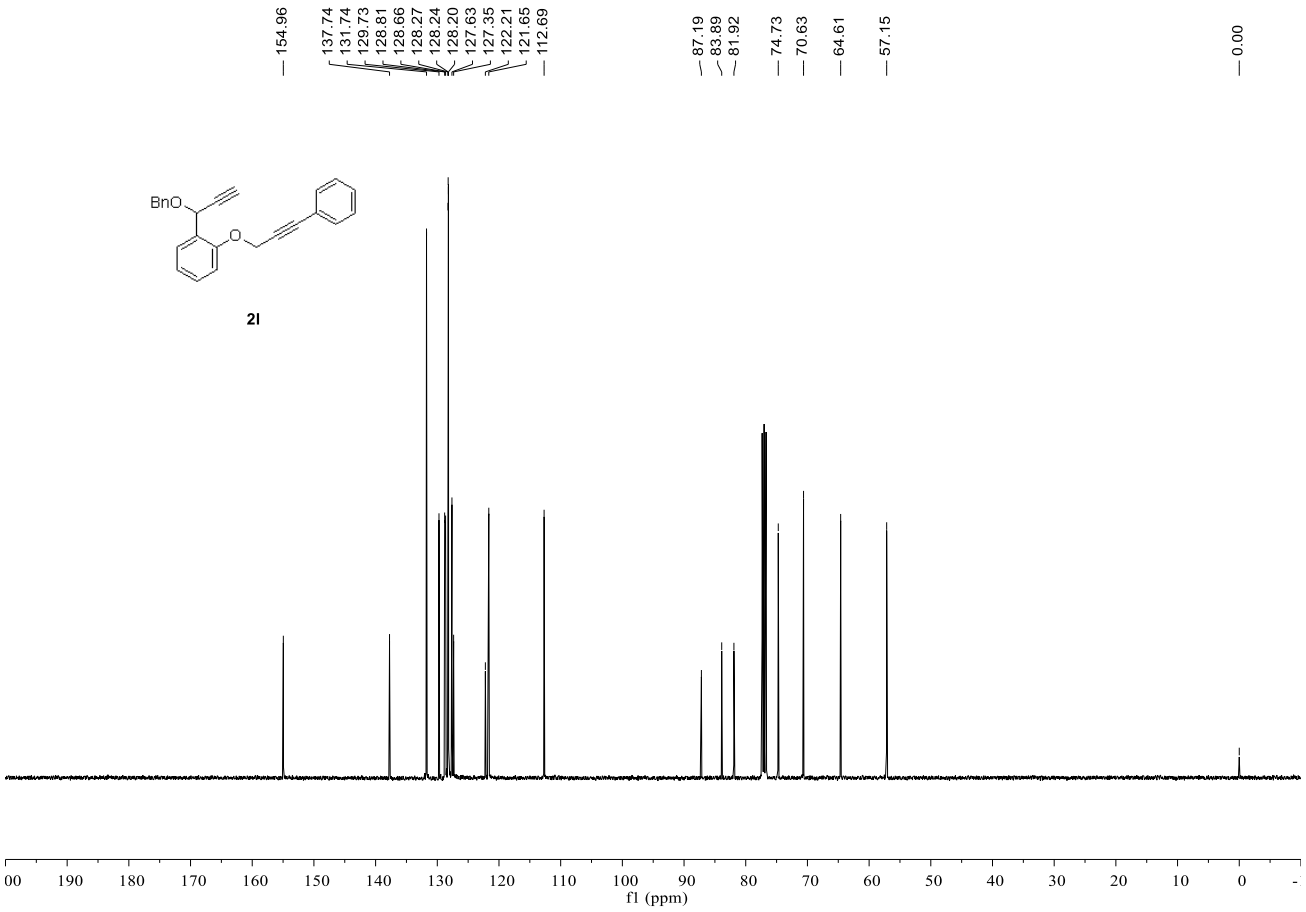
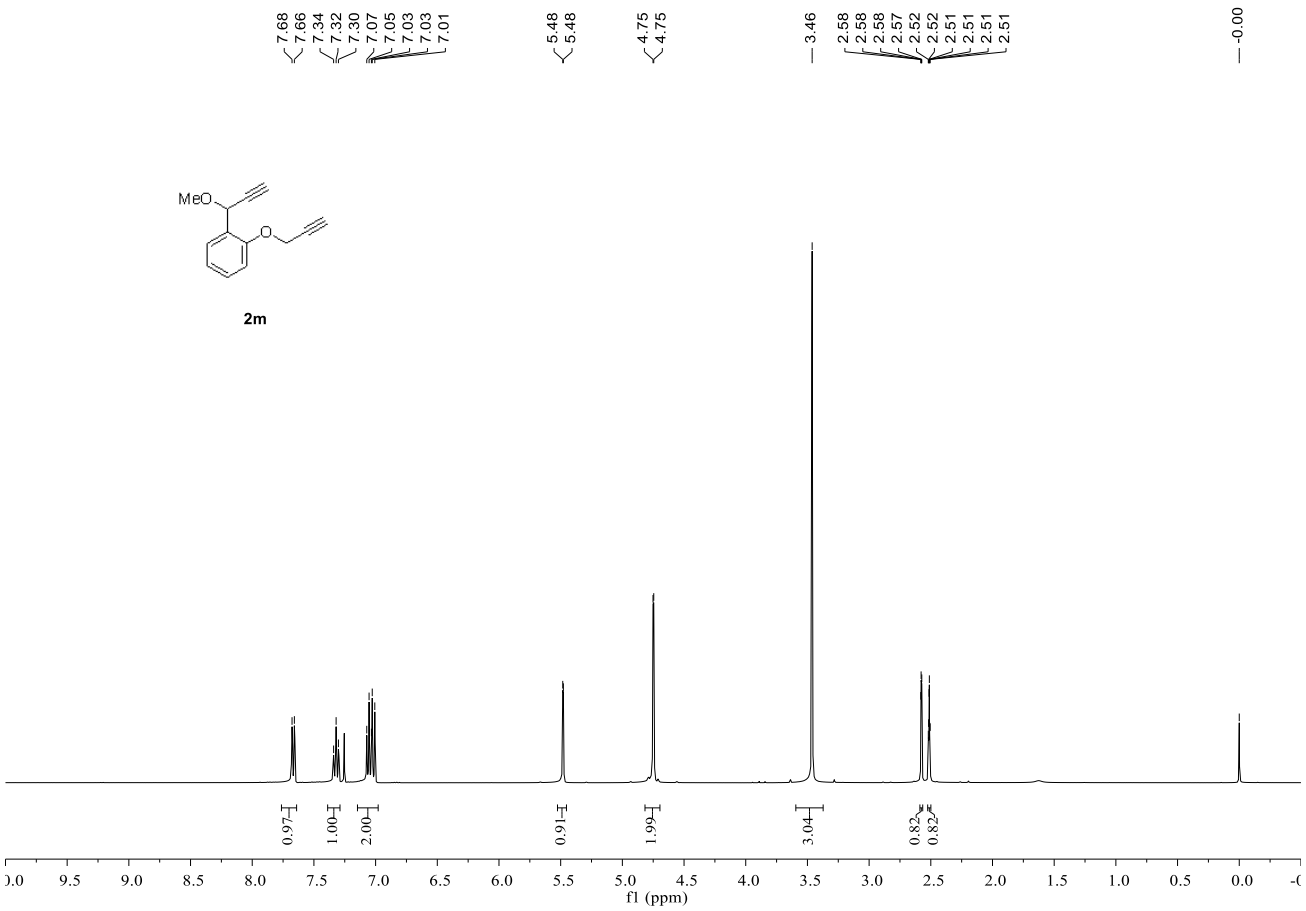
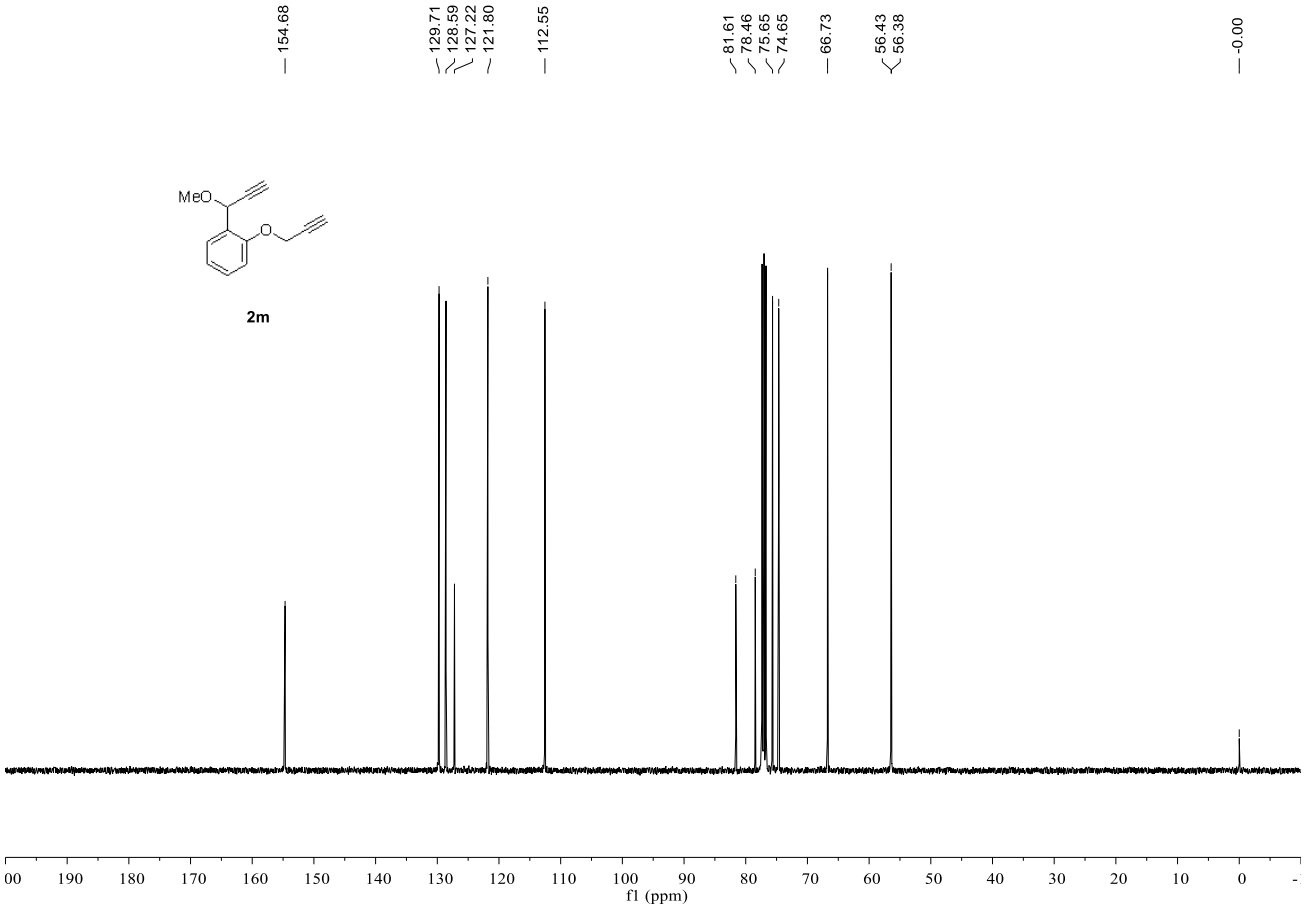


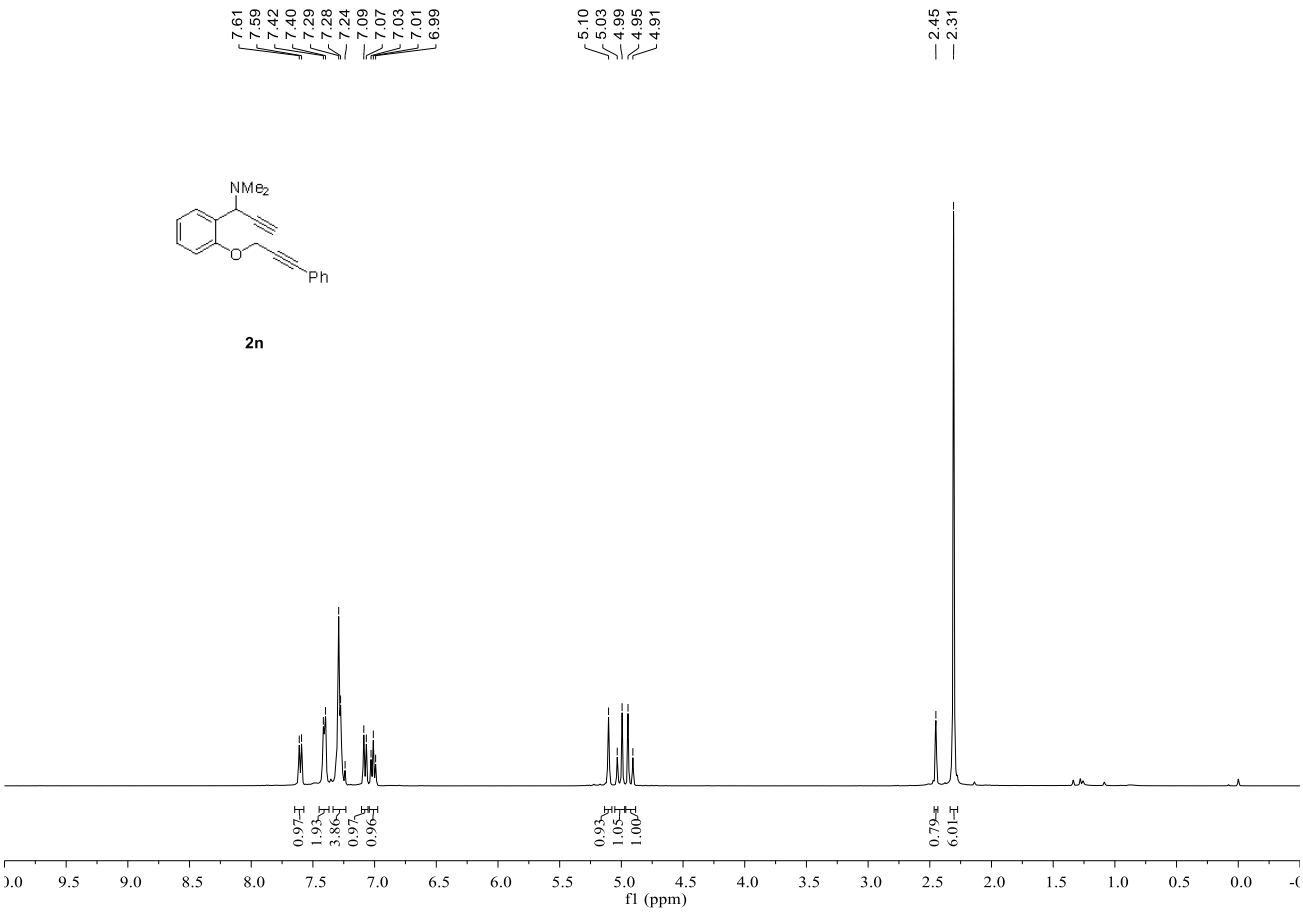
^{1}H NMR (400 MHz) of **2m** in $CDCl_3$



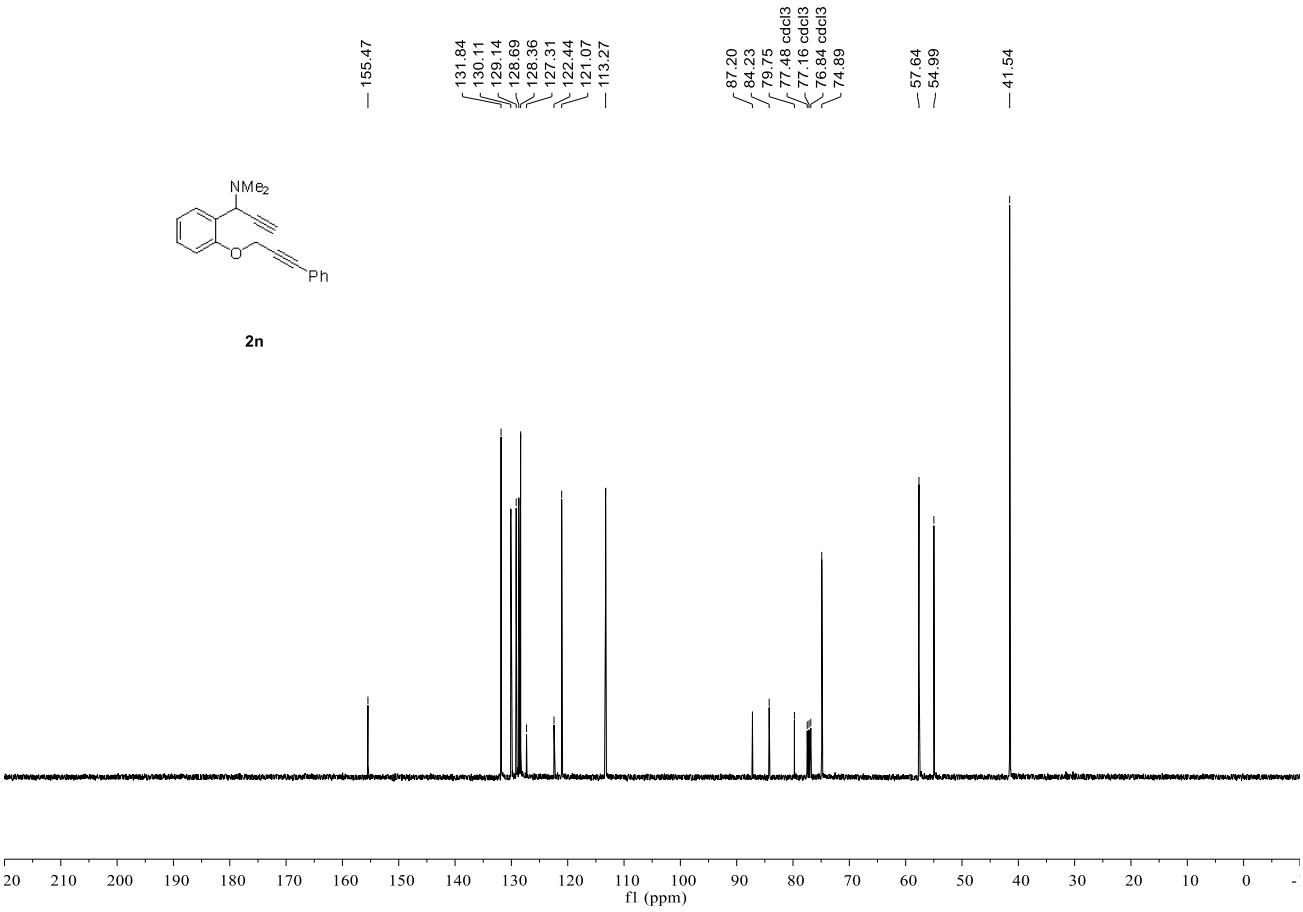
^{13}C NMR (100 MHz) of **2m** in $CDCl_3$



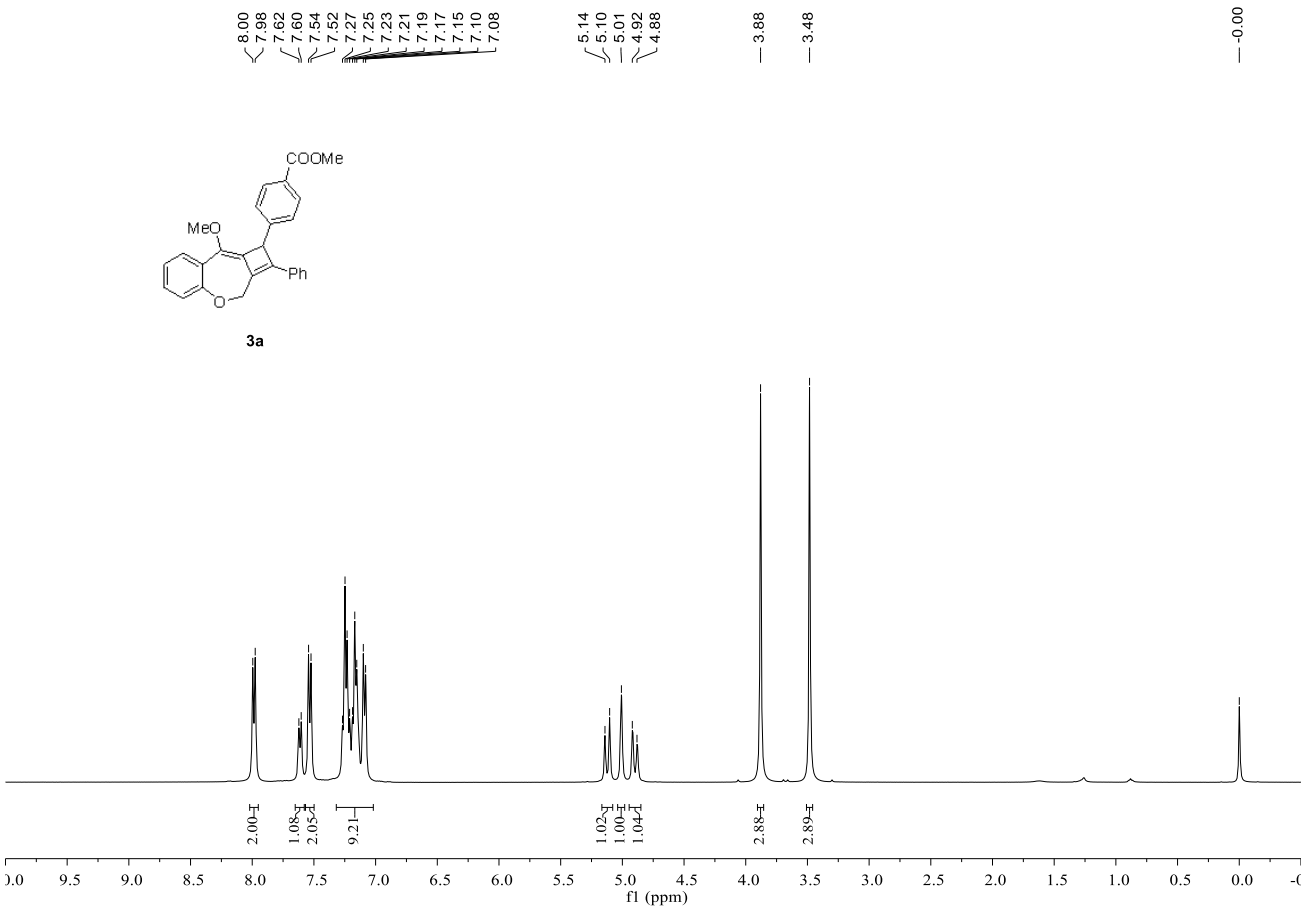
^{1}H NMR (400 MHz) of **2n** in $CDCl_3$



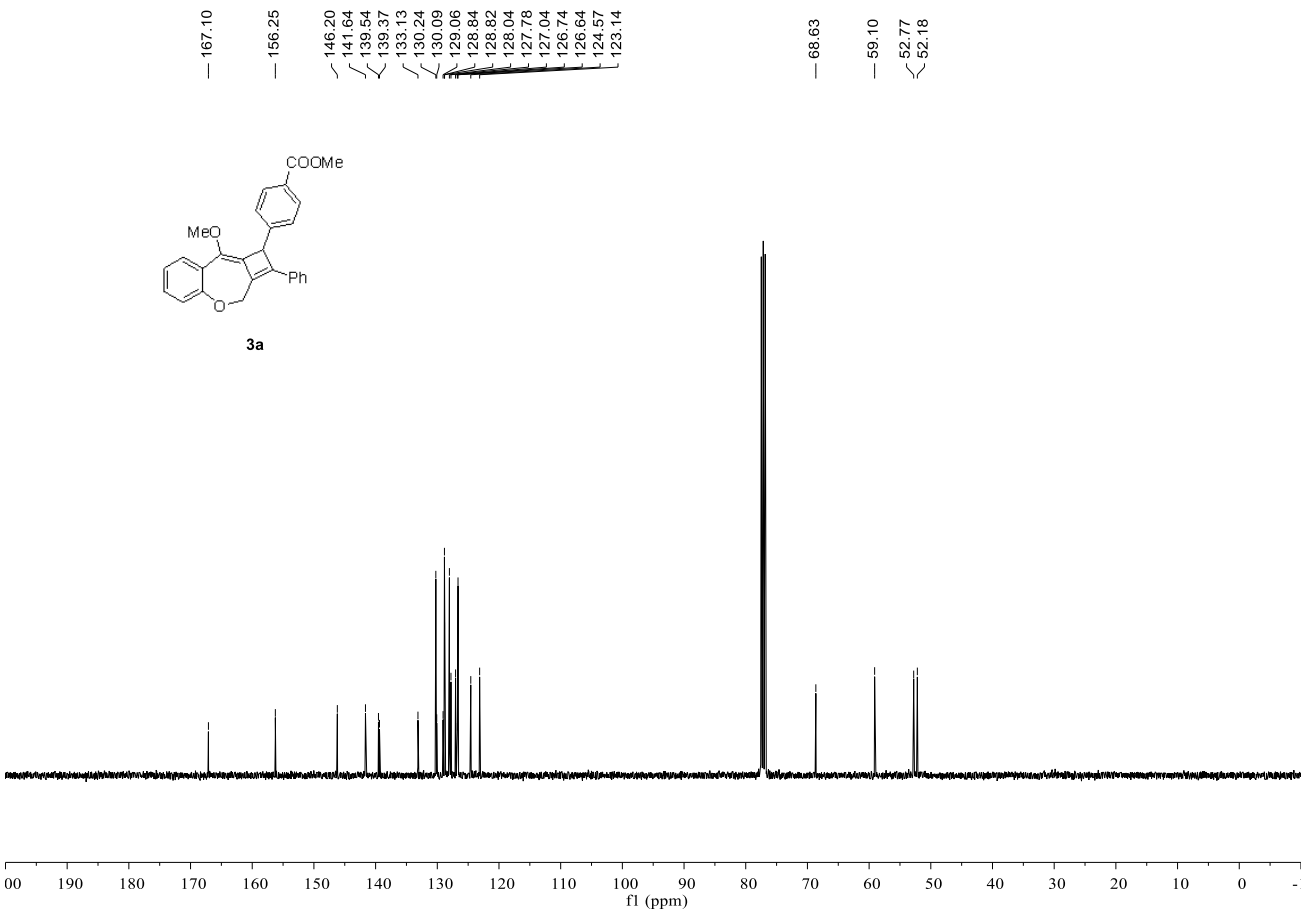
^{13}C NMR (100 MHz) of **2n** in $CDCl_3$



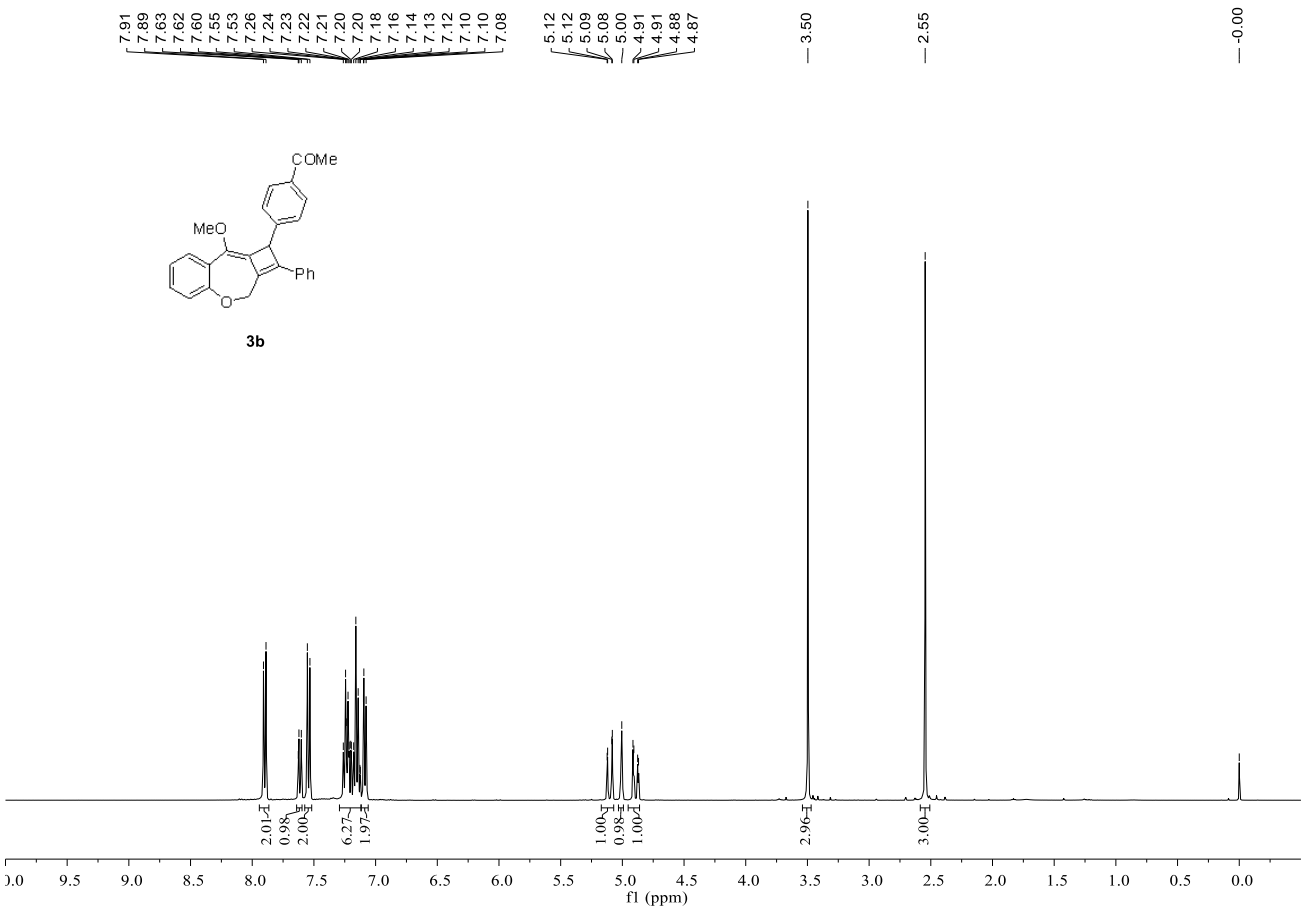
^{1}H NMR (400 MHz) of **3a** in $CDCl_3$



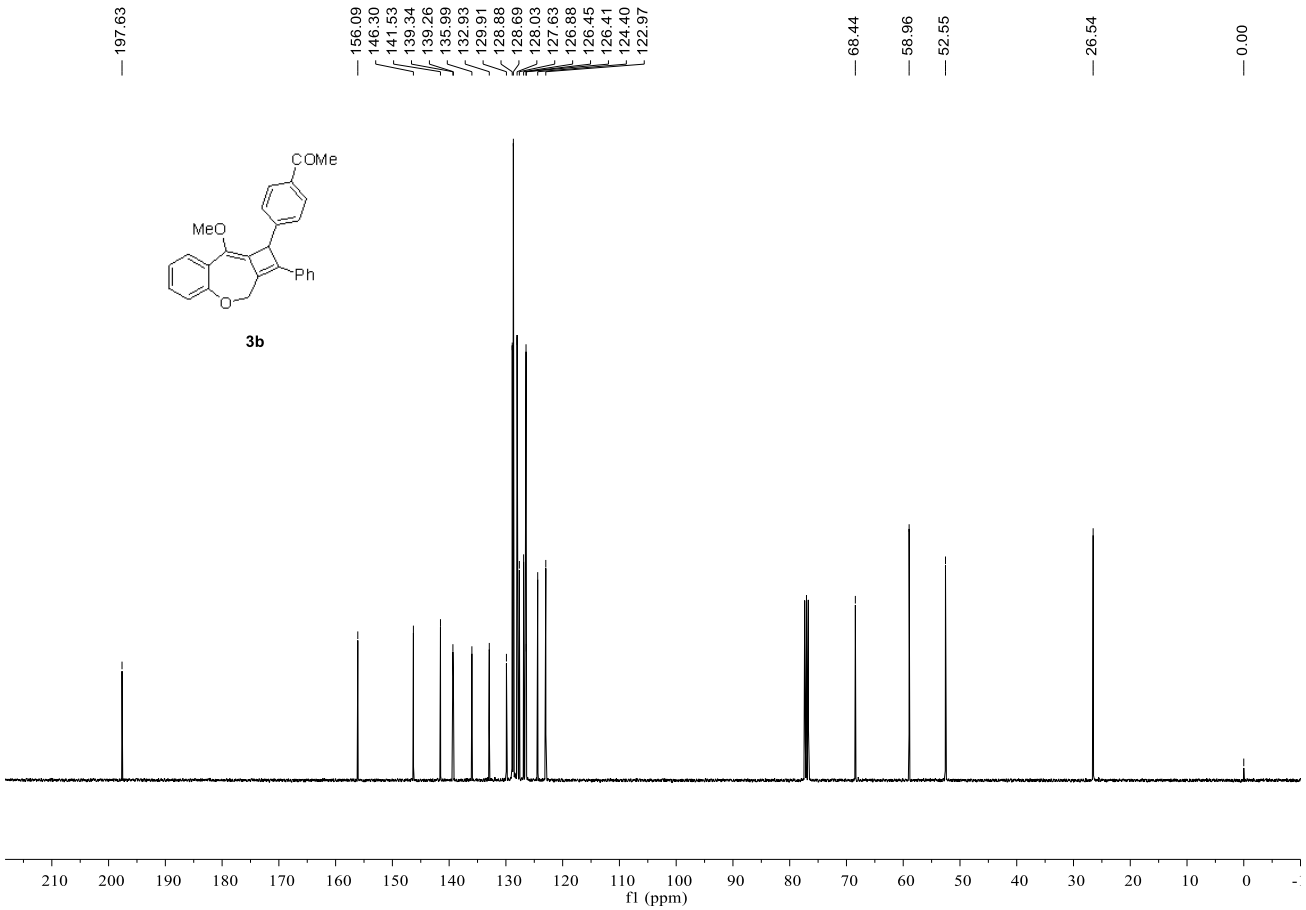
^{13}C NMR (100 MHz) of **3a** in $CDCl_3$



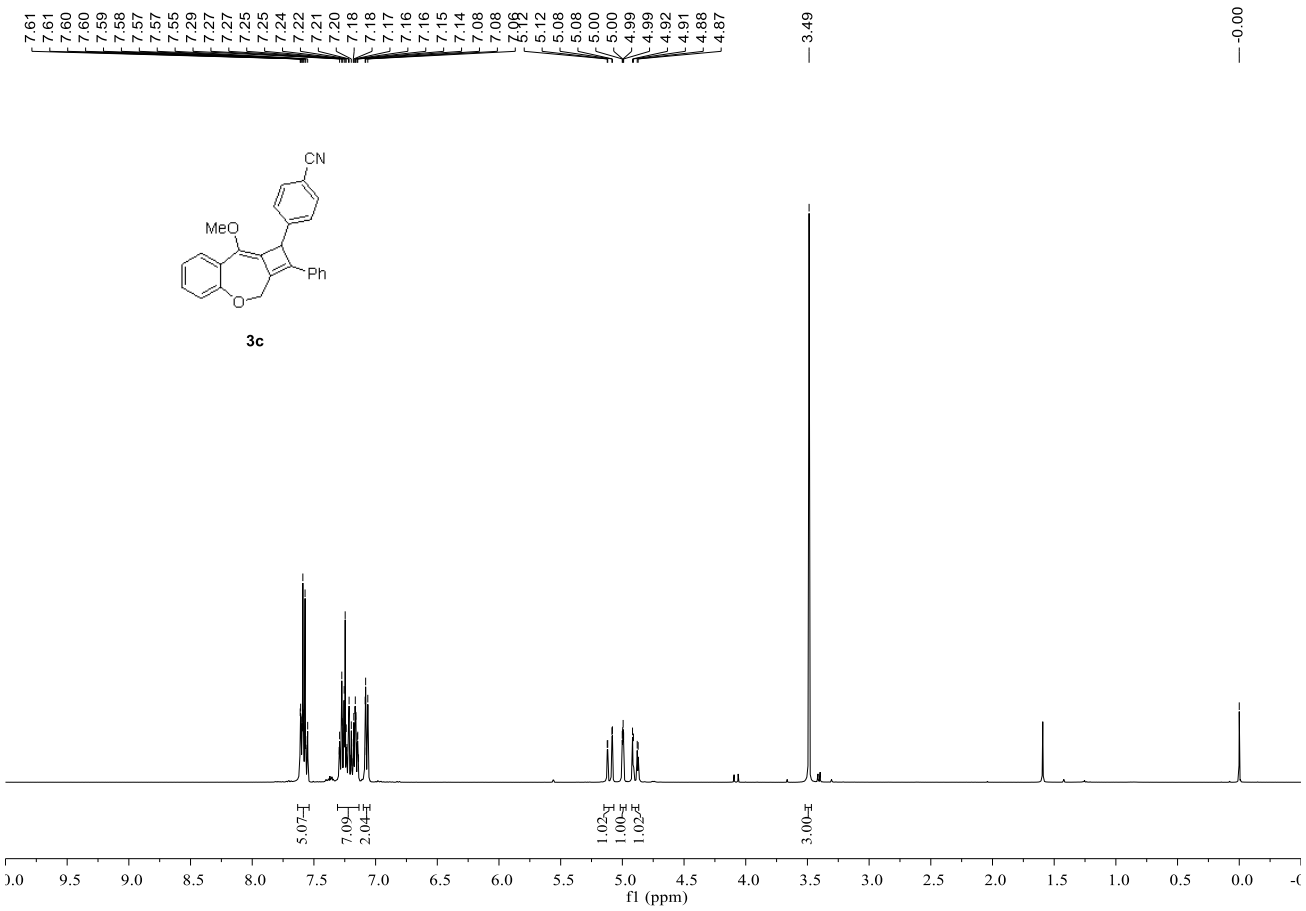
^{1}H NMR (400 MHz) of **3b** in $CDCl_3$



