A palladium-catalyzed decarboxylative (5 + 5) cyclization reaction of vinyloxazolidine-2,4-diones: access to ten-membered *N*,*O*-containing heterocycles

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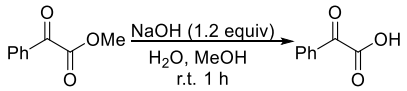
1. General information.

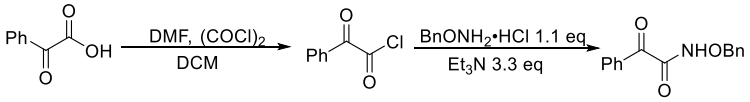
Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Flash column chromatography was performed over silica gel (H, purchased from Qingdao Ocean Chemical Co., Ltd. Qingdao, China). Analytical thin layer chromatography (TLC) was performed on silica gel HSGF254 glass plates (purchased from Yantai Xinuo Chemical Co., Ltd. Yantai, China) containing a 254 nm fluorescent indicator. ^{1}H NMR spectra were measured on a Bruker AVANCE NEO 400 MHz spectrometer at the ambient temperature of 400 MHz. Proton chemical shifts are reported in parts per million (δ scale) and referenced using tetramethylsilane (TMS) as an internal standard or residual protium in the NMR solvent [$CDCl_3$: δ 7.26 ($CHCl_3$) or DMSO-d_6: δ 2.50 (CD_2HSOCD_3)]. Data are reported as follows: chemical shift [multi-plicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets,brs = broad singlet), coupling constant(s) (Hz), integration]. ^{13}C NMR spectra were also measured on a Bruker AVANCE NEO 400 MHz spectrometer at the ambient temperature of ^{13}C at 101MHz. Carbon chemical shifts are reported in parts per million (δ scale), and referenced using the carbon resonances of the solvent [δ 77.16 ($CDCl_3$) or δ 39.52 (DMSO-d_6)]. The melting points of products were recorded on a Büchi Melting Point B-545 and temperatures were not corrected. High-resolution mass spectra (HRMS) were recorded by Agilent 6545 LC/Q-TOF mass spectrometer by using an electrospray ionization (ESI) ionization source analyzed by quadrupole time-of-flight (Q-TOF).

2. General procedures for the synthesis of compounds 1a-1r.



S1 **S2**

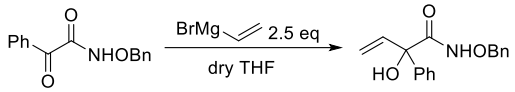
To a solution of **S1** (6.0 mL, 42 mmol, 1.0 equiv) in methanol (100 mL) and water (40 mL) was added NaOH (2.1 g, 1.2 equiv) under ice-bath. The mixture was stirred at room temperature for 1 h. After the completion of the reaction, methanol was removed in vacuo and the residue was acidified by conc. HCl to pH 1 under ice bath. The mixture was extracted with ethyl acetate (50 mL × 3) and washed with water (30 mL × 2), the combined organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was used in the next step without further purification (**S2** as an off-white solid, 6.2 g, 98% yield).



S2 **S3** **S4**

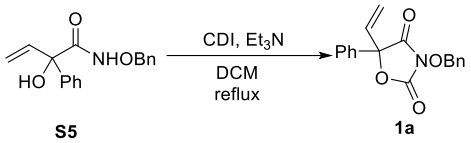
Oxalyl chloride (4.0 mL, 1.1 equiv) and two drops of DMF were added to a solution of **S2** (6.2 g, 41 mmol, 1.0 equiv) in dichloromethane (200 mL) under ice bath conditions and stirred at room temperature for 6 h. After the completion of the reaction, the suspension of 2-oxo-2-phenylacetyl chloride in DCM, was added *O*-benzylhydroxylamine hydrochloride (7.2 g, 1.1 equiv) and Et_3N (19.0 mL, 3.3 equiv) at 0 ^{o}C. The reaction was stirred at room temperature for 12 h and monitored by TLC. When the material **S3** was completely disappeared, the reaction was quenched with water, and extracted with DCM (100 mL × 3). The combined organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1)

to provide **S4** (8.4 g, 80% yield).



S4 **S5**

S4 (2.4 g, 10 mmol, 1.0 equiv) was suspended in anhydrous THF (50 mL) under argon atmosphere and then cooled to 0 ºC. Then 1 M solution of vinylmagnesiumbromide (25 mL, 25 mmol, 2.5 equiv) was added slowly via cannulating needle and the solution was stirred for 2 h at room temperature. The mixture was quenched with saturated aqueous NH_4Cl and extracted with DCM (100 mL × 3). The extracts were successively washed with water and brine, dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by chromatography over silica gel eluting with 20% ethyl acetate in hexane to afford the desired product **S5** (brown oil, 2.0 g, 70% yield).



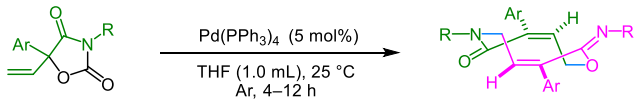
S5 **1a**

Et_3N (2.0 mL, 2.0 equiv) and CDI (3.4 g, 3.0 equiv) were added to a solution of **S5** (2.0 g, 7 mmol, 1.0 equiv) in DCM (25 mL). The resulting solution was refluxed for 6 h. The residue was cooled to room temperature and then purified by flash column chromatography (ethyl acetate/hexane = 1:10) to afford 1.8 g of **1a** as a white solid (82% yield). If necessary, the crude product can be recrystallized in ethyl acetate and hexane.

1b-**1u** were prepared according to the above method for the preparation of **1a**.

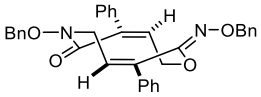
3. General procedure for the synthesis of compounds 2a-2u.

To an oven-dried 25 mL of Schlenk tube equipped with a stir bar, $Pd(PPh_3)_4$ (5 mol%) and 5-vinyloxazolidine-2,4-diones **1a-1u** (0.2 mmol) was added along with THF (1.0 mL). The reaction was stirred at 25 ℃ under argon atmosphere until complete consumption of **1a-1u** as monitored by thin layer chromatography. The reaction mixture was directly purified by silica gel column chromatography to afford the desired products **2a-2u**.



1 **2a-w**

(3*Z*,8*Z*,10*E*)-6-(benzyloxy)-10-((benzyloxy)imino)-4,9-diphenyl-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2a)



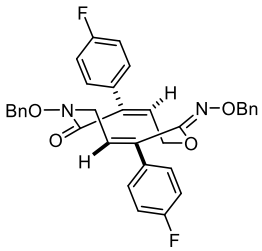
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (61.6 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2a** as white solid, 37.1 mg, 70% yield, m.p. 149.8 – 150.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 6H), 7.25 (d, *J* = 6.3 Hz, 7H), 7.20 (d, *J* = 4.5 Hz, 4H), 7.08 (dd, *J* = 16.0, 7.1 Hz, 3H), 6.62 (dd, *J* = 11.1, 4.4 Hz, 1H), 6.23 (t, *J* = 7.9 Hz, 1H), 5.01 (d, *J* = 17.0 Hz, 3H), 4.90 (d, *J* = 10.8 Hz, 1H), 4.58 – 4.43 (m, 3H), 3.54 (dd, *J* = 15.1, 4.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 152.9, 140.6, 137.8, 136.0, 135.2, 135.1, 134.4, 129.7, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.4, 128.2, 128.1, 127.9, 126.7, 126.3, 125.4, 76.6, 76.3, 67.3, 48.6.

HRMS (ESI) calcd. for $C_{34}H_{31}N_2O_4$ $[M + H]^+$ 531.2278; found: 531.2282.

(3*Z*,8*Z*,10*E*)-6-(benzyloxy)-10-((benzyloxy)imino)-4,9-bis(4-fluorophenyl)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2b)



Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (65.4 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2b** as white solid, 22.4 mg, 40% yield, m.p. 153.9 – 154.1 °C.

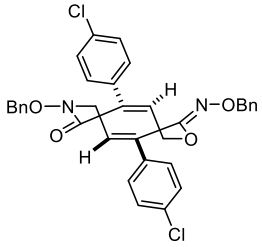
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.39 – 7.32 (m, 6H), 7.29 – 7.10 (m, 6H), 7.07 – 6.95 (m, 4H), 6.64 (dd, *J* = 10.9, 4.5 Hz, 1H), 6.23 (dd, *J* = 10.7, 4.9 Hz, 1H), 5.12 (s, 2H), 5.10 – 4.97 (m, 2H), 4.64 – 4.47 (m, 3H), 3.61 (dd, *J* = 14.9, 4.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 164.6 (d, *J* =3.0 Hz), 163.4 (d, *J* = 249.2 Hz), 162.2(d, *J* =2.8 Hz), 162.1, 152.8, 139.8, 137.8, 135.0, 133.6, 132.0 (d, *J* = 3.3 Hz), 131.3 (d, *J* = 3.3 Hz), 129. 8, 129.2, 128.7 (d, *J* = 8.4 Hz), 128.6, 128.5, 128.4, 128.2, 128.1, 125.3, 116.1(d, *J* = 21.8 Hz), 115.8 (d, *J* = 21.7 Hz), 76.8, 76.4, 67.3, 47.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.77, -112.21.

HRMS (ESI) calcd. for $C_{34}H_{29}F_2N_2O_4$ $[M + H]^+$ 567.2090; found: 567.2092.

(3*Z*,8*Z*,10*E*)-6-(benzyloxy)-10-((benzyloxy)imino)-4,9-bis(4-chlorophenyl)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2c)



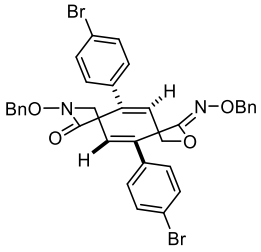
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (68.6 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 7:1) to give the product **2c** as white solid, 18.1 mg, 30% yield, m.p. 157.9 – 158.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.35 (m, 2H), 7.30 (d, *J* = 5.4 Hz, 3H), 7.27 – 7.19 (m, 8H), 7.17 – 7.14(m, 5H), 6.60 (dd, *J* = 10.8, 4.5 Hz, 1H), 6.18 (dd, *J* = 10.9, 4.8 Hz, 1H), 5.03 (s, 2H), 5.01 – 4.87 (m, 2H), 4.54 – 4.41 (m, 3H), 3.53 (dd, *J* = 14.9, 4.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 152.5, 139.8, 137.7, 135.4, 135.2, 134.9, 134.4, 133.6, 133.5, 129.8, 129.4, 129.3, 129.0, 128.8, 128.6, 128.5, 128.4, 128.2, 128.1, 127.7, 125.8, 76.8, 76.4, 67.2, 48.5.

HRMS (ESI) calcd. for $C_{34}H_{29}Cl_2N_2O_4$ $[M + H]^+$ 599.1499; found: 599.1502.

(3*Z*,8*Z*,10*E*)-6-(benzyloxy)-10-((benzyloxy)imino)-4,9-bis(4-bromophenyl)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2d)



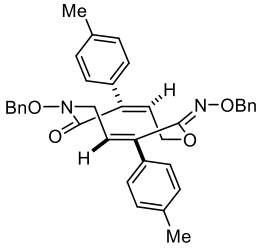
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (77.4 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2d** as white solid, 37.1 mg, 54% yield, m.p. 160.2 – 160.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 8H), 7.35 – 7.31 (m, 2H), 7.26 – 7.18 (m, 6H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.68 (dd, *J* = 10.8, 4.5 Hz, 1H), 6.27 (dd, *J* = 10.9, 4.8 Hz, 1H), 5.11 (s, 2H), 5.08 – 4.96 (m, 2H), 4.61 – 4.49 (m, 3H), 3.68 – 3.61 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 152.5, 139.9, 136.8, 134.9, 134.9, 134.0, 133.7, 132.2, 132.0, 129.8, 129.3, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 125.9, 123.6, 123.5, 77.4, 76.4, 67.3, 49.2.

HRMS (ESI) calcd. for $C_{34}H_{29}Br_2N_2O_4$ $[M + H]^+$ 687.0489; found: 687.0486.