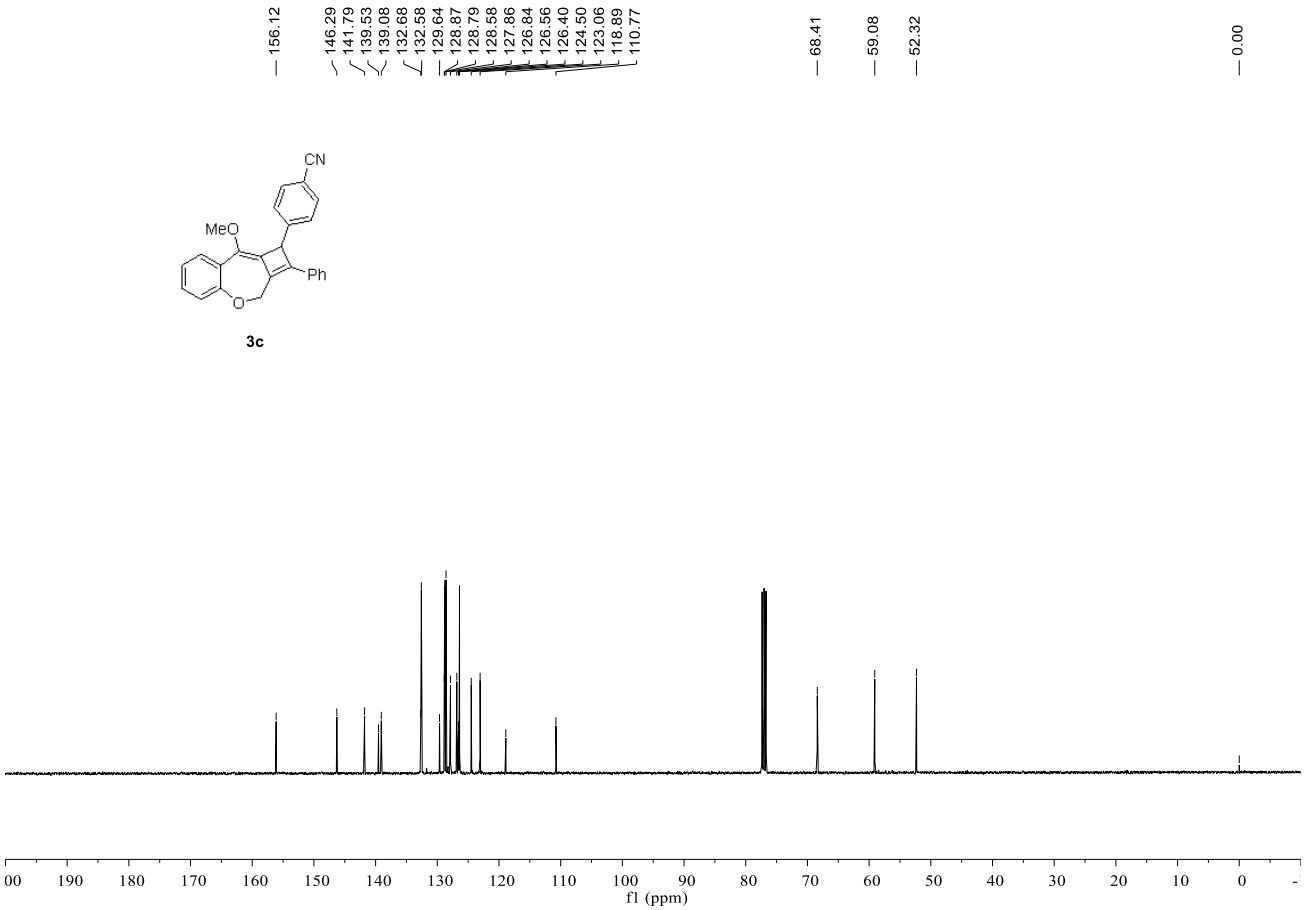
^{13}C NMR (100 MHz) of **3b** in $CDCl_3$



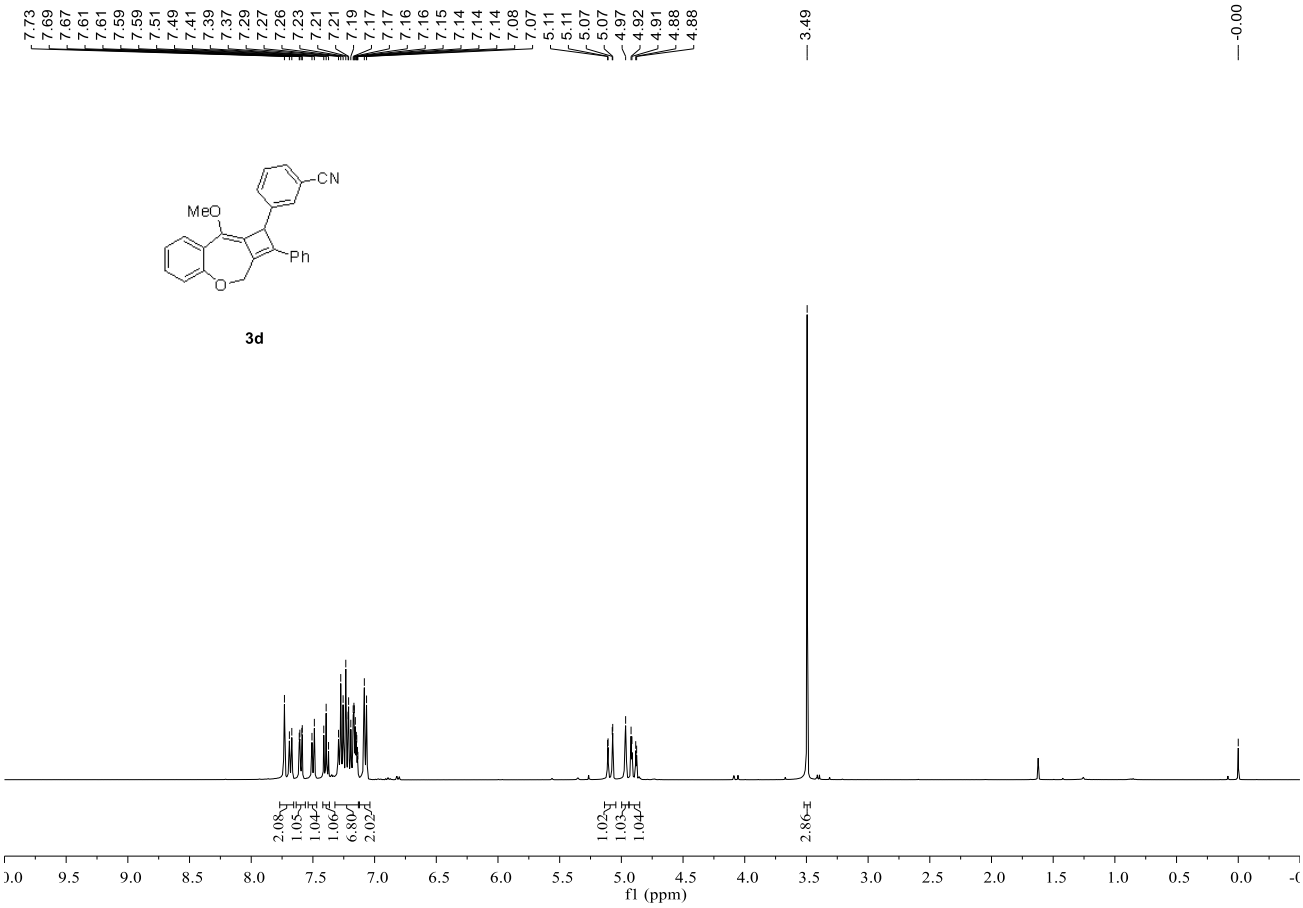
^{1}H NMR (400 MHz) of **3c** in $CDCl_3$



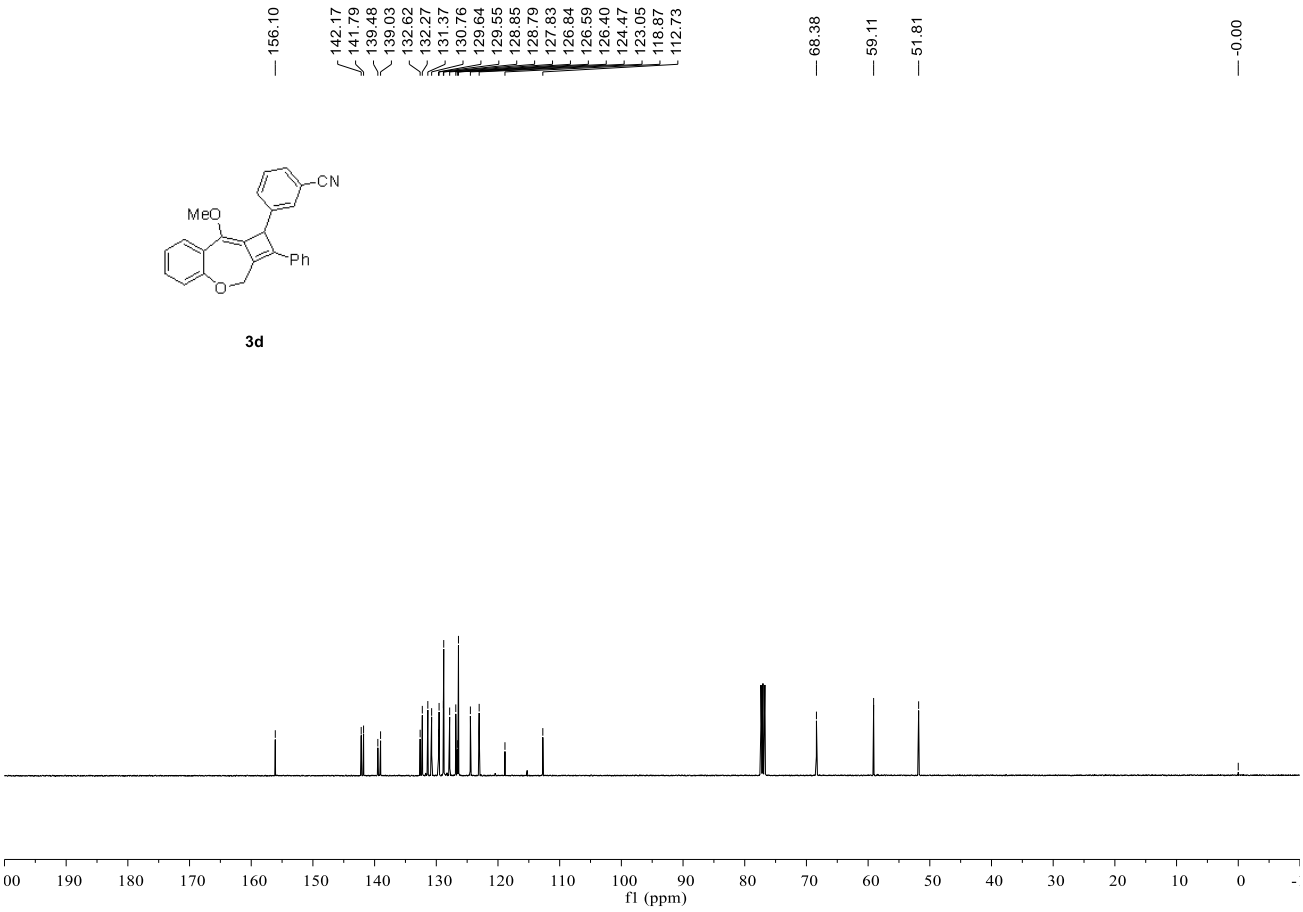
^{13}C NMR (100 MHz) of **3c** in $CDCl_3$



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



^{13}C NMR (100 MHz) of **3d** in $CDCl_3$



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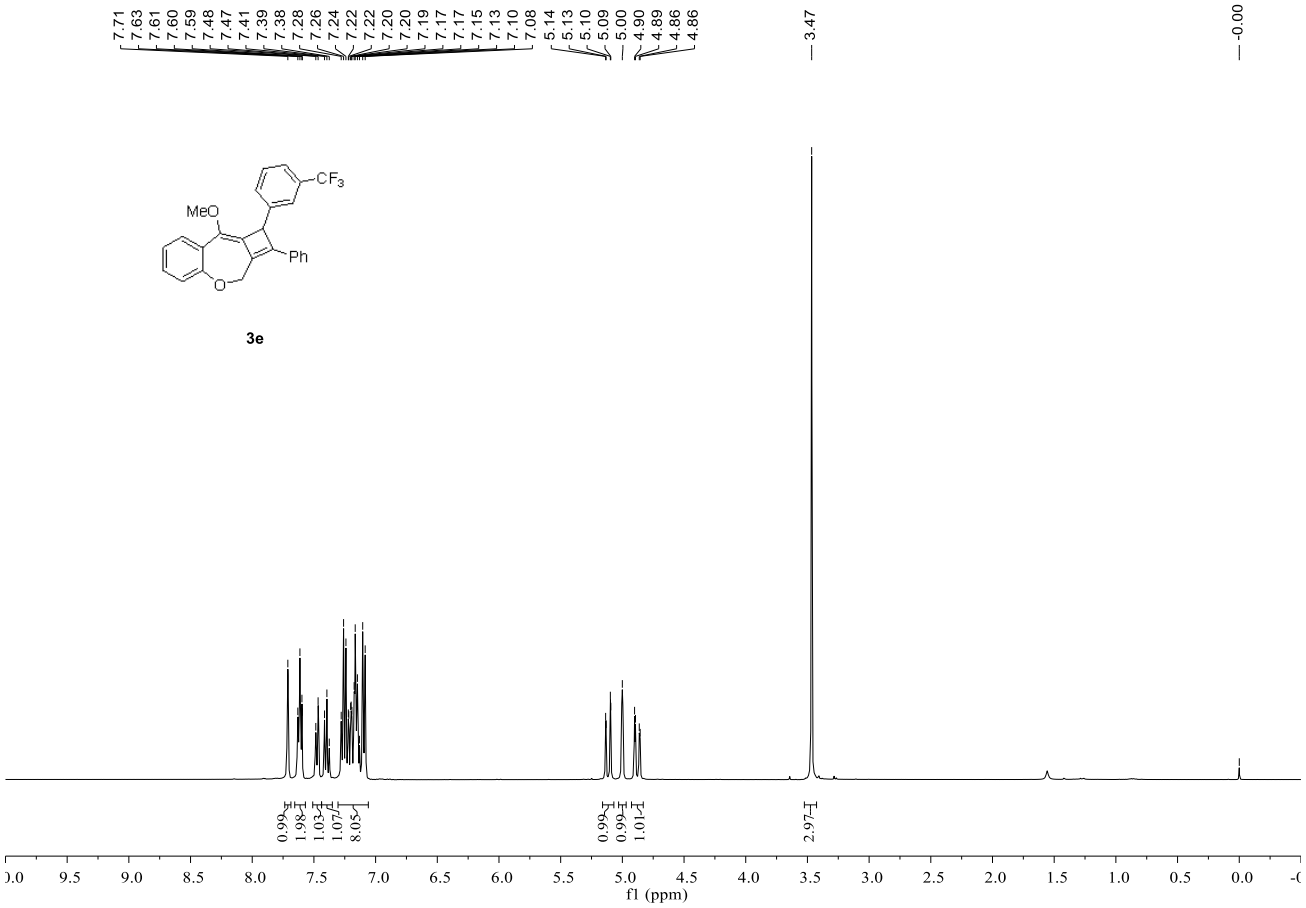
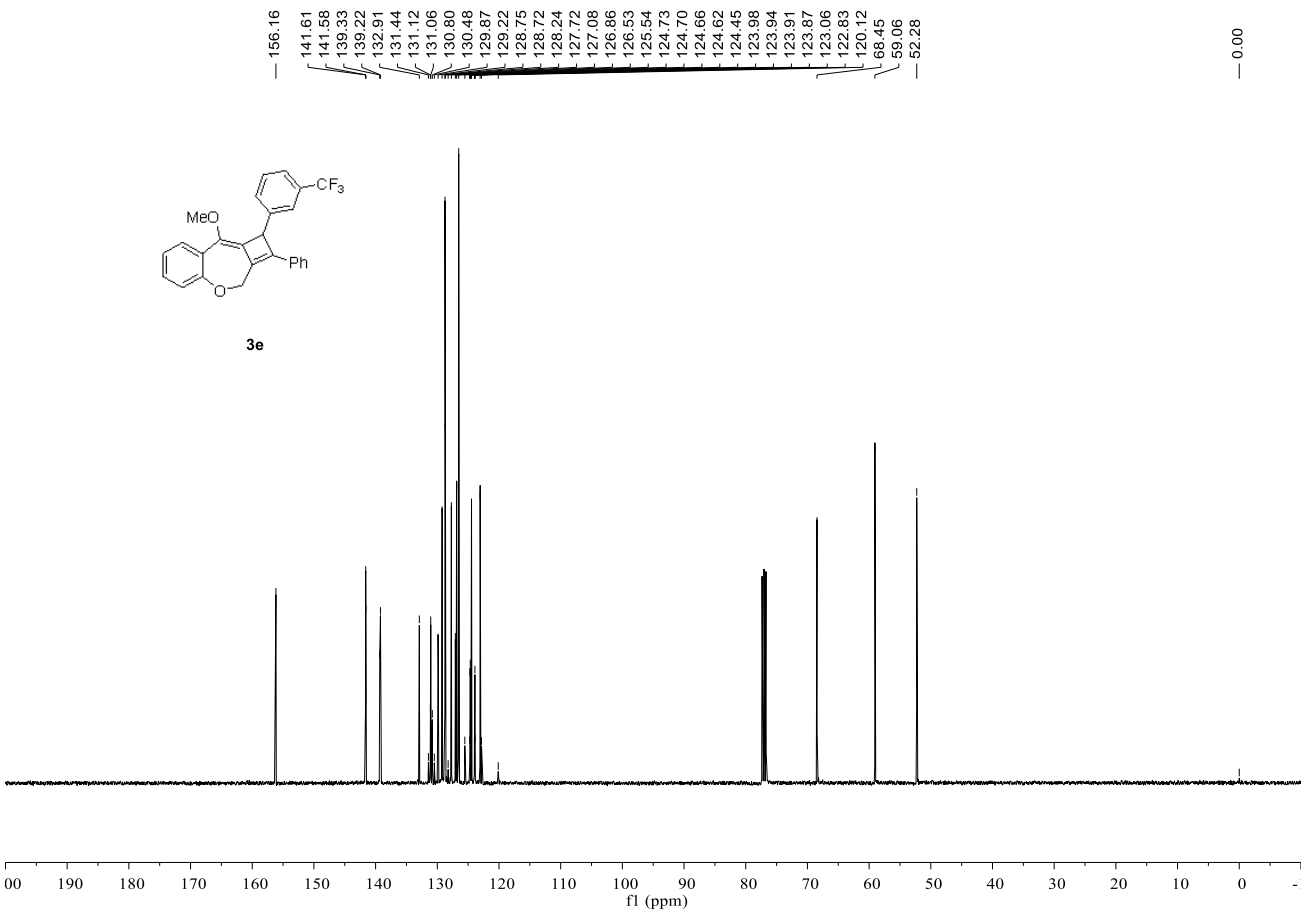
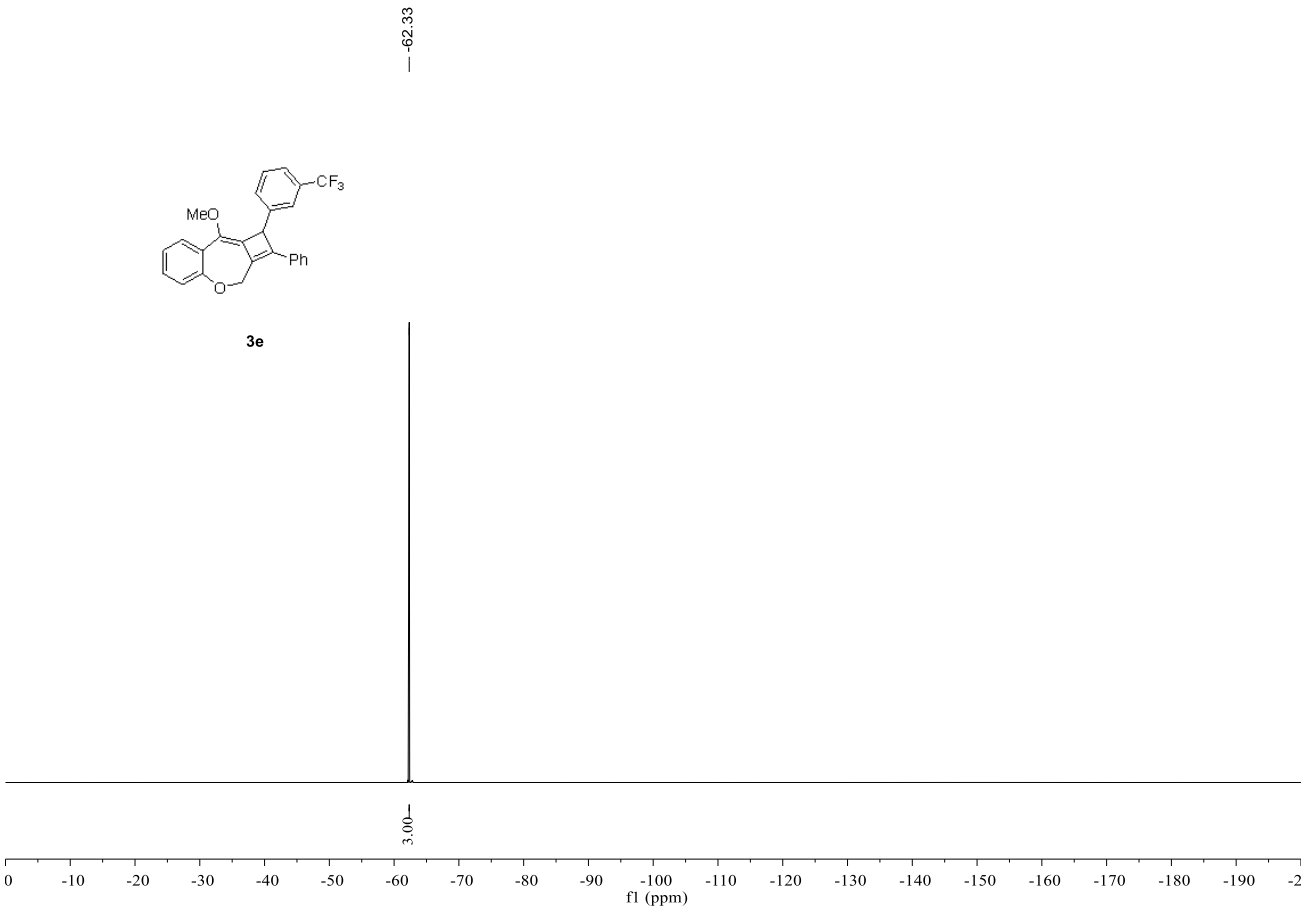


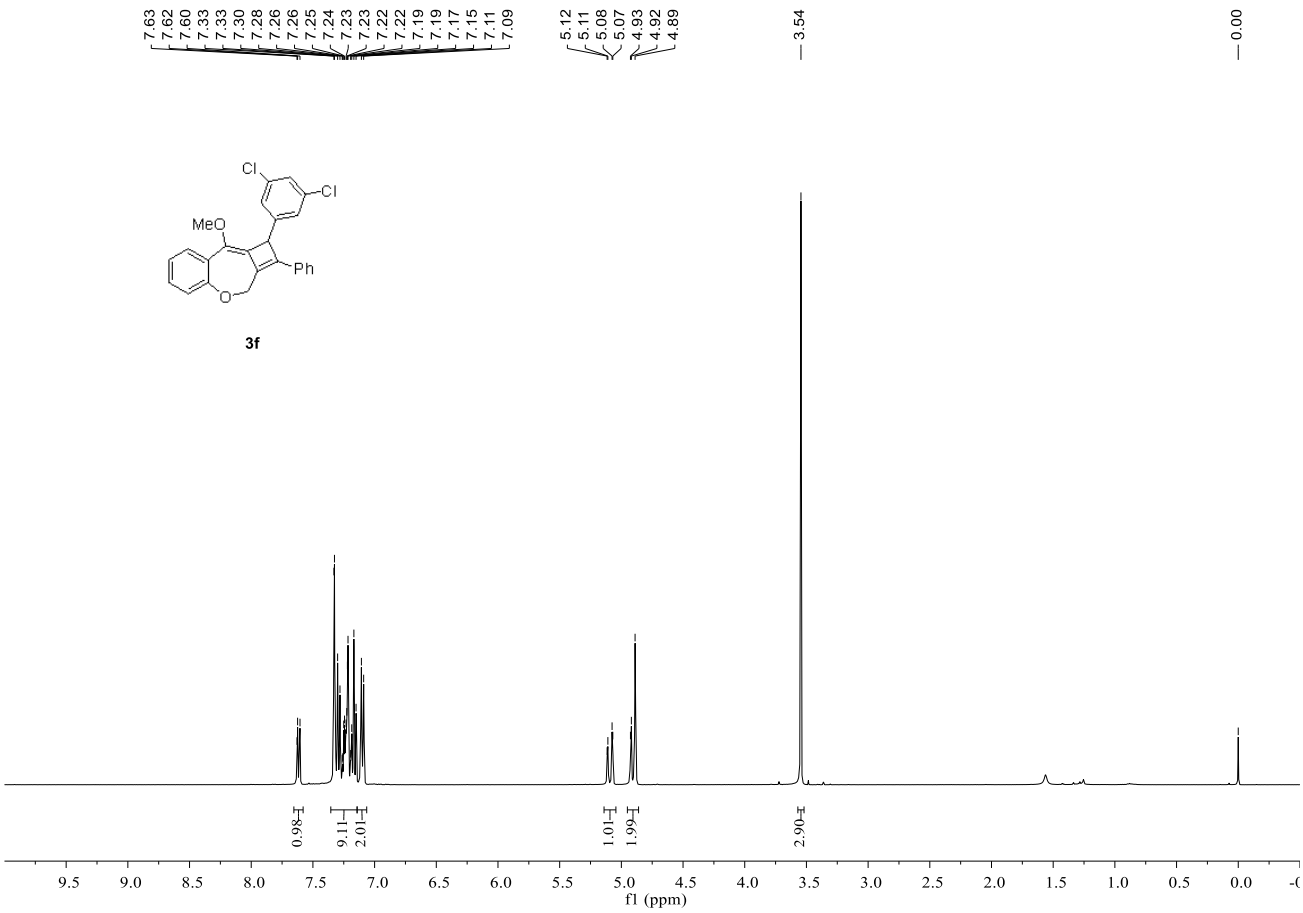
^{13}C NMR (100 MHz) of **3e** in $CDCl_3$



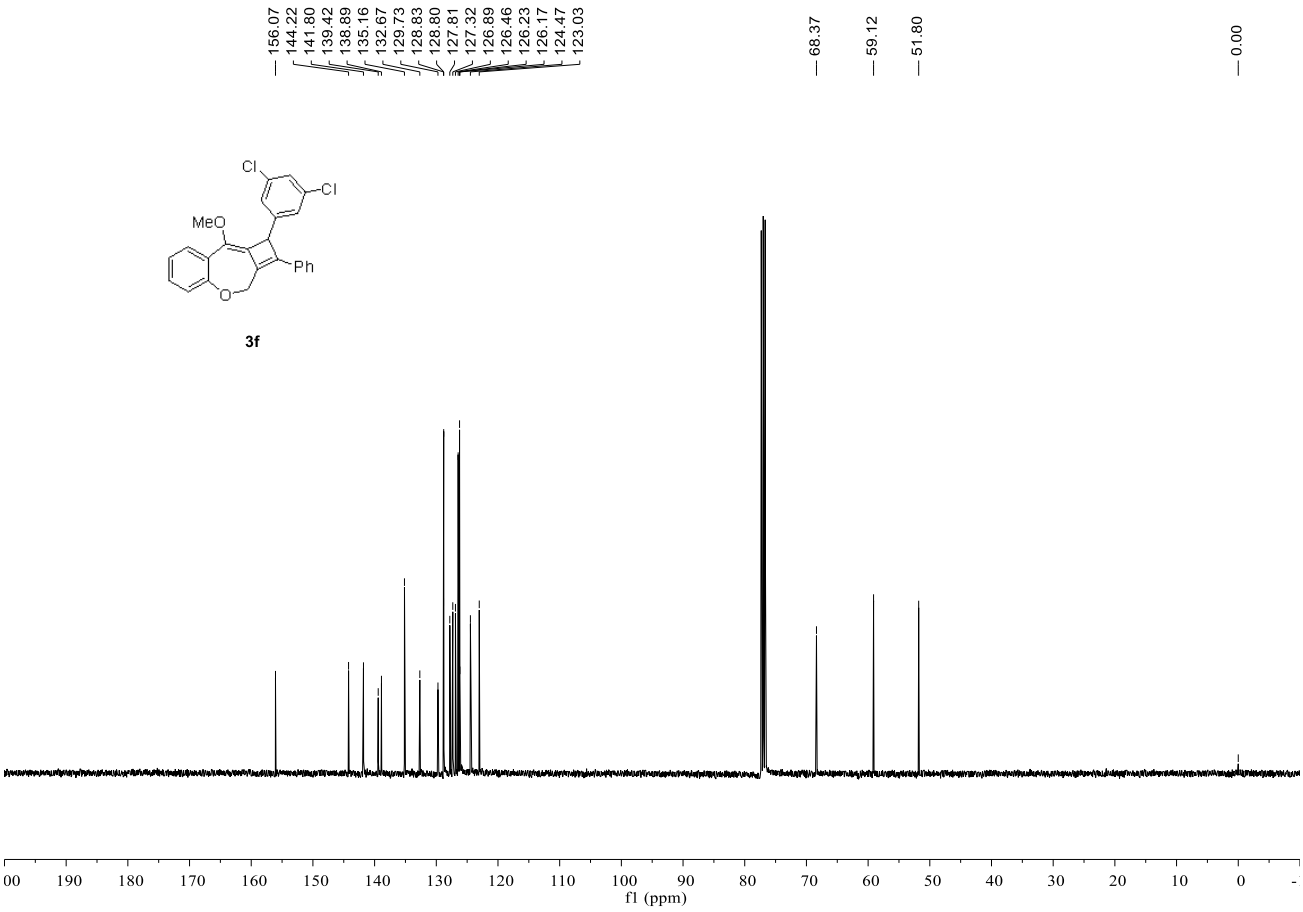
^{19}F NMR (376 MHz) of **3e** in $CDCl_3$



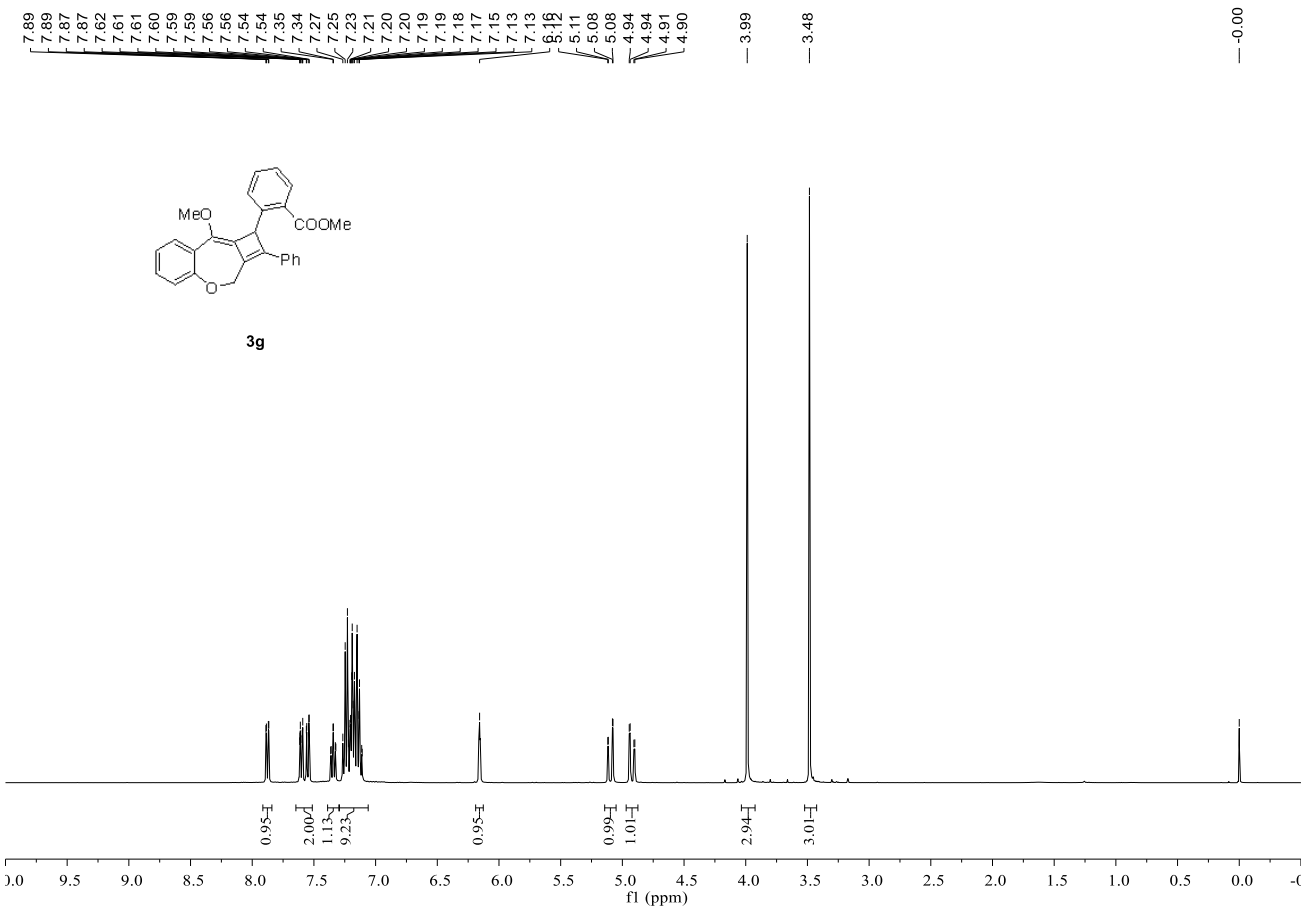
^{1}H NMR (400 MHz) of **3f** in $CDCl_3$



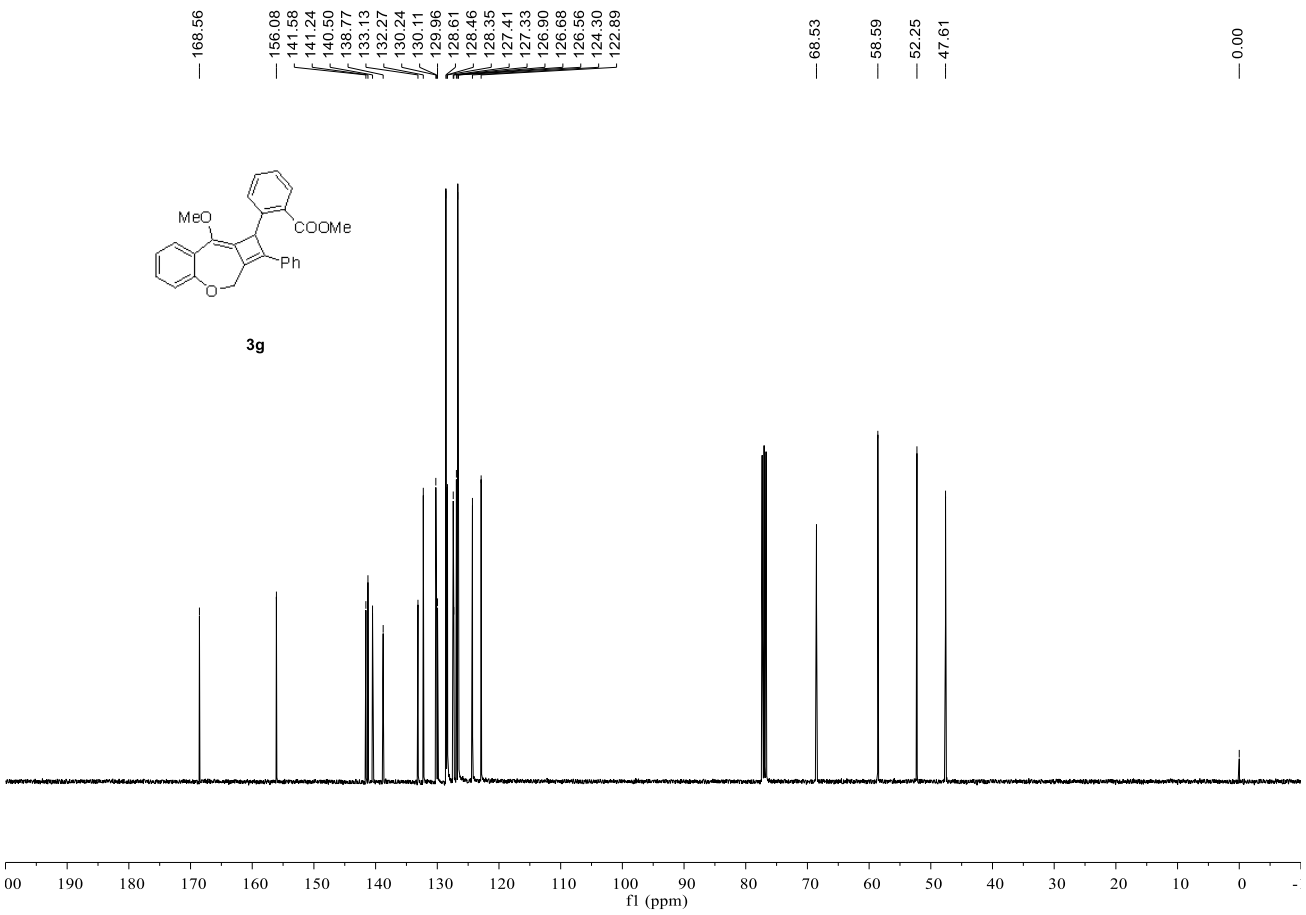
^{13}C NMR (100 MHz) of **3f** in $CDCl_3$



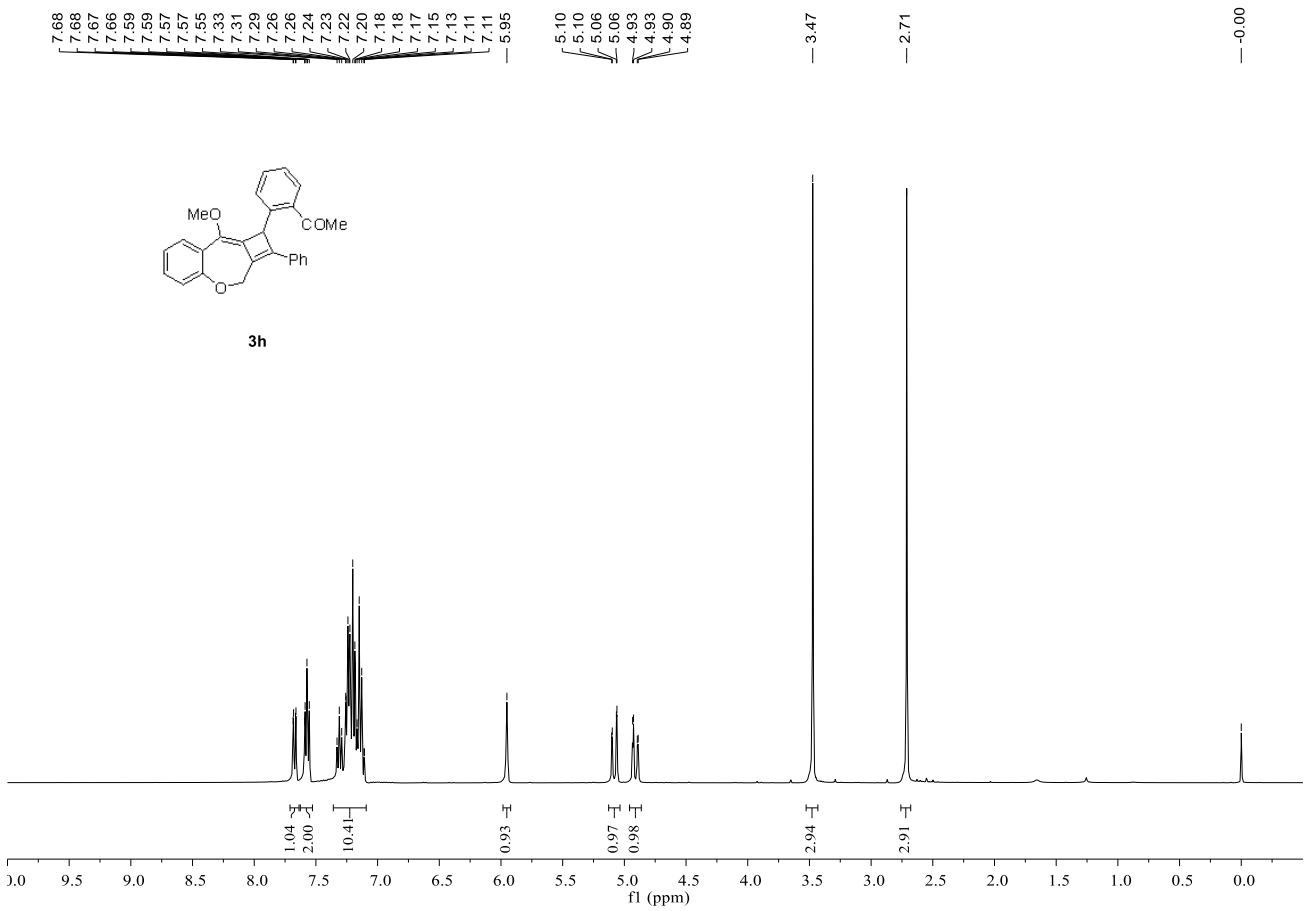
^{1}H NMR (400 MHz) of **3g** in $CDCl_3$



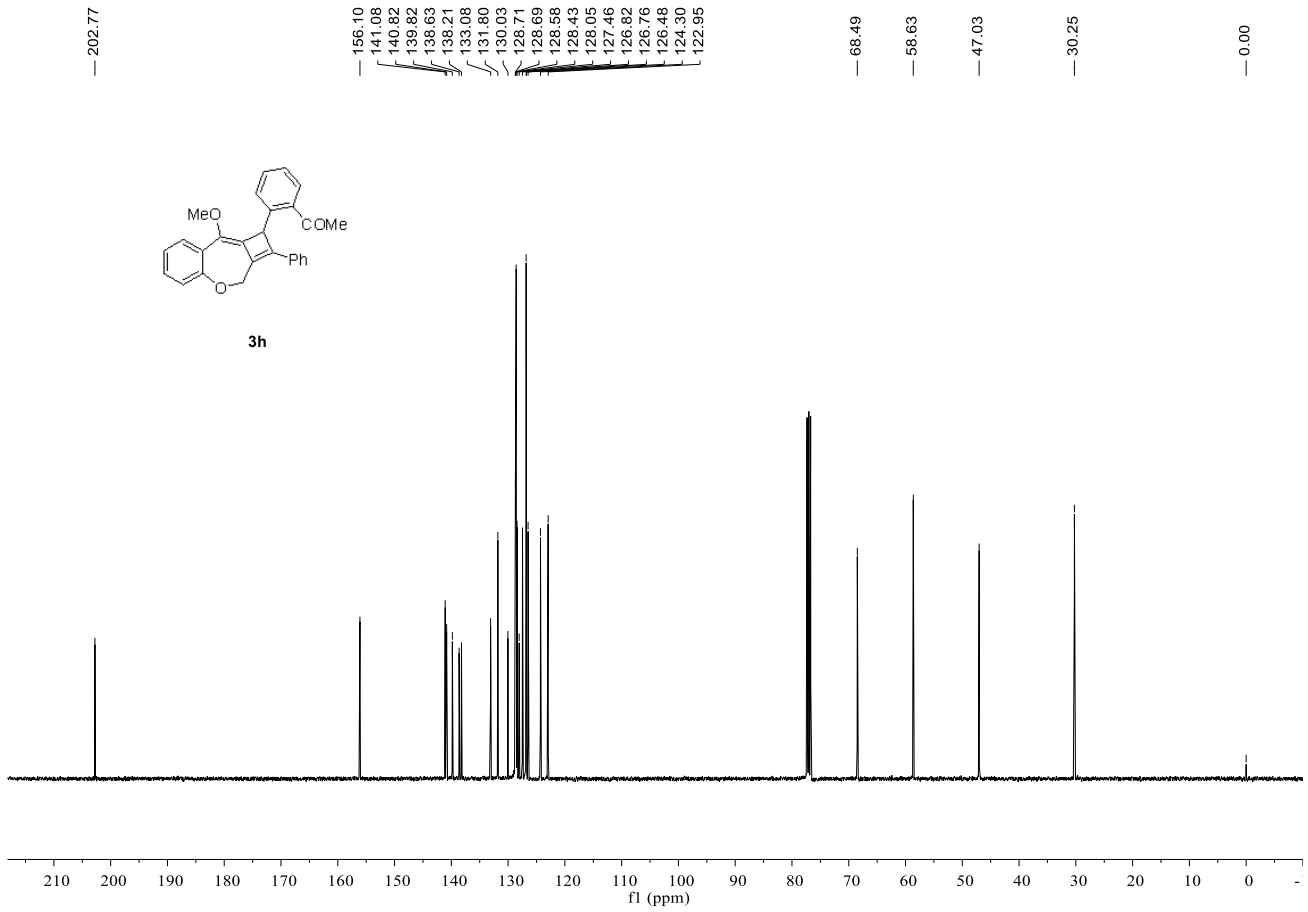
^{13}C NMR (100 MHz) of **3g** in $CDCl_3$



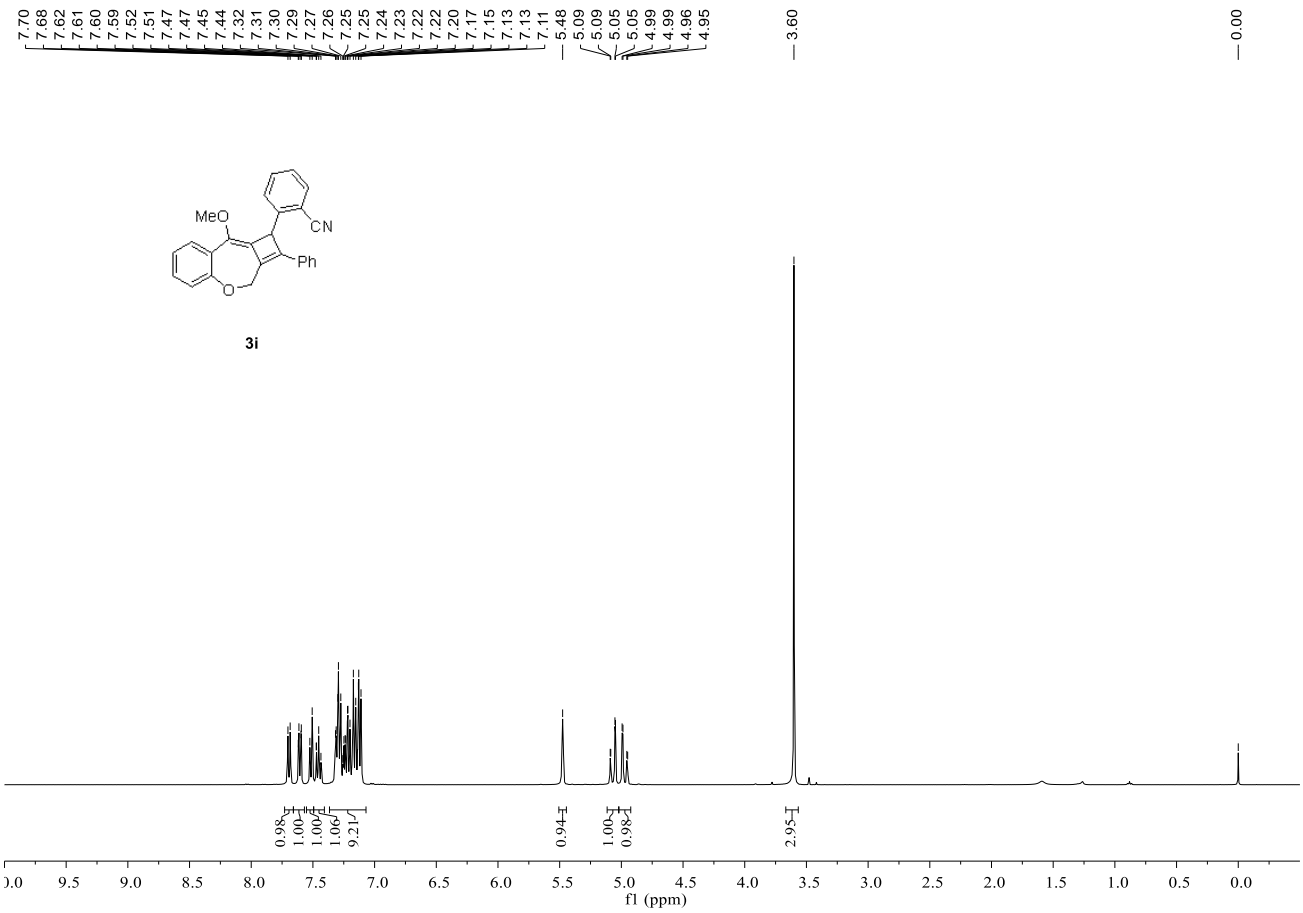
^{13}C NMR (100 MHz) of **3h** in $CDCl_3$



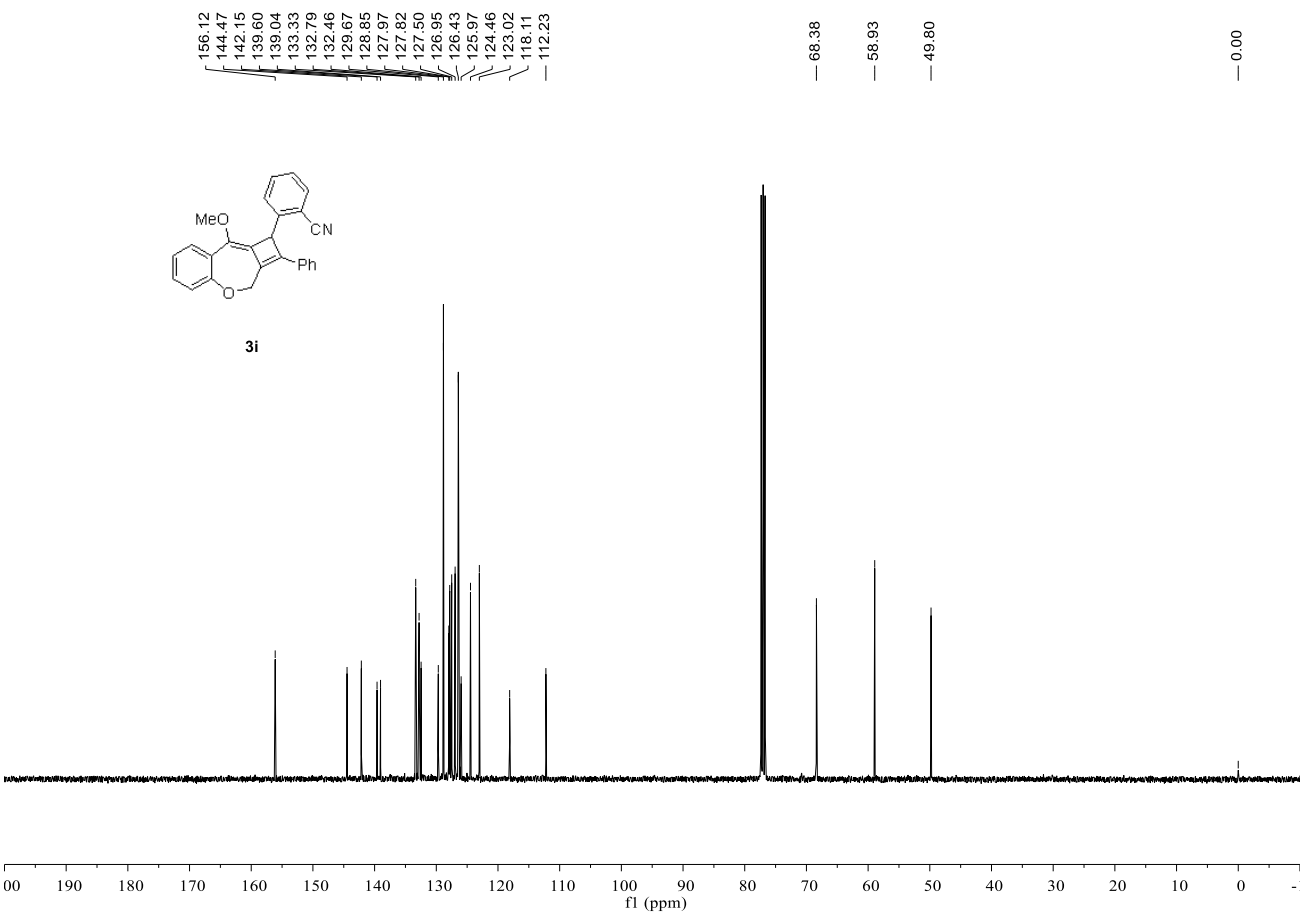
^{13}C NMR (100 MHz) of **3h** in $CDCl_3$



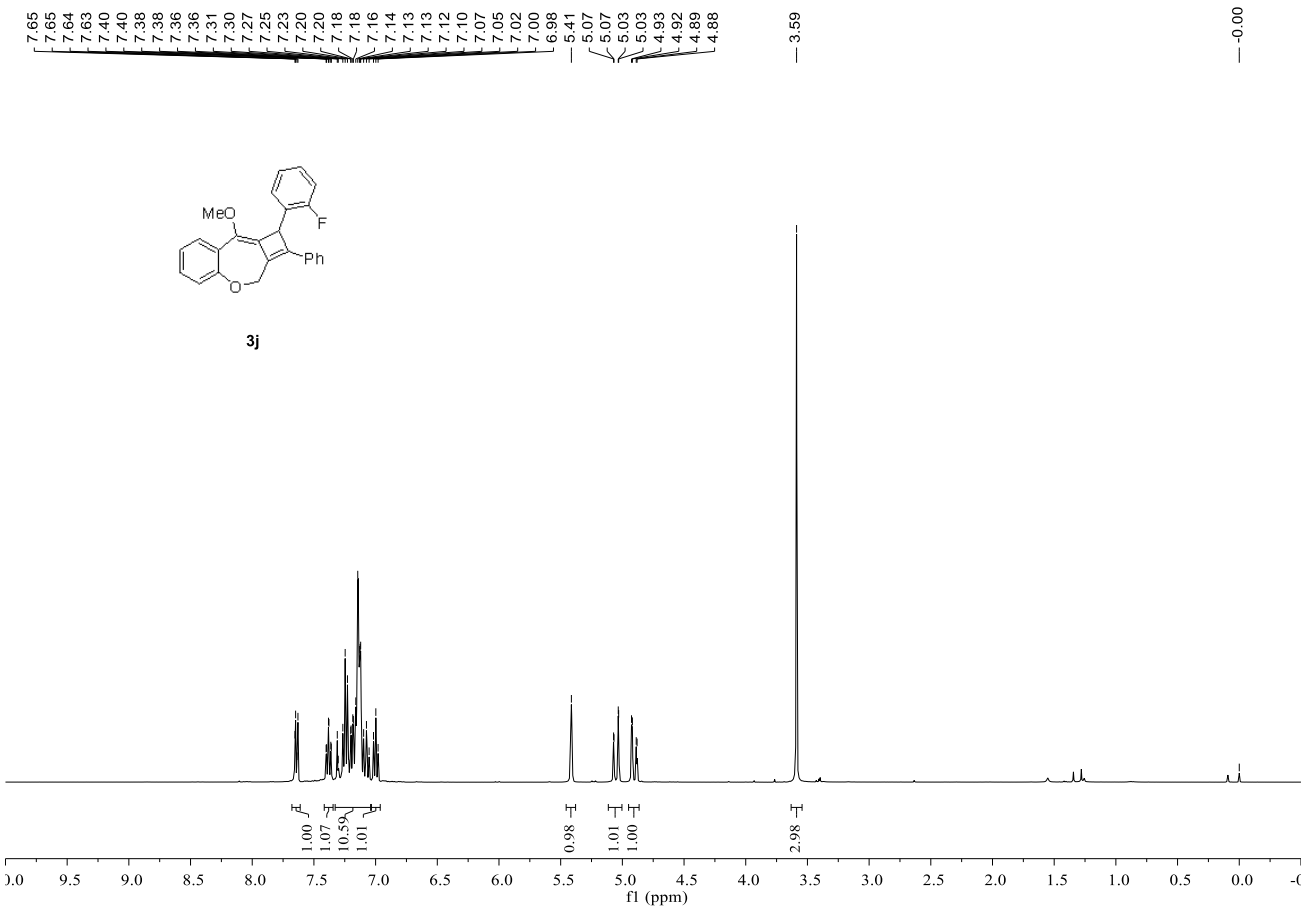
^{13}C NMR (100 MHz) of **3i** in $CDCl_3$



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



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



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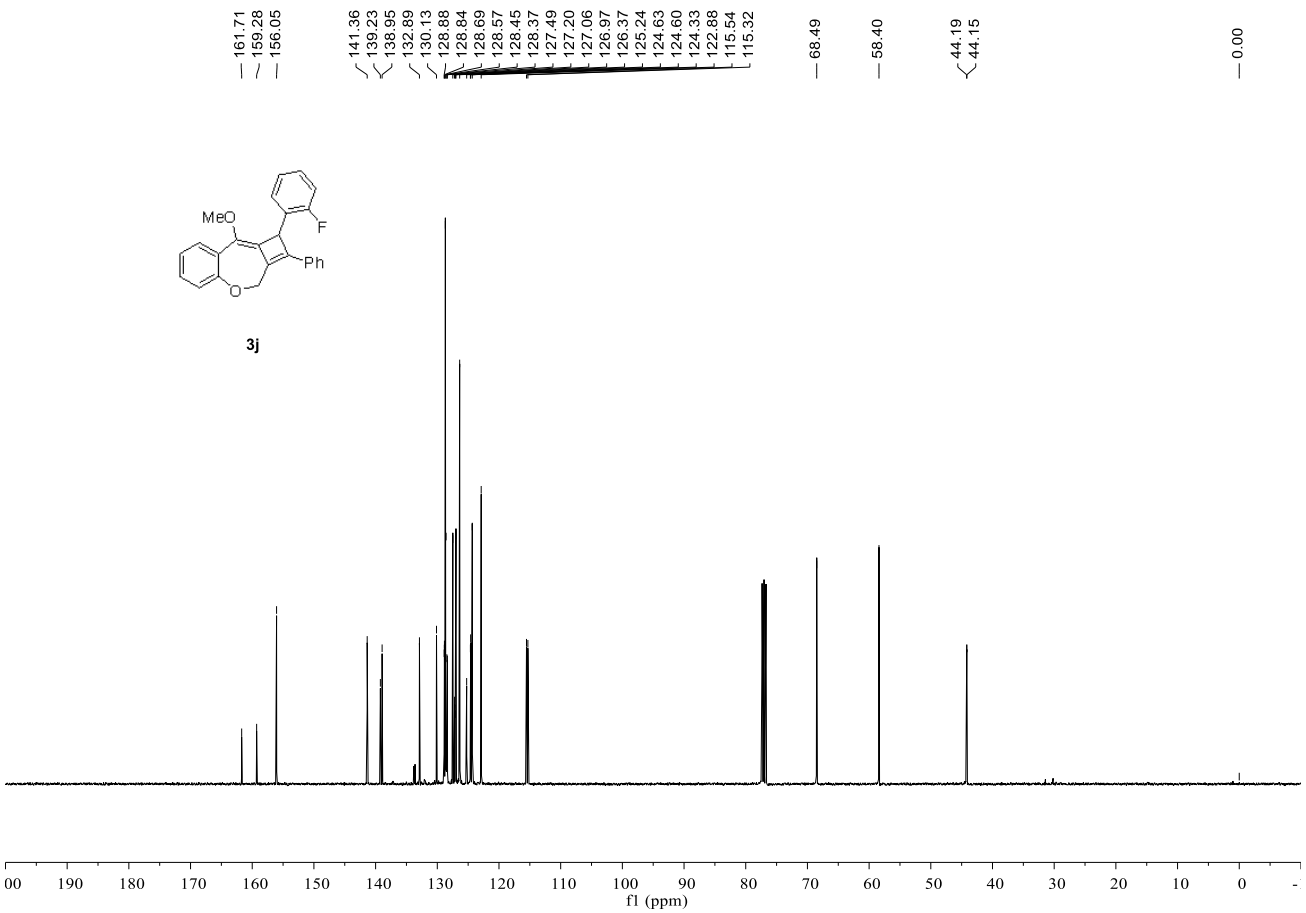
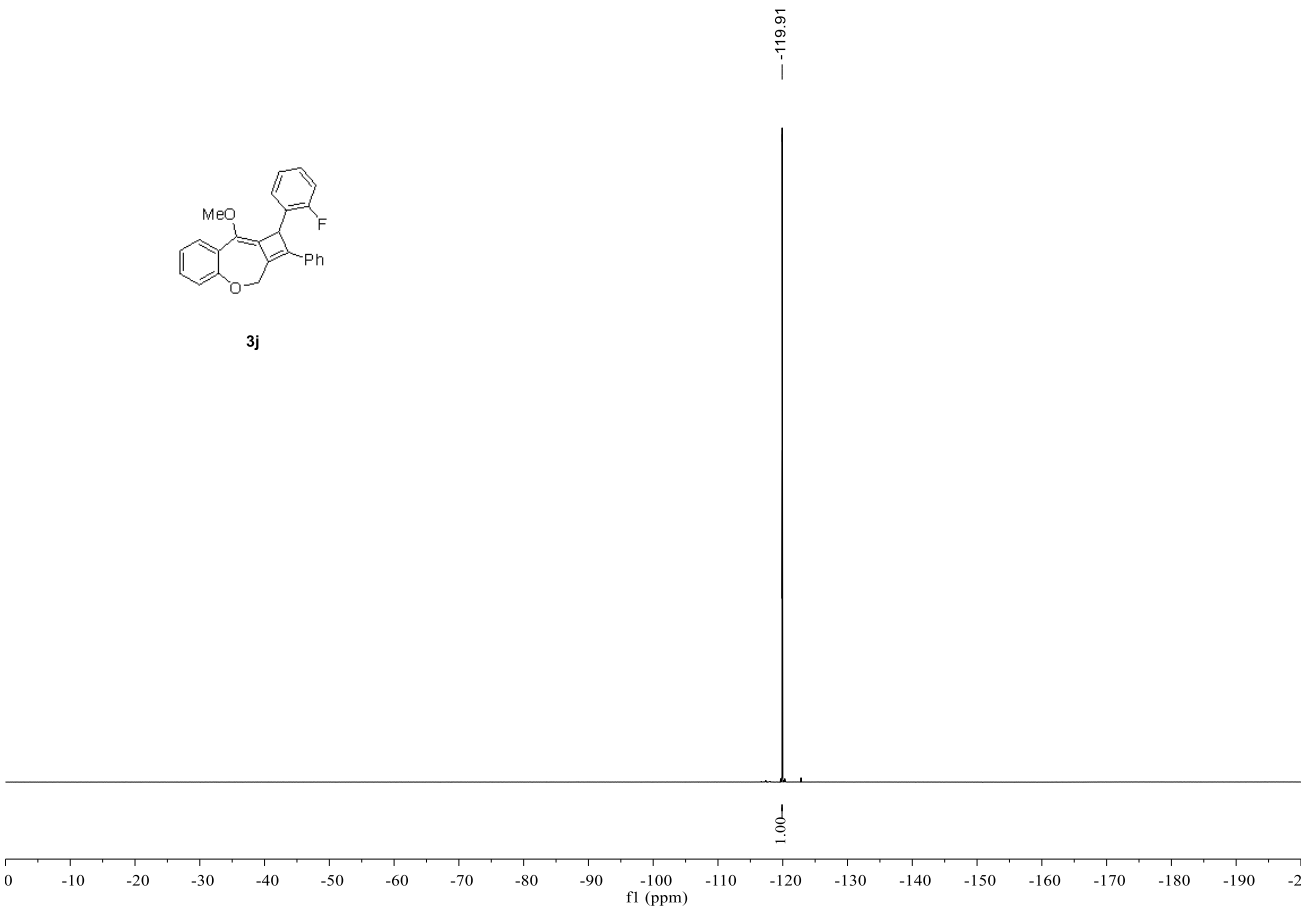
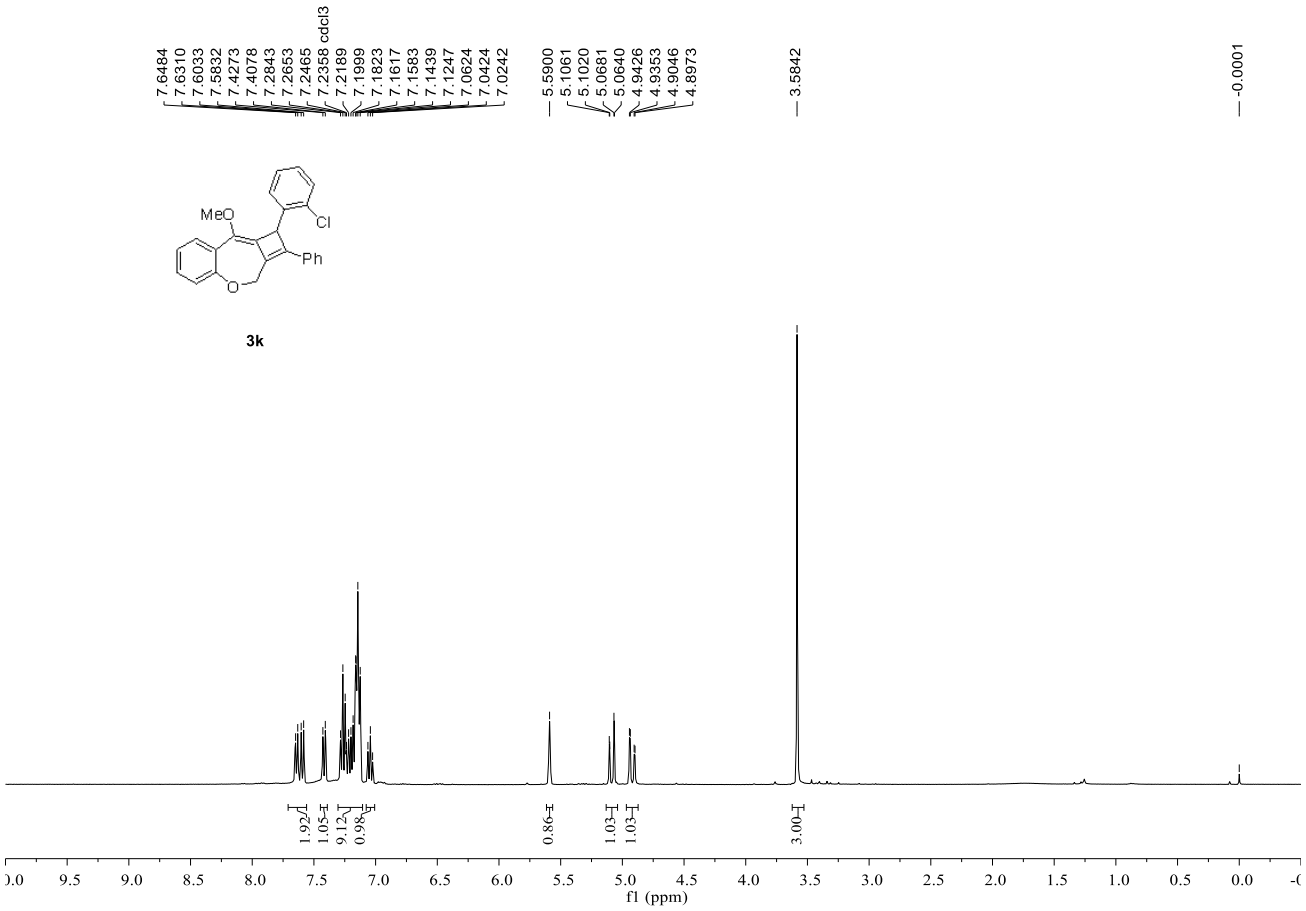


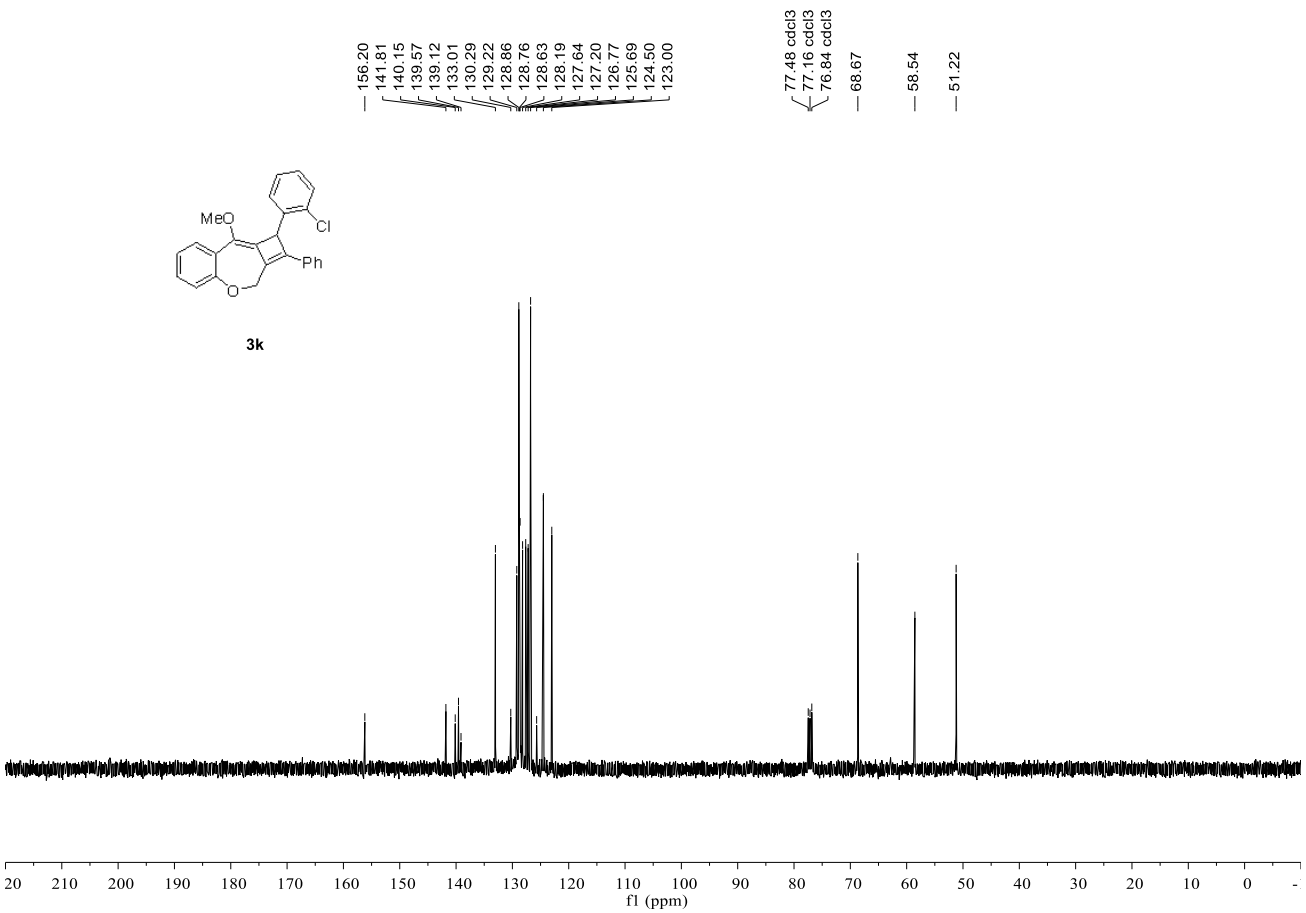
^{19}F NMR (376 MHz) of **3j** in $CDCl_3$



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



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



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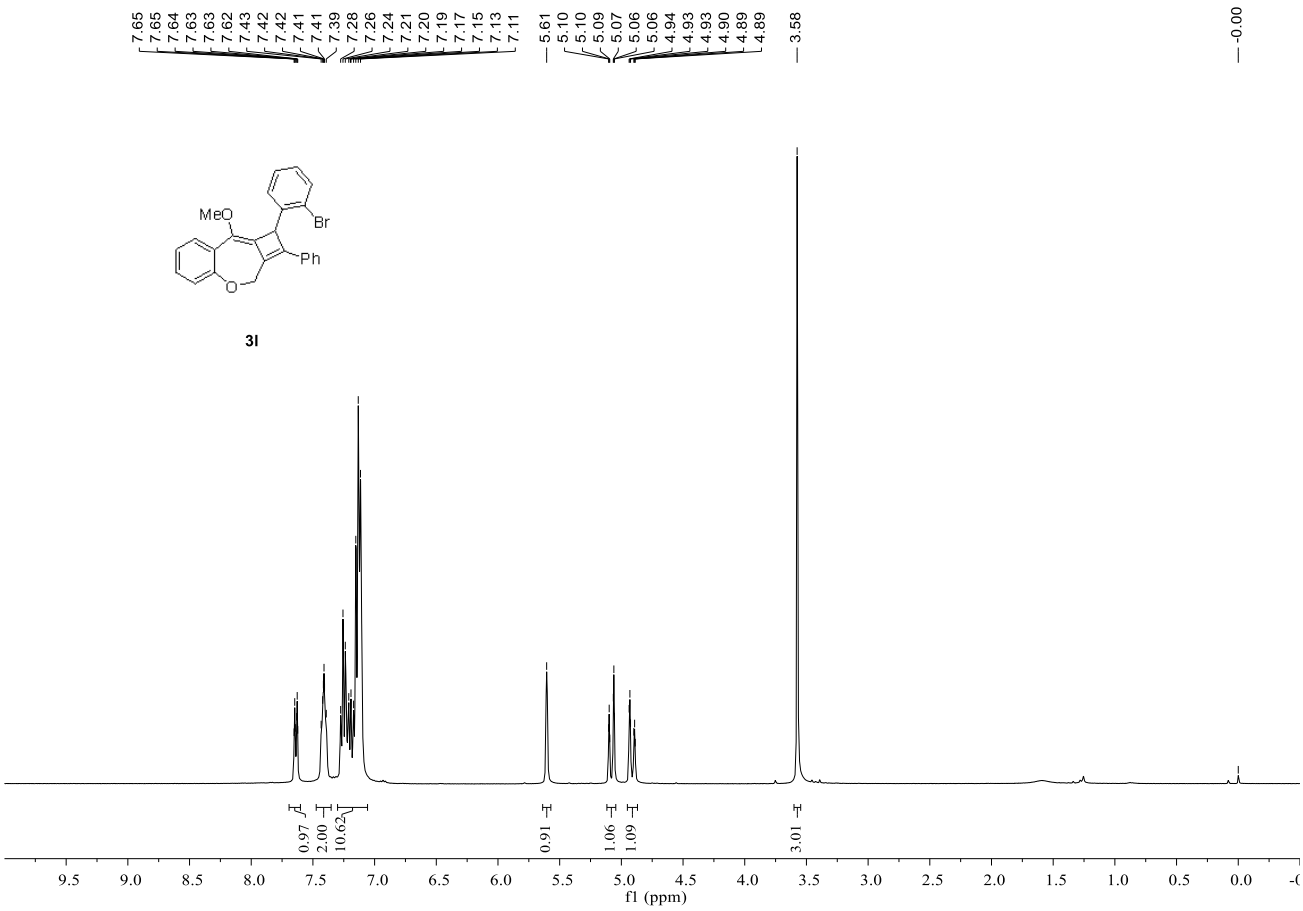
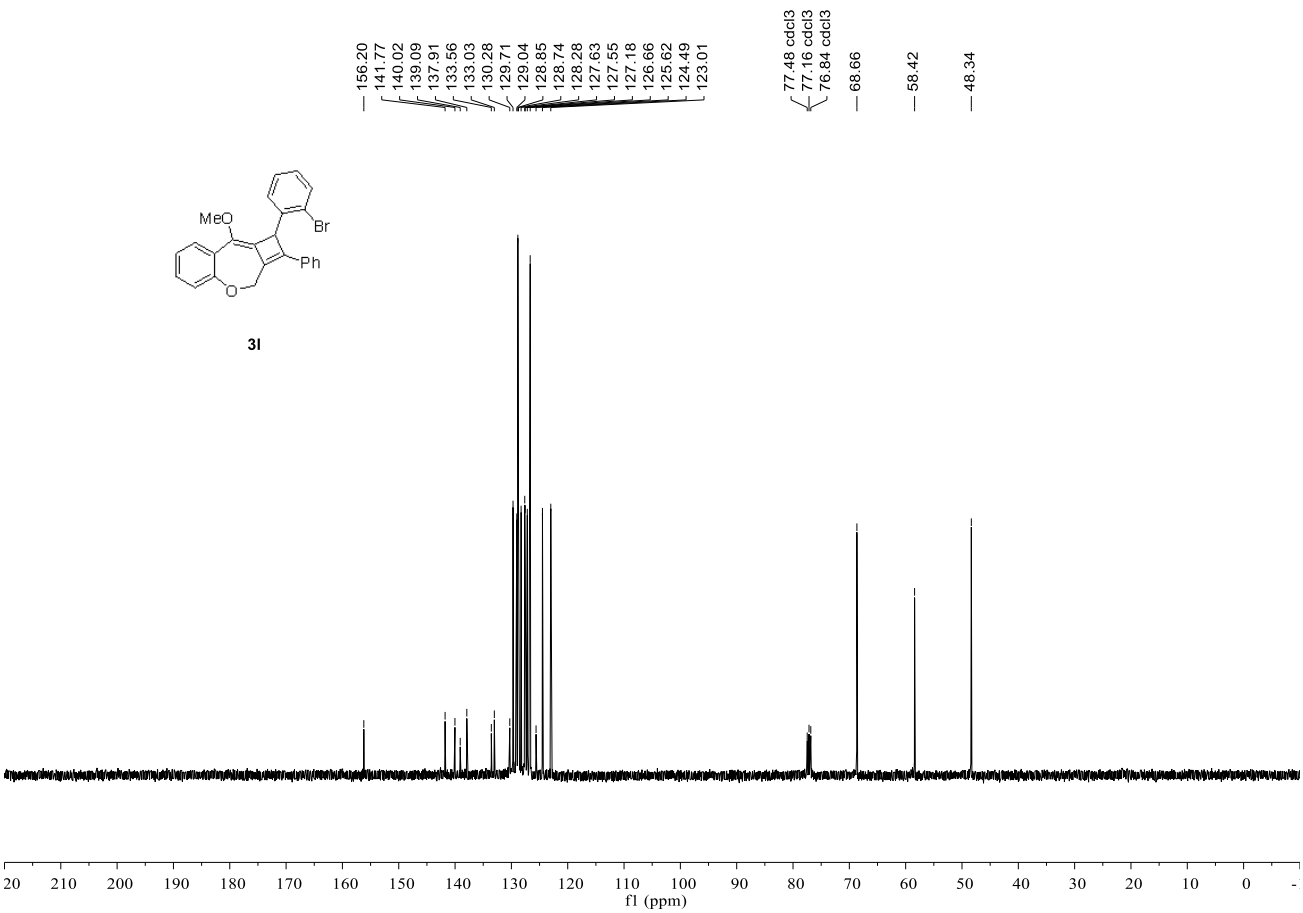
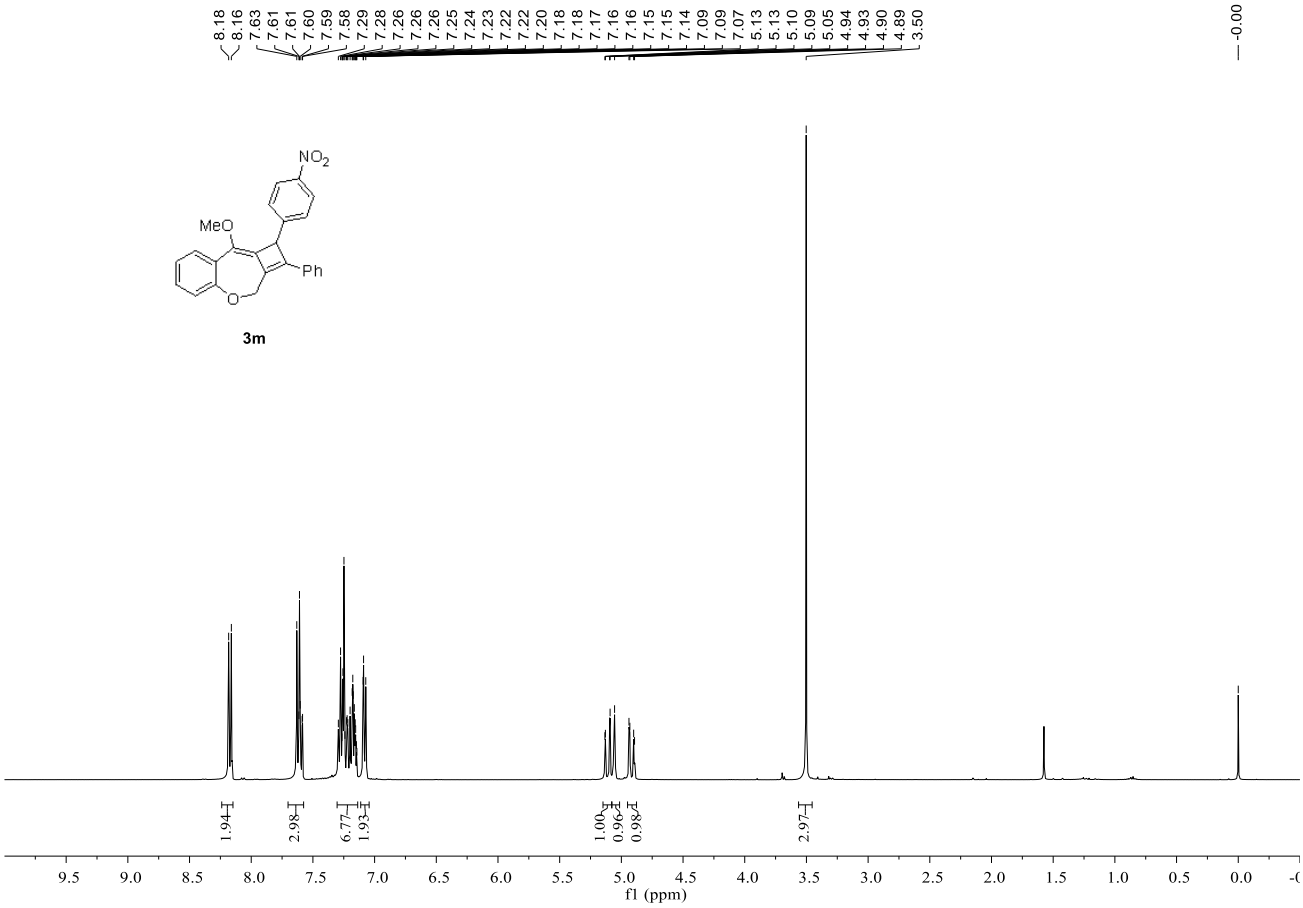