(3*Z*,8*Z*,10*E*)-6-(benzyloxy)-10-((benzyloxy)imino)-4,9-di-*p*-tolyl-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2e)



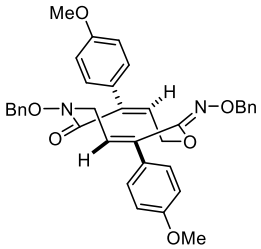
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (64.6 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2e** as white solid, 32.2 mg, 58% yield, m.p. 144.0 – 144.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H), 7.39 – 7.36 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 4H), 7.25 – 7.14 (m, 6H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.67 (dd, *J* = 10.9, 4.5 Hz, 1H), 6.29 (dd, *J* = 8.6, 7.1 Hz, 1H), 5.19 – 5.06 (m, 3H), 4.99 (d, *J* = 10.8 Hz, 1H), 4.67 – 4.46 (m, 3H), 3.62 (dd, *J* = 14.9, 4.5 Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 152.6, 140.0, 139.4, 139.2, 138.5, 135.9, 134.3, 133.2, 131.9, 129.7, 129.6, 129.2, 129.1, 128.8, 128.5, 128.2, 127.9, 127.2, 126.7, 126.3, 124.2, 76.6, 76.4, 67.4, 48.7, 21.4, 21.4.

HRMS (ESI) calcd. for $C_{36}H_{35}N_2O_4$ $[M + H]^+$ 559.2591; found: 559.2588.

(3*Z*,8*Z*,10*E*)-6-(benzyloxy)-10-((benzyloxy)imino)-4,9-bis(4-methoxyphenyl)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2f)



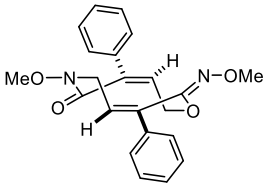
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (67.8 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2f** as white solid, 18.3 mg, 31% yield, m.p. 161.8 – 162.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.40 – 7.32 (m, 6H), 7.31 – 7.28 (m, 3H), 7.24 – 7.14 (m, 3H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.61 (dd, *J* = 11.0, 4.5 Hz, 1H), 6.23 (dd, *J* = 9.3, 6.4 Hz, 1H), 5.17 – 5.08 (m, 3H), 5.00 (d, *J* = 10.8 Hz, 1H), 4.64 – 4.51 (m, 3H), 3.86 (s, 3H), 3.80 (s, 3H), 3.60 (dd, *J* = 14.9, 4.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 160.5, 160.4, 153.3, 140.1, 138.0, 135.2, 133.9, 129.7, 129.1, 128.8, 128.6, 128.5, 128.3, 128.2, 127.9, 127.8, 127.7, 126.2, 123.5, 114.4, 114.2, 76.6, 76.3, 67.5, 55.6, 55.5, 48.6.

HRMS (ESI) calcd. for $C_{36}H_{34}N_2O_6Na$ $[M + Na]^+$ 613.2309; found: 613.2309.

(3*Z*,8*Z*,10*Z*)-6-methoxy-10-(methoxyimino)-4,9-diphenyl-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2g)



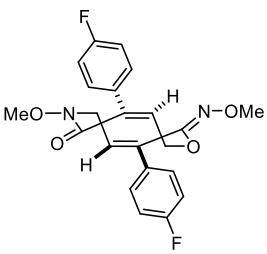
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (46.6 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2g** as white solid, 34.0 mg, 90% yield, m.p. 146.2 – 146.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 4H), 7.44 – 7.31 (m, 6H), 6.75 (dd, *J* = 10.8, 4.6 Hz, 1H), 6.36 (dd, *J* = 9.9, 5.6 Hz, 1H), 4.81 (dd, *J* = 15.0, 10.8 Hz, 1H), 4.66 – 4.55 (m, 2H), 4.02 (dd, *J* = 15.0, 4.6 Hz, 1H), 3.98 (s, 3H), 3.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 152.4, 140.0, 136.2, 135.2, 134.6, 129.4, 129.3, 129.2, 128.9, 128.3, 126.8, 126.3, 125.4, 67.3, 62.9, 61.1, 47.4.

HRMS (ESI) calcd. for $C_{22}H_{23}N_2O_4$ $[M + H]^+$ 379.1652; found: 379.1651.

(3*Z*,8*Z*,10*Z*)-4,9-bis(4-fluorophenyl)-6-methoxy-10-(methoxyimino)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2h)



Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (50.2 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2h** as colorless oil, 27.6 mg, 67% yield.

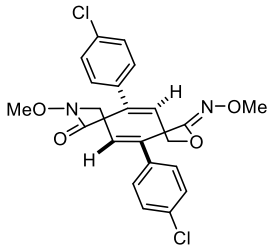
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 4H), 7.10 – 7.01 (m, 4H), 6.68 (dd, *J* = 10.7, 4.7 Hz, 1H), 6.28 (dd, *J* = 10.9, 4.7 Hz, 1H), 4.76 (dd, *J* = 14.9, 10.7 Hz, 1H), 4.66 – 4.50 (m, 2H), 4.05 – 3.94 (m, 4H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 163.4 (dd, *J* = 242.5 Hz, *J* = 242.4 Hz), 152.2, 139.8, 133.8, 132.3 (d, *J* = 3.3 Hz), 131.3 (d, *J* = 3.2 Hz) , 128.8 (d, *J* = 8.3 Hz), 128.7 (d, *J* = 8.4 Hz), 128.1, 128.0, 125.2, 116.2 (d, *J* = 21.8 Hz), 115.9 (d, *J* = 21.7 Hz), 67.3, 62.9, 61.7, 47.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.6, -112.1.

HRMS (ESI) calcd. for $C_{22}H_{20}F_2N_2O_4Na$ $[M + Na]^+$ 437.1283; found: 437.1301.

(3*Z*,8*Z*,10*Z*)-4,9-bis(4-chlorophenyl)-6-methoxy-10-(methoxyimino)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2i)



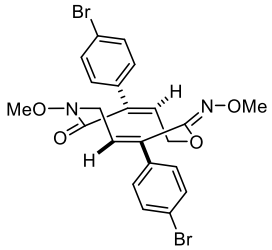
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (53.4 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2i** as colorless oil, 31.8 mg, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 6H), 7.35 – 7.31 (m, 2H), 6.71 (dd, *J* = 10.6, 4.7 Hz, 1H), 6.32 (dd, *J* = 10.9, 4.6 Hz, 1H), 4.74 (dd, *J* = 15.0, 10.7 Hz, 1H), 4.65 – 4.51 (m, 2H), 4.03 – 3.98 (m, 1H), 3.96 (s, 3H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 152.0, 139.8, 135.6, 135.3, 134.6, 133.8, 133.5, 129.4, 129.1, 128.6, 128.1, 127.6, 125.7, 67.2, 62.9, 61.7, 47.2.

HRMS (ESI) calcd. for $C_{22}H_{21}{}^{35}Cl_2N_2O_4$ $[M + H]^+$ 447.0873; found: 447.0878.

(3*Z*,8*Z*,10*Z*)-4,9-bis(4-bromophenyl)-6-methoxy-10-(methoxyimino)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2j)



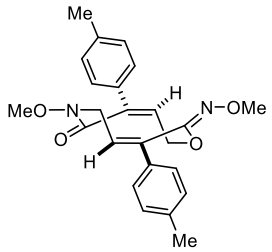
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (62.4 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2j** as white solid, 17.1 mg, 32% yield. m.p. 158.3 – 159.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 4H), 7.33 (dd, *J* = 8.6, 1.6 Hz, 4H), 6.72 (dd, *J* = 10.6, 4.7 Hz, 1H), 6.33 (dd, *J* = 10.9, 4.6 Hz, 1H), 4.74 (dd, *J* = 15.0, 10.6 Hz, 1H), 4.66 – 4.47 (m, 2H), 3.96 (s, 4H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 151.9, 139.9, 135.1, 134.0, 133.8, 132.4, 132.1, 128.6, 128.4, 127.8, 125.8, 123.8, 123.6, 67.3, 63.0, 61.7, 47.3.

HRMS (ESI) calcd. for $C_{22}H_{21}Br_2N_2O_4$ $[M + H]^+$ 534.9863; found: 534.9863.

(3*Z*,8*Z*,10*Z*)-6-methoxy-10-(methoxyimino)-4,9-di-*p*-tolyl-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2k)



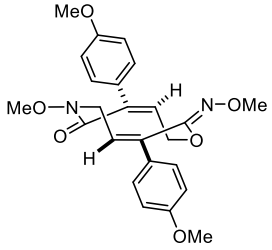
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (49.4 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2k** as white solid, 27.7 mg, 68% yield, m.p. 165.1-165.7 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 4H), 7.19 (dd, *J* = 16.8, 7.9 Hz, 4H), 6.71 (dd, *J* = 10.9, 4.6 Hz, 1H), 6.31 (dd, *J* = 10.1, 5.6 Hz, 1H), 4.78 (dd, *J* = 14.9, 10.9 Hz, 1H), 4.64 – 4.52 (m, 2H), 3.97 (s, 4H), 3.89 (s, 3H), 2.35 (d, *J* = 9.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 152.6, 140.5, 139.5, 139.3, 134.5, 133.3, 132.4, 129.8, 129.6, 127.3, 126.7, 126.2, 124.5, 67.4, 62.8, 61.6, 47.3, 21.4, 21.4.

HRMS (ESI) calcd. for $C_{24}H_{26}N_2O_4Na$ $[M + Na]^+$ 429.1785; found: 429.1783.

(3*Z*,8*Z*,10*Z*)-6-methoxy-10-(methoxyimino)-4,9-bis(4-methoxyphenyl)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2l)



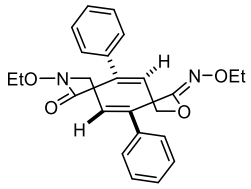
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (52.6 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 3:1) to give the product **2l** as colorless oil, 26.6 mg, 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 4H), 6.92 – 6.89 (m, 4H), 6.64 (dd, *J* = 10.9, 4.6 Hz, 1H), 6.24 (dd, *J* = 10.4, 5.2 Hz, 1H), 4.76 (dd, *J* = 14.9, 10.9 Hz, 1H), 4.64 – 4.51 (m, 2H), 3.98 (d, *J* = 17.0 Hz, 4H), 3.89 (s, 3H), 3.82 (d, *J* = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 160.6, 160.4, 152.7, 140.1, 134.0, 128.6, 128.1, 127.6, 126.2, 123.4, 114.5, 114.2, 77.4, 67.4, 62.8, 61.6, 55.5, 55.4, 47.3.

HRMS (ESI) calcd. for $C_{24}H_{27}N_2O_6$ $[M + H]^+$ 439.1864; found: 439.1872.

(3*Z*,8*Z*,10*E*)-6-ethoxy-10-(ethoxyimino)-4,9-diphenyl-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2m)



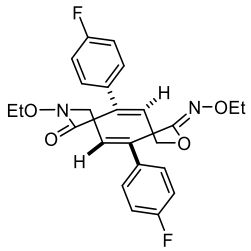
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (49.4 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2m** as white solid, 22.9 mg, 56% yield, m.p. 131.4 – 131.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 4H), 7.42 – 7.32 (m, 6H), 6.78 (dd, *J* = 10.8, 4.6 Hz, 1H), 6.36 (dd, *J* = 10.0, 5.7 Hz, 1H), 4.84 (dd, *J* = 14.8, 10.9 Hz, 1H), 4.70 – 4.51 (m, 2H), 4.28 – 4.13 (m, 3H), 4.08 (dd, *J* = 8.7, 7.0 Hz, 1H), 3.97 (dd, *J* = 14.9, 4.6 Hz, 1H), 1.40 – 1.32 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 152.3, 140.8, 136.2, 135.3, 134.8, 129.3, 129.2, 129.1, 128.9, 128.3, 126.8, 126.3, 125.5, 70.5, 69.8, 67.3, 48.0, 15.0, 13.9.

HRMS (ESI) calcd. for $C_{24}H_{26}N_2O_4Na$ $[M + Na]^+$ 429.1785; found: 429.1785.

(3*Z*,8*Z*)-6-ethoxy-10-(ethoxyimino)-4,9-bis(4-fluorophenyl)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2n)



Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (50.2 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2n** as colorless oil, 30.0 mg, 68% yield.