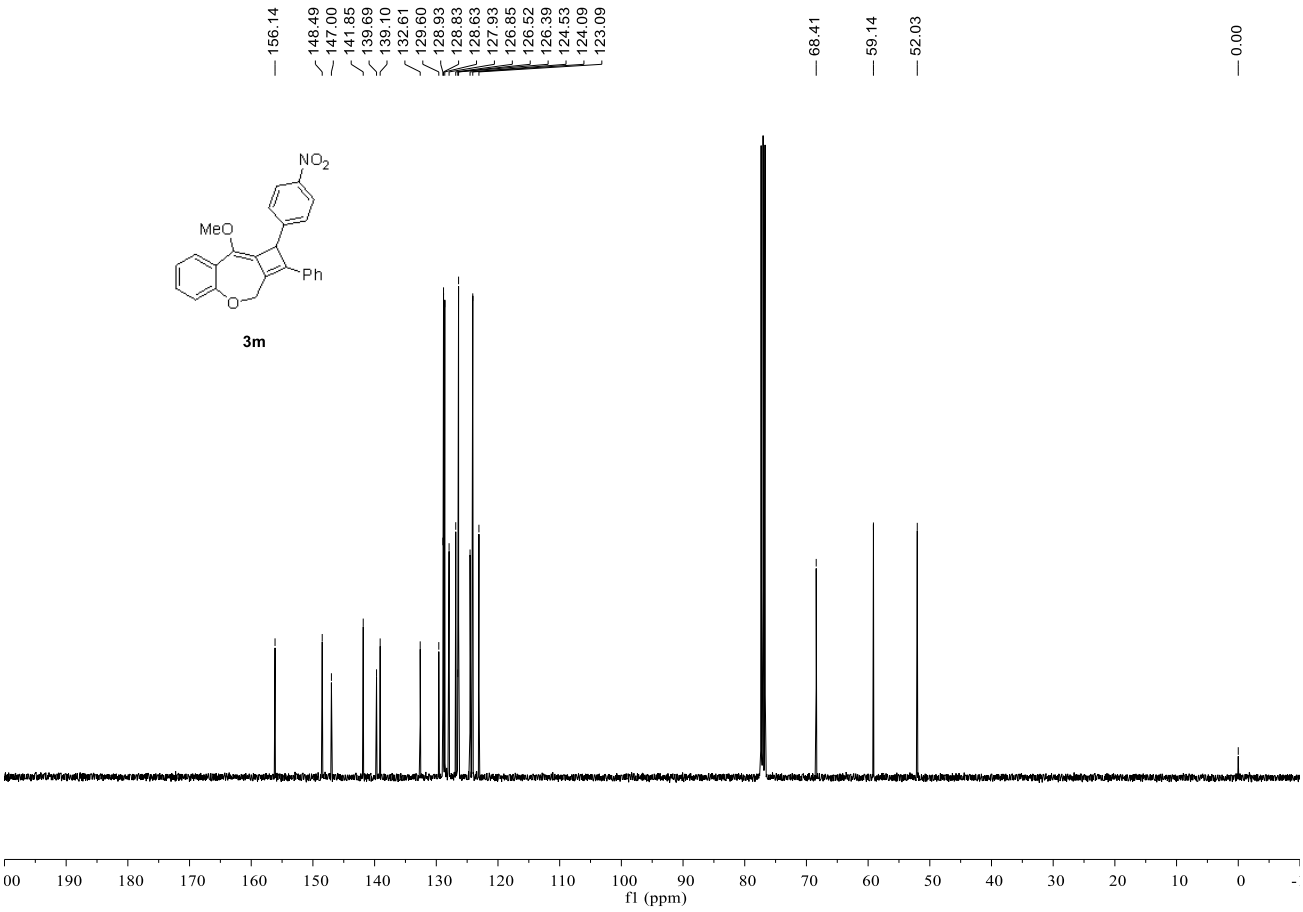
^{13}C NMR (100 MHz) of **3l** in $CDCl_3$



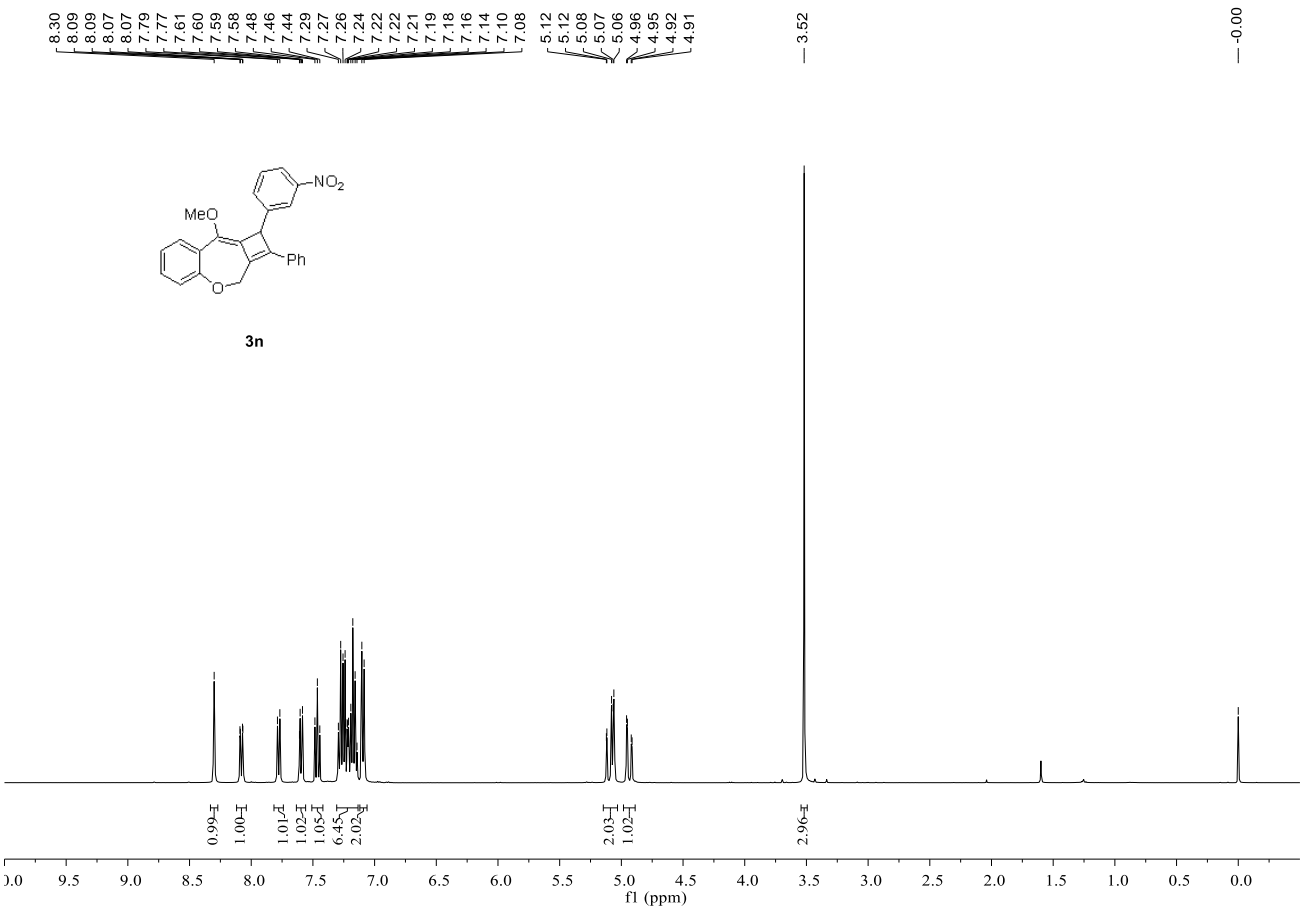
^{1}H NMR (400 MHz) of **3m** in $CDCl_3$



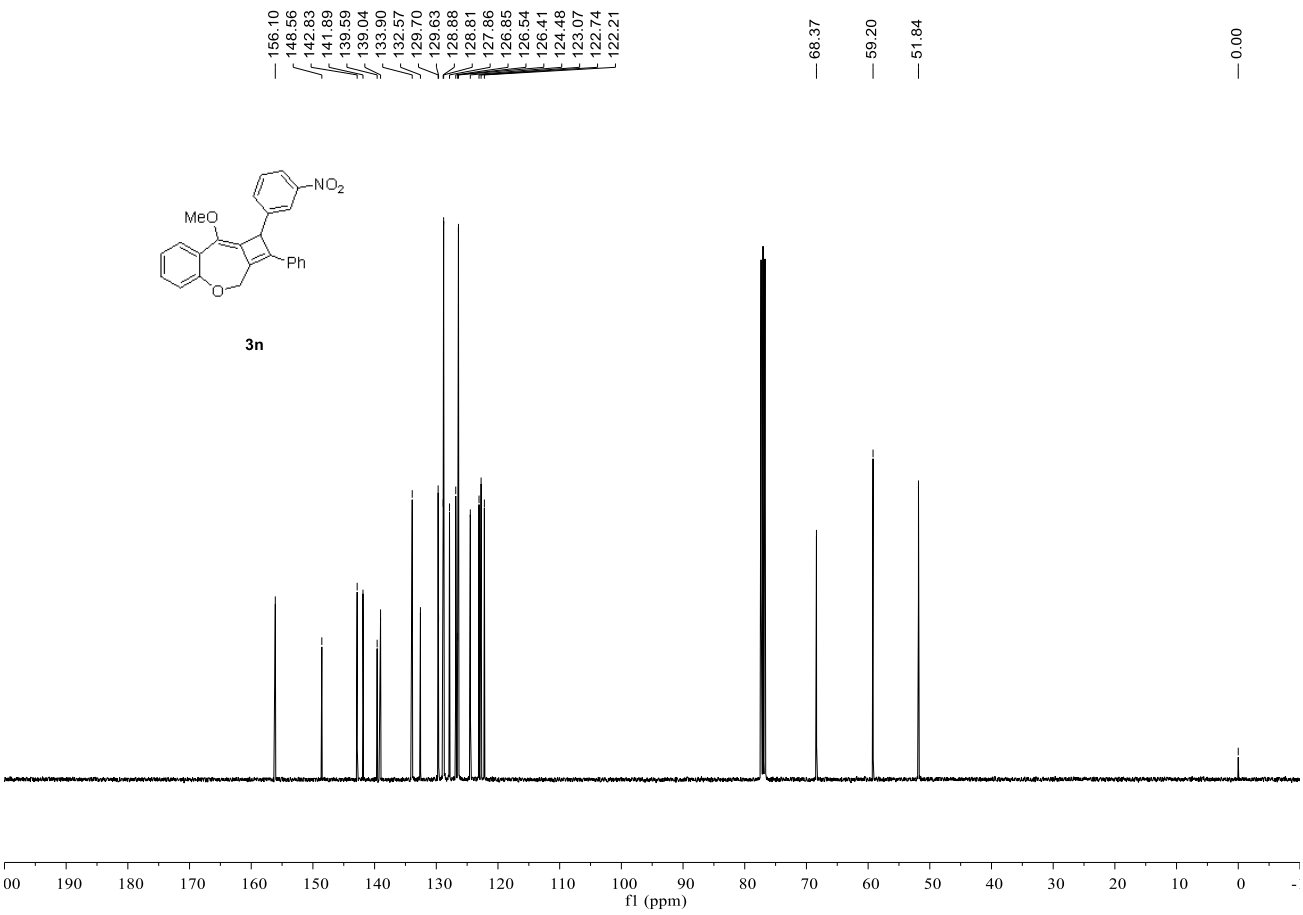
^{13}C NMR (100 MHz) of **3m** in $CDCl_3$



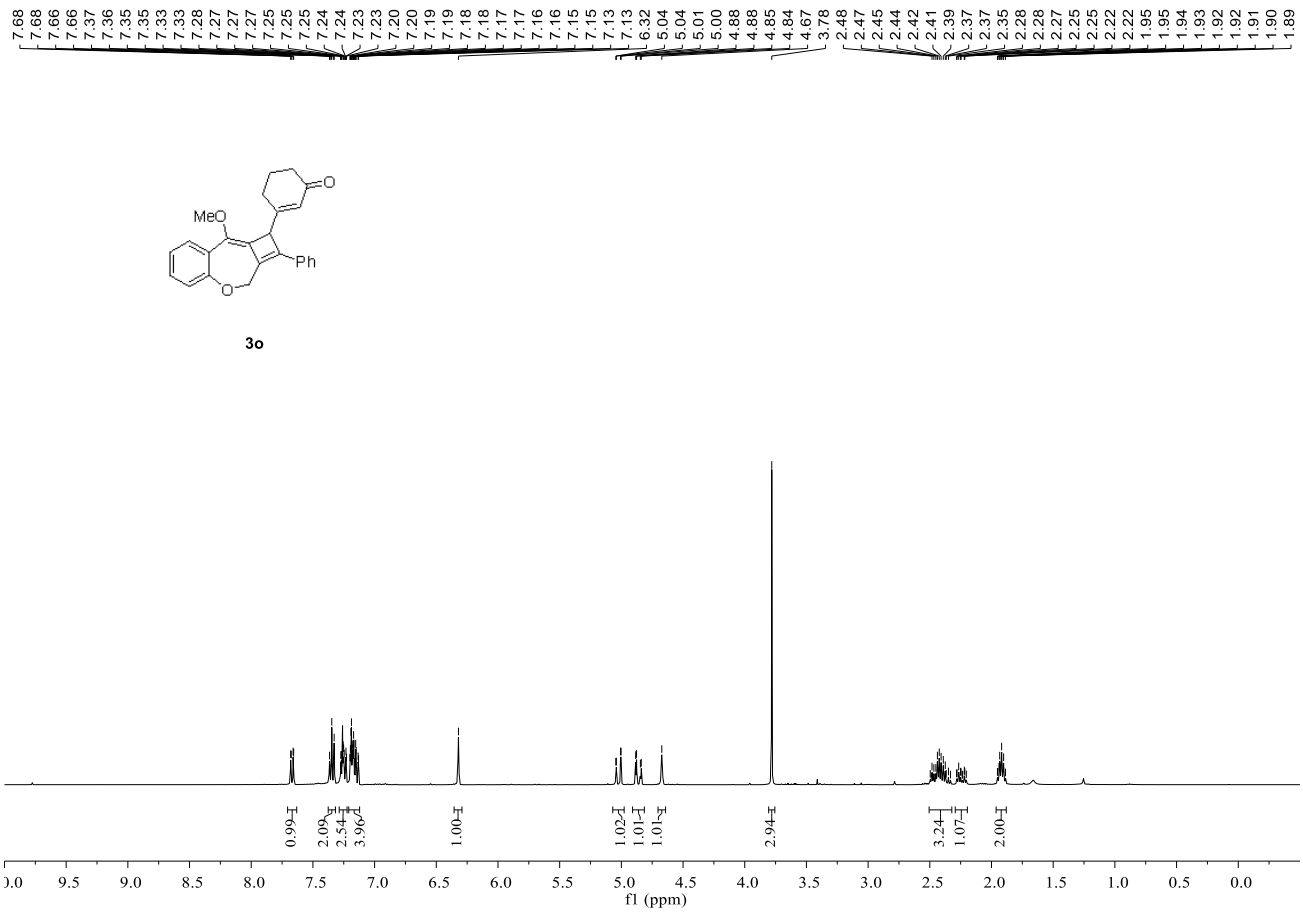
^{1}H NMR (400 MHz) of **3n** in $CDCl_3$



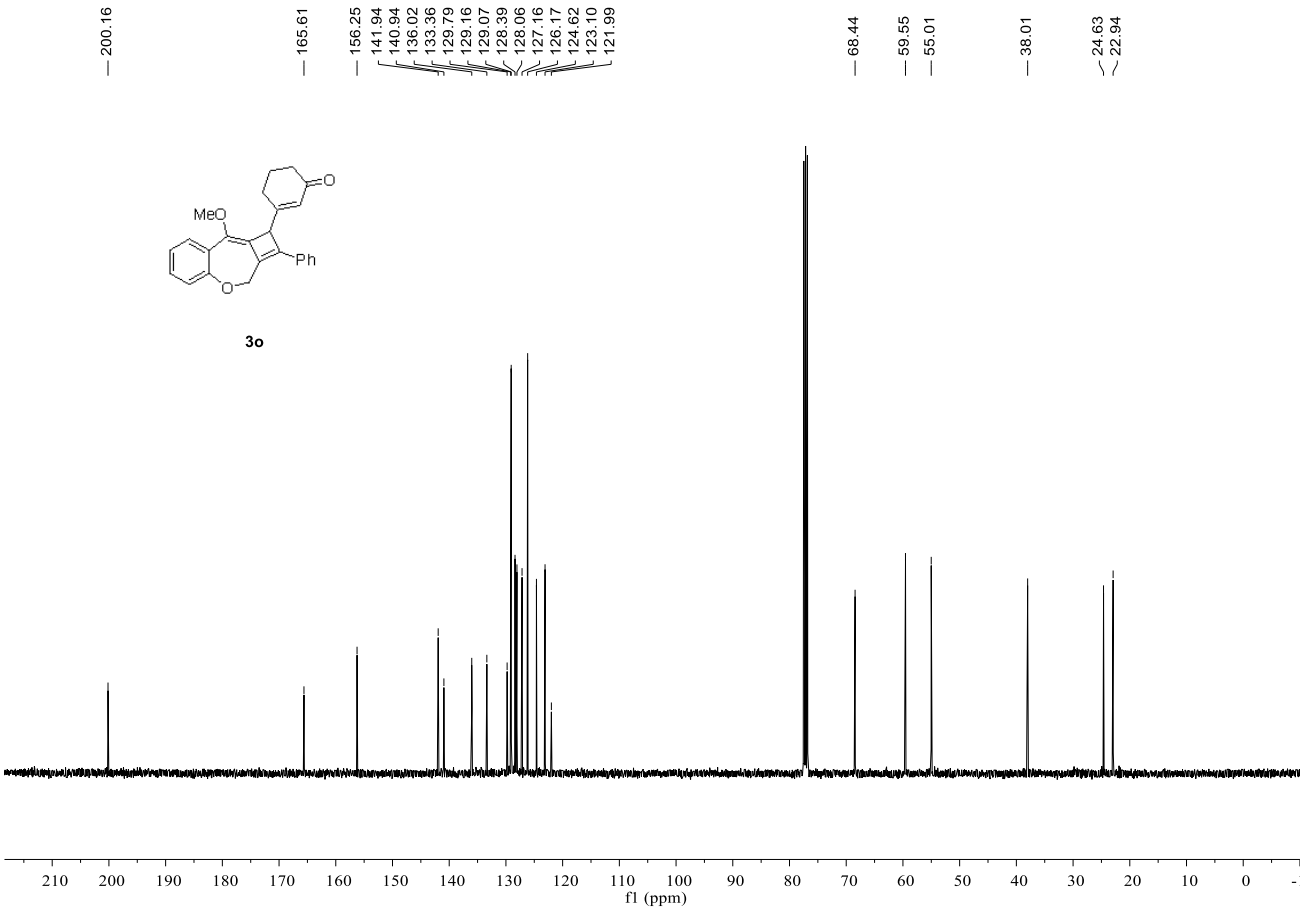
^{13}C NMR (100 MHz) of **3n** in $CDCl_3$



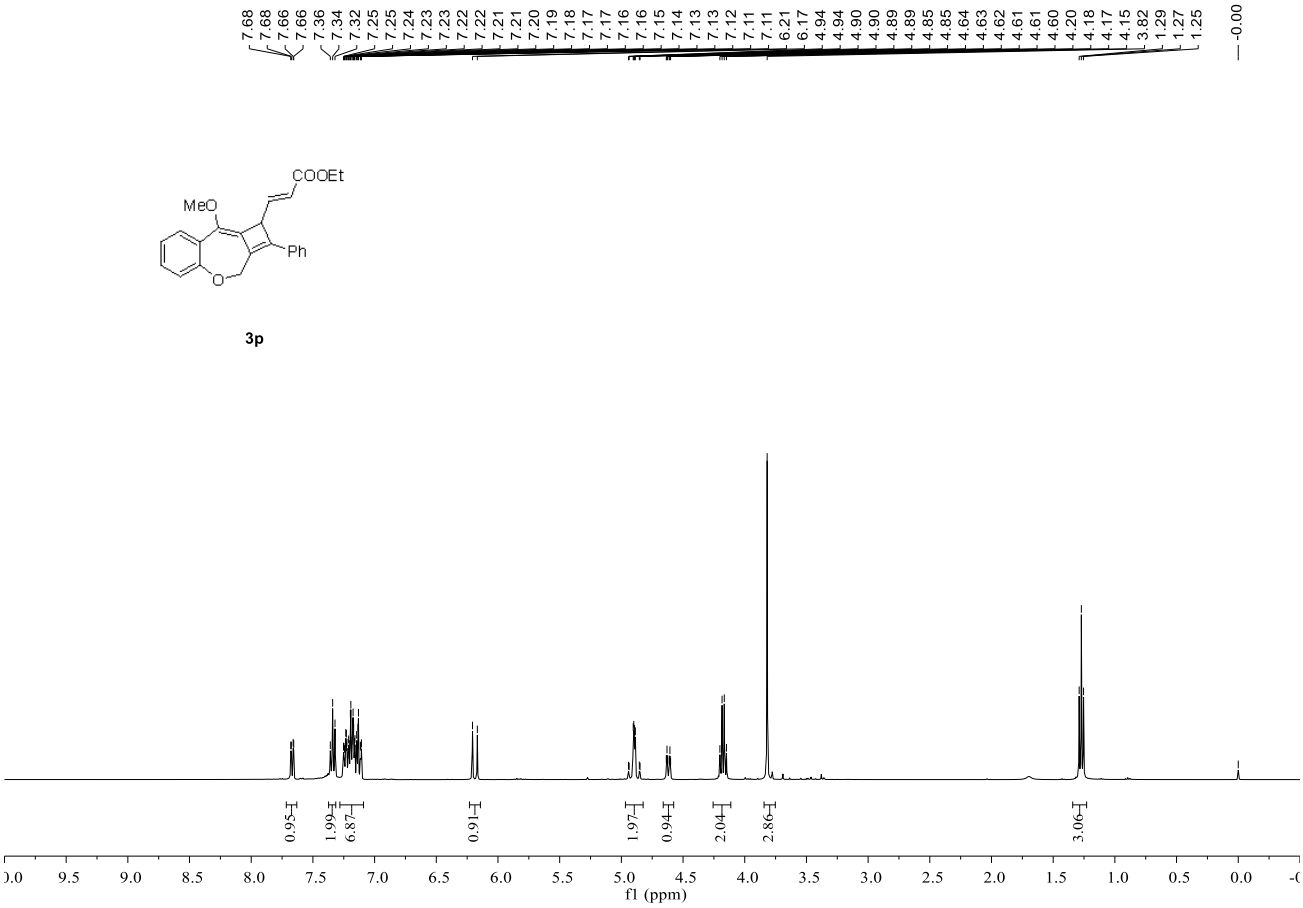
^{1}H NMR (400 MHz) of **3o** in $CDCl_3$



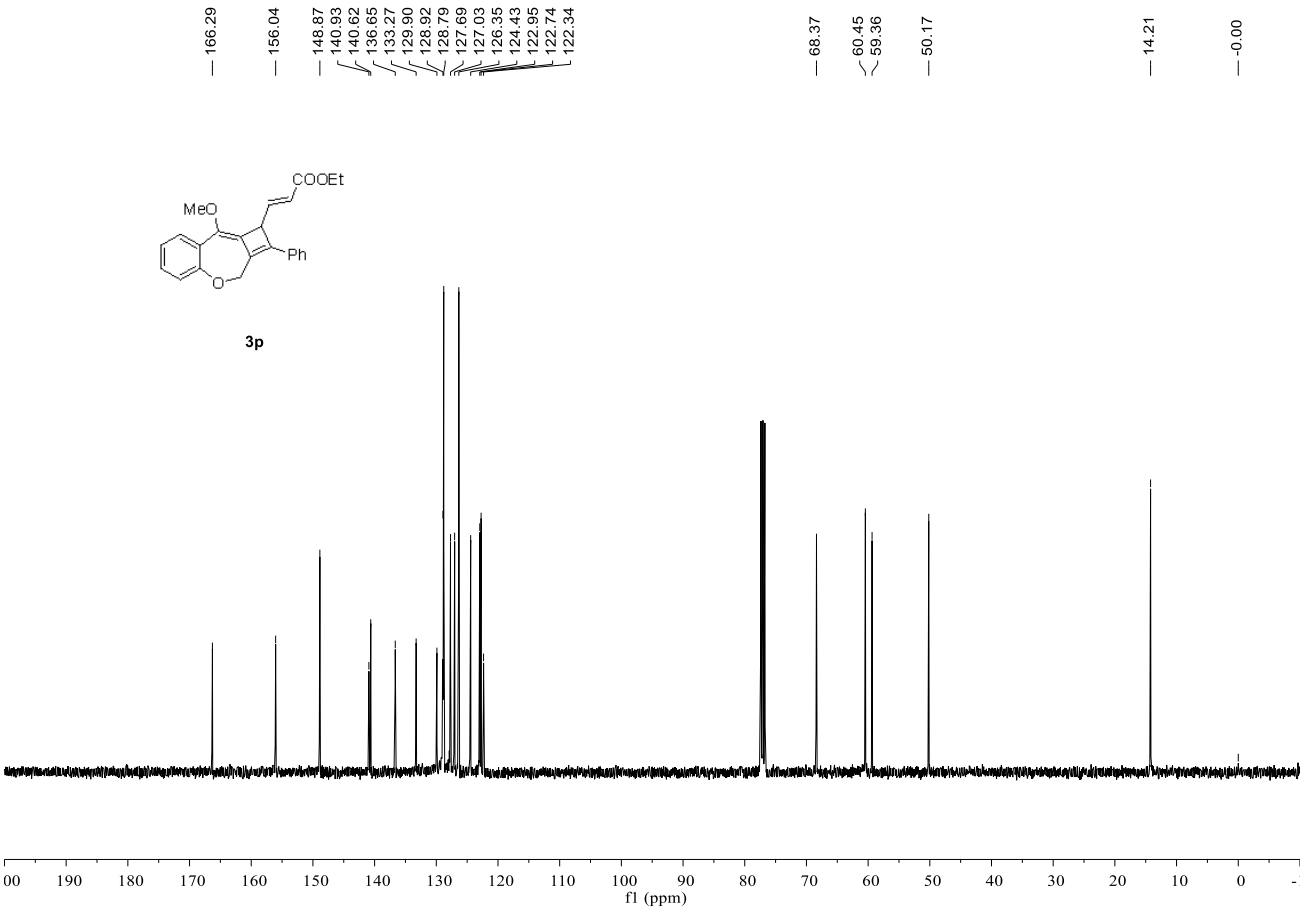
^{13}C NMR (100 MHz) of **3o** in $CDCl_3$



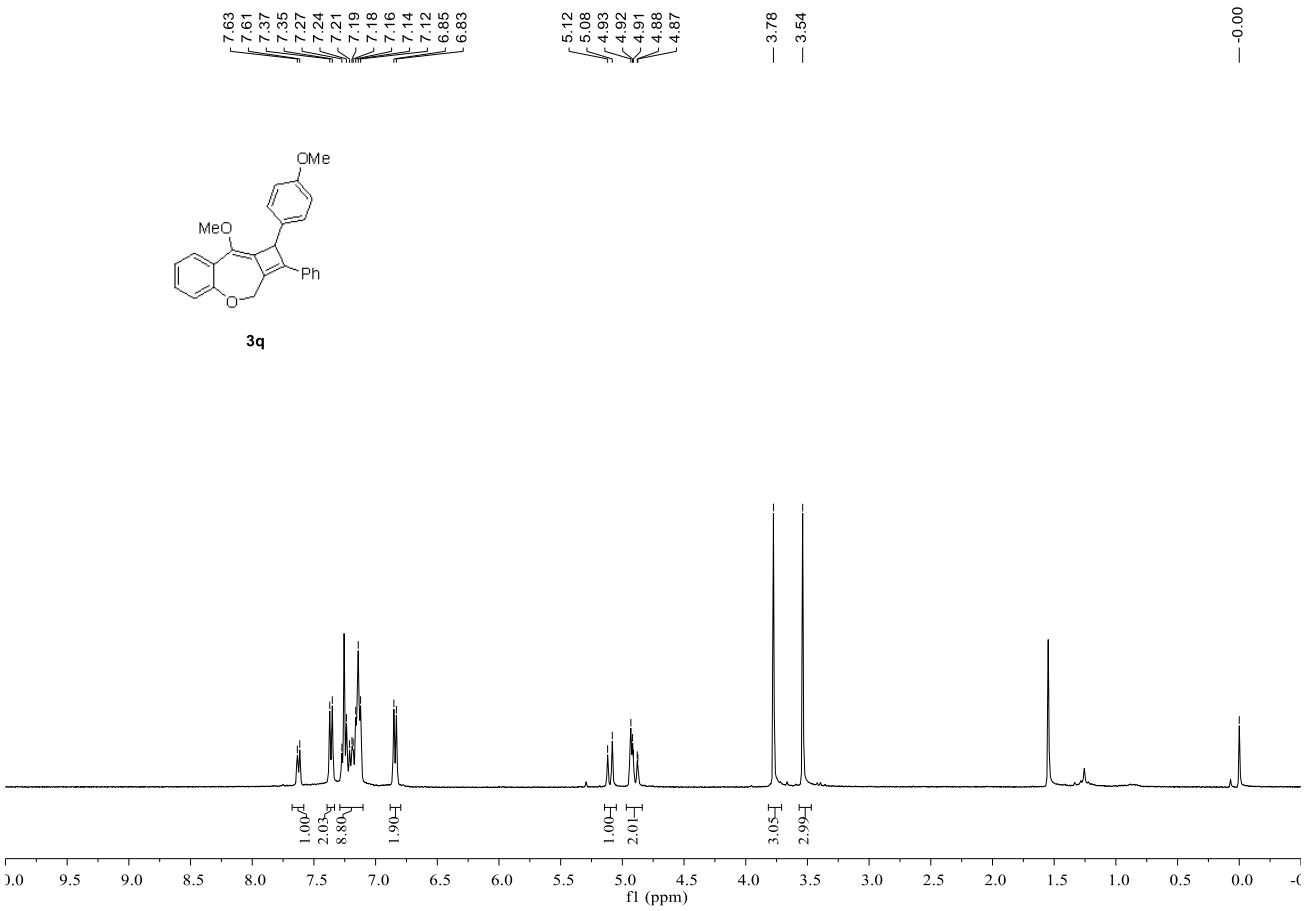
^{1}H NMR (400 MHz) of **3p** in $CDCl_3$



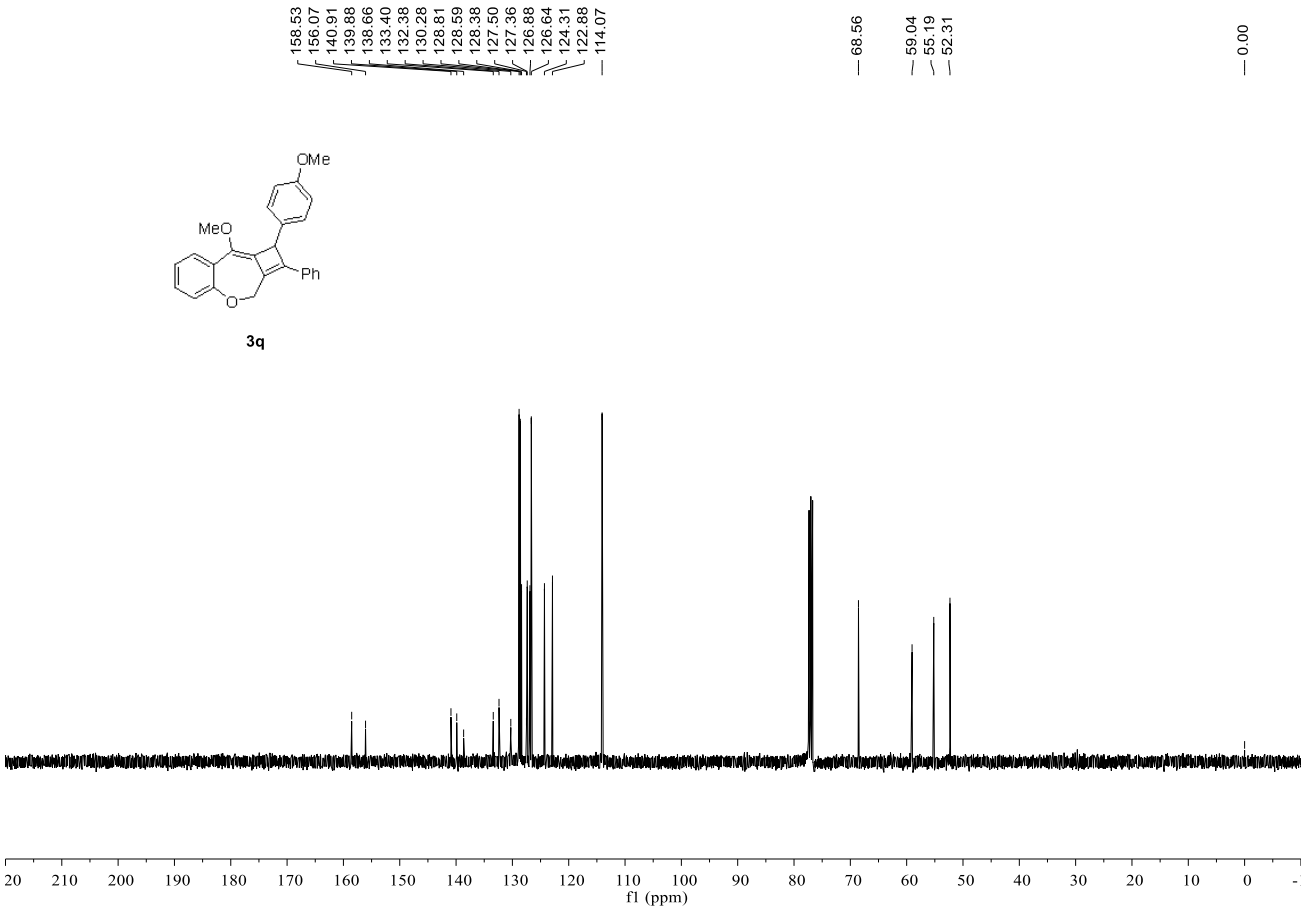
^{13}C NMR (100 MHz) of **3p** in $CDCl_3$



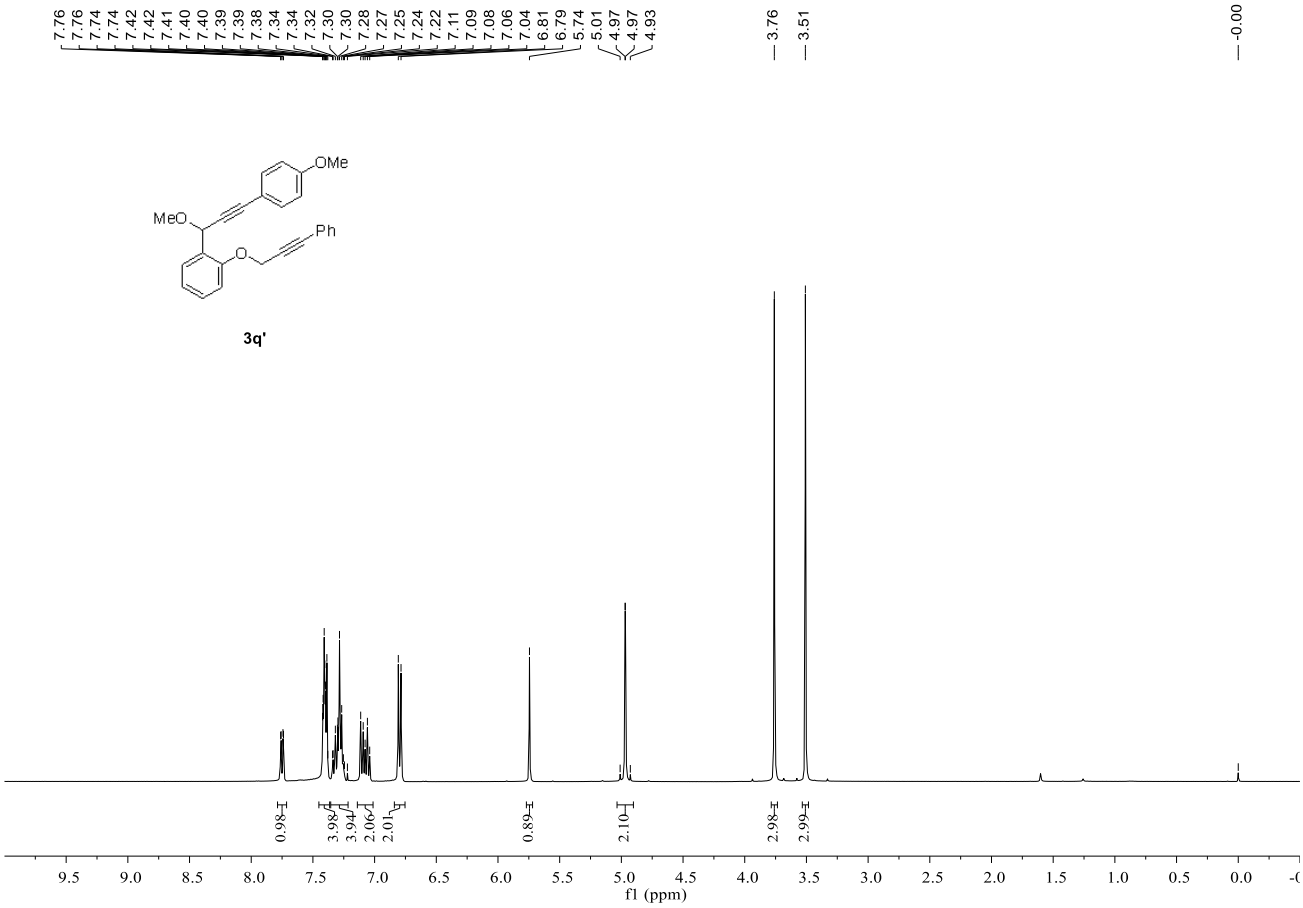
^{1}H NMR (400 MHz) of **3q** in $CDCl_3$



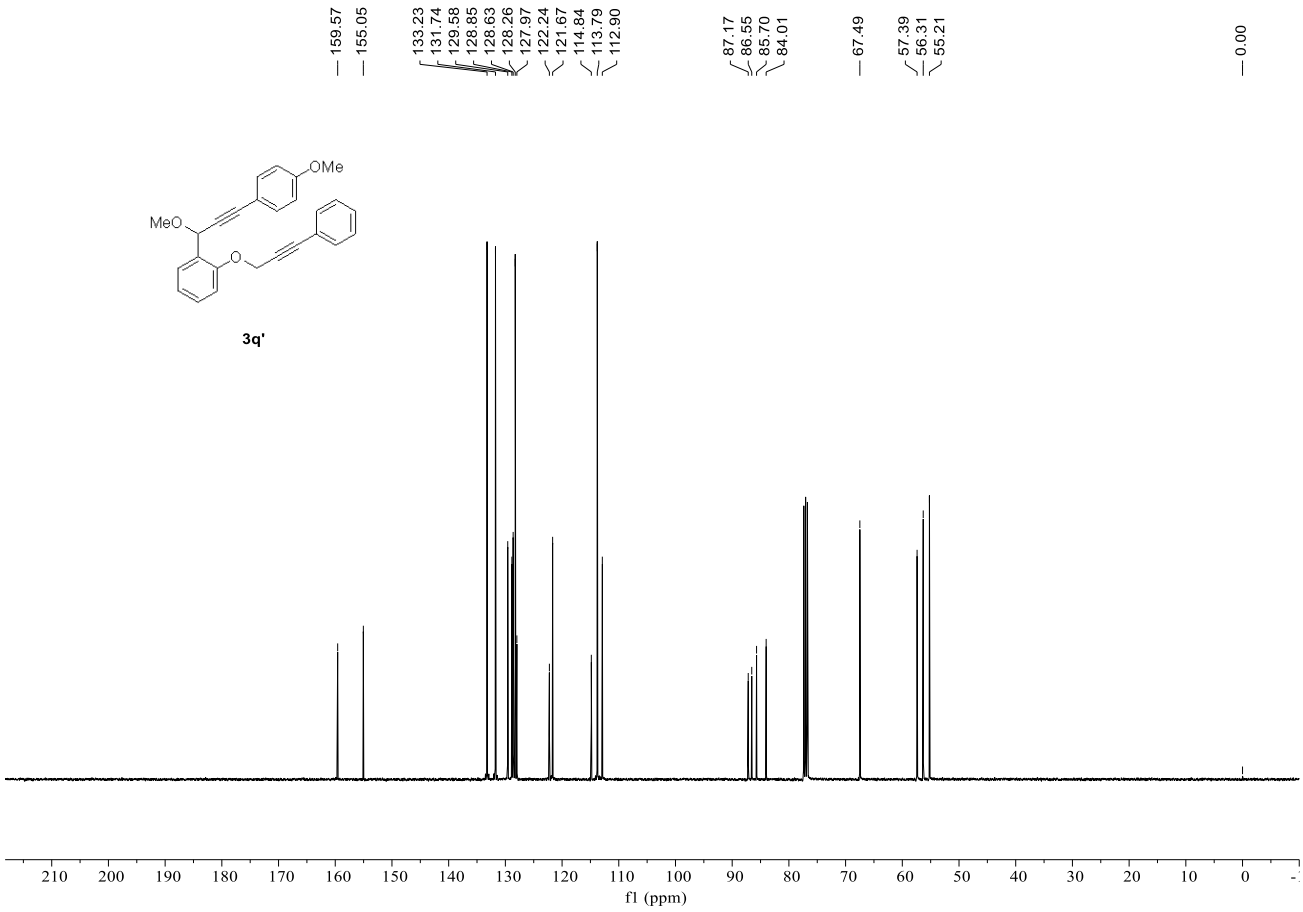
^{13}C NMR (100 MHz) of **3q** in $CDCl_3$



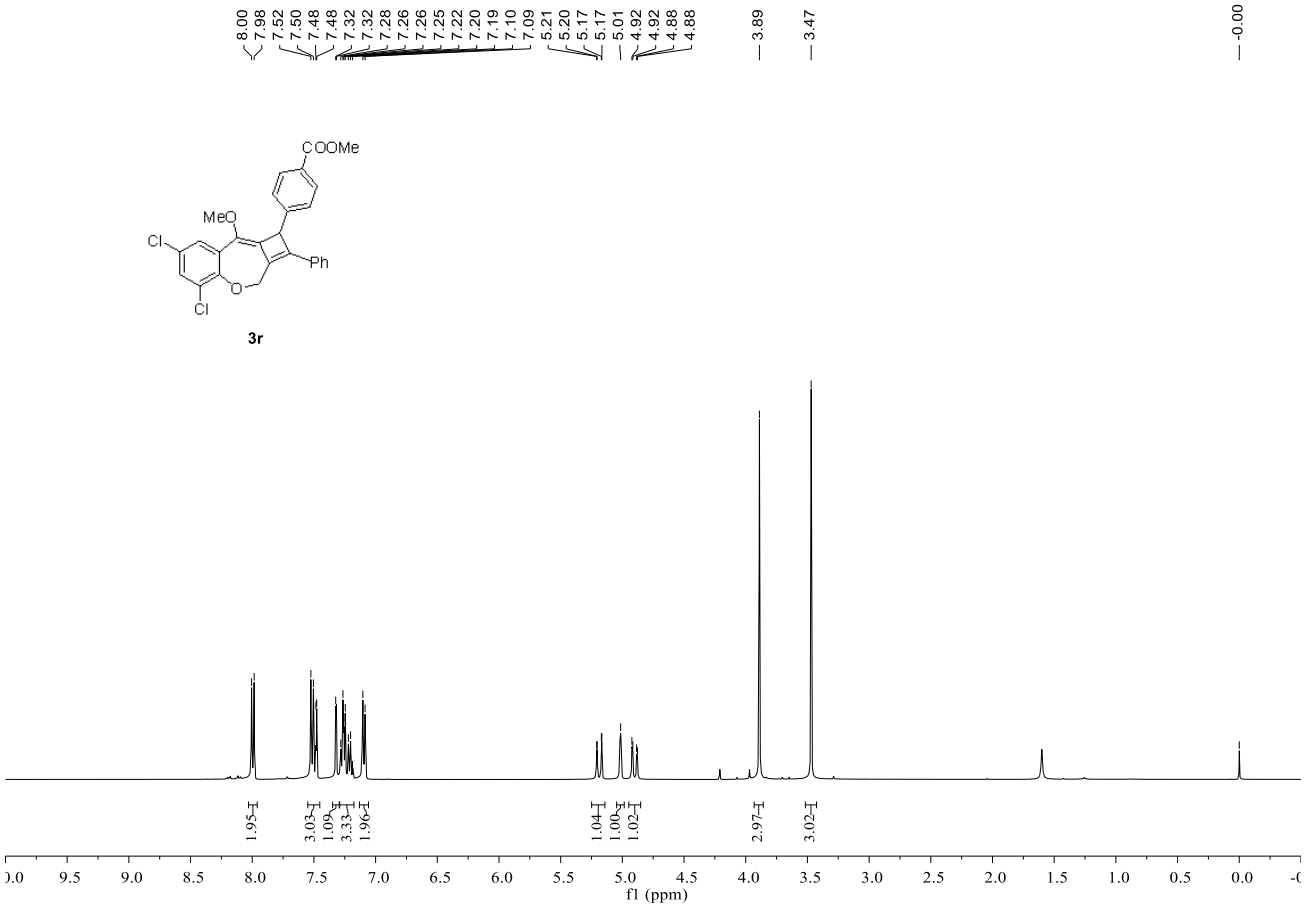
^{1}H NMR (400 MHz) of **3q'** in $CDCl_3$



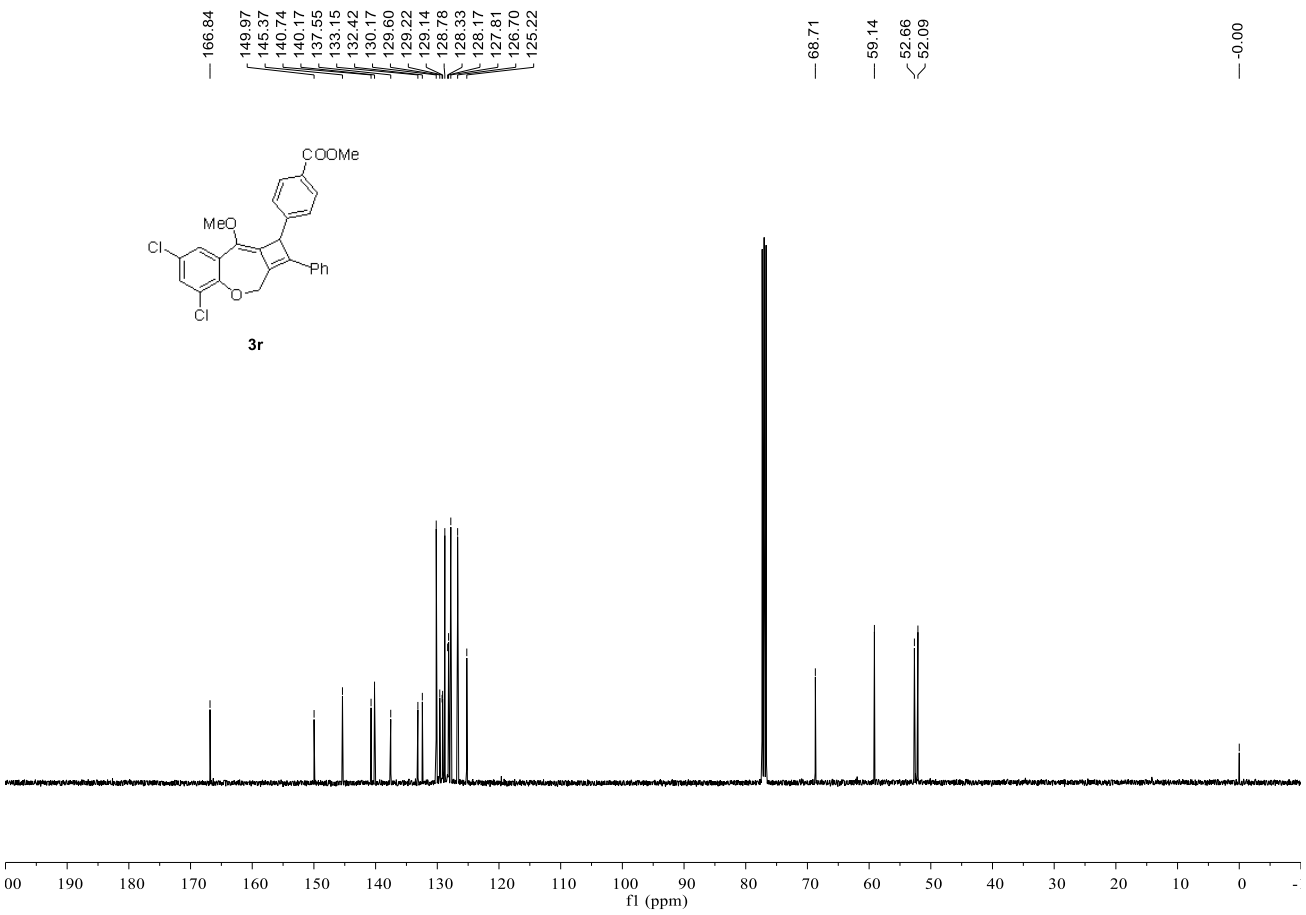
^{13}C NMR (100 MHz) of **3q'** in $CDCl_3$



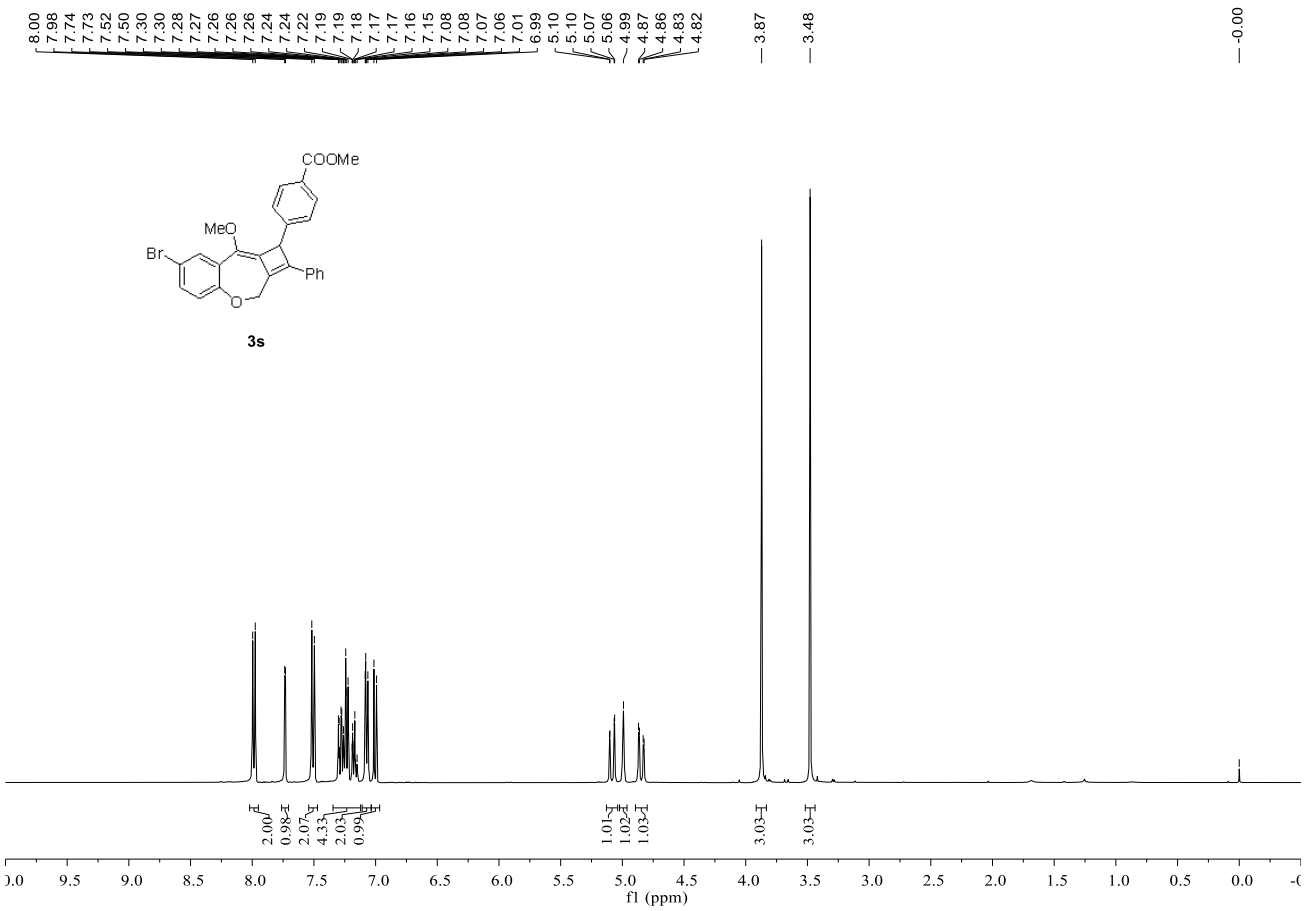
^{1}H NMR (400 MHz) of **3r** in $CDCl_3$



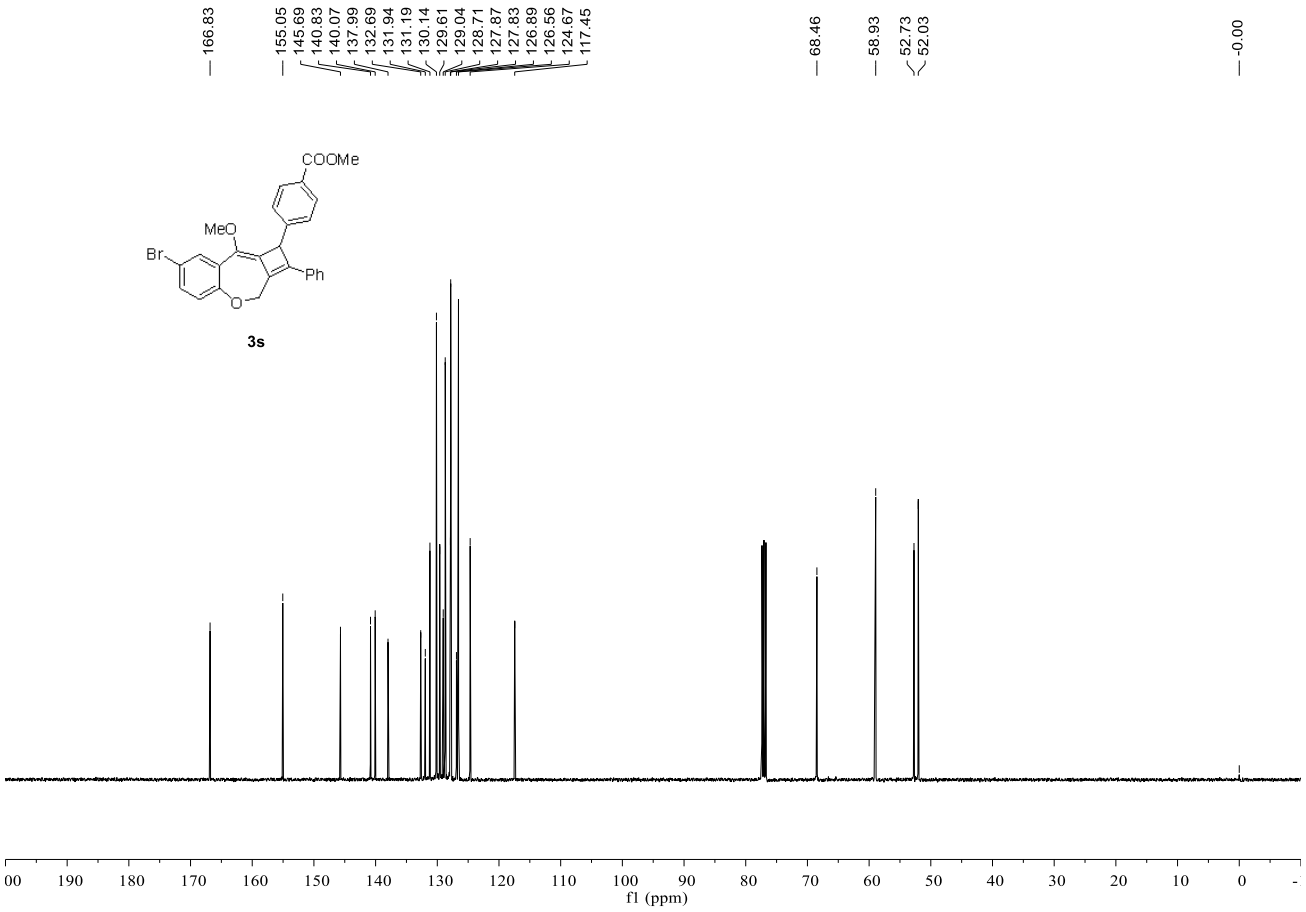
^{13}C NMR (100 MHz) of **3r** in $CDCl_3$



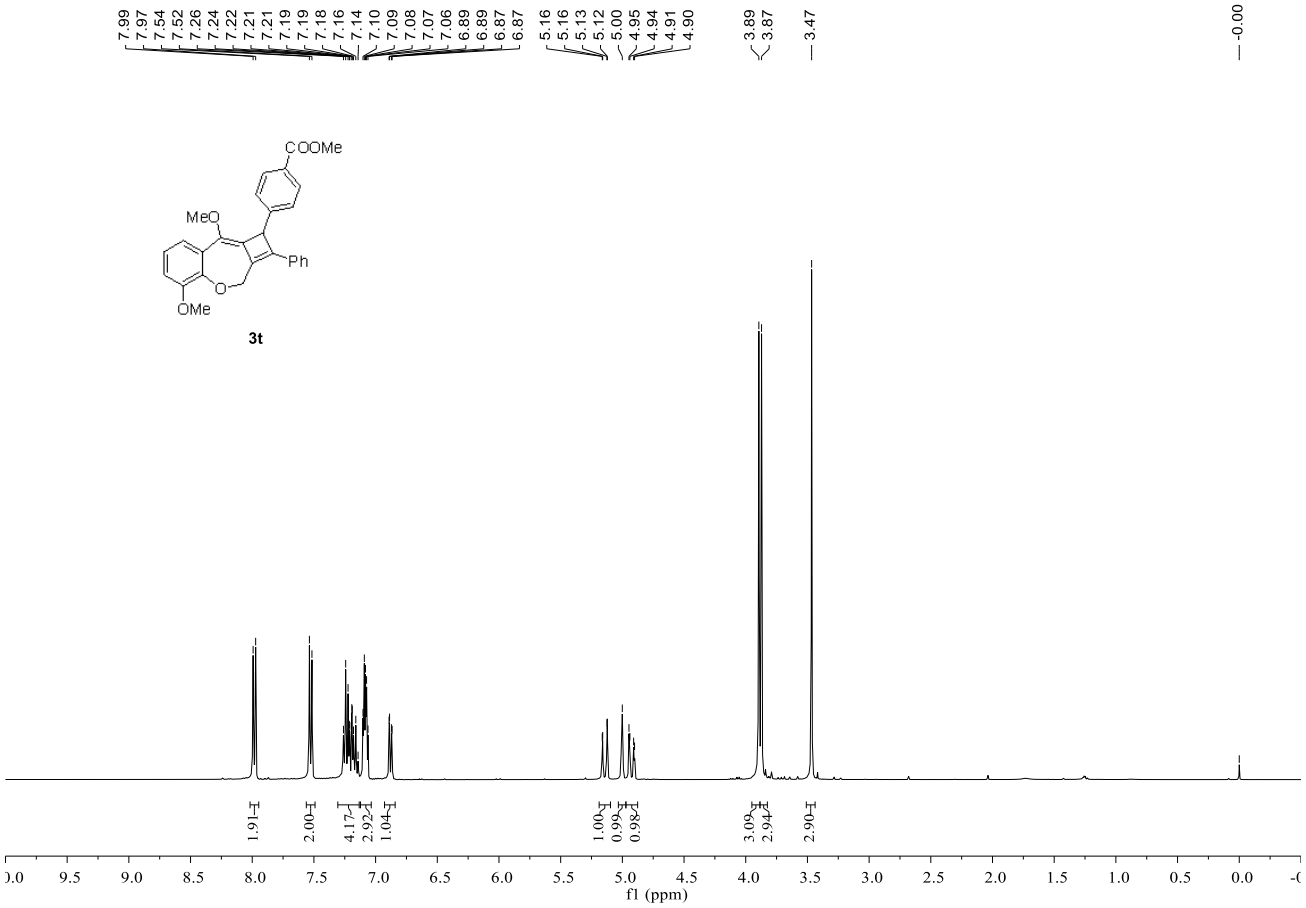
^{1}H NMR (400 MHz) of **3s** in $CDCl_3$



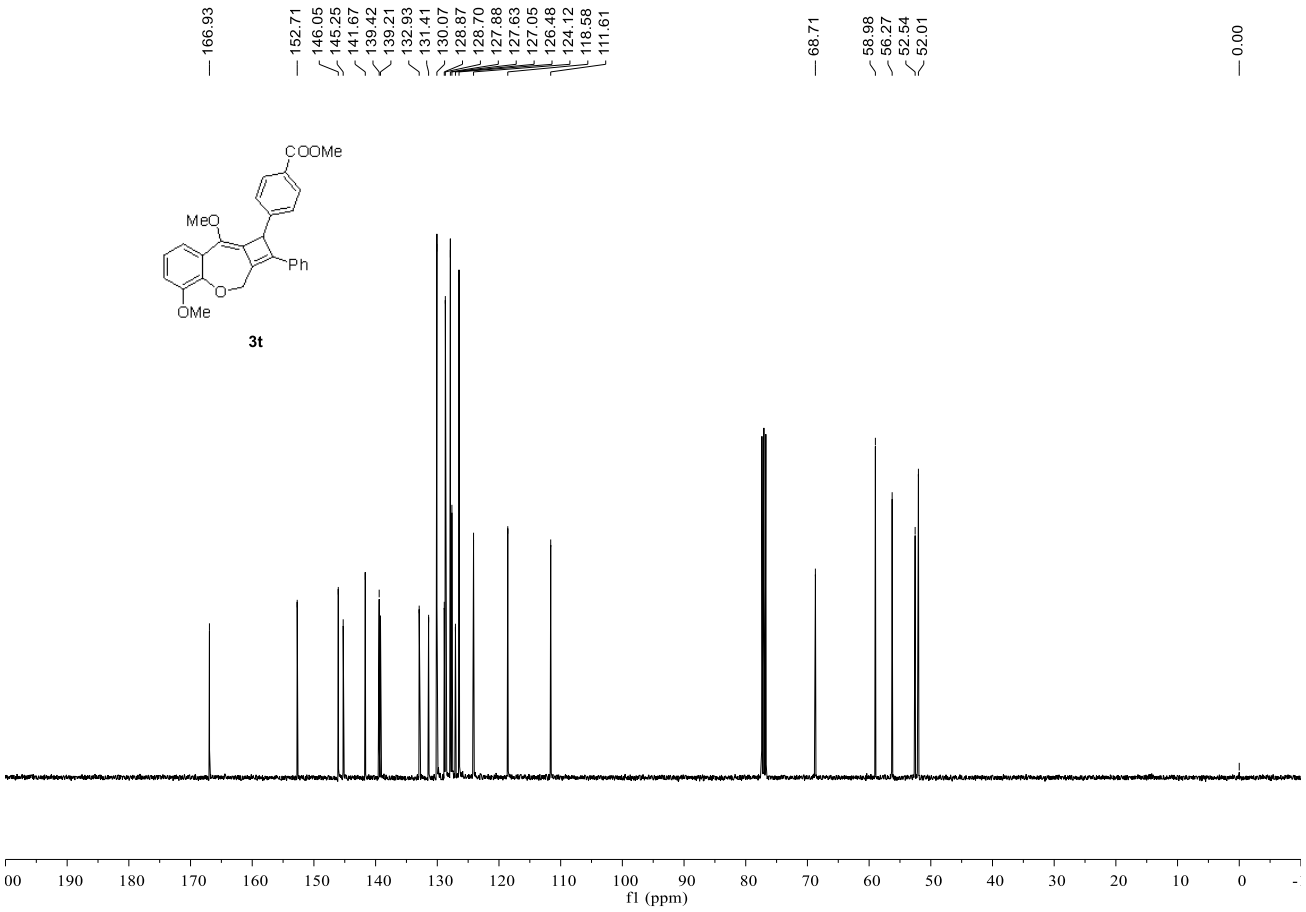
^{13}C NMR (100 MHz) of **3s** in $CDCl_3$



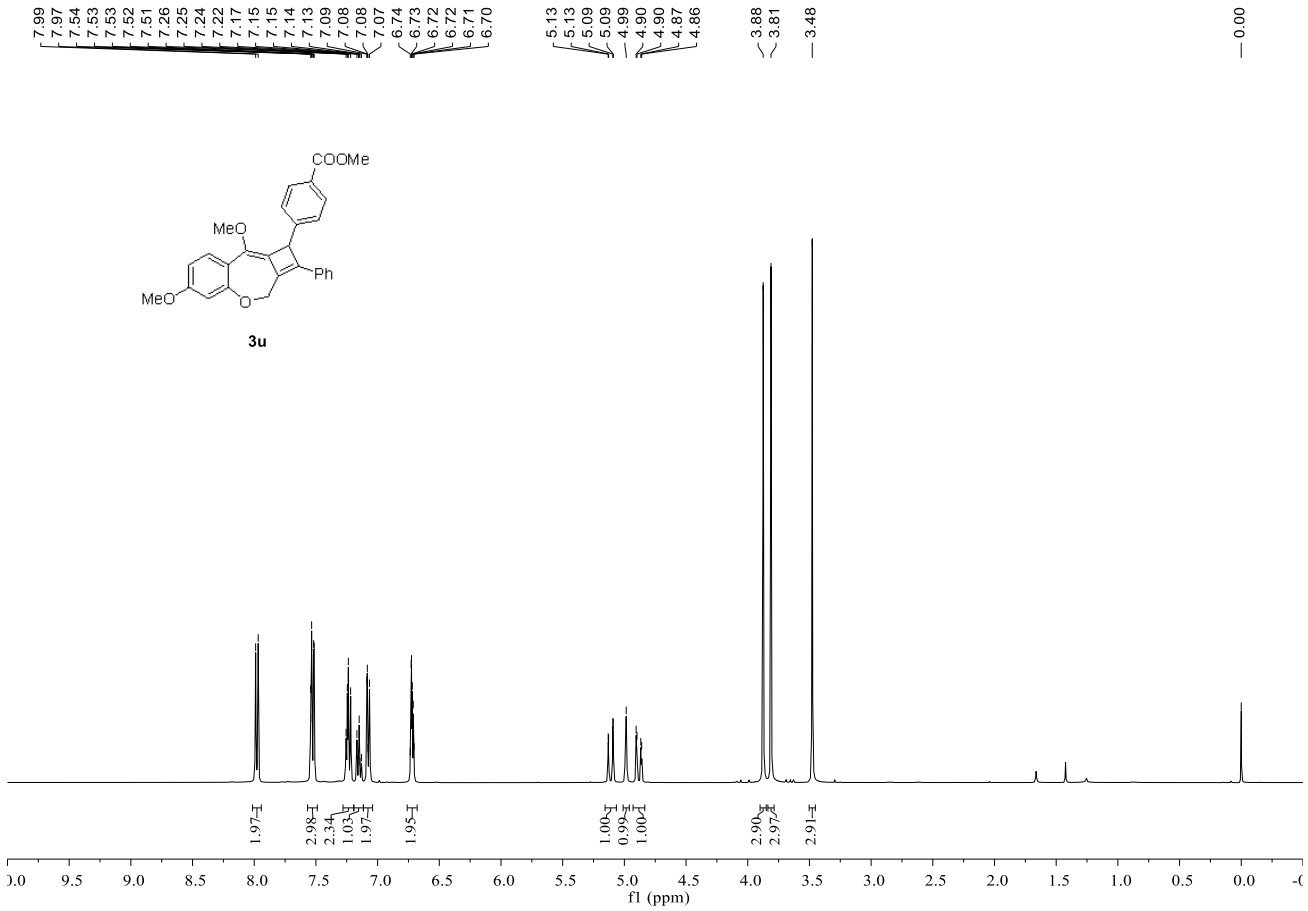
^{1}H NMR (400 MHz) of **3t** in $CDCl_3$



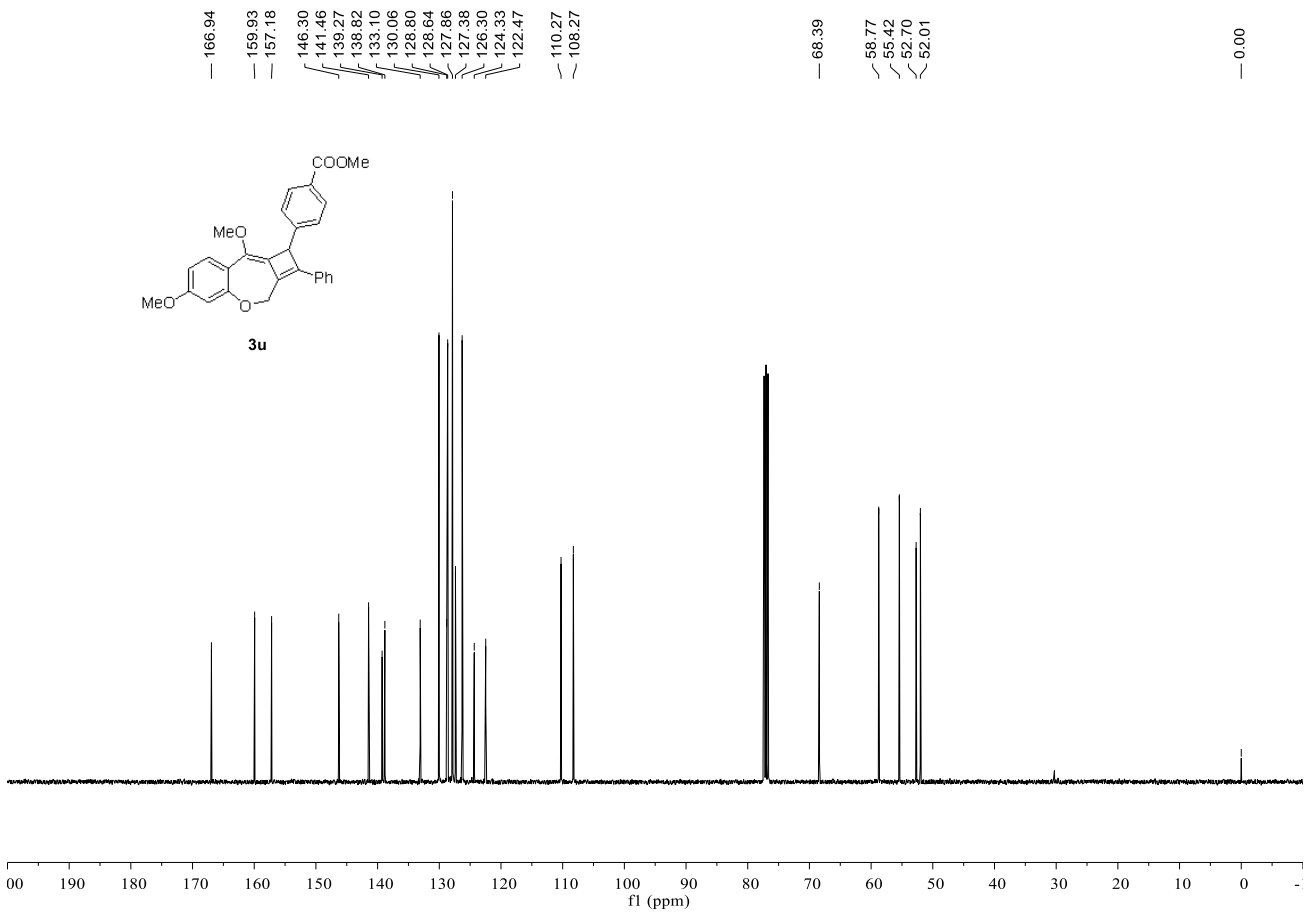
^{13}C NMR (100 MHz) of **3t** in $CDCl_3$



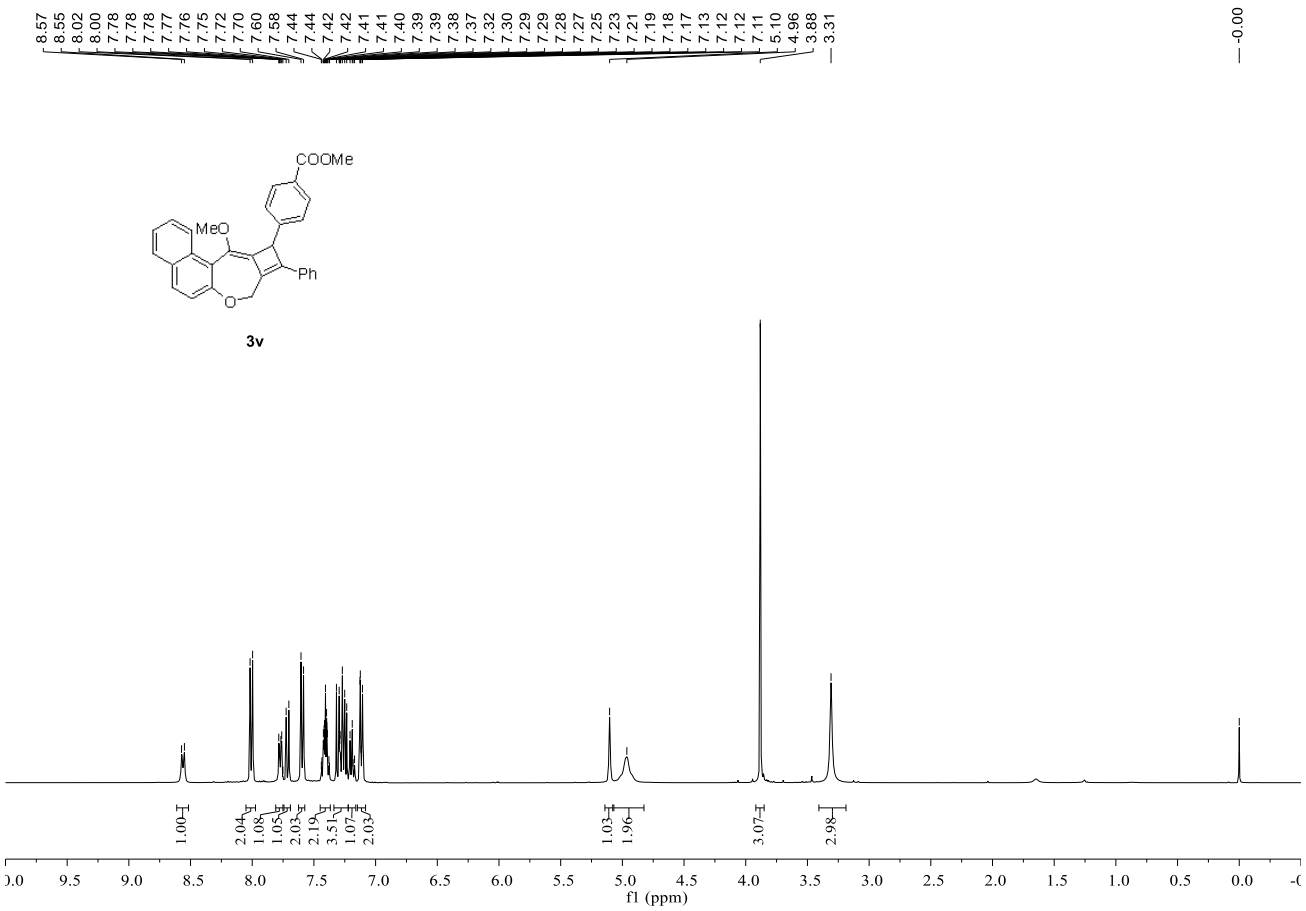
^{1}H NMR (400 MHz) of **3u** in $CDCl_3$