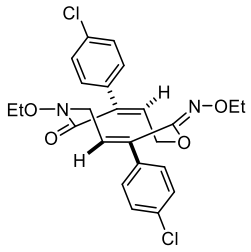
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.33 (m, 4H), 7.12 – 6.97 (m, 4H), 6.70 (dd, *J* = 10.9, 4.6 Hz, 1H), 6.29 (dd, *J* = 11.1, 4.6 Hz, 1H), 4.79 (dd, *J* = 14.8, 10.8 Hz, 1H), 4.65 – 4.50 (m, 2H), 4.25 – 3.93 (m, 5H), 1.32 (dt, *J* = 10.7, 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 164.6 (d, *J* = 6.9 Hz), 162.1 (d, *J* = 6.2 Hz), 152.1, 139.9, 133.9, 132.3 (d, *J* = 3.4 Hz), 131.4 (d, *J* = 3.3 Hz), 128.7, 128.6, 128.1, 128.1, 128.0, 125.2, 116.3, 116.0, 116.0, 115.8, 70.5, 69.9, 67.2, 47.9, 14.9, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.77, -112.23.

HRMS (ESI) calcd. for $C_{24}H_{25}F_2N_2O_4$ $[M + H]^+$ 443.1777; found: 443.1779.

(3*Z*,8*Z*,10*E*)-4,9-bis(4-chlorophenyl)-6-ethoxy-10-(ethoxyimino)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2o)



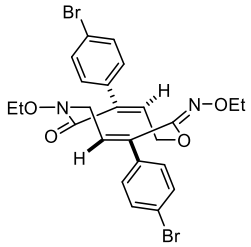
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (56.2 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2o** as colorless oil, 27.2 mg, 57% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 8H), 6.74 (dd, *J* = 10.8, 4.7 Hz, 1H), 6.33 (dd, *J* = 11.1, 4.6 Hz, 1H), 4.77 (dd, *J* = 14.9, 10.7 Hz, 1H), 4.65 – 4.50 (m, 2H), 4.23 – 3.93 (m, 5H), 1.32 (dt, *J* = 10.0, 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 151.8, 139.9, 135.5, 135.3, 134.6, 133.9, 133.7, 129.4, 129.1, 128.6, 128.1, 127.6, 125.8, 70.6, 69.9, 67.2, 47.9, 15.0, 13.9.

HRMS (ESI) calcd. for $C_{24}H_{24}Cl_2N_2O_4Na$ $[M + Na]^+$ 497.1005; found: 497.1010.

(3*Z*,8*Z*)-4,9-bis(4-bromophenyl)-6-ethoxy-10-(ethoxyimino)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2p)



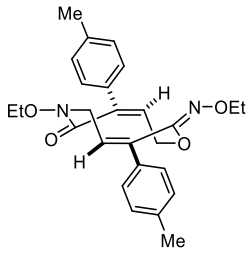
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (65.2 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2p** as colorless oil, 25.0 mg, 44% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 4H), 7.34 (dd, *J* = 8.6, 2.5 Hz, 4H), 6.75 (dd, *J* = 10.7, 4.7 Hz, 1H), 6.34 (dd, *J* = 11.1, 4.6 Hz, 1H), 4.77 (dd, *J* = 14.9, 10.8 Hz, 1H), 4.65 – 4.48 (m, 2H), 4.24 – 4.02 (m, 4H), 3.95 (dd, *J* = 14.8, 4.7 Hz, 1H), 1.32 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 151.8, 140.1, 135.1, 134.2, 134.0, 132.3, 132.1, 128.7, 128.4, 127.8, 125.9, 123.7, 123.5, 70.6, 70.0, 67.2, 47.9, 15.0, 13.9.

HRMS (ESI) calcd. for $C_{24}H_{24}Br_2N_2O_4Na$ $[M + Na]^+$ 584.9995; found: 585.0003.

(3*Z*,8*Z*)-6-ethoxy-10-(ethoxyimino)-4,9-di-*p*-tolyl-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2q)

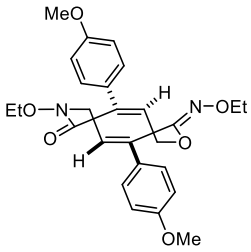


Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (52.2 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2q** as white solid, 31.0 mg, 71% yield, 134.2 – 134.8℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.37 (m, 4H), 7.20 – 7.15 (m, 4H), 6.73 (dd, *J* = 10.9, 4.6 Hz, 1H), 6.32 (dd, *J* = 10.0, 5.7 Hz, 1H), 4.82 (dd, *J* = 14.8, 10.9 Hz, 1H), 4.63 – 4.52 (m, 2H), 4.26 – 4.12 (m, 3H), 4.11 – 4.03 (m, 1H), 3.94 (dd, *J* = 14.8, 4.6 Hz, 1H), 2.36 (d, *J* = 8.0 Hz, 6H), 1.41 – 1.32 (m, 6H).

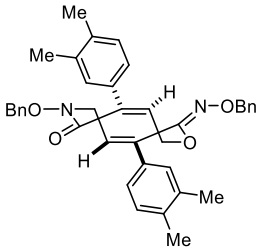
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 152.5, 140.7, 139.4, 139.2, 134.6, 133.4, 132.5, 129.7, 129.5, 127.3, 126.7, 126.2, 124.6, 70.4, 69.7, 67.3, 48.0 (2C), 21.3, 14.9, 13.9.
HRMS (ESI) calcd. for $C_{26}H_{30}N_2O_4Na$ $[M + Na]^+$ 457.2098; found: 457.2109.

(3*Z*,8*Z*,10*Z*)-6-methoxy-10-(ethoxyimino)-4,9-bis(4-methoxyphenyl)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2r)



Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (55.4 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2r** as colorless oil, 29.3 mg, 63% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 9.0, 3.0 Hz, 4H), 6.94 – 6.85 (m, 4H), 6.68 (dd, *J* = 10.9, 4.6 Hz, 1H), 6.26 (dd, *J* = 10.5, 5.3 Hz, 1H), 4.81 (dd, *J* = 14.8, 11.0 Hz, 1H), 4.59 (dd, *J* = 13.3, 7.8 Hz, 2H), 4.22 – 3.92 (m, 5H), 3.82 (d, *J* = 6.2 Hz, 6H), 1.41 – 1.33 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 152.5, 140.7, 139.4, 139.2, 134.6, 133.4, 132.5, 129.7, 129.5, 129.1, 127.3, 126.7, 126.2, 124.6, 70.4, 69.7, 67.3, 48.0, 21.3, 14.9, 13.9.
HRMS (ESI) calcd. for $C_{26}H_{30}N_2O_6Na$ $[M + Na]^+$ 489.1996; found: 489.2010.

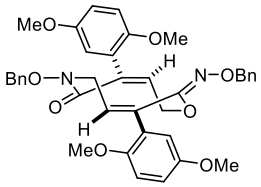
(3*Z*,8*Z*,10*E*)-6-(benzyloxy)-10-((benzyloxy)imino)-4,9-bis(3,4-dimethylphenyl)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2s)



Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (67.4 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2s** as white solid, 20.1 mg, 34% yield, m.p. 168.5 – 169.0 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.40 – 7.31 (m, 5H), 7.29 – 7.20 (m, 2H), 7.20 – 7.06 (m, 7H), 6.66 (dd, *J* = 11.0, 4.4 Hz, 1H), 6.31 (t, *J* = 7.9 Hz, 1H), 5.12 (d, *J* = 9.9 Hz, 3H), 5.00 (d, *J* = 10.8 Hz, 1H), 4.67 – 4.54 (m, 3H), 3.62 (dd, *J* = 15.0, 4.5 Hz, 1H), 2.30 (d, *J* = 9.1 Hz, 6H), 2.21 (d, *J* = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 153.3, 140.6, 138.1, 137.9, 137.2, 137.1, 135.2, 134.5, 133.6, 132.8, 130.3, 130.0, 129.7, 129.1, 128.9, 128.8, 128.4, 128.1, 128.0, 127.9, 127.4, 127.1, 124.4, 124.3, 123.9, 76.5, 76.4, 67.4, 48.8, 20.1, 19.9, 19.8, 19.7.
HRMS (ESI) calcd. for $C_{38}H_{39}N_2O_4$ $[M + H]^+$ 587.2904; found: 587.2908.

(3*Z*,8*Z*,10*E*)-6-(benzyloxy)-10-((benzyloxy)imino)-4,9-bis(2,5-dimethoxyphenyl)-7,10-dihydro-2*H*-

1,6-oxazecin-5(6*H*)-one (2t)



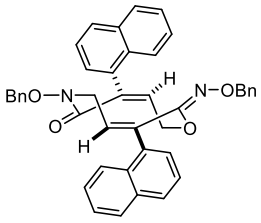
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (73.8 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2t** as white solid, 32.4 mg, 50% yield, m.p. 79.9 – 80.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 –7.46 (m, 2H), 7.33 – 7.30 (m, 3H), 7.26 – 7.14 (m, 5H), 6.96 – 6.74 (m, 6H), 6.46 – 6.39 (m, 1H), 6.32 (dd, *J* = 10.8, 5.6 Hz, 1H), 5.11 – 5.01 (m, 3H), 4.98 – 4.79 (m, 4H), 3.97 (dd, *J* = 15.6, 5.6 Hz, 1H), 3.79 (s, 3H), 3.74 (d, *J* = 7.0 Hz, 6H), 3.63 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 154.3, 154.0, 153.5, 151.3, 150.9, 139.7, 137.9, 135.5, 133.1, 131.5, 129.6, 128.8, 128.6, 128.4, 128.3, 128.0, 127.7, 127.6, 127.0, 116.0, 115.7, 115.3, 114.3, 112.4, 112.2, 76.6, 76.5, 67.6, 56.4, 56.3, 56.0, 55.8, 49.3.

HRMS (ESI) calcd. for $C_{38}H_{39}N_2O_8$ $[M+H]^+$ 651.2701; found: 651.2704.

(3*Z*,8*Z*,10*E*)-6-(benzyloxy)-10-((benzyloxy)imino)-4,9-di(naphthalen-1-yl)-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (2u)



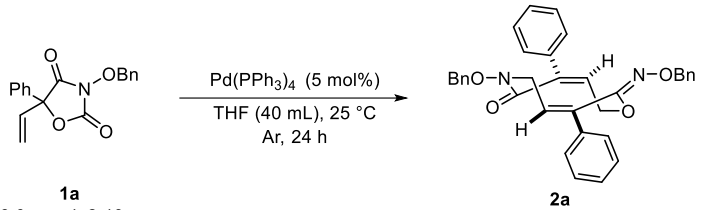
Prepared according to general procedure using corresponding 5-vinyloxazolidine-2,4-dione (71.8 mg, 0.20 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 5:1) to give the product **2a** as yellow oil, 18.6 mg, 30% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.35 (m, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.96 – 7.87 (m, 2H), 7.85 – 7.82 (m, 2H), 7.62 – 7.38 (m, 9H), 7.36 – 7.27 (m, 4H), 7.25 – 7.21 (m, 1H), 7.15 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 2H), 6.56 (dd, *J* = 10.2, 4.9 Hz, 1H), 6.36 (dd, *J* = 10.9, 4.6 Hz, 1H), 5.26 – 5.13 (m, 3H), 5.03 – 4.85 (m, 2H), 4.83 – 4.71 (m, 2H), 3.57 (dd, *J* = 14.5, 4.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 154.2, 141.2, 137.8, 135.2, 134.7, 134.4, 134.2, 134.1, 134.0, 131.6, 131.3, 130.7, 129.9, 129.6, 129.4, 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.3, 127.1, 126.7, 126.5, 126.4, 126.0, 125.5, 125.4, 125.3, 125.2, 77.4, 76.3, 67.7, 49.2.

HRMS (ESI) calcd. for $C_{42}H_{34}N_2O_4K$ $[M+K]^+$ 669.2150; found: 669.2148.

4. Scale-up reaction for the synthesis of 2a.

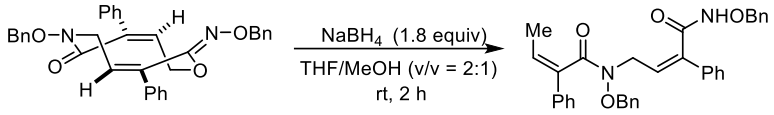


1a
8.0 mmol, 2.46 g

2a
1.05 g, 50% yield

In an ordinary vial equipped with a magnetic stirring bar, $Pd(PPh_3)_4$ (5 mol%), **1a** (8.0 mol, 2.46 g) and dry THF (40 mL). The reaction stirred at rt under argon atmosphere for 24 h. The reaction mixture was directly purified by alumina column chromatography (ethyl acetate/petroleum ether = 1:20) to afford the desired **2a** with 50% yield.