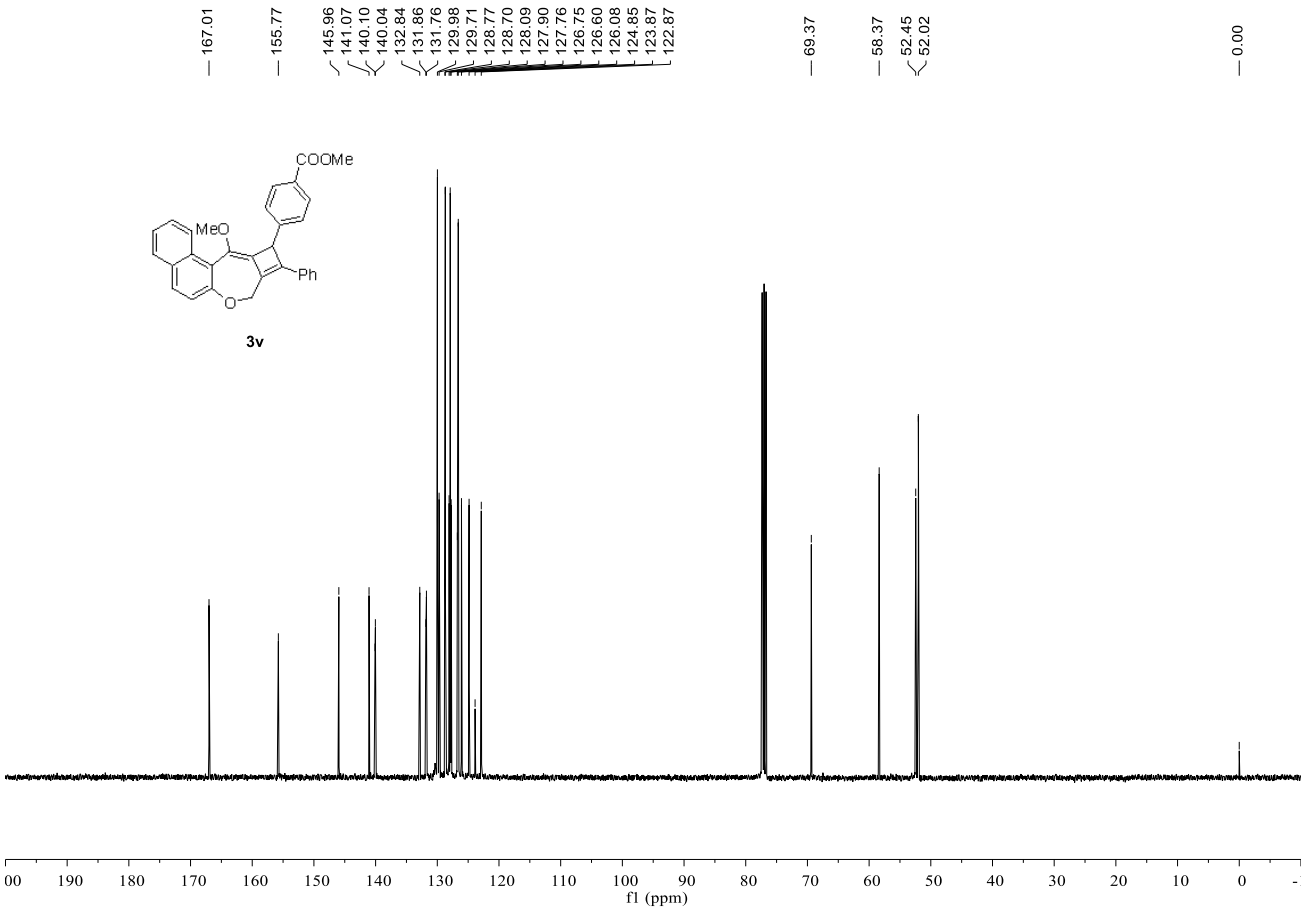
^{13}C NMR (100 MHz) of **3u** in $CDCl_3$



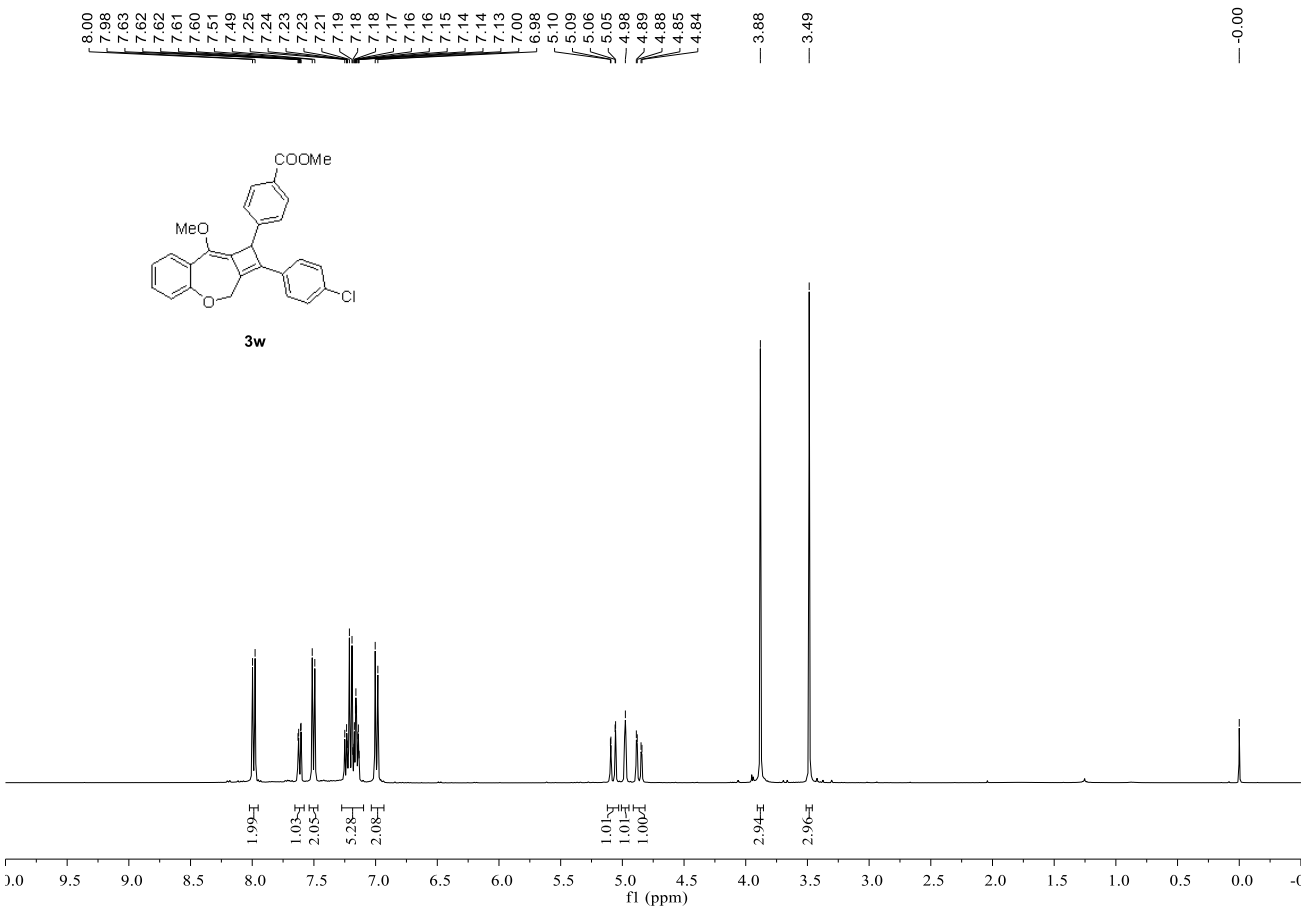
^{1}H NMR (400 MHz) of **3v** in $CDCl_3$



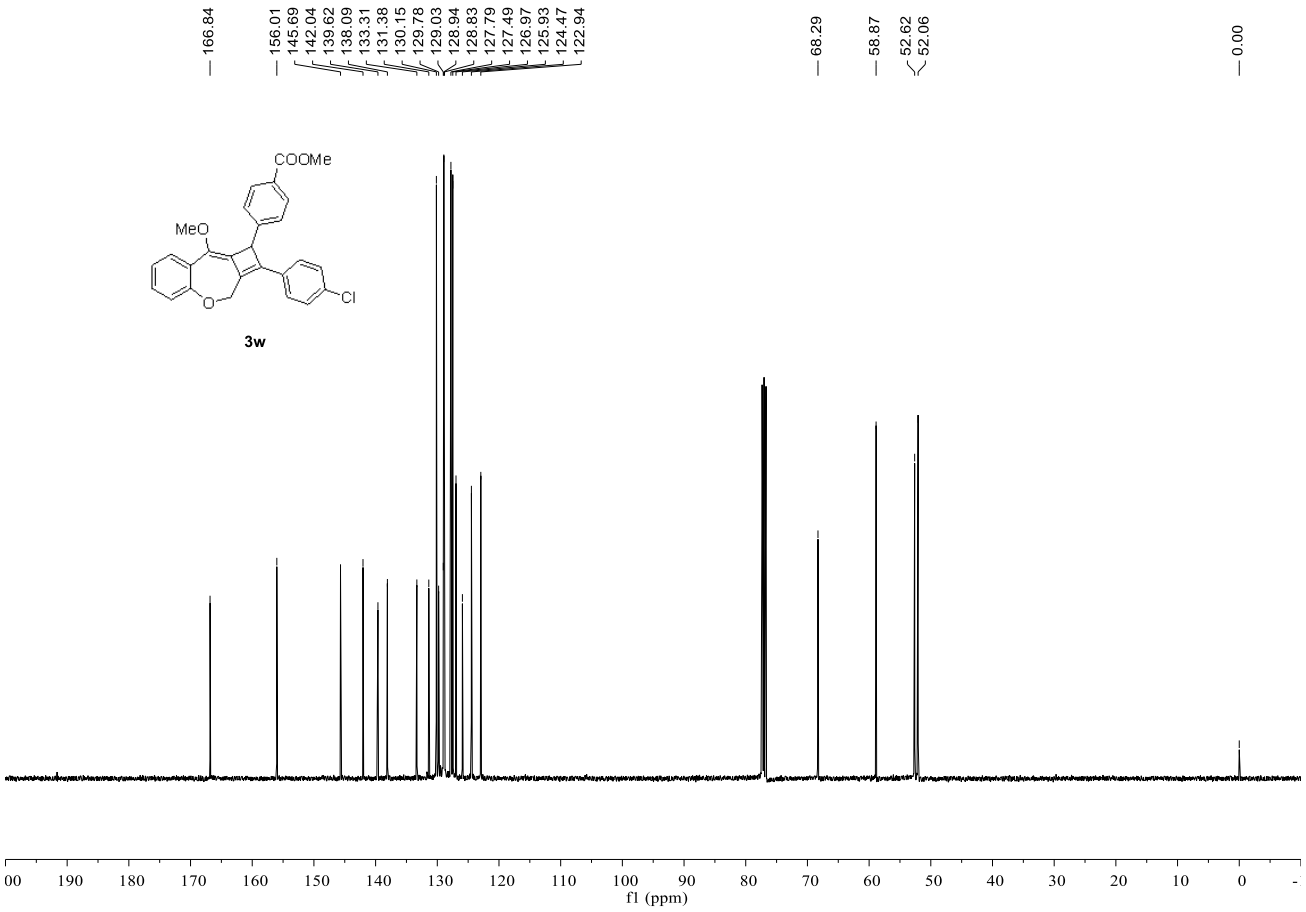
^{13}C NMR (100 MHz) of **3v** in $CDCl_3$



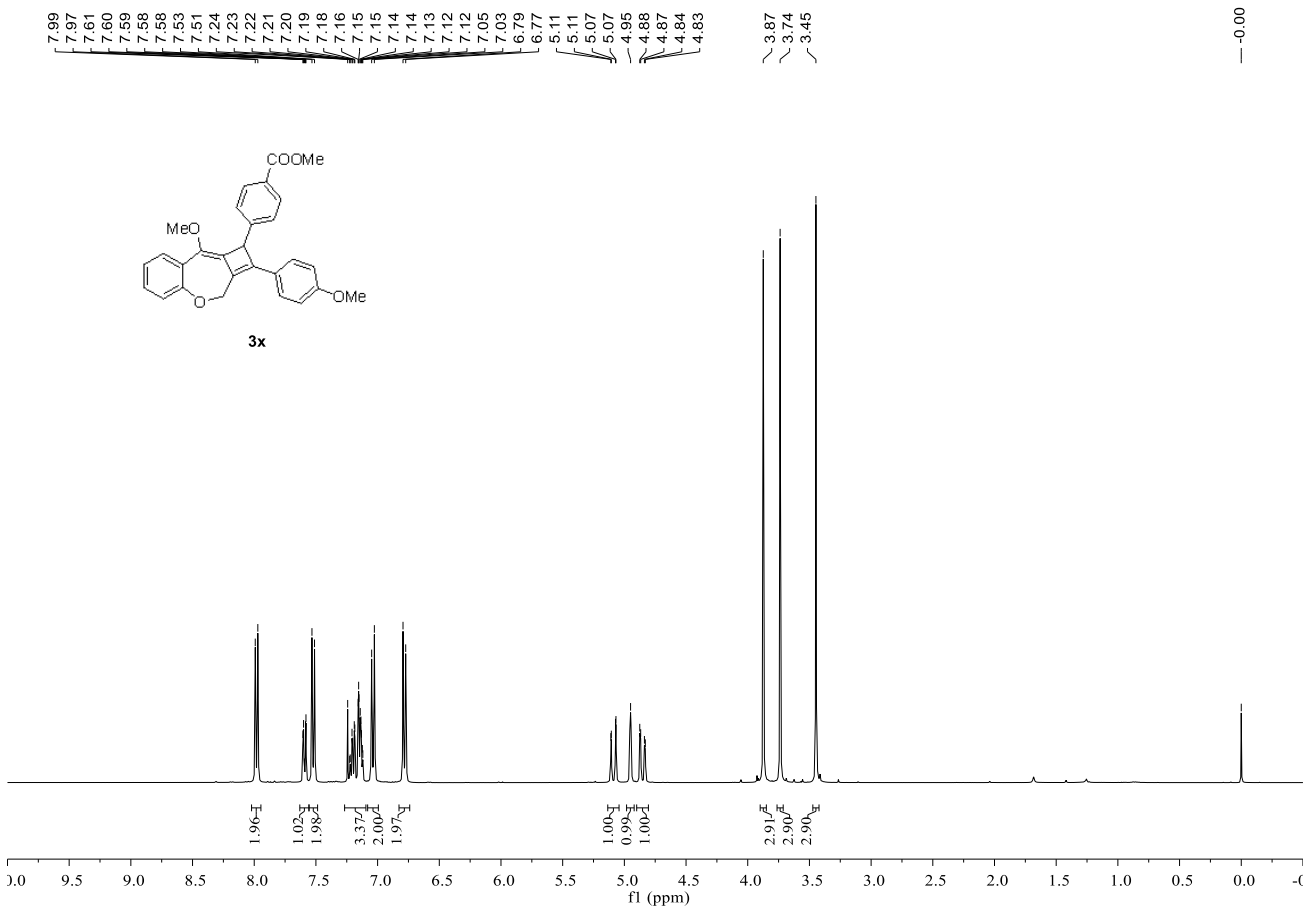
^{1}H NMR (400 MHz) of **3w** in $CDCl_3$



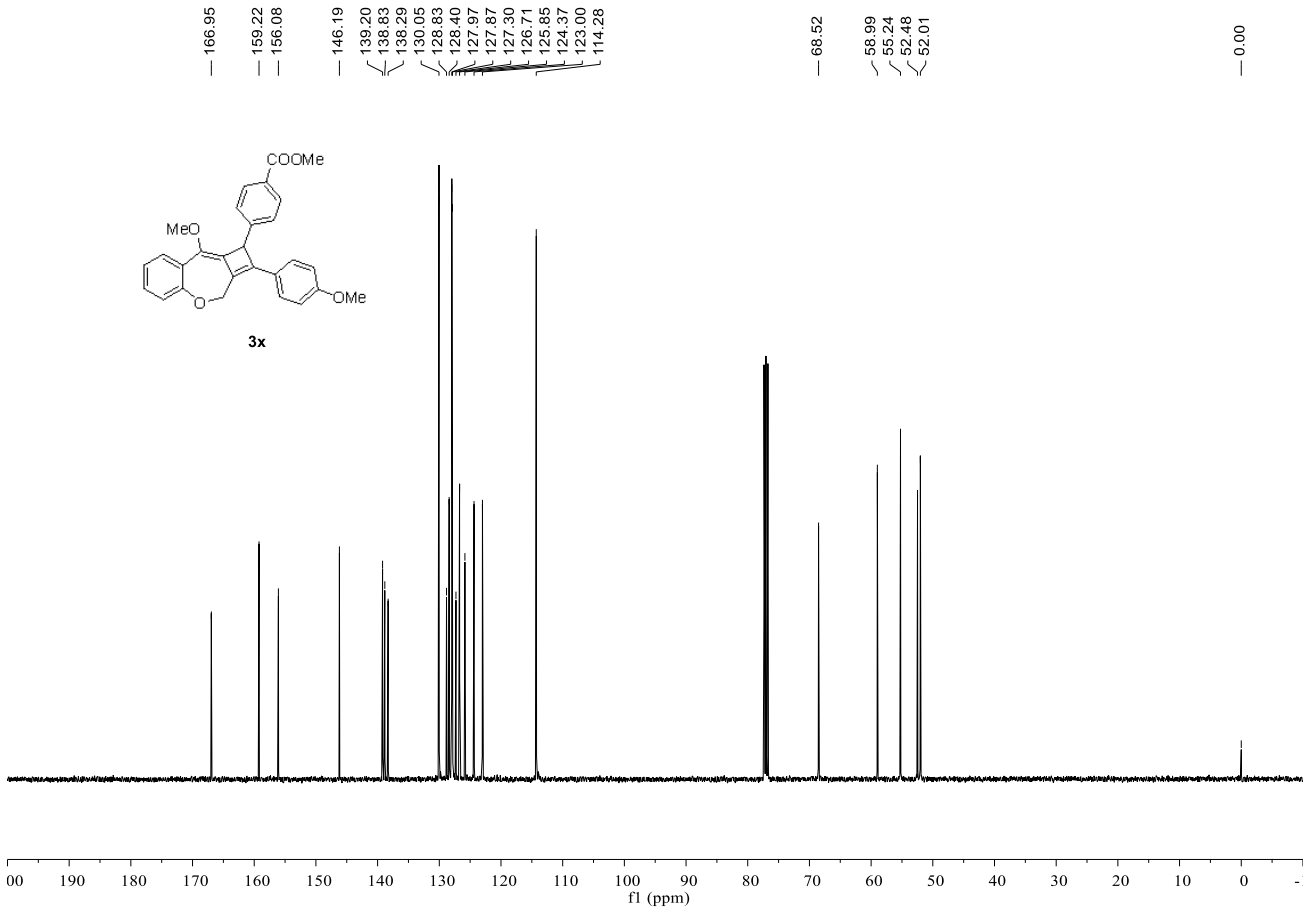
^{13}C NMR (100 MHz) of **3w** in $CDCl_3$



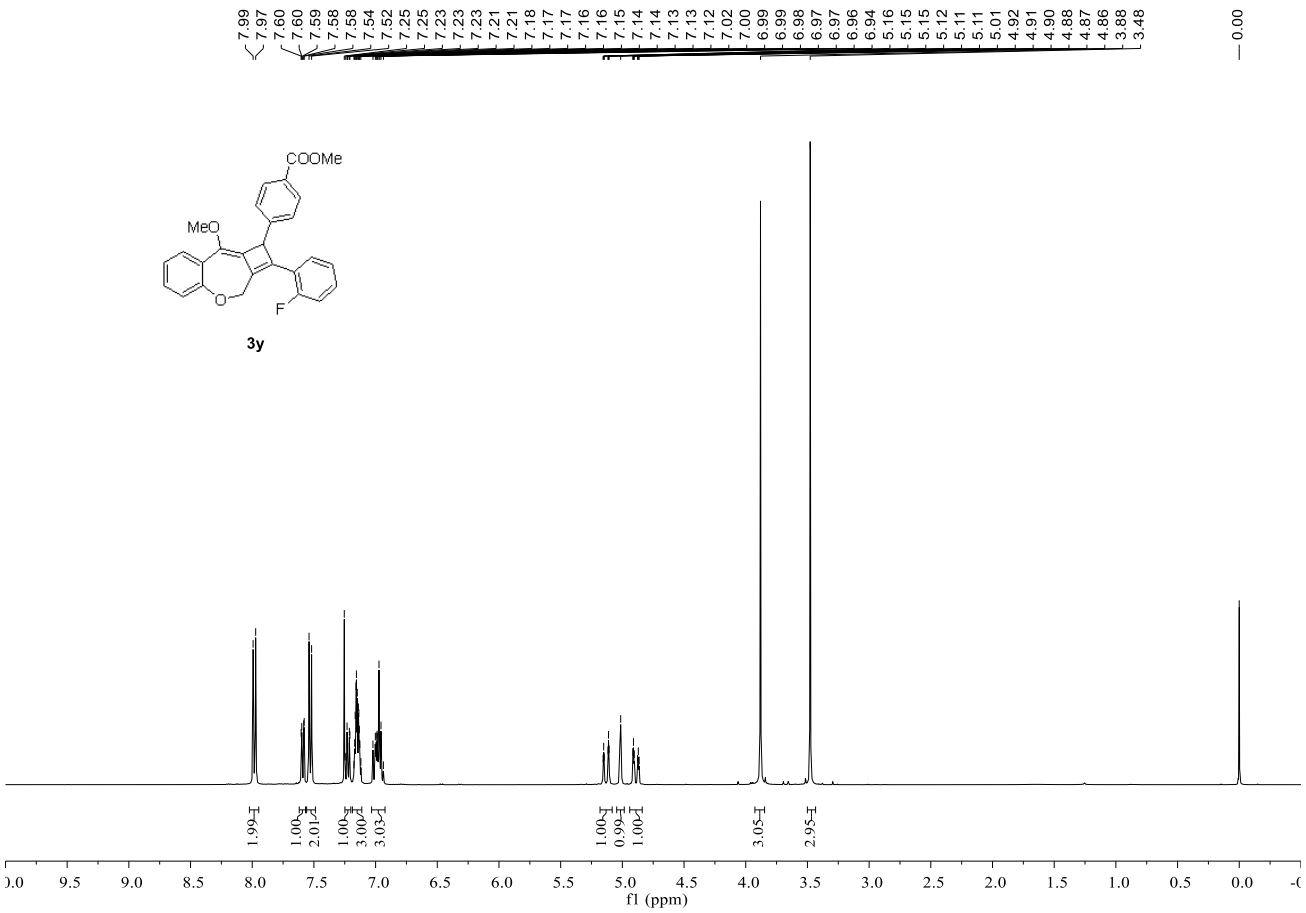
^{1}H NMR (400 MHz) of **3x** in $CDCl_3$



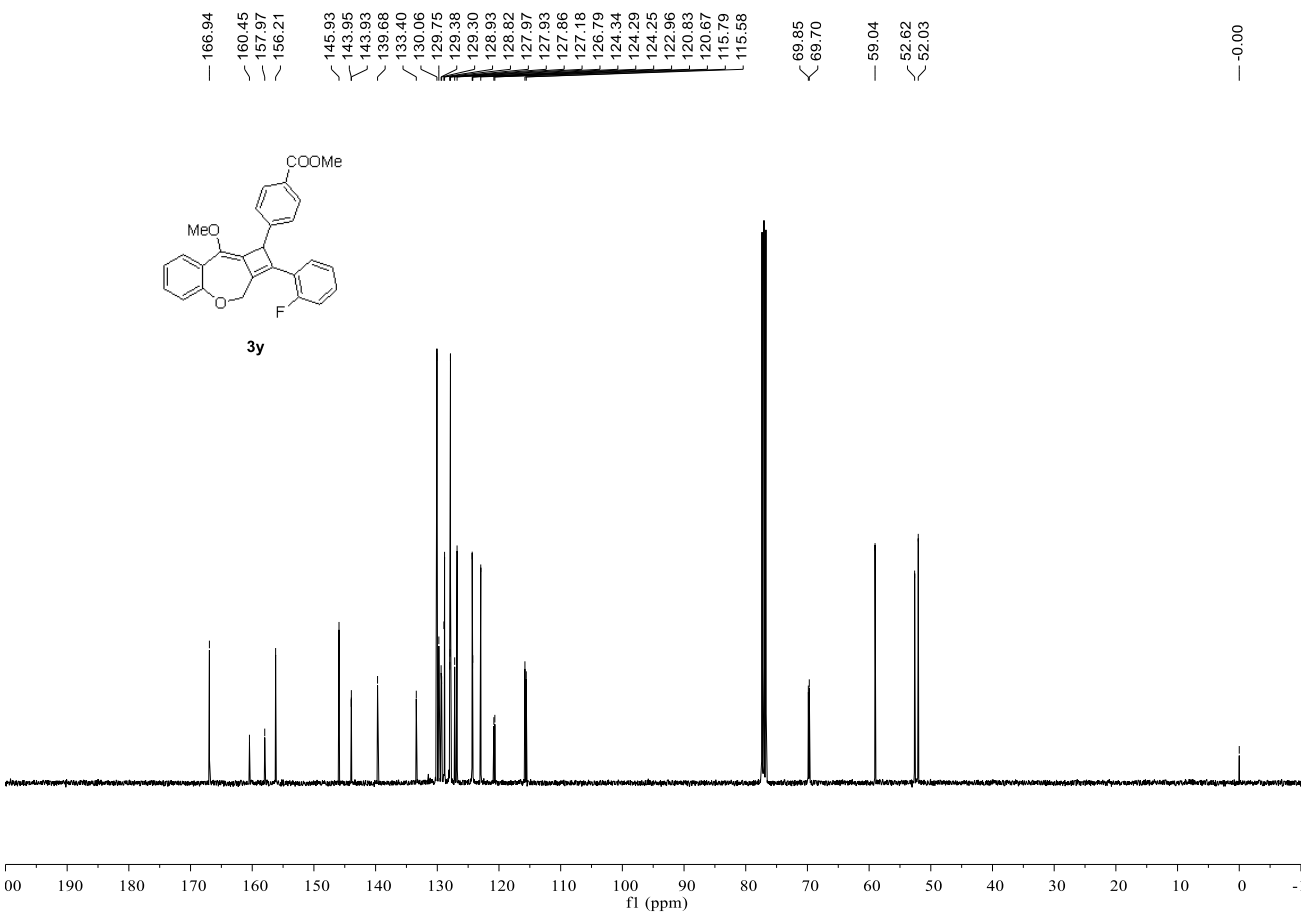
^{13}C NMR (100 MHz) of **3x** in $CDCl_3$



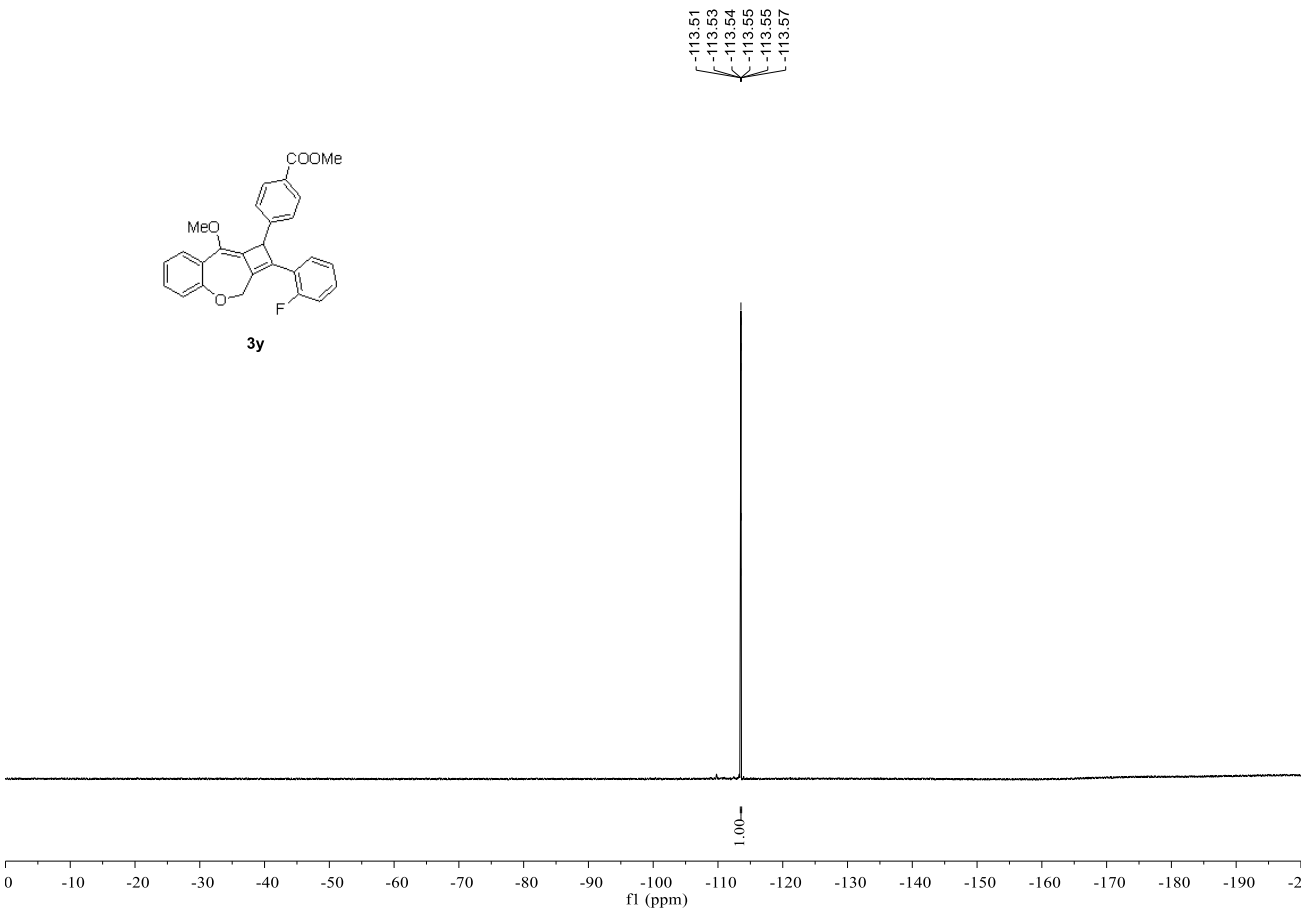
^{1}H NMR (400 MHz) of **3y** in $CDCl_3$



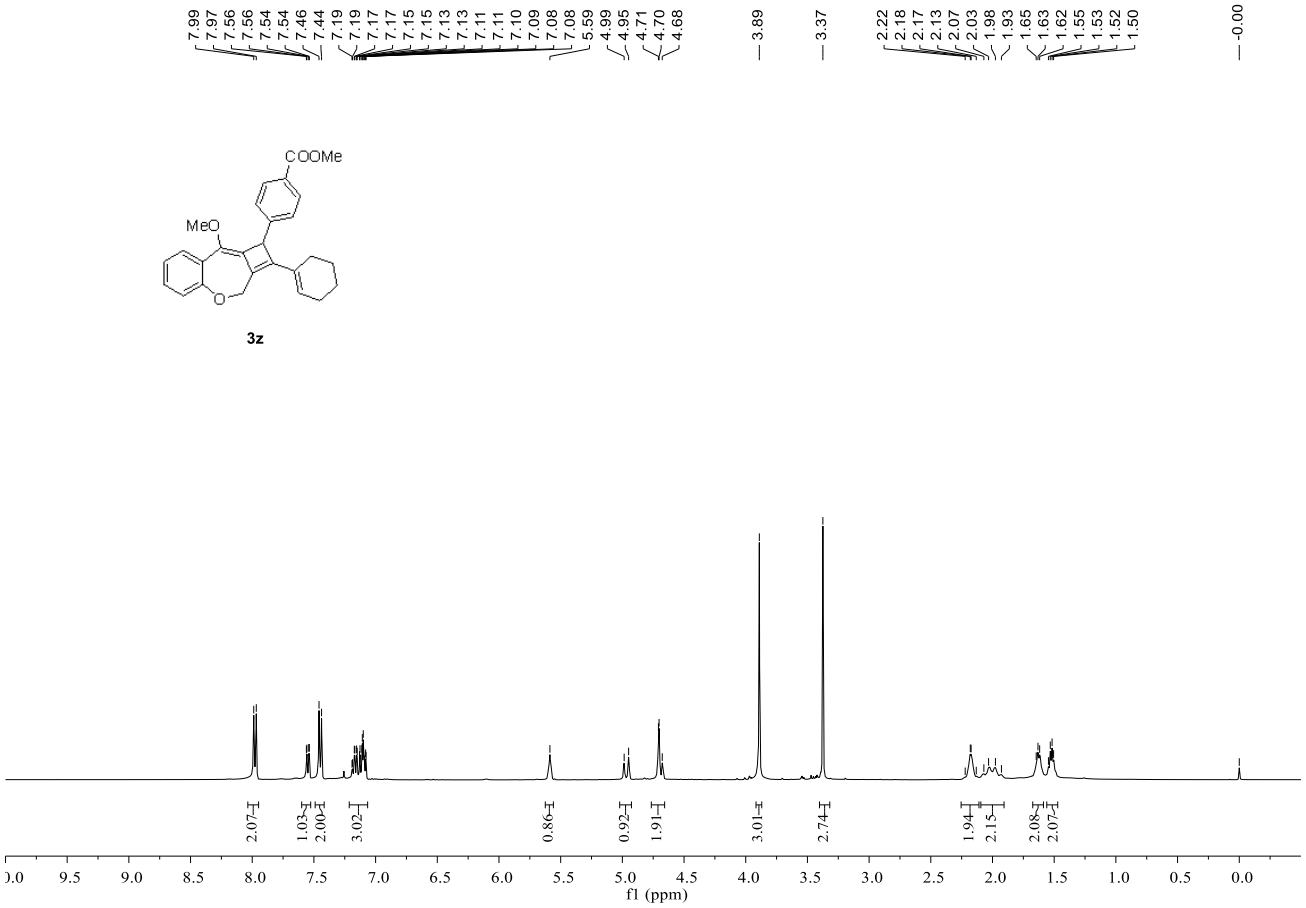
^{13}C NMR (100 MHz) of **3y** in $CDCl_3$



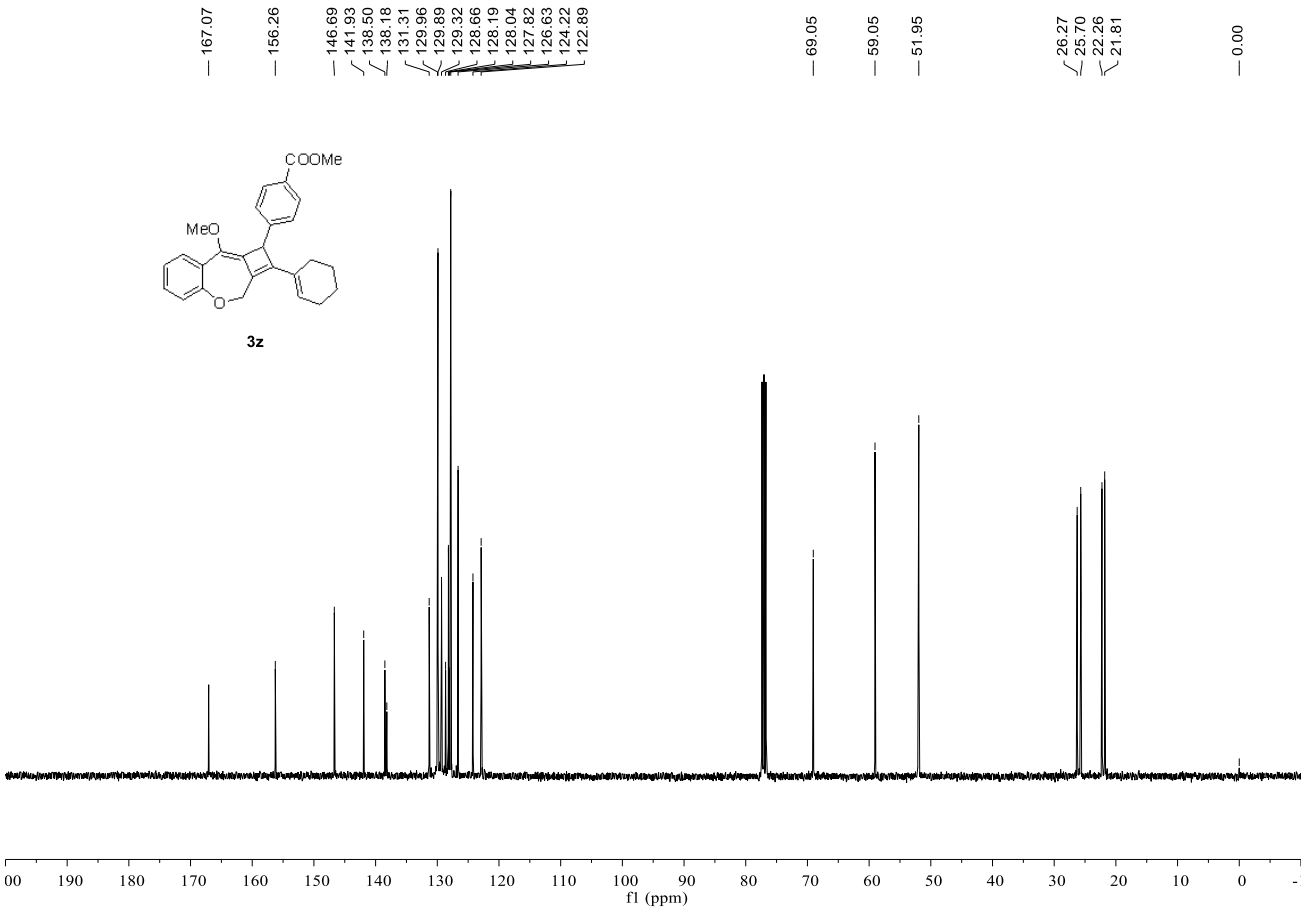
^{19}F NMR (376 MHz) of **3y** in $CDCl_3$



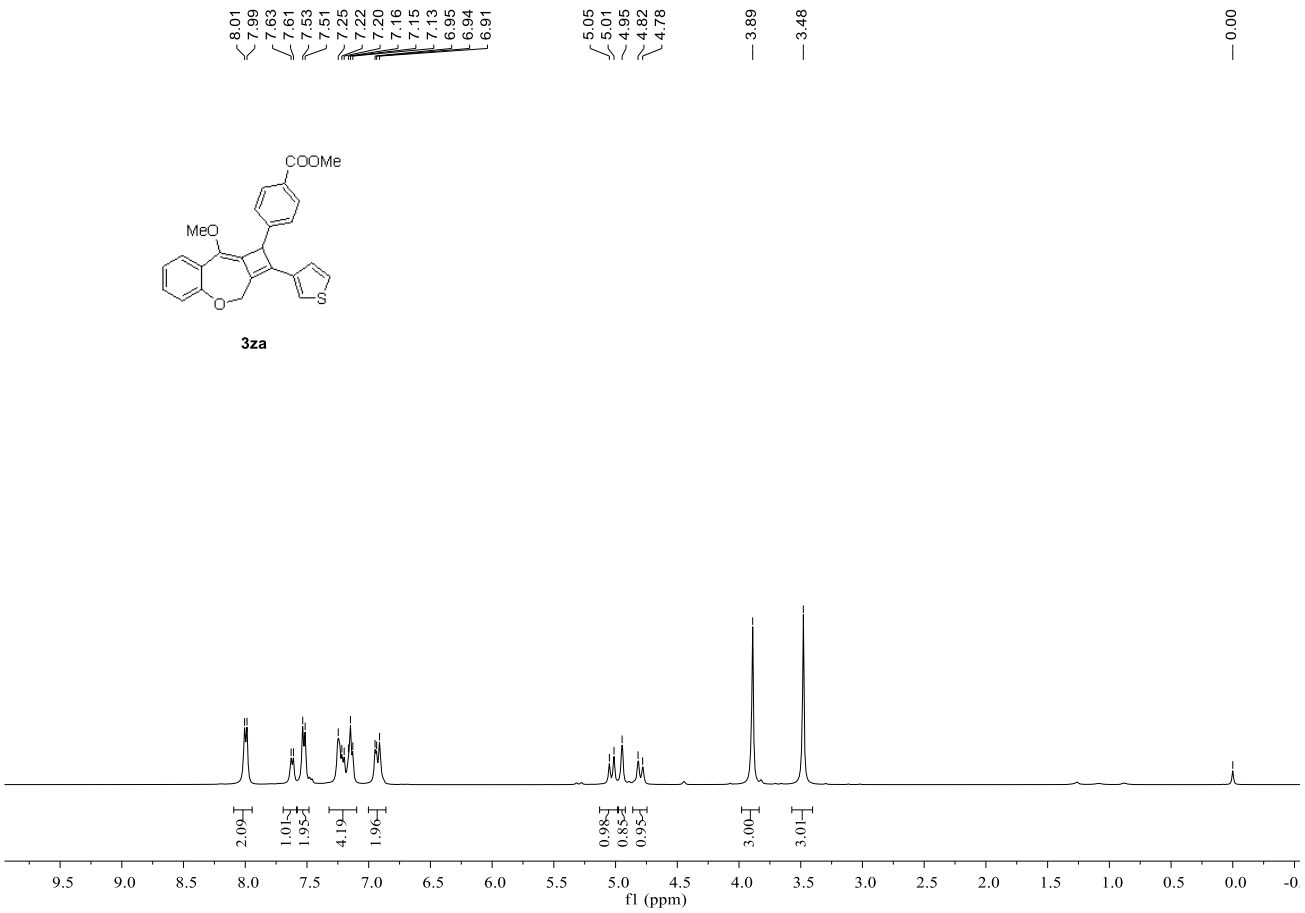
^{1}H NMR (400 MHz) of **3z** in $CDCl_3$