5. Procedures for further transformations.

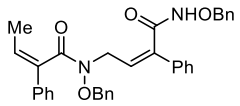


2a

3, 55%

To a stirred solution of **2a** (53.0 mg, 0.1 mmol) in THF/MeOH (*v*/*v*=2:1, 3 mL) were added $NaBH_4$ (68 mg, 1.8 eq). The resultant reaction mixture was stirred at rt for 2 h. After the reaction was finished, the mixture was poured into water (3 mL), and extracted with EtOAc (3 ×5 mL). The combined organic layers were further washed with aqueous sodium bicarbonate (2 ×5 mL), brine and dried over Na_2SO_4, and concentrated under reduced pressure. The pure product **3** was isolated by flash chromatography: 29.2 mg, 55% yield.

(*Z*)-*N*-(benzyloxy)-4-((*Z*)-*N*-(benzyloxy)-2-phenylbut-2-enamido)-2-phenylbut-2-enamide (3)

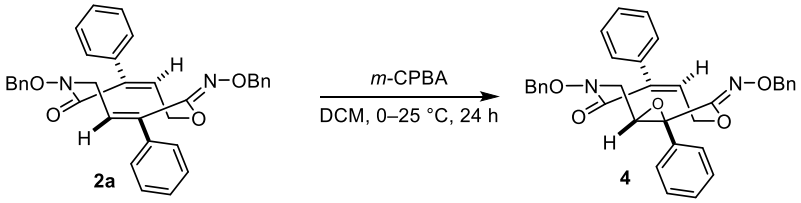


It was purified by flash chromatography (petroleum ether/ethyl acetate = 3:1) to give the product **3** as colorless oil, 29.2 mg, 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.52 – 7.47 (m, 2H), 7.40 – 7.28 (m, 14H), 7.27 – 7.18 (m, 2H), 7.14 (d, *J* = 6.6 Hz, 2H), 6.21 (q, *J* = 7.2 Hz, 1H), 5.99 (t, *J* = 7.7 Hz, 1H), 5.06 (s, 2H), 4.56 (s, 2H), 4.32 (d, *J* = 7.8 Hz, 2H), 1.87 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 165.5, 139.1, 137.4, 136.5, 136.0, 135.5, 133.9, 129.4, 129.4, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 127.9, 126.7, 126.6, 125.5, 124.1, 78.2, 77.6, 48.3, 16.0.

HRMS (ESI) calcd. for $C_{34}H_{33}N_2O_4$ $[M + H]^+$ 533.2435; found: 533.2444.



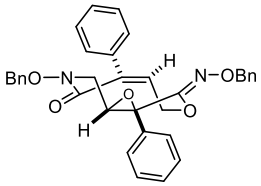
2a

4

To a stirred solution of **2a** (53.0 mg, 0.1 mmol) in DCM (1 mL) were added *m*-chloroperbenzoic acid (86.0 mg, 0.5 mmol) under ice bath. The resultant reaction mixture was stirred at 25 ℃ for 24 h. After the reaction was finished, the mixture was poured into water (3 mL), and extracted with EtOAc

(3 ×5 mL). The combined organic layers were further washed with aqueous sodium bicarbonate (2 ×5 mL), brine and dried over Na_2SO_4, and concentrated under reduced pressure. The pure product **4** was isolated by flash chromatography: 34.2 mg, 63% yield.

(3*Z*,8*Z*,10*Z*)-6-methoxy-10-(methoxyimino)-4,9-diphenyl-7,10-dihydro-2*H*-1,6-oxazecin-5(6*H*)-one (4)



It was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1) to give the product **4** white solid, 34.2 mg, 63% yield, m.p. 75.2 – 75.8 ℃.

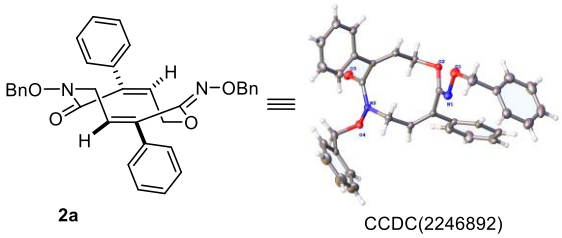
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 4H), 7.28 – 7.27(m, 10H), 7.18 – 7.17 (m, 6H), 6.21 (dd, *J* = 8.9, 6.1 Hz, 1H), 5.08 – 5.00 (m, 4H), 4.76 – 4.74 (m, 2H), 3.83 (t, *J* = 6.1 Hz, 1H), 3.59 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 151.4, 141.0, 137.1, 135.0, 134.6, 134.5, 129.8, 129.5, 129.4, 129.3, 129.1, 128.9, 128.8, 128.7, 128.6, 128.2, 127.2, 126.2, 125.6, 76.5, 67.5, 61.3, 59.6, 48.2, 29.8.

HRMS (ESI) calcd. for $C_{34}H_{31}N_2O_5$ $[M + H]^+$ 547.2227; found: 547.2230.

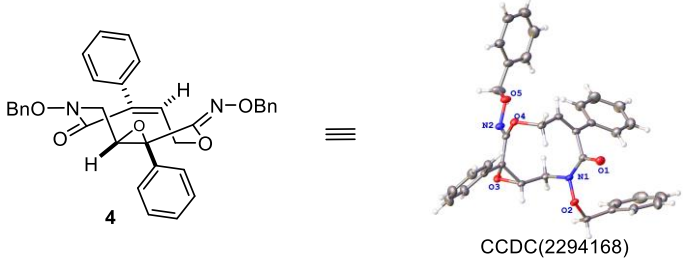
6. X-ray crystallographic data of 2a and 4.

Single crystals of compound **2a** were prepared from the mixture solvent of dichloromethane and EtOH. A suitable crystal was selected for structure determination on a Xcalibur, Eos, Gemini diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2[1], the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.



Identification code	**2a**
Empirical formula	$C_{34}H_{30}N_2O_4$
Formula weight	530.60
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.264(5)
b/Å	11.216(3)
c/Å	13.734(4)
α/°	90
β/°	106.847(6)
γ/°	90
Volume/Å^3	2840.2(13)
Z	4
ρ_{calc}g/cm^3	1.241
μ/mm^{-1}	0.082
F(000)	1120.0
Crystal size/mm^3	0.14 × 0.11 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.868 to 50.108
Index ranges	-22 ≤ h ≤ 20, -11 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	31215
Independent reflections	4983 [R_{int} = 0.1080, R_{sigma} = 0.1015]
Data/restraints/parameters	4983/0/361
Goodness-of-fit on F^2	0.996
Final R indexes [I>=2σ (I)]	R_1 = 0.0567, wR_2 = 0.1136

Final R indexes [all data]	R_1 = 0.1501, wR_2 = 0.1475
Largest diff. peak/hole / e Å^{-3}	0.14/-0.20



Identification code	**4**
Empirical formula	$C_{34}H_{30}N_2O_5$
Formula weight	546.60
Temperature/K	294.39(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.3940(2)
b/Å	14.6109(5)
c/Å	15.1875(2)
α/°	96.358(2)
β/°	90.1140(10)
γ/°	102.034(2)
Volume/Å^3	2888.01(12)
Z	4
ρ_{calc}g/cm^3	1.257
μ/mm^{-1}	0.685
F(000)	1152.0
Crystal size/mm^3	0.16 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.858 to 133.198
Index ranges	-15 ≤ h ≤ 13, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18
Reflections collected	40872
Independent reflections	10168 [R_{int} = 0.0524, R_{sigma} = 0.0391]
Data/restraints/parameters	10168/0/739
Goodness-of-fit on F^2	1.553
Final R indexes [I>=2σ (I)]	R_1 = 0.1100, wR_2 = 0.3414
Final R indexes [all data]	R_1 = 0.1169, wR_2 = 0.3487
Largest diff. peak/hole / e Å^{-3}	0.42/-0.34

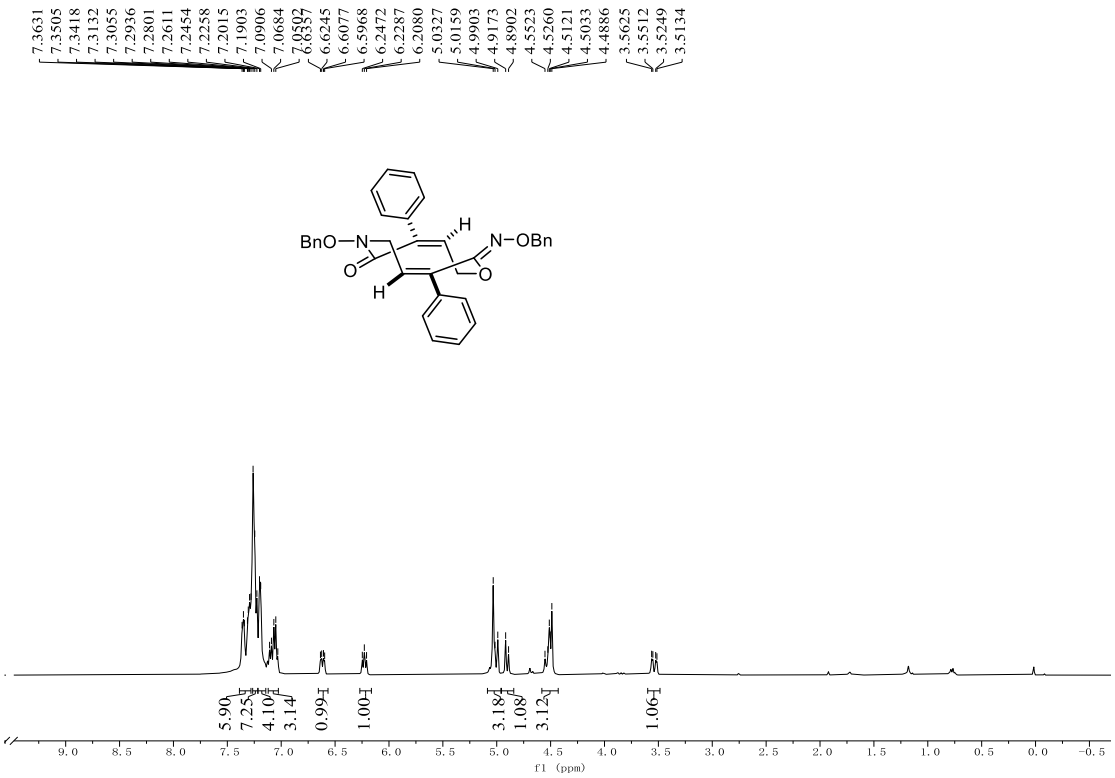
[1] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J, Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst*. **2009**, *42*, 339-341.

[2] Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112-122.

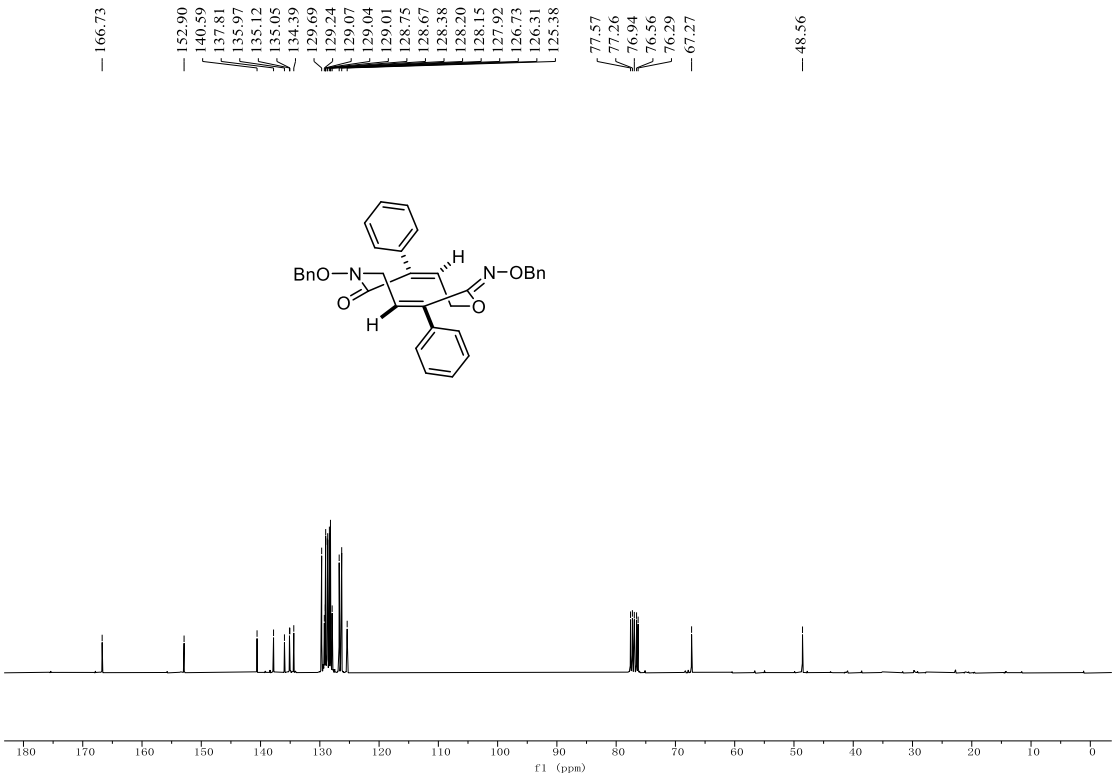
[3] Sheldrick, G. M. *Acta Cryst*. **2015**, C71, 3-8.

7. ^{1}H NMR, ^{13}C NMR for compounds 2, 3, and 4.

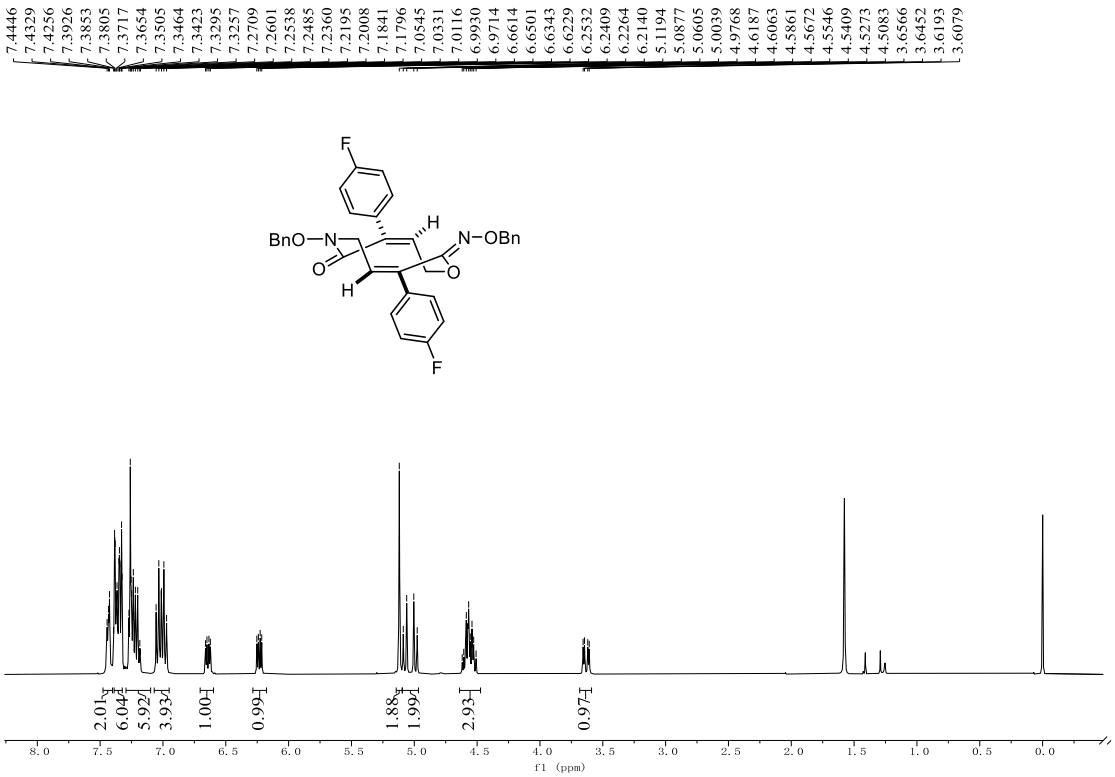
^{1}H NMR (400 MHz, $CDCl_3$) of **2a**



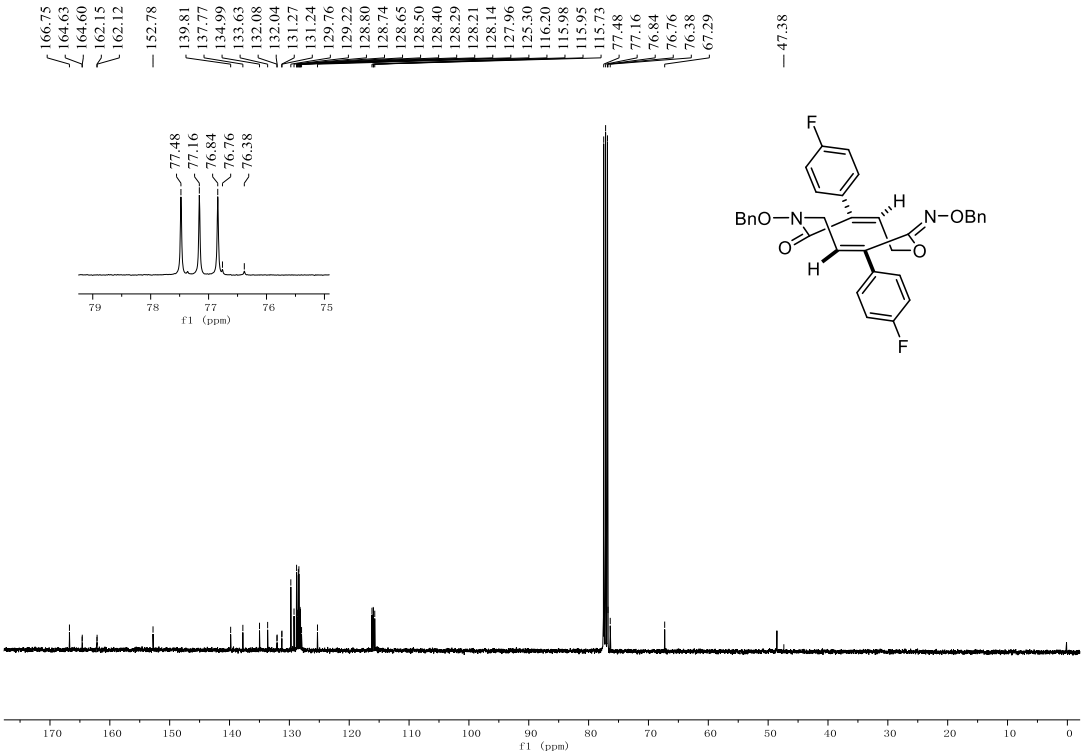
^{13}C NMR (101 MHz, $CDCl_3$) of **2a**



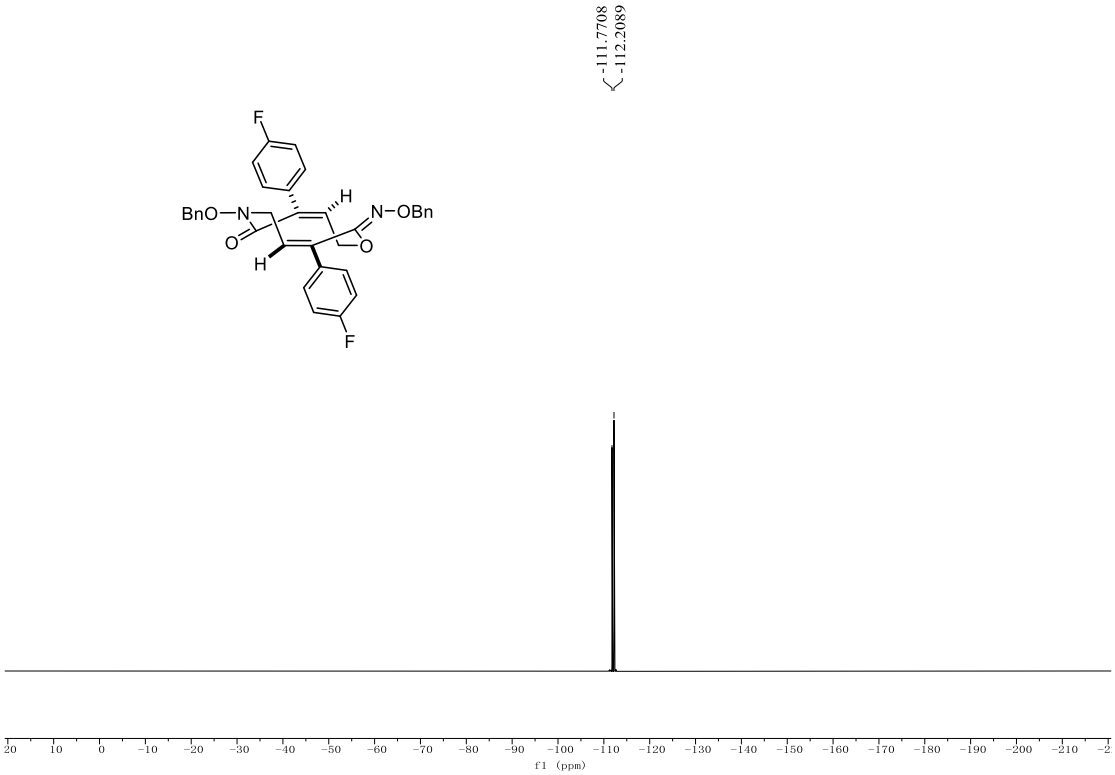
^{1}H NMR (400 MHz, $CDCl_3$) of **2b**



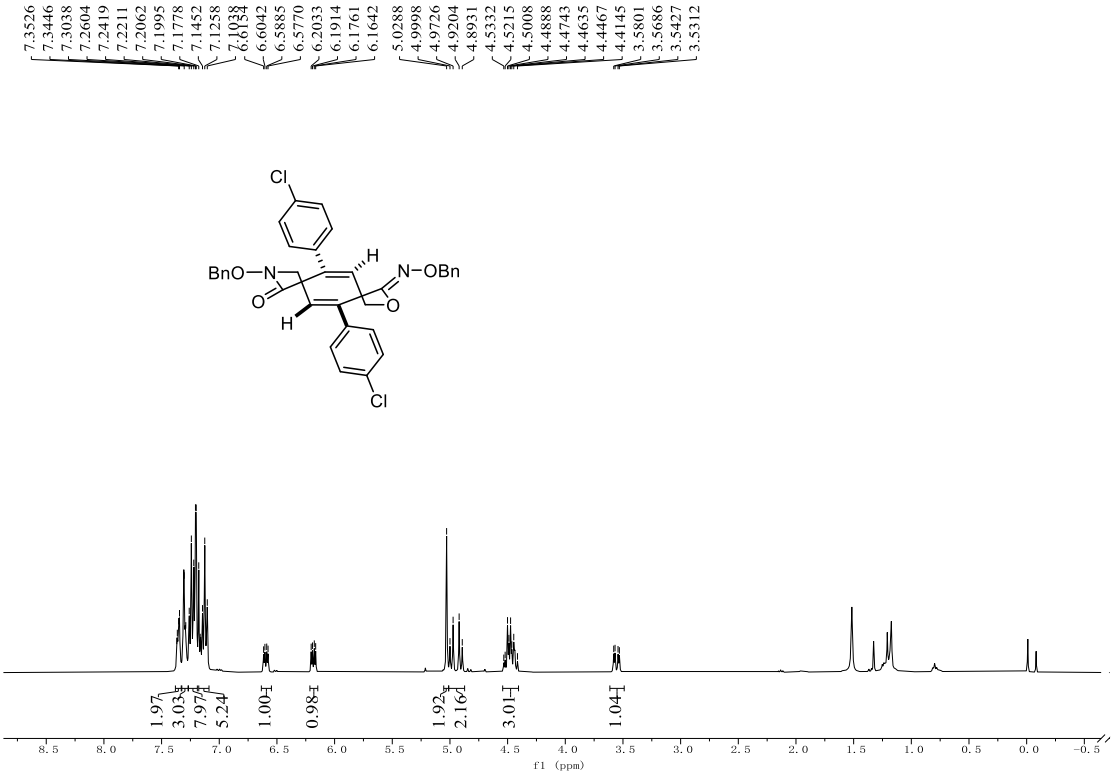
^{13}C NMR (101 MHz, $CDCl_3$) of **2b**