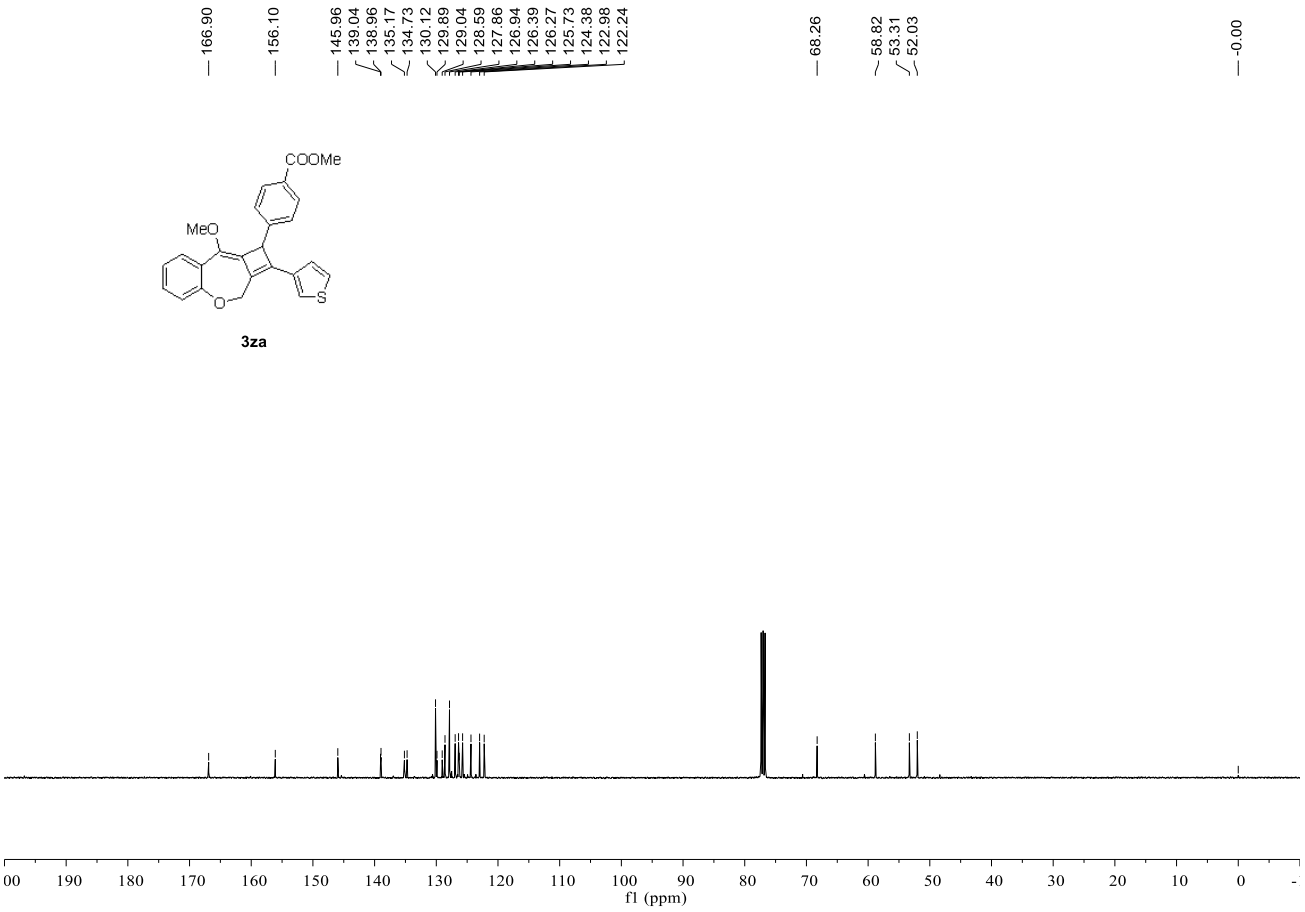
^{13}C NMR (100 MHz) of **3z** in $CDCl_3$



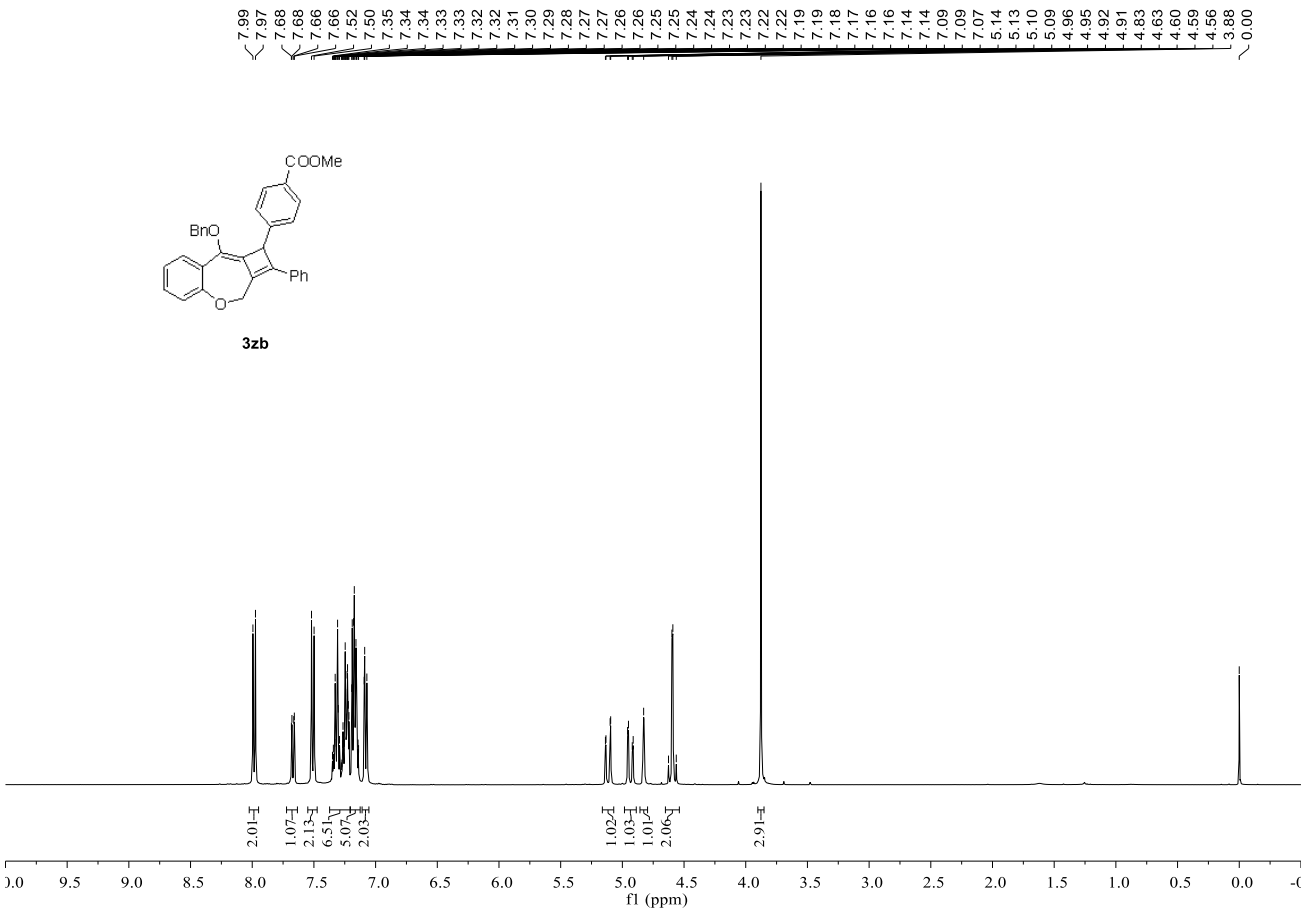
^{1}H NMR (400 MHz) of **3za** in $CDCl_3$



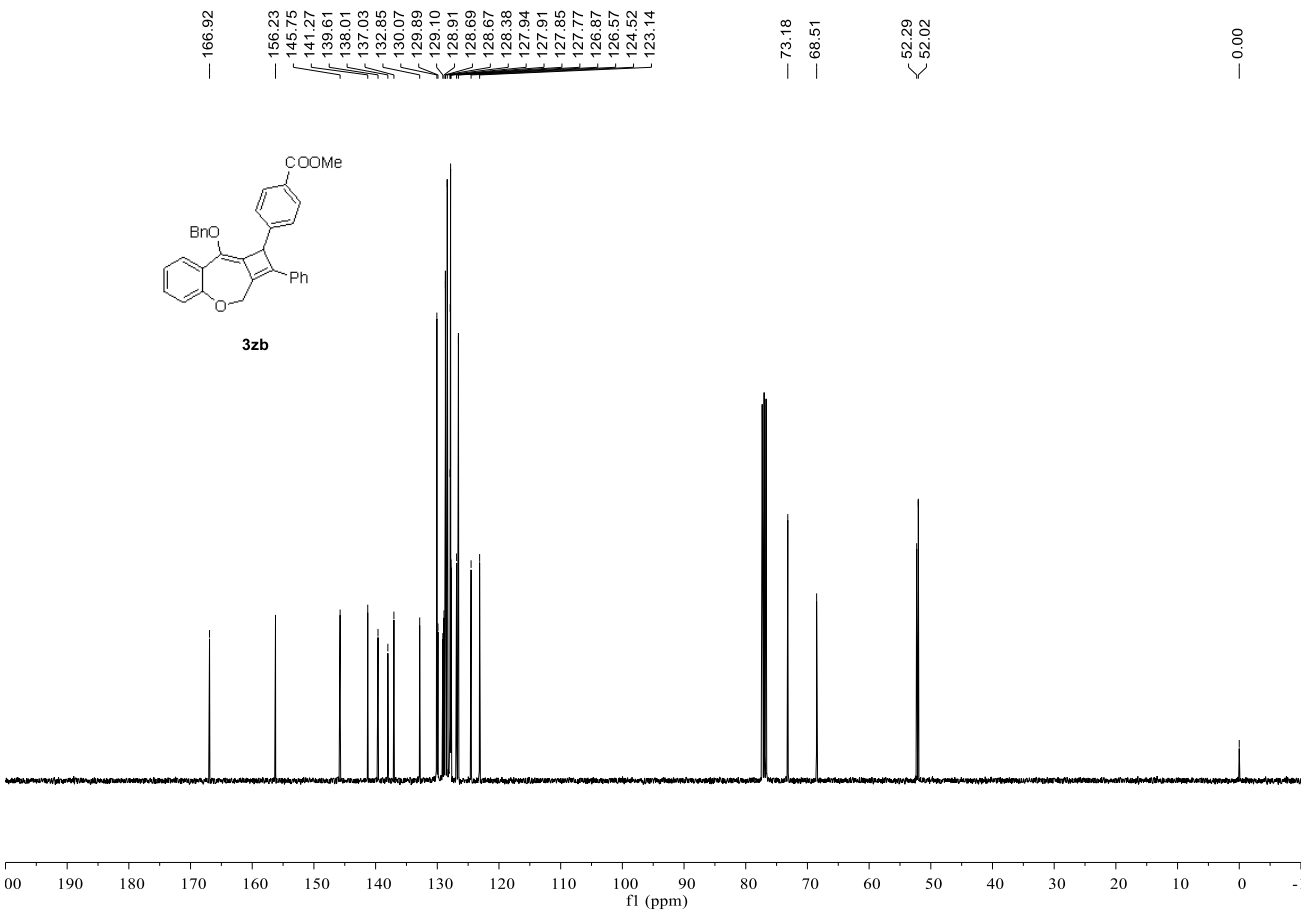
^{13}C NMR (100 MHz) of **3za** in $CDCl_3$



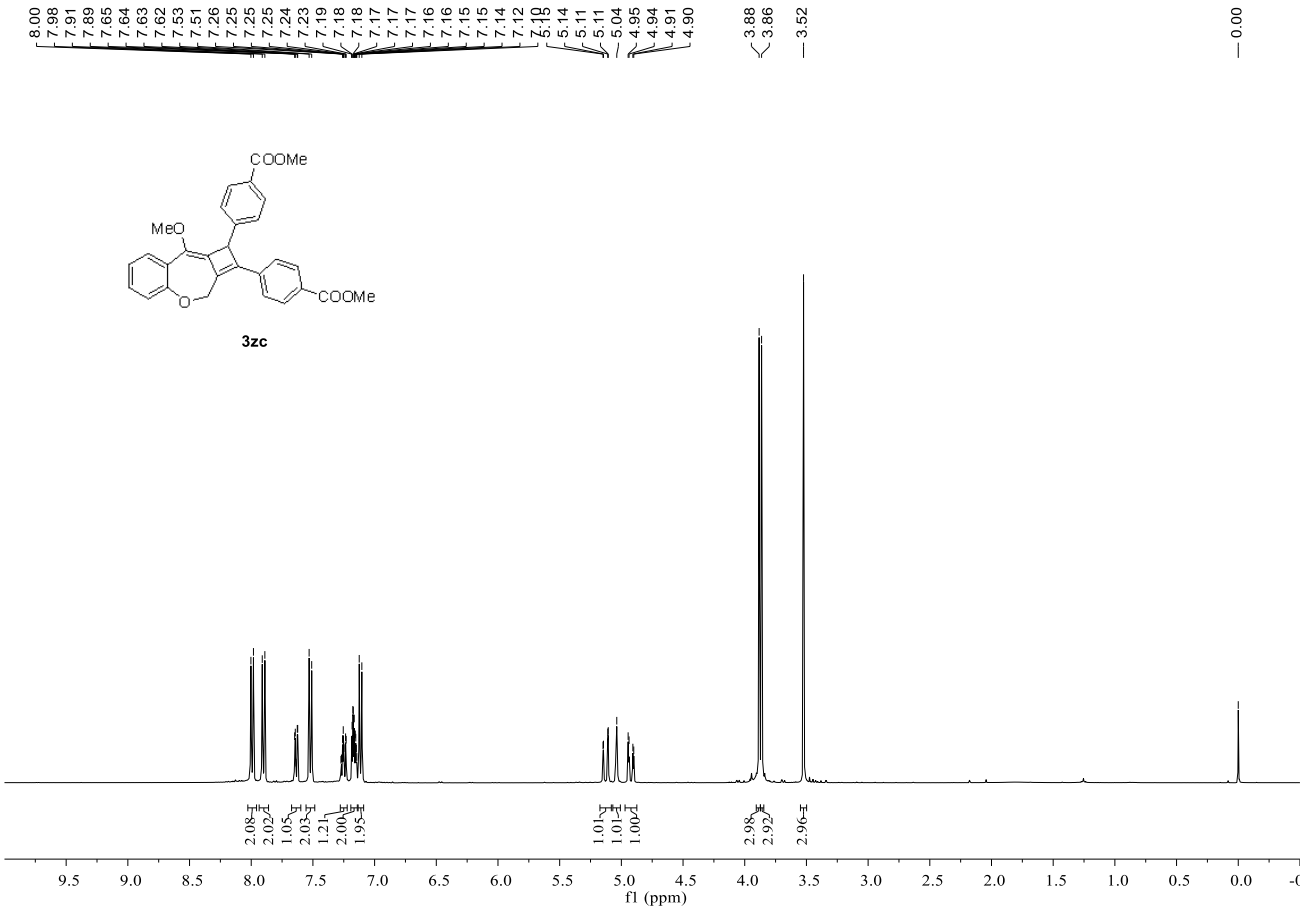
^{1}H NMR (400 MHz) of **3zb** in $CDCl_3$



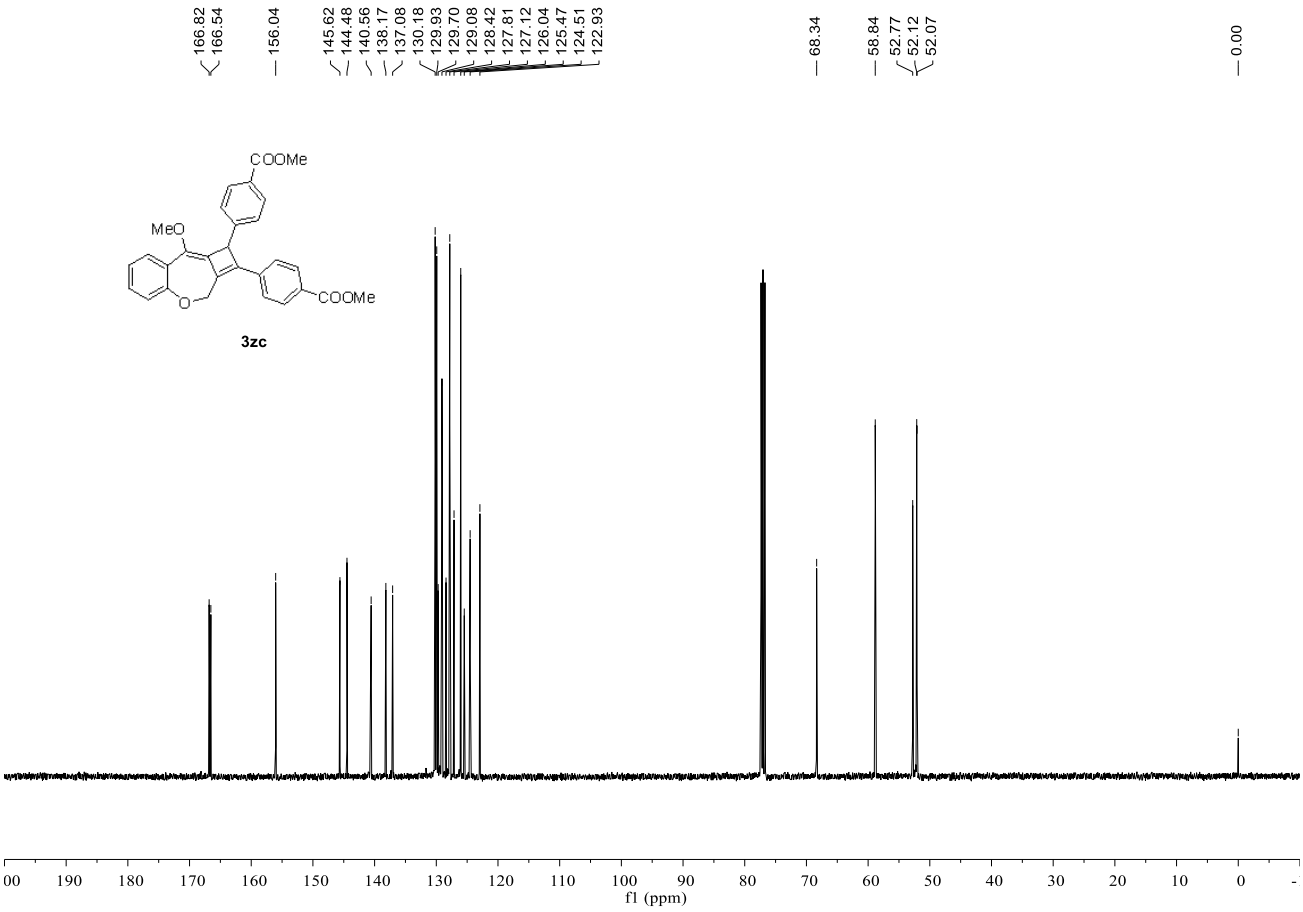
^{13}C NMR (100 MHz) of **3zb** in $CDCl_3$



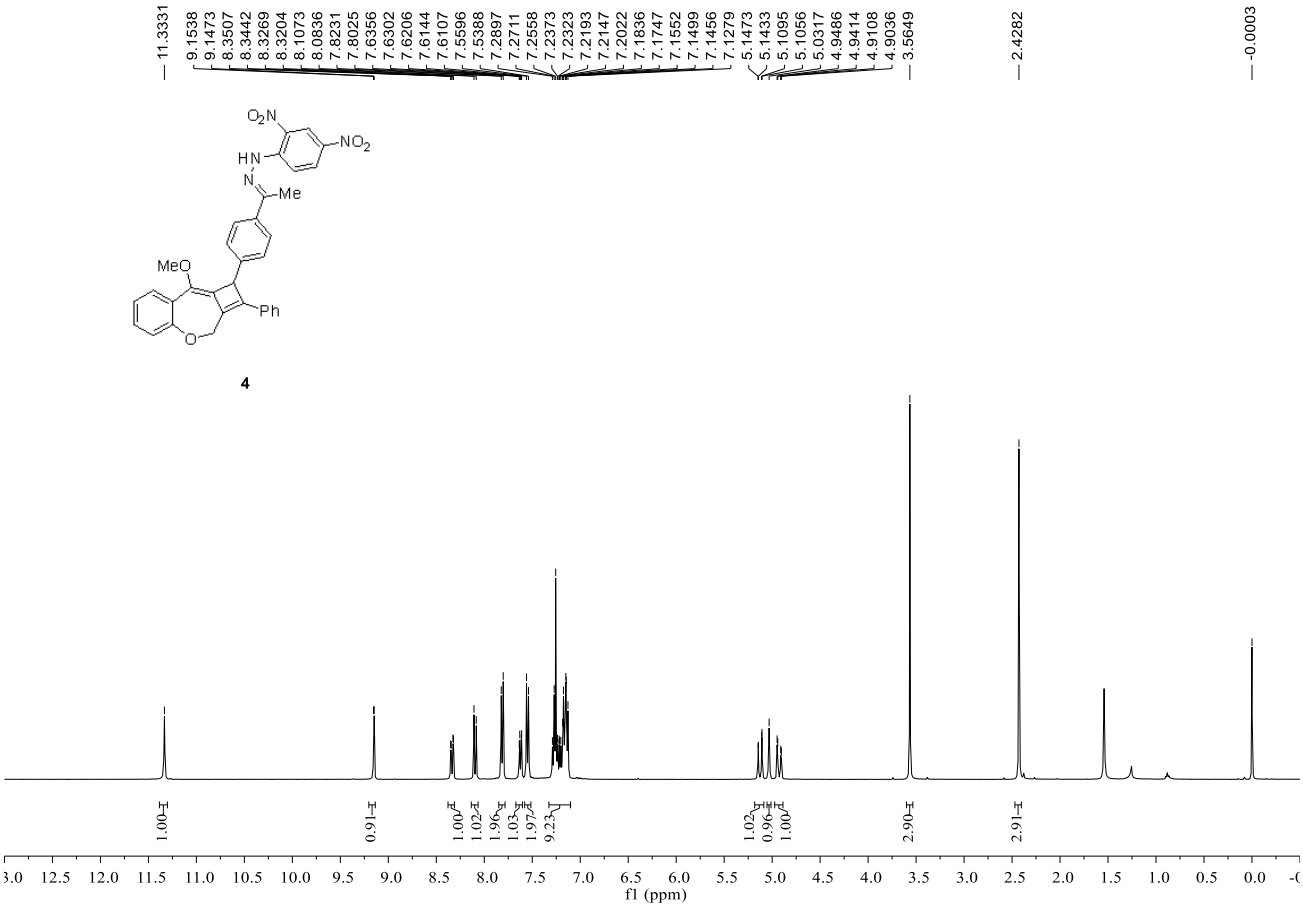
^{1}H NMR (400 MHz) of **3zc** in $CDCl_3$



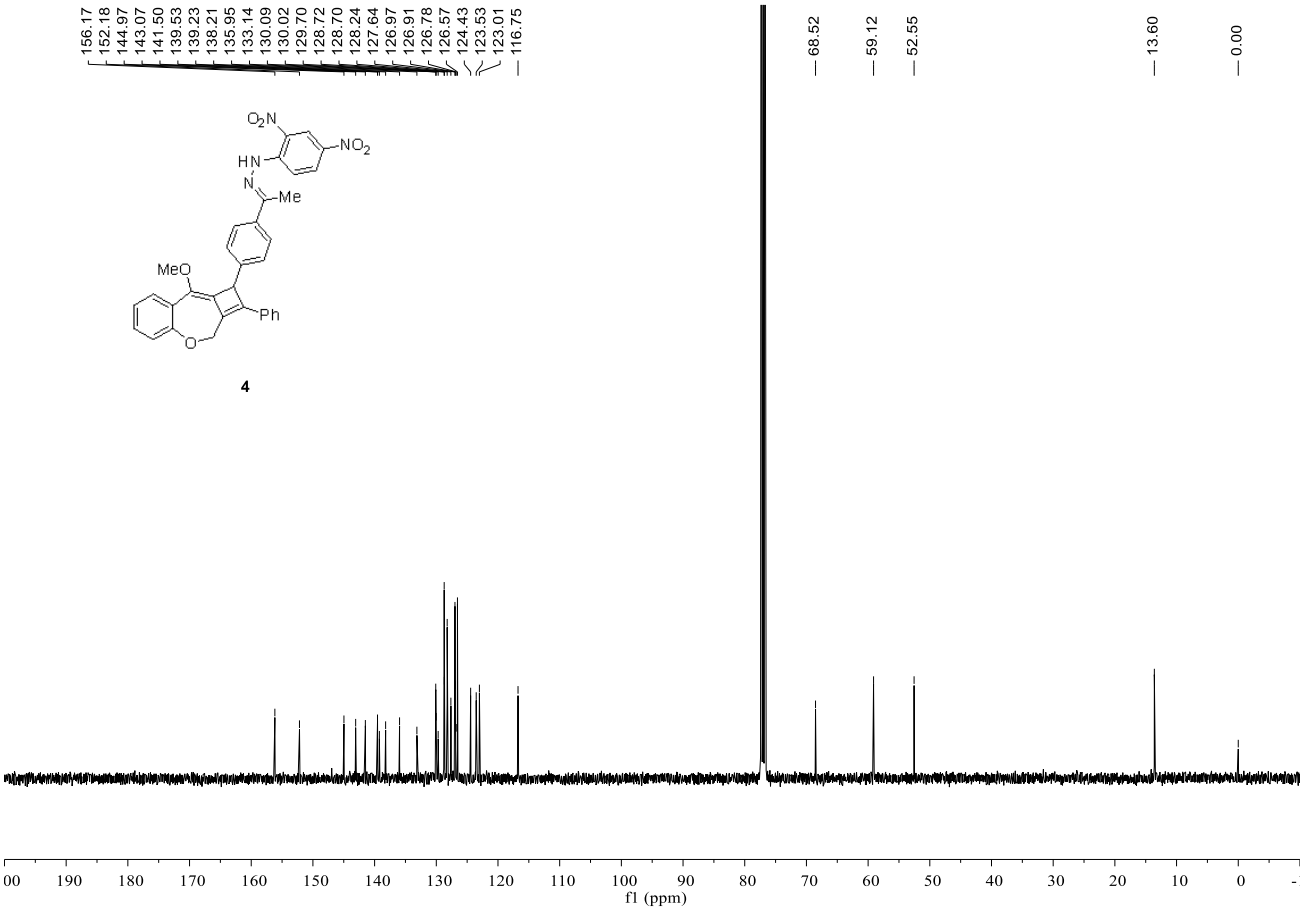
^{13}C NMR (100 MHz) of **3zc** in $CDCl_3$



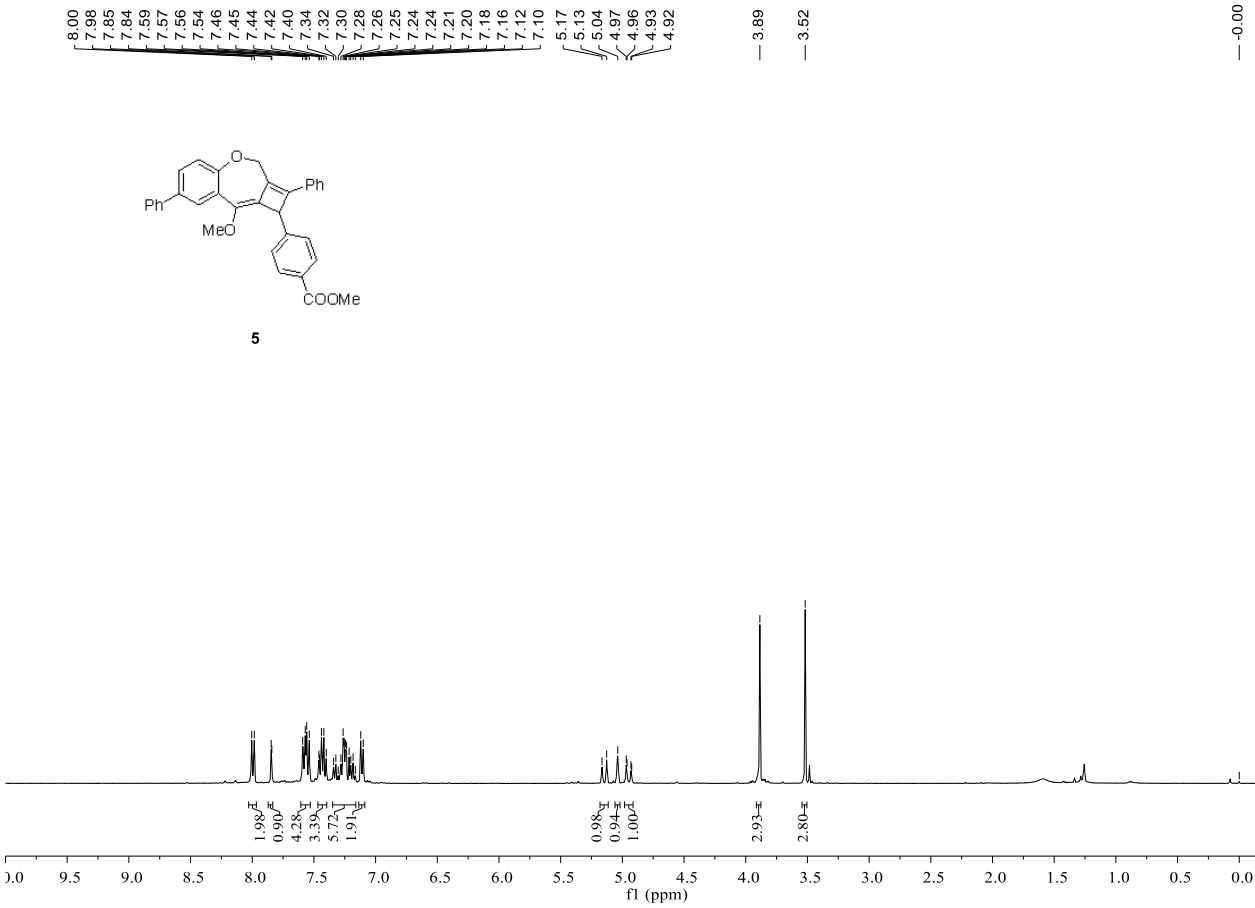
^{1}H NMR (400 MHz) of **4** in $CDCl_3$



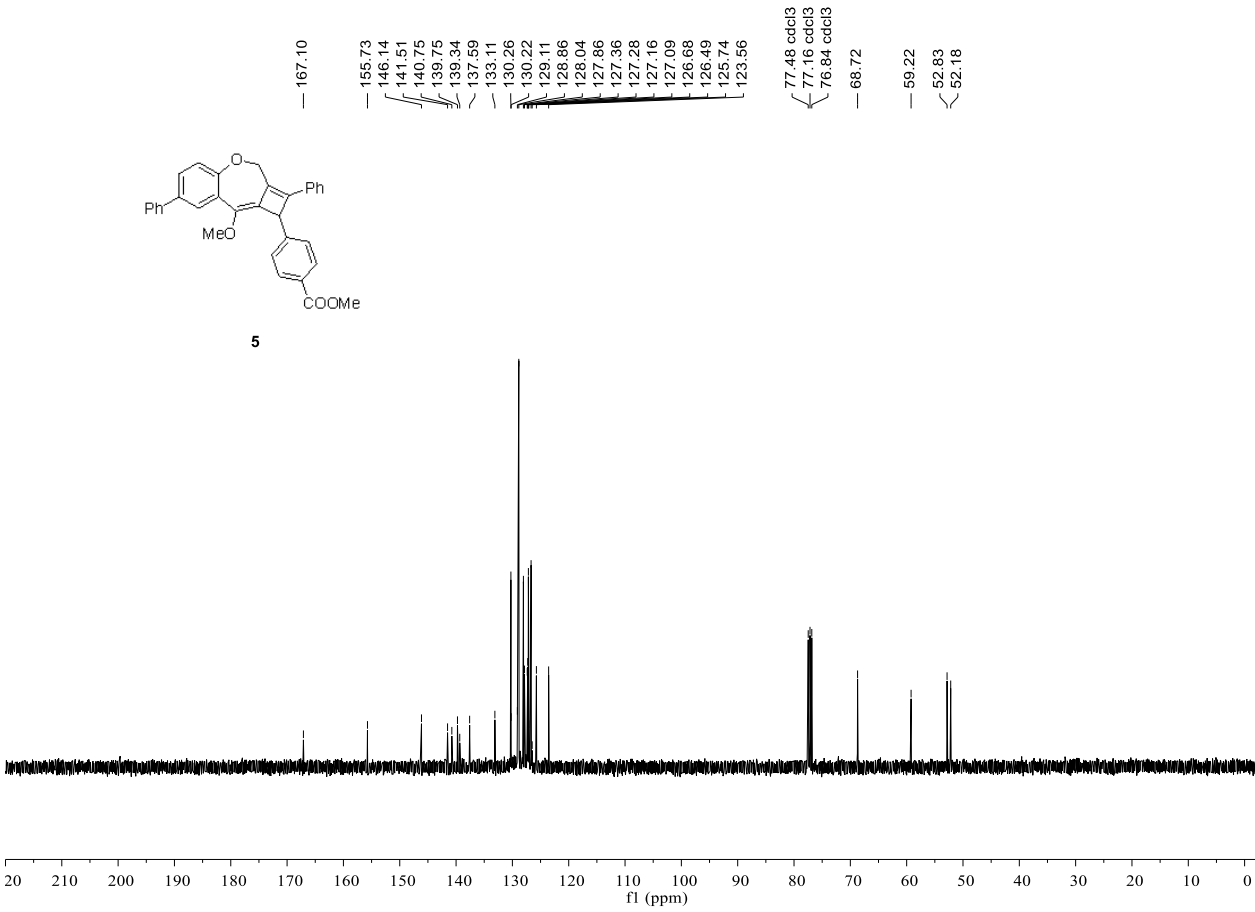
^{13}C NMR (100 MHz) of **4** in $CDCl_3$



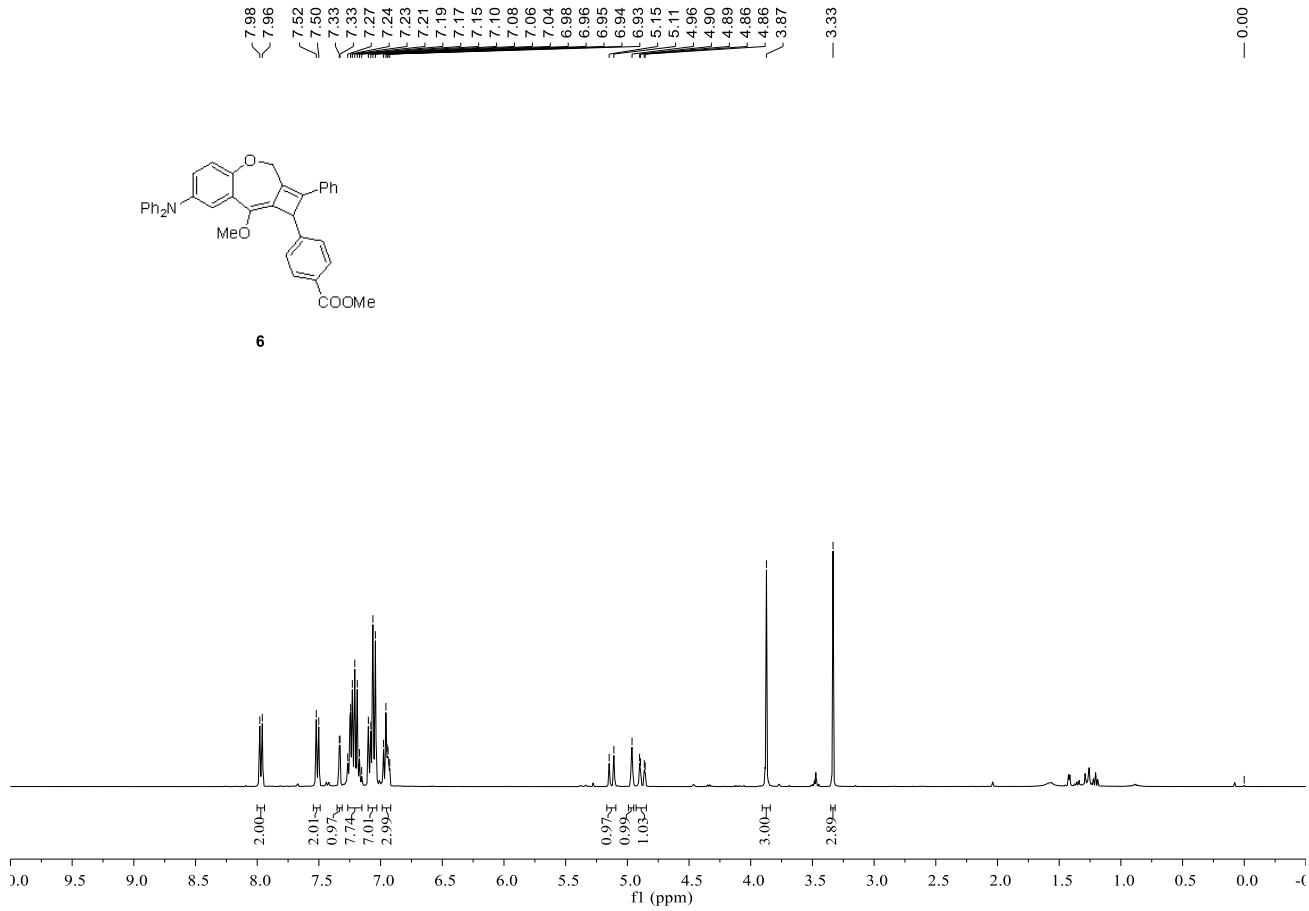
^{1}H NMR (400 MHz) of **5** in $CDCl_3$