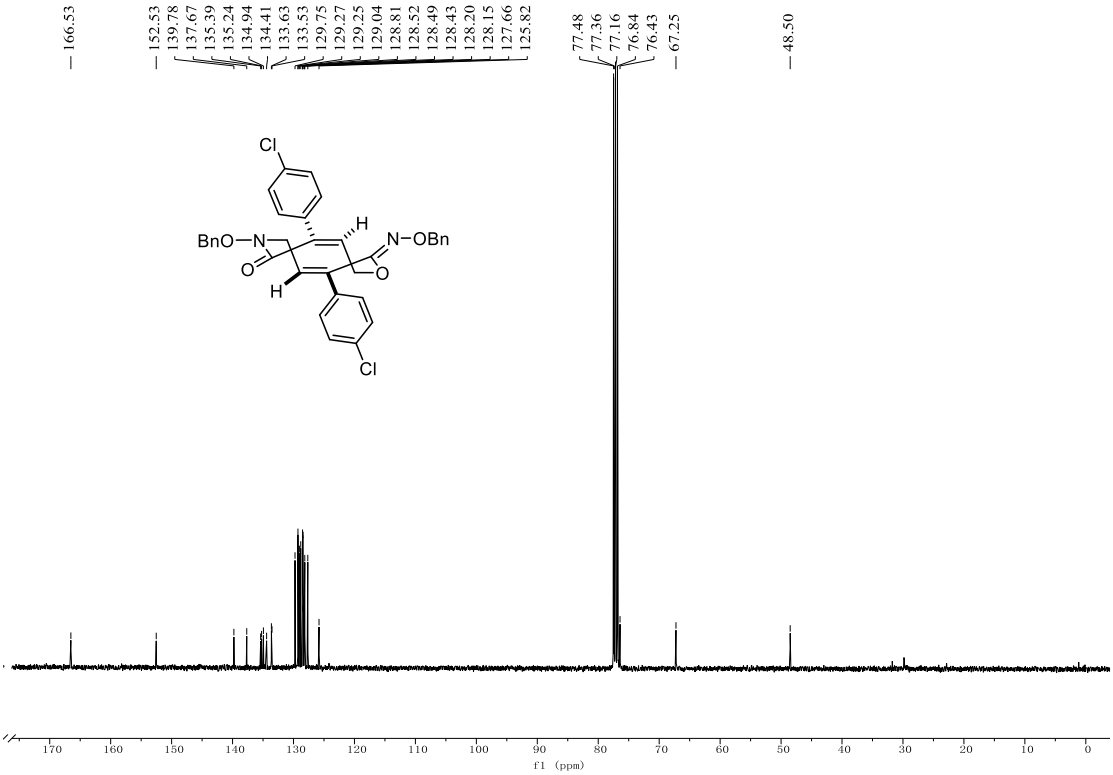
^{19}F NMR (376 MHz, $CDCl_3$) of **2b**



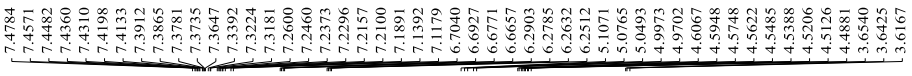
^{1}H NMR (400 MHz, $CDCl_3$) of **2c**

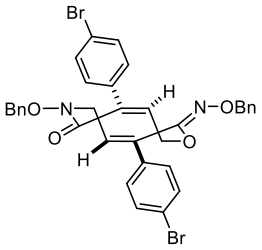


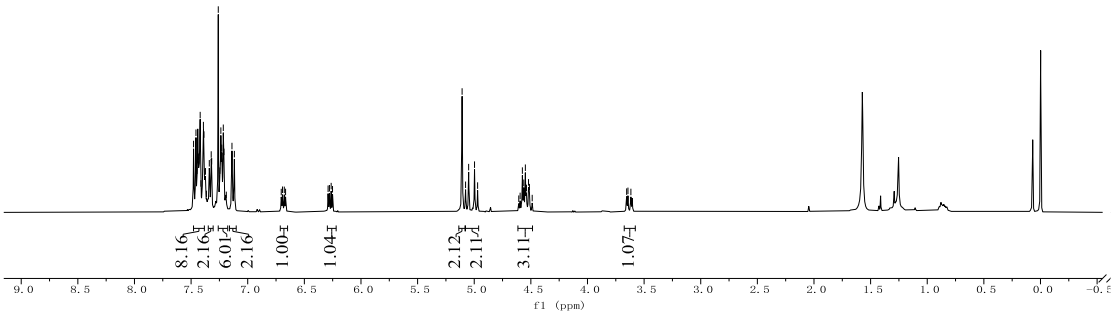
^{13}C NMR (101 MHz, $CDCl_3$) of **2c**



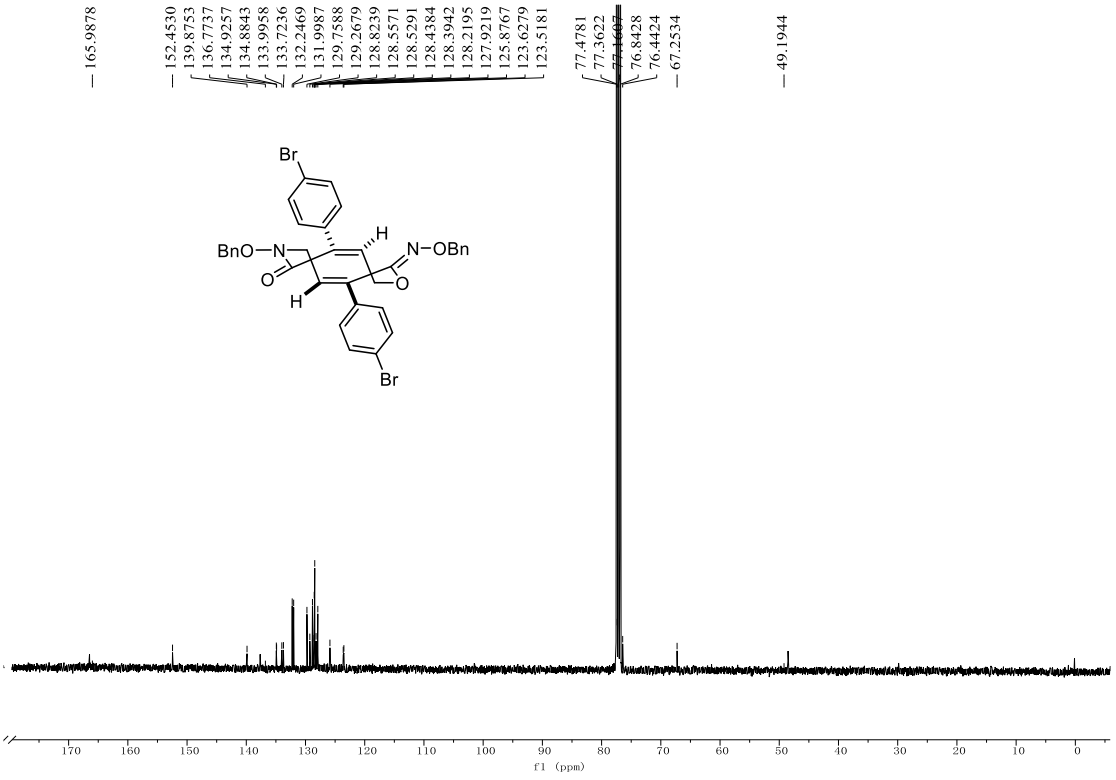
^{1}H NMR (400 MHz, $CDCl_3$) **2d**



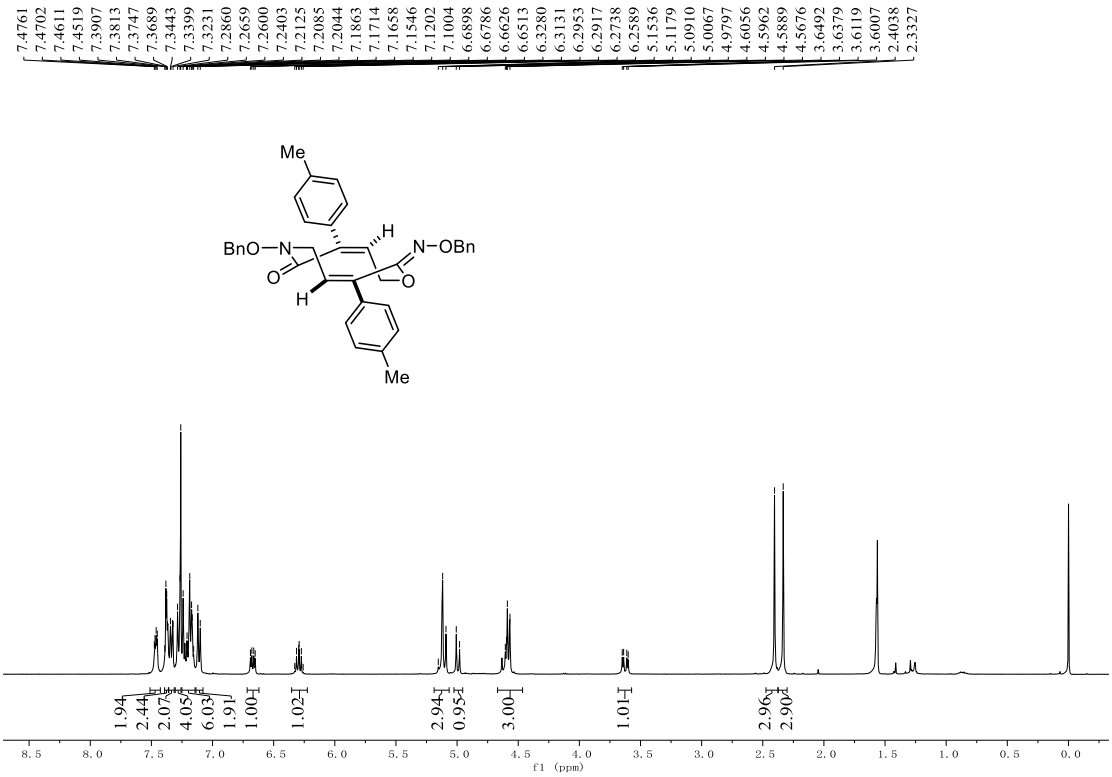




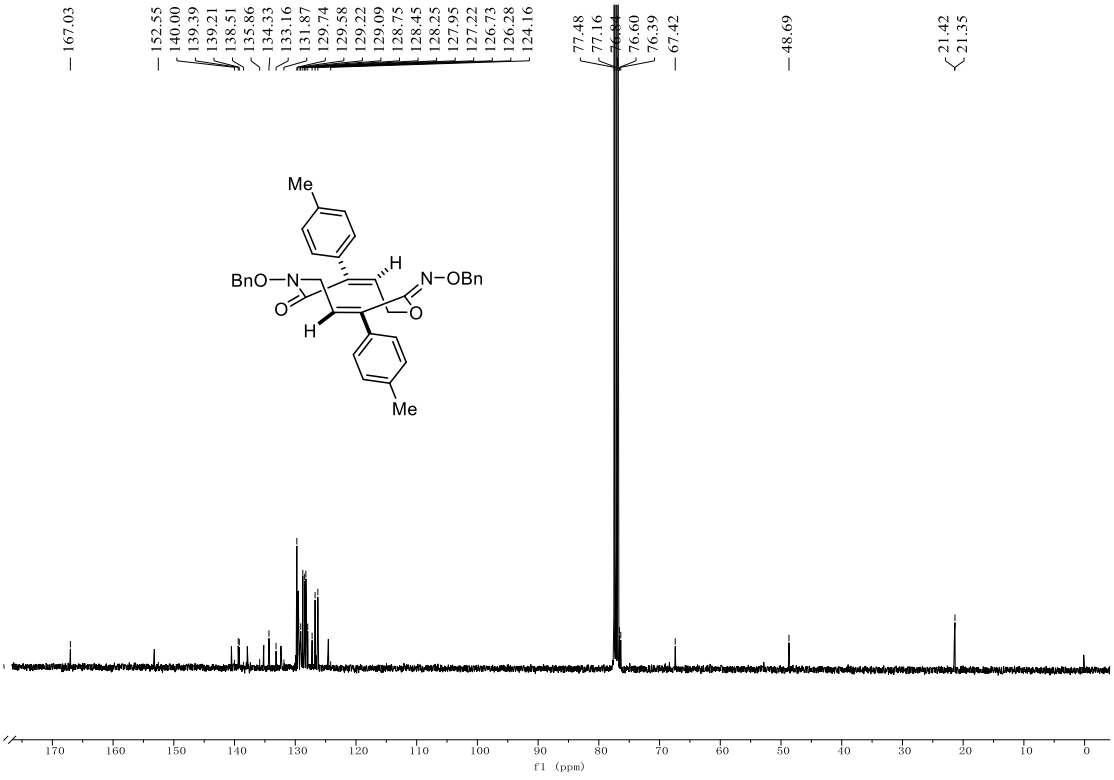
^{13}C NMR (101 MHz, $CDCl_3$) of **2d**



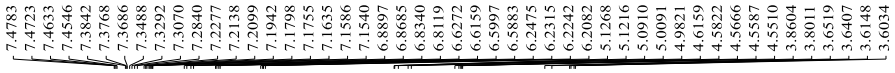
^{1}H NMR (400 MHz, $CDCl_3$) of **2e**

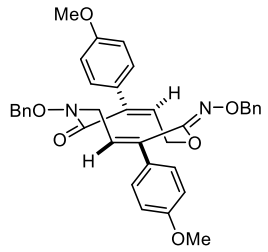


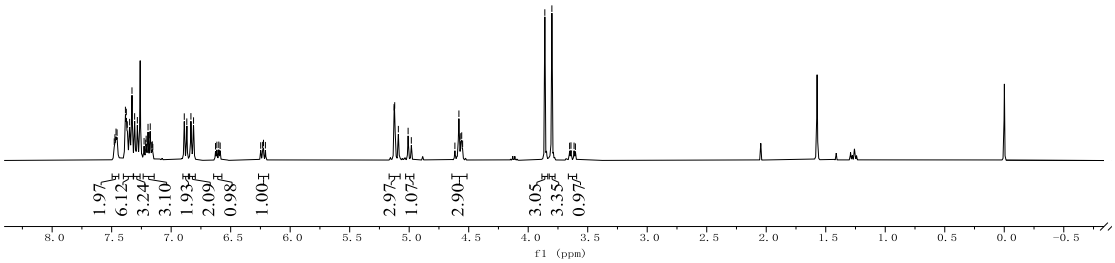
^{13}C NMR (101 MHz, $CDCl_3$) of **2e**



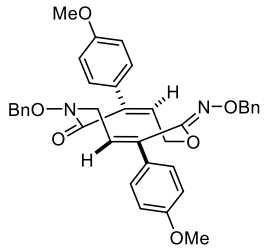
^{1}H NMR (400 MHz, $CDCl_3$) of **2f**



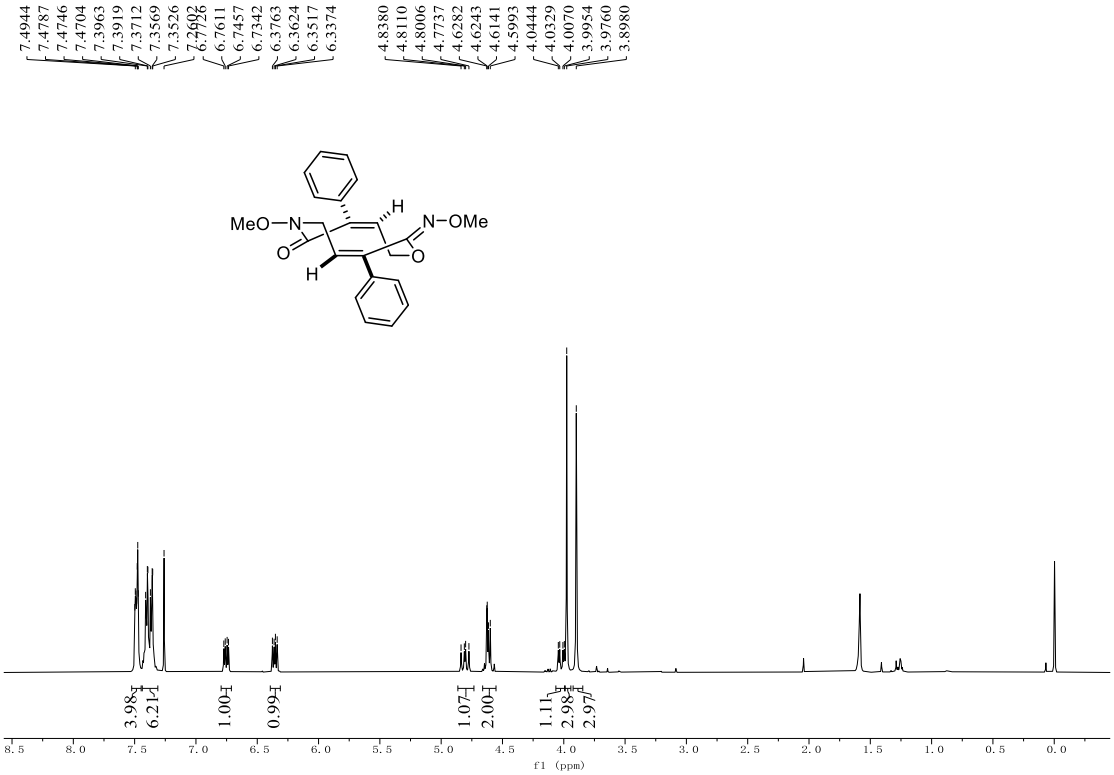




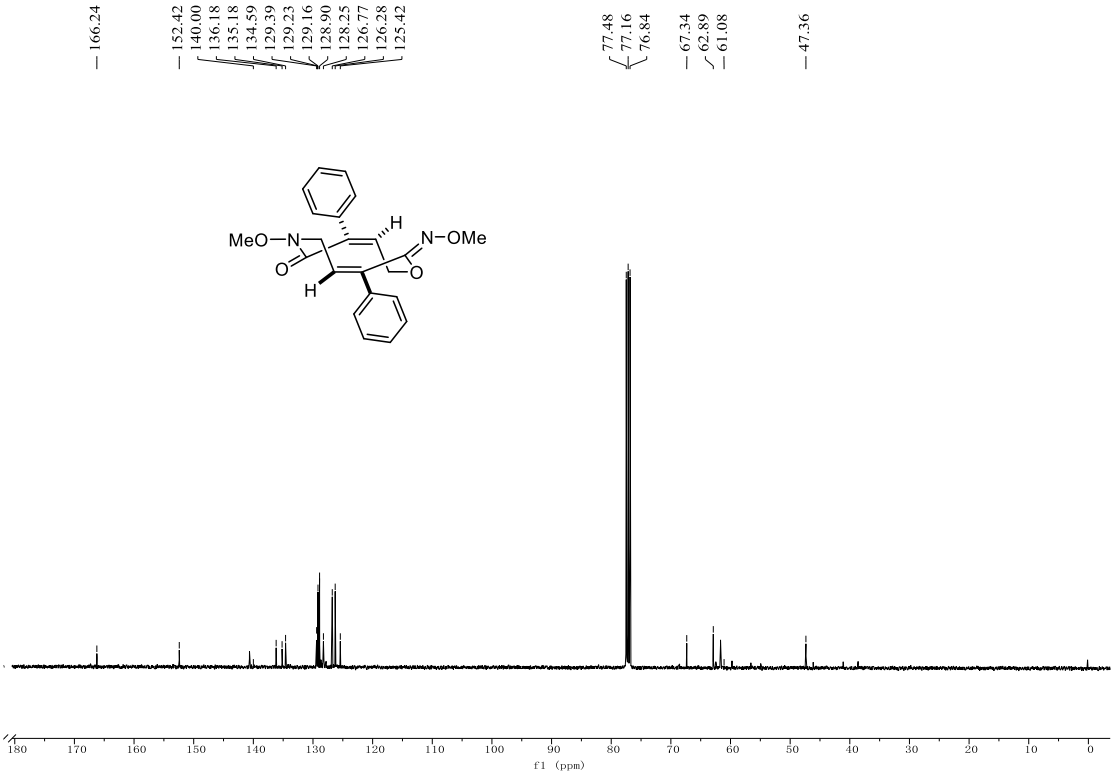
^{13}C NMR (101 MHz, $CDCl_3$) of **2f**



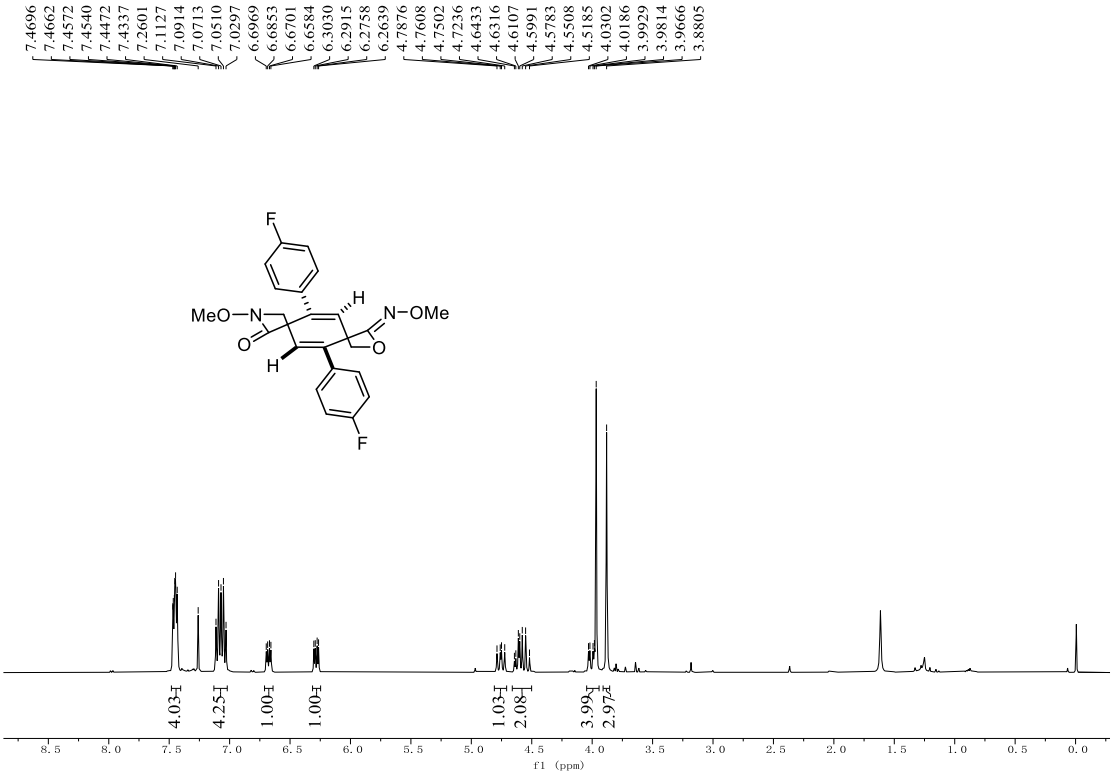
^{1}H NMR (400 MHz, $CDCl_3$) of **2g**



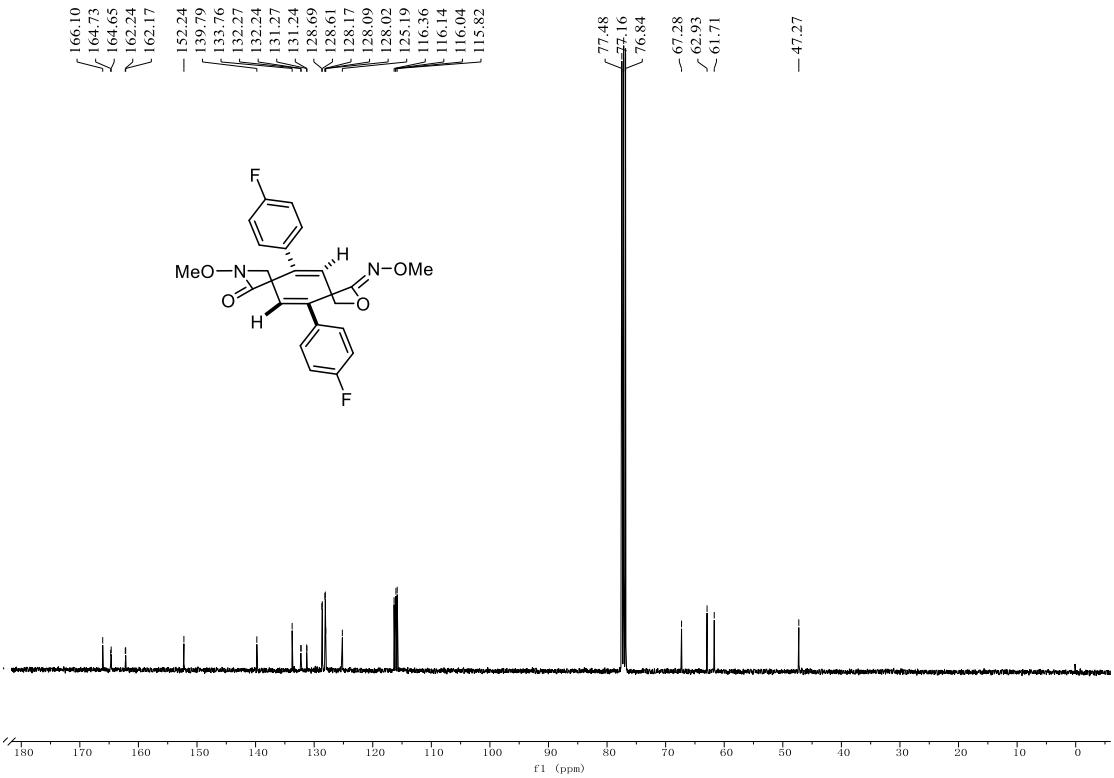
^{13}C NMR (101 MHz, $CDCl_3$) of **2g**