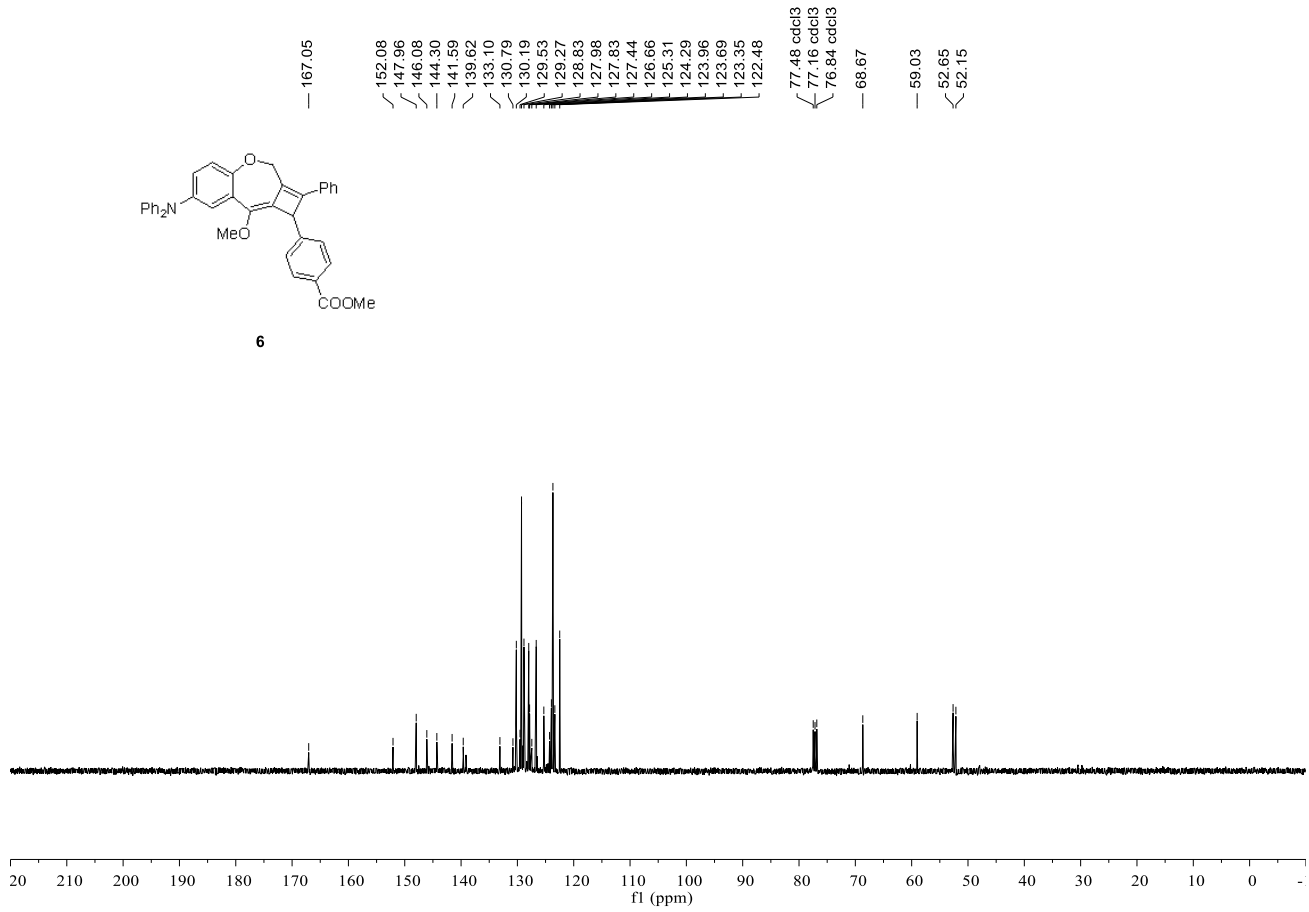
^{13}C NMR (100 MHz) of **5** in $CDCl_3$



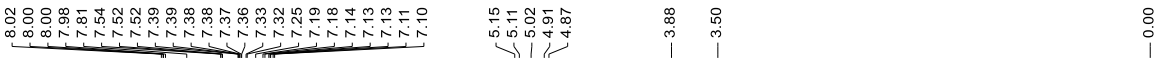
^{1}H NMR (400 MHz) of **6** in $CDCl_3$

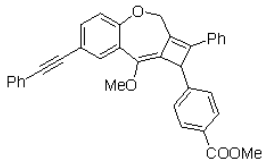


^{13}C NMR (100 MHz) of **6** in $CDCl_3$



^{1}H NMR (400 MHz) of **7** in $CDCl_3$





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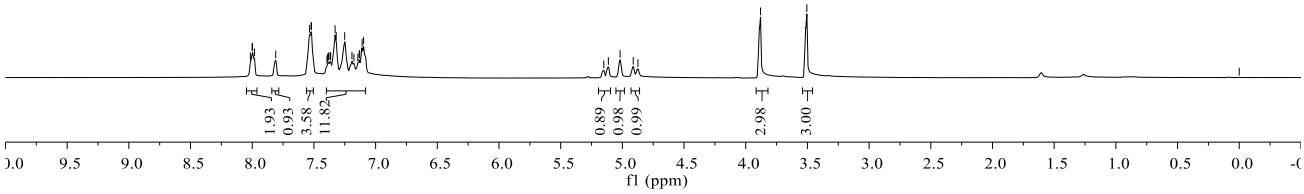
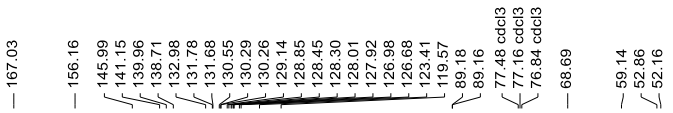
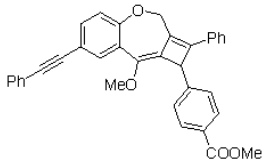


^{13}C NMR (100 MHz) of **7** in $CDCl_3$





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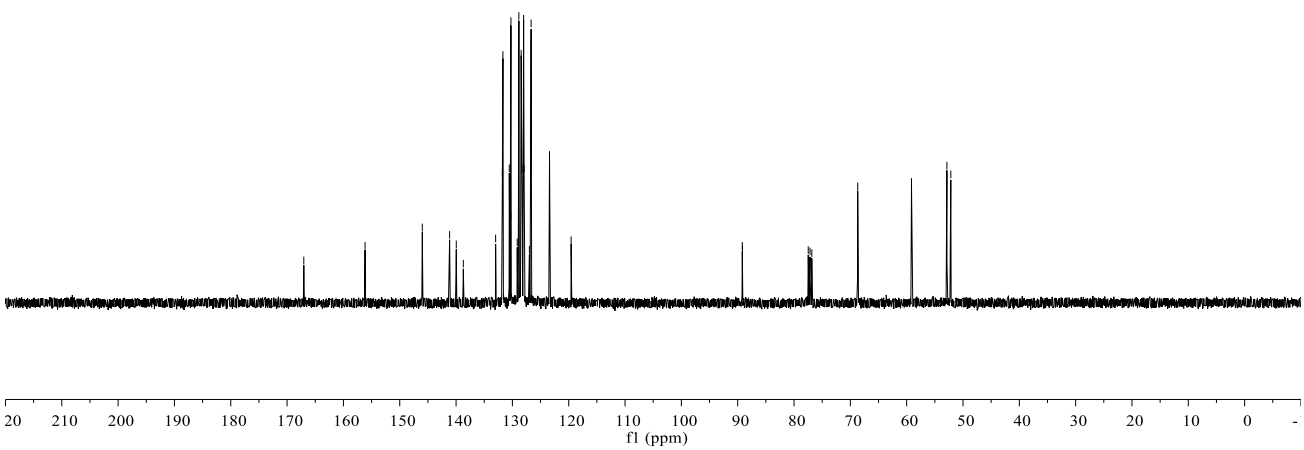
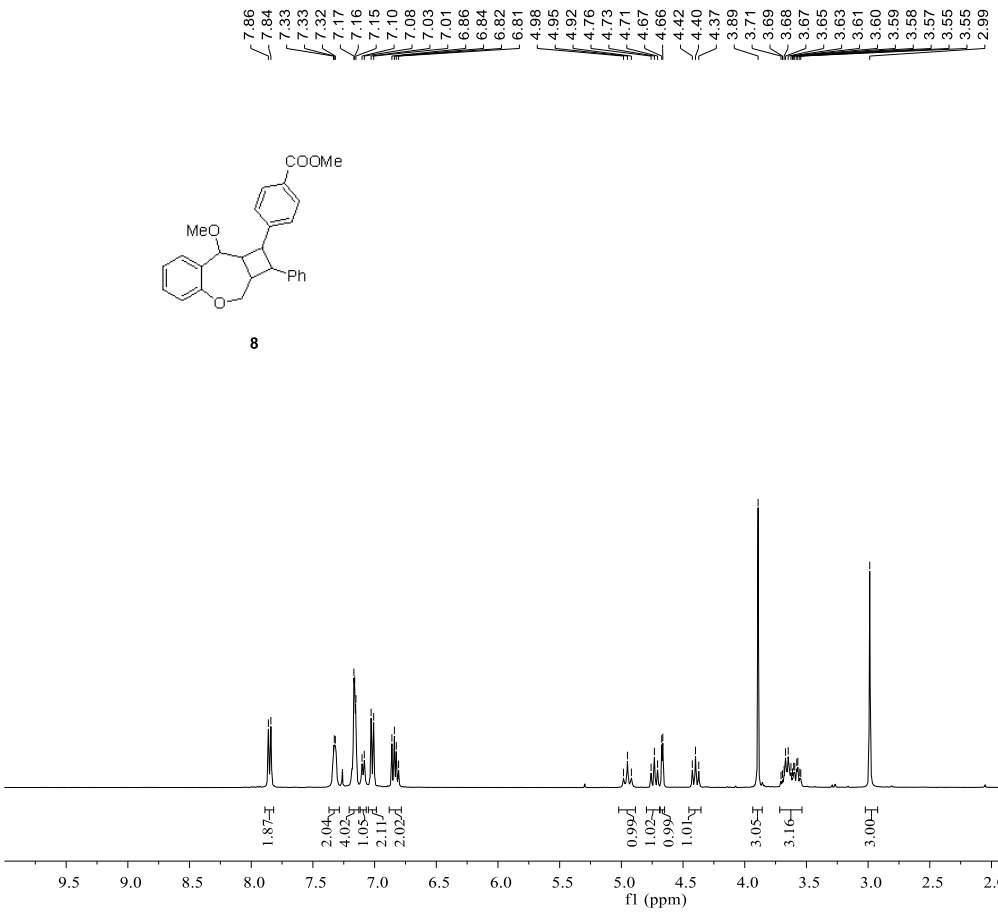
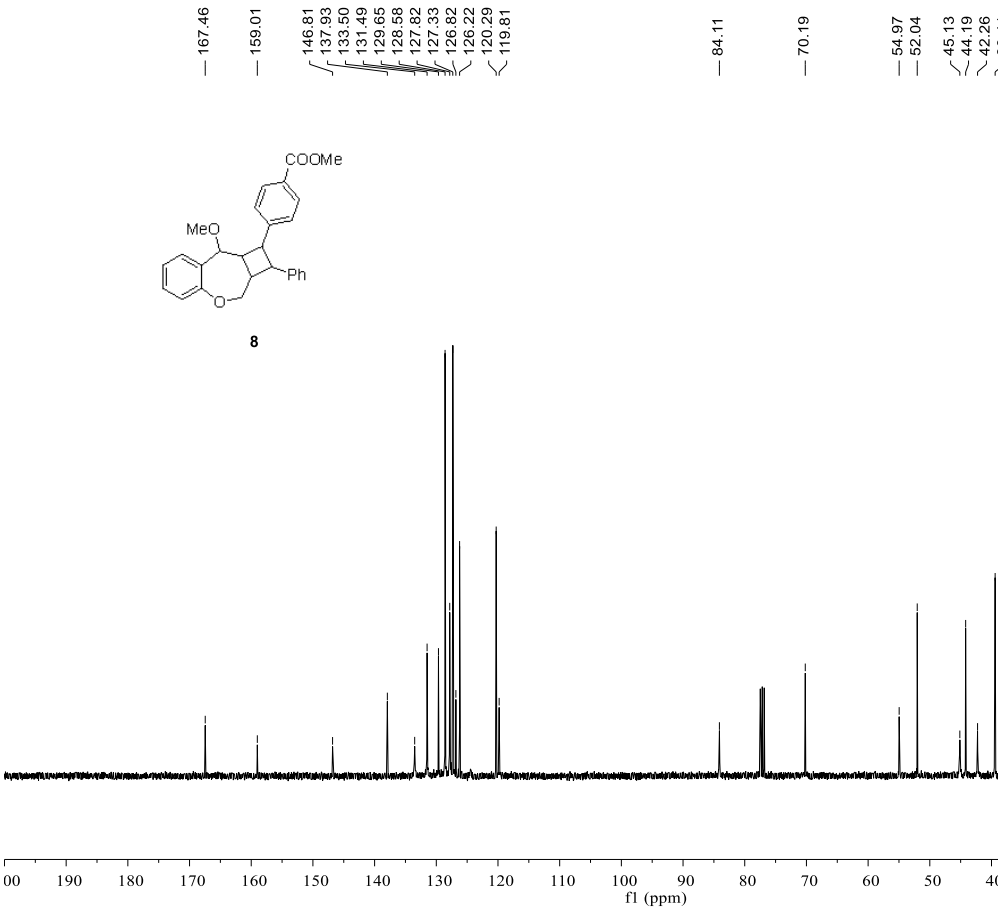


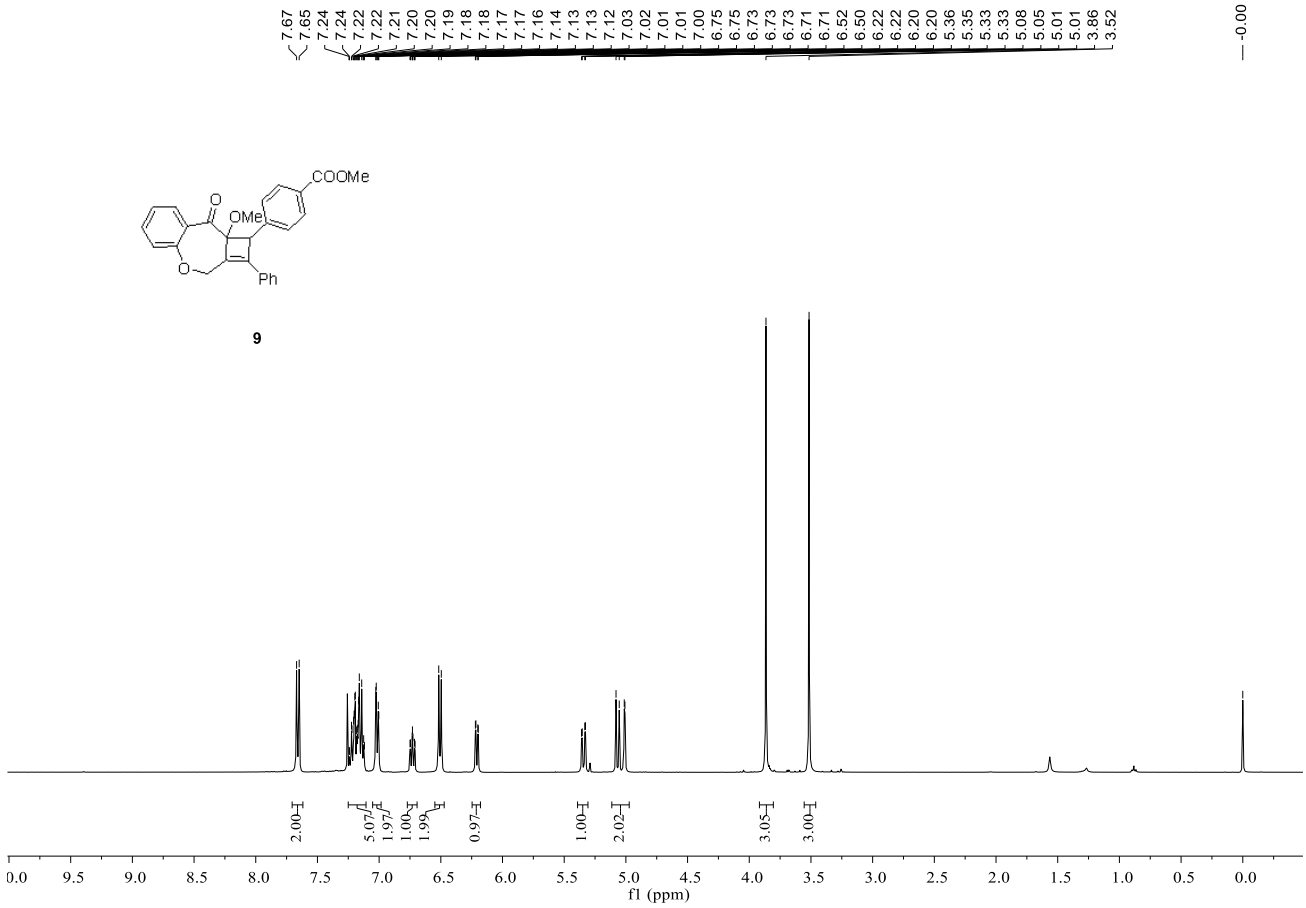
^{1}H NMR (400 MHz) of **8** in $CDCl_3$



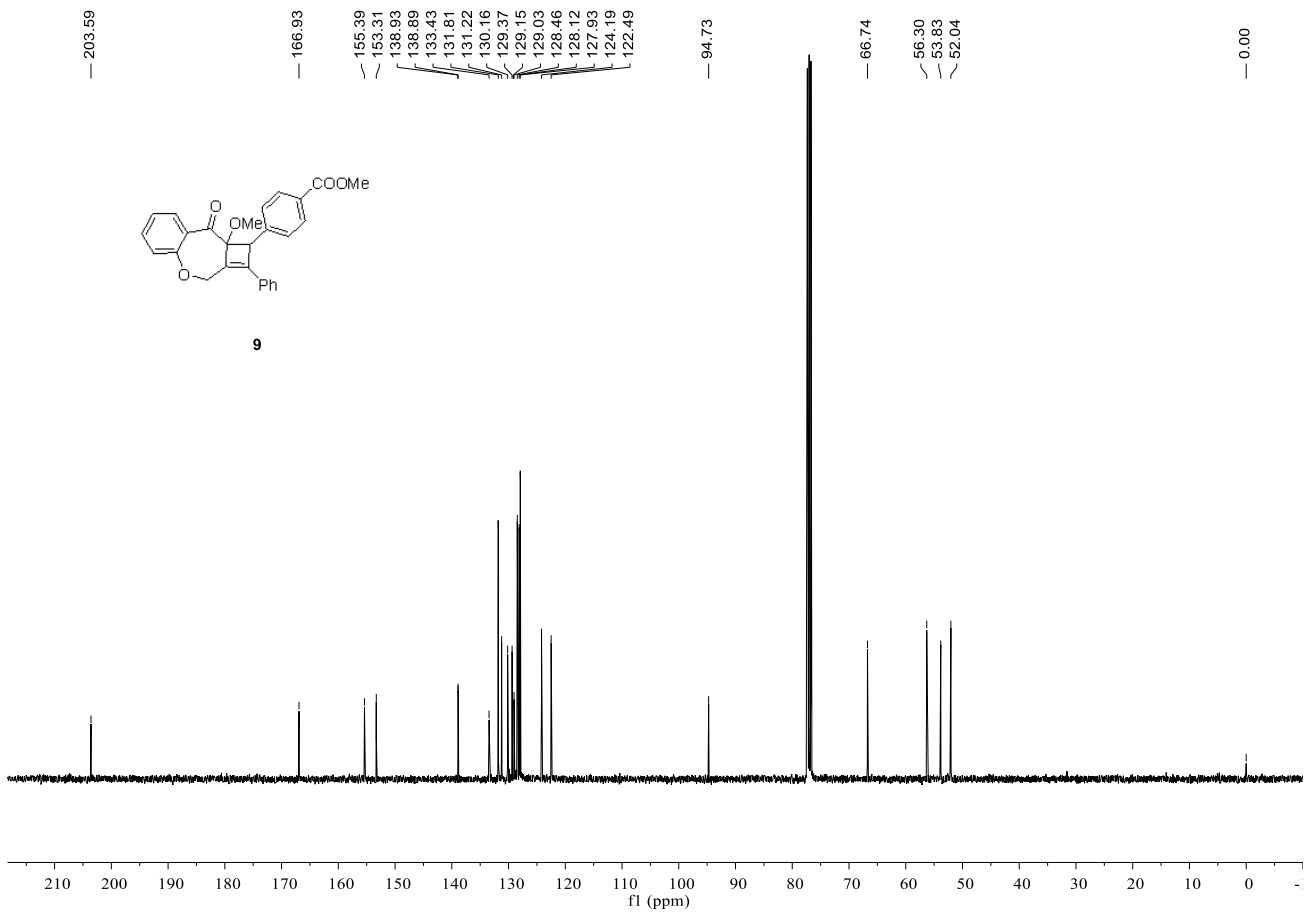
^{13}C NMR (100 MHz) of **8** in $CDCl_3$



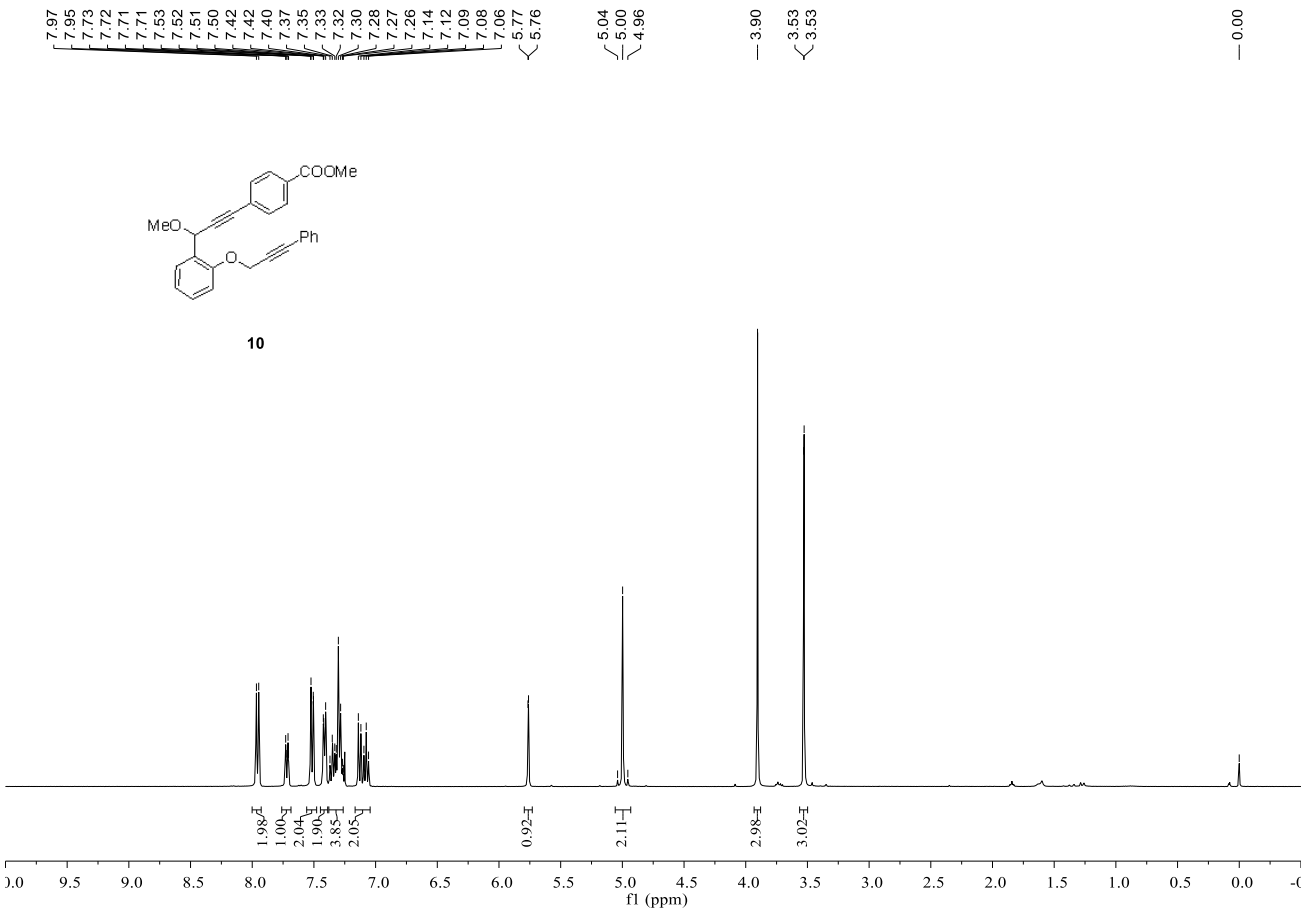
^{1}H NMR (400 MHz) of **9** in $CDCl_3$



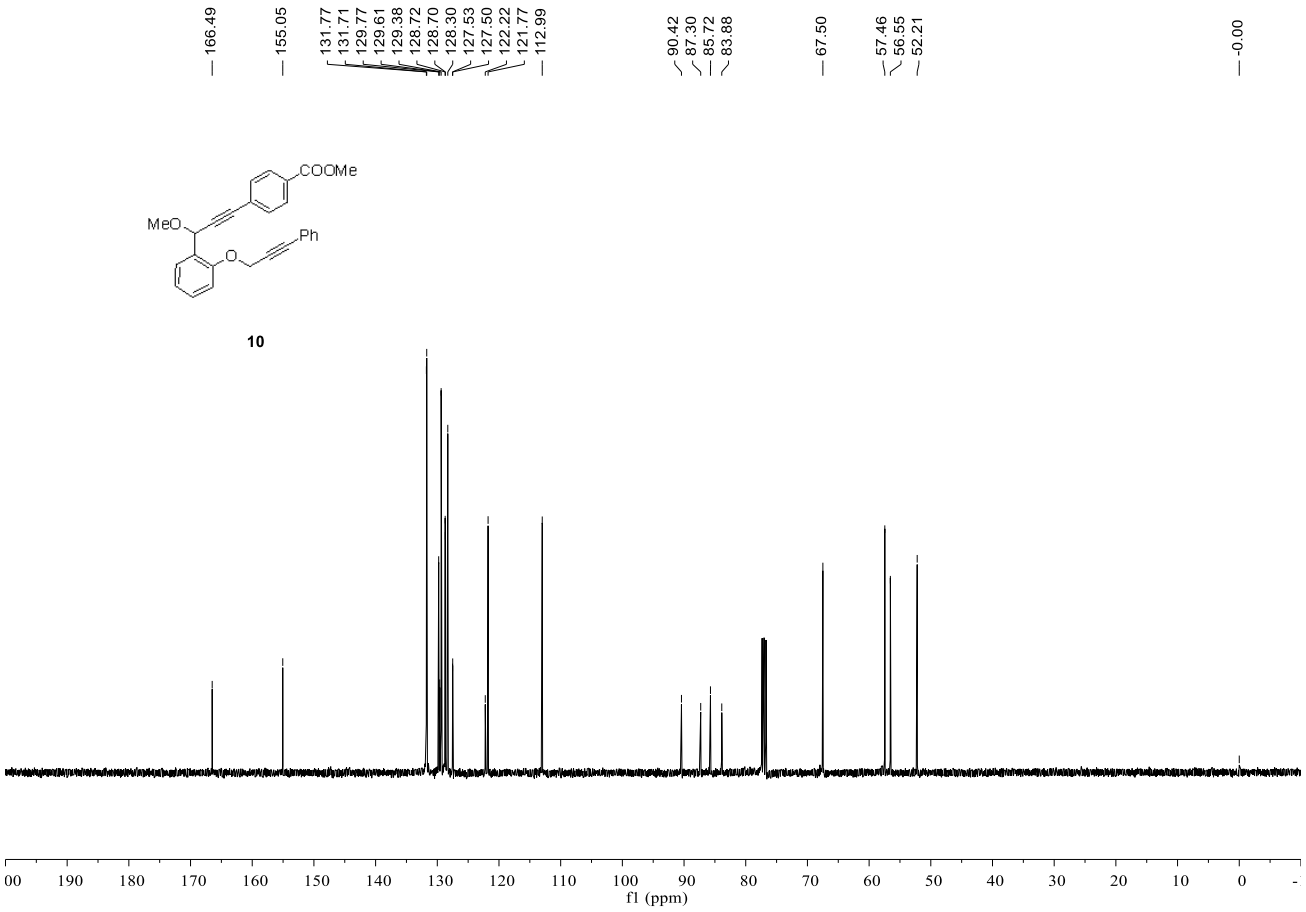
^{13}C NMR (100 MHz) of **9** in $CDCl_3$



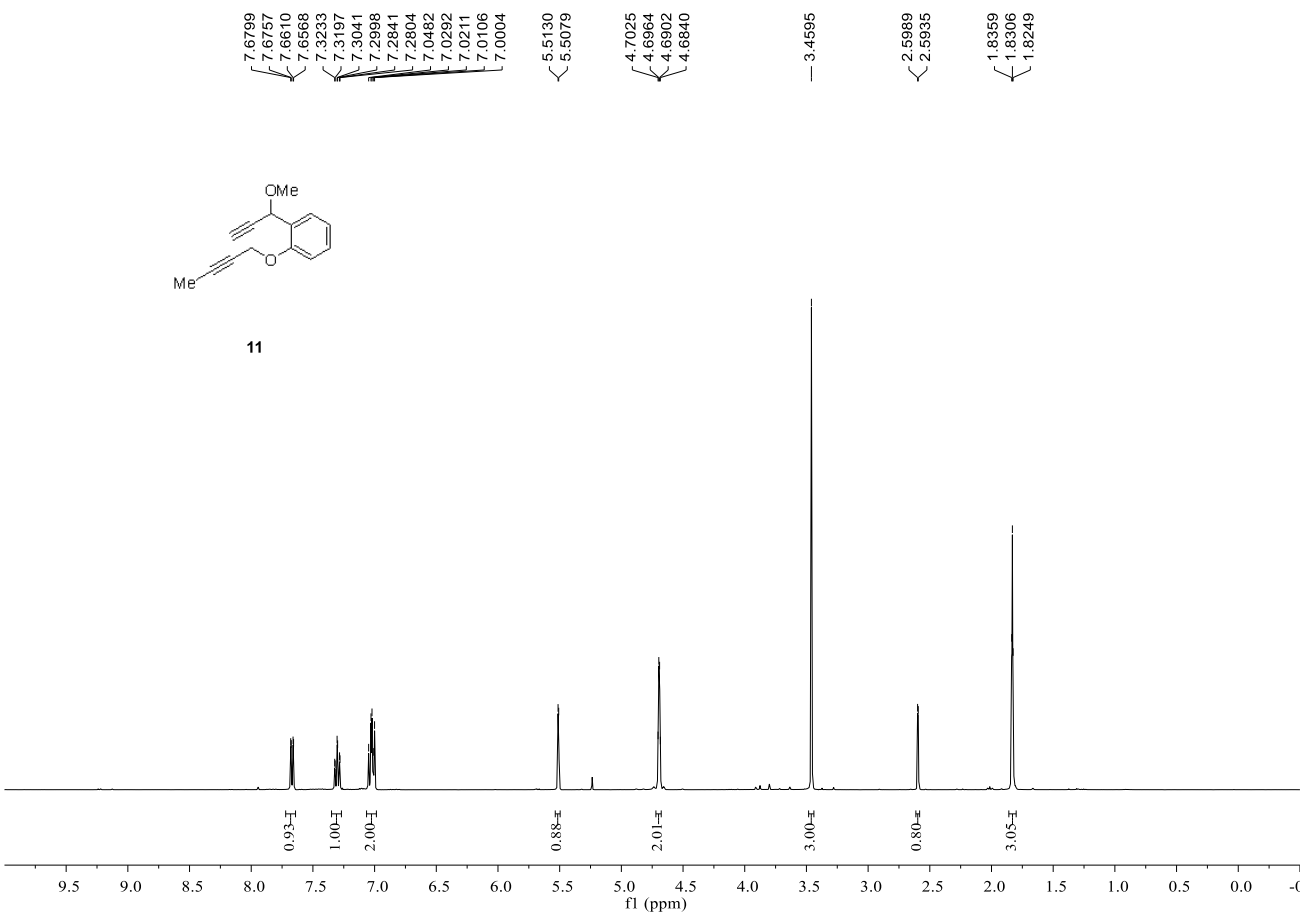
^{1}H NMR (400 MHz) of **10** in $CDCl_3$



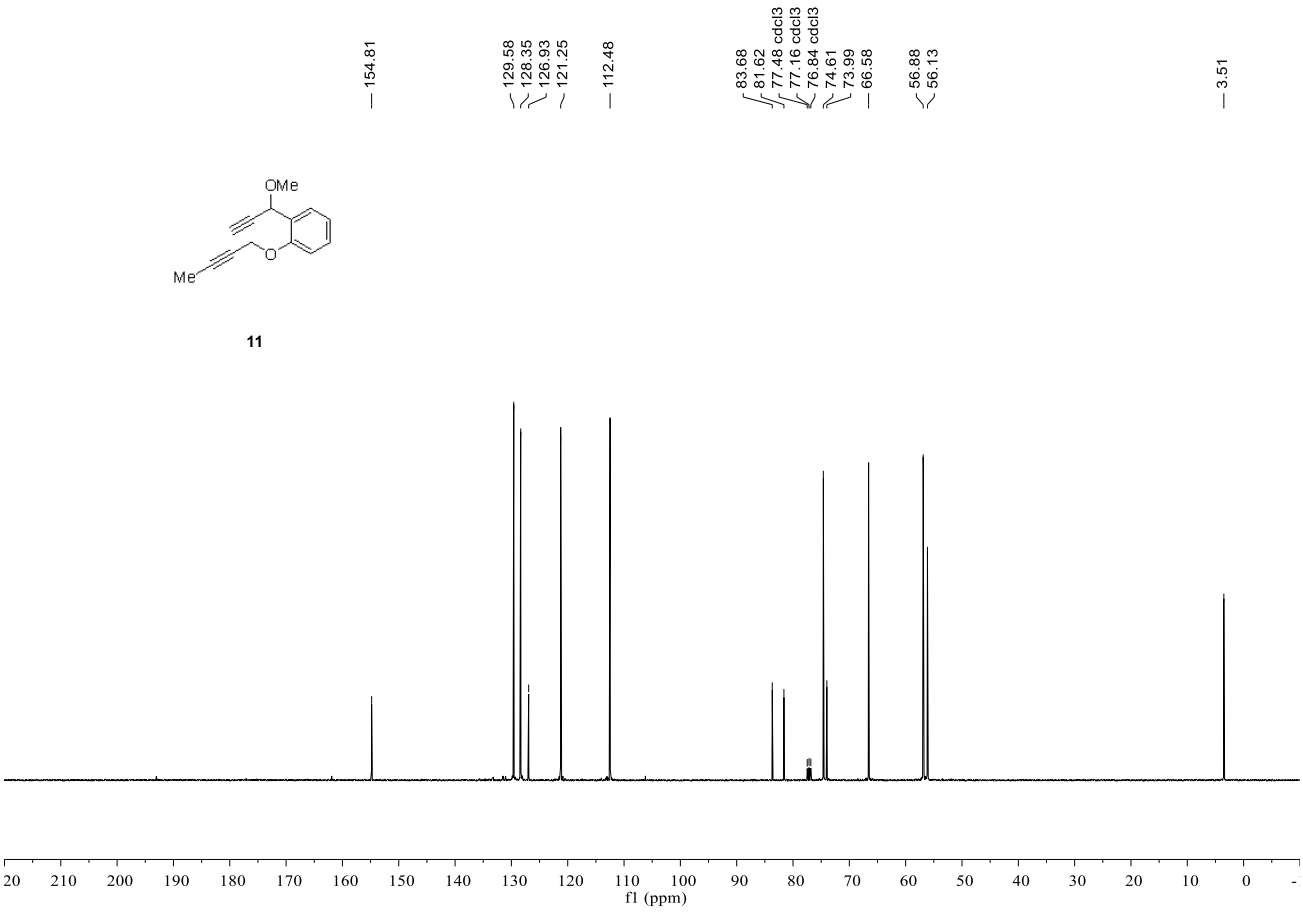
^{13}C NMR (100 MHz) of **10** in $CDCl_3$



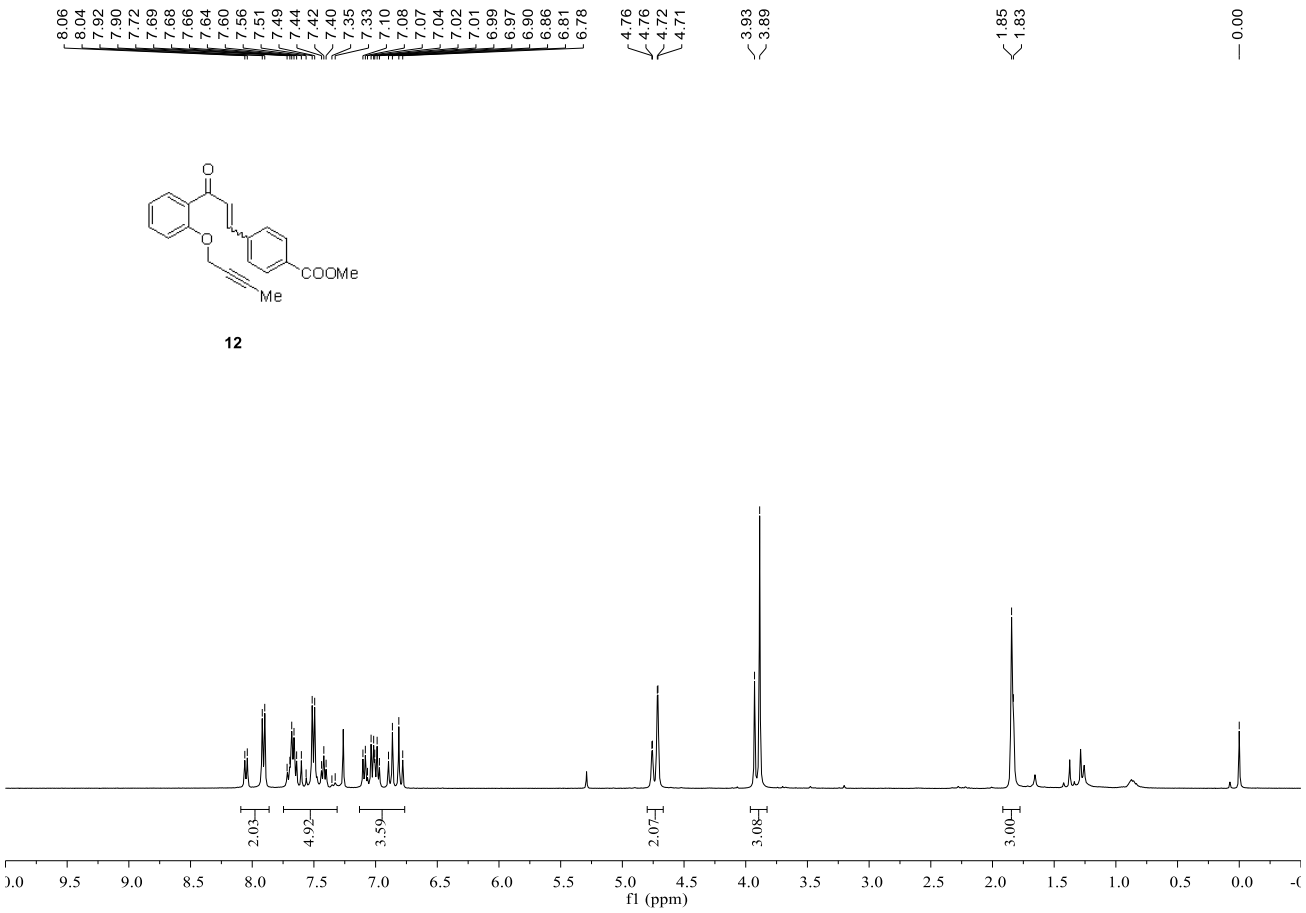
^{1}H NMR (400 MHz) of **11** in $CDCl_3$



^{13}C NMR (100 MHz) of **11** in $CDCl_3$



^{1}H NMR (400 MHz) of **12** in $CDCl_3$



^{13}C NMR (100 MHz) of **12** in $CDCl_3$