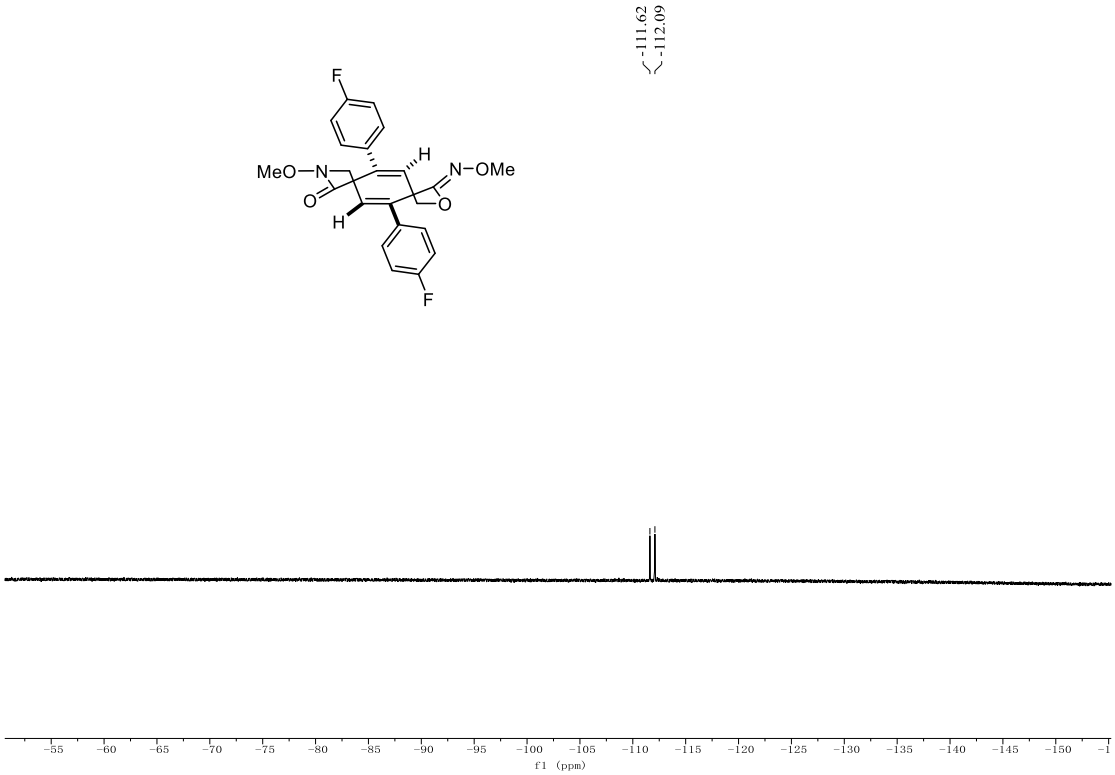
^{1}H NMR (400 MHz, $CDCl_3$) of **2h**



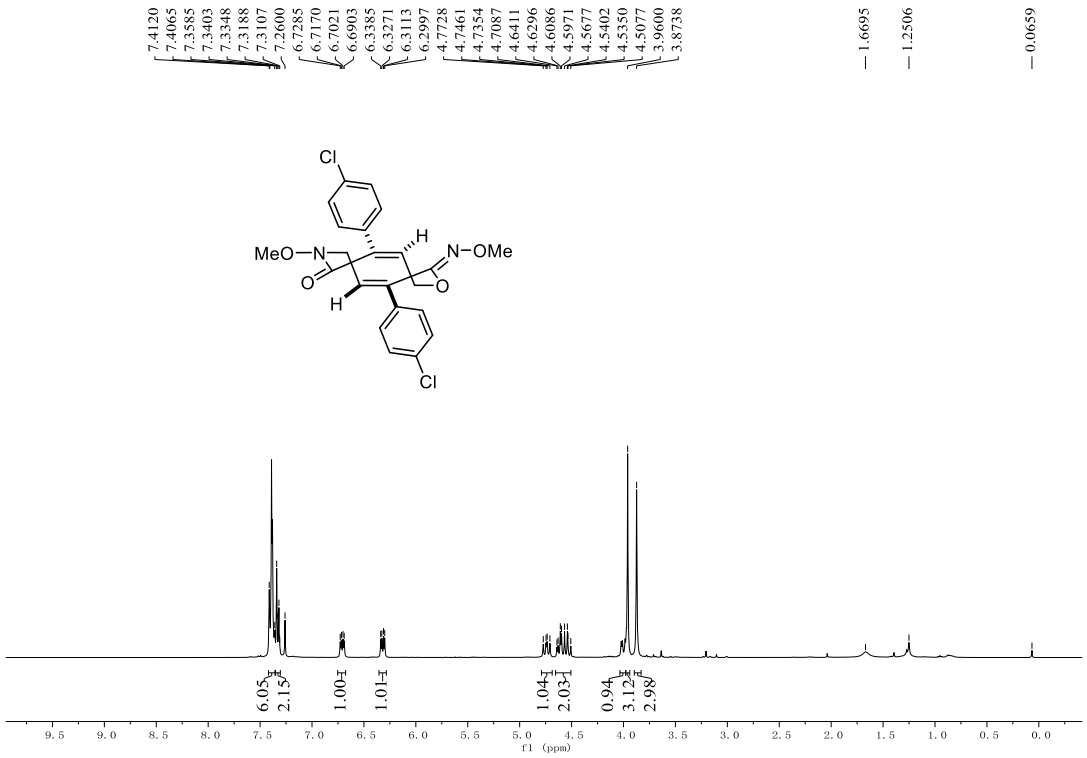
^{13}C NMR (101 MHz, $CDCl_3$) of **2h**



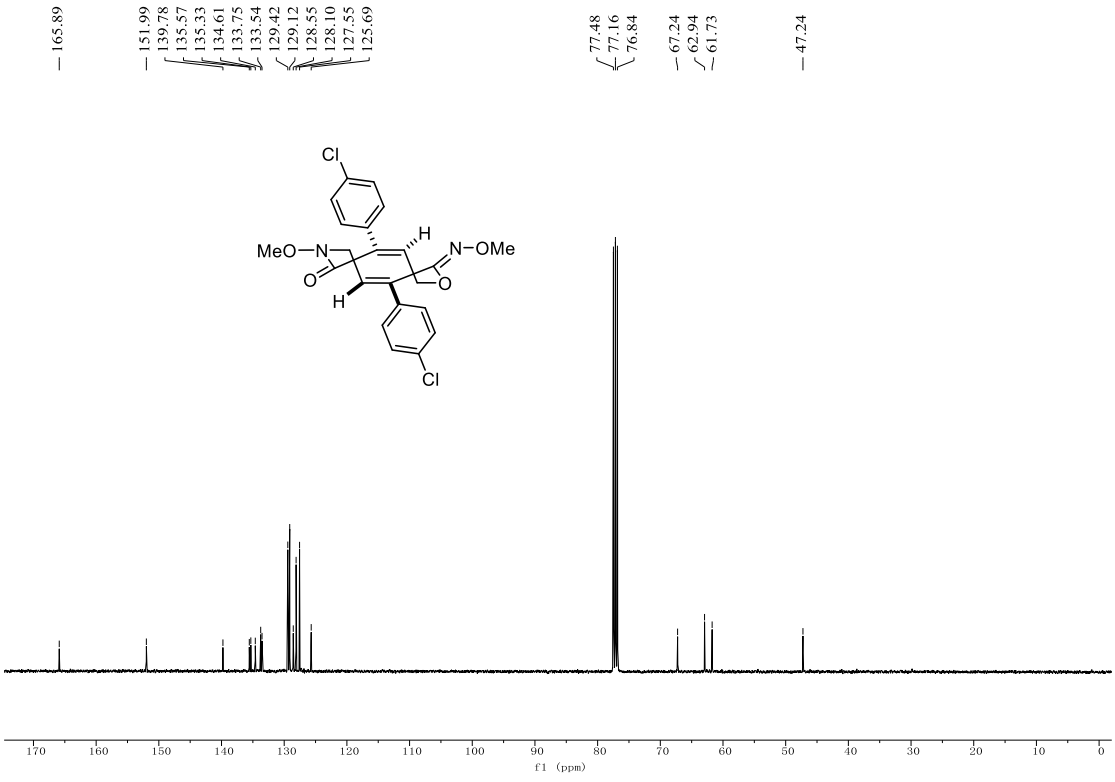
^{19}F NMR (376 MHz, $CDCl_3$) of **2h**



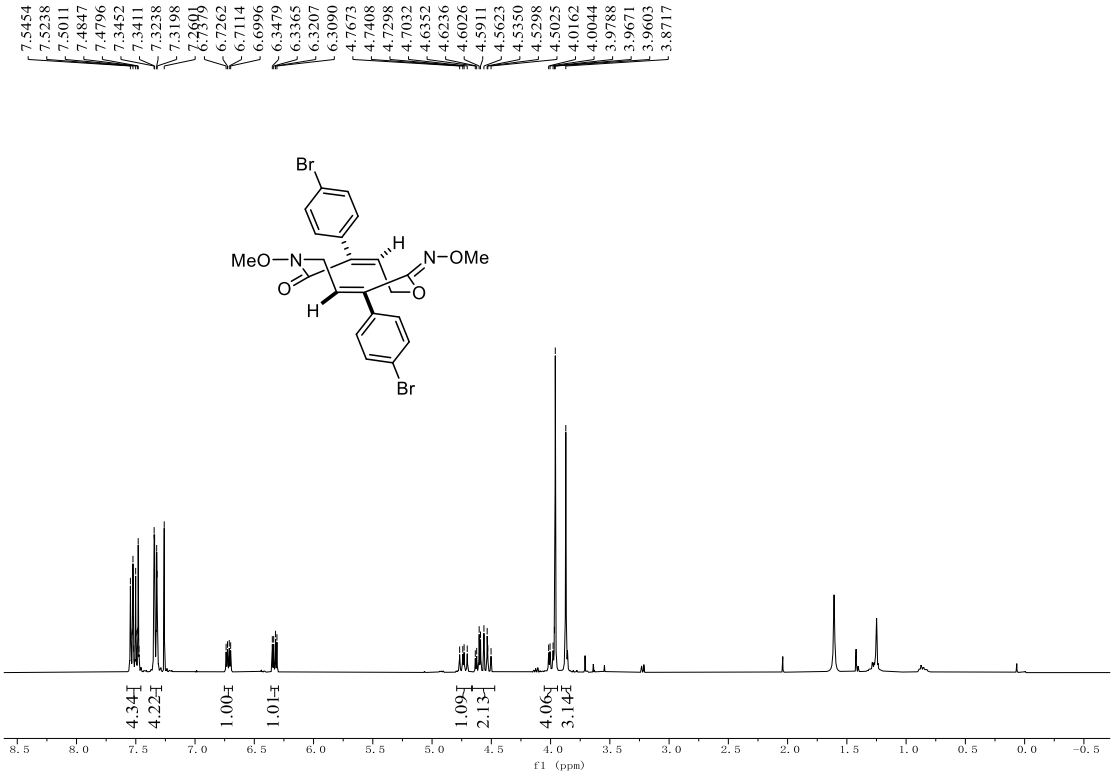
^{1}H NMR (400 MHz, $CDCl_3$) of **2i**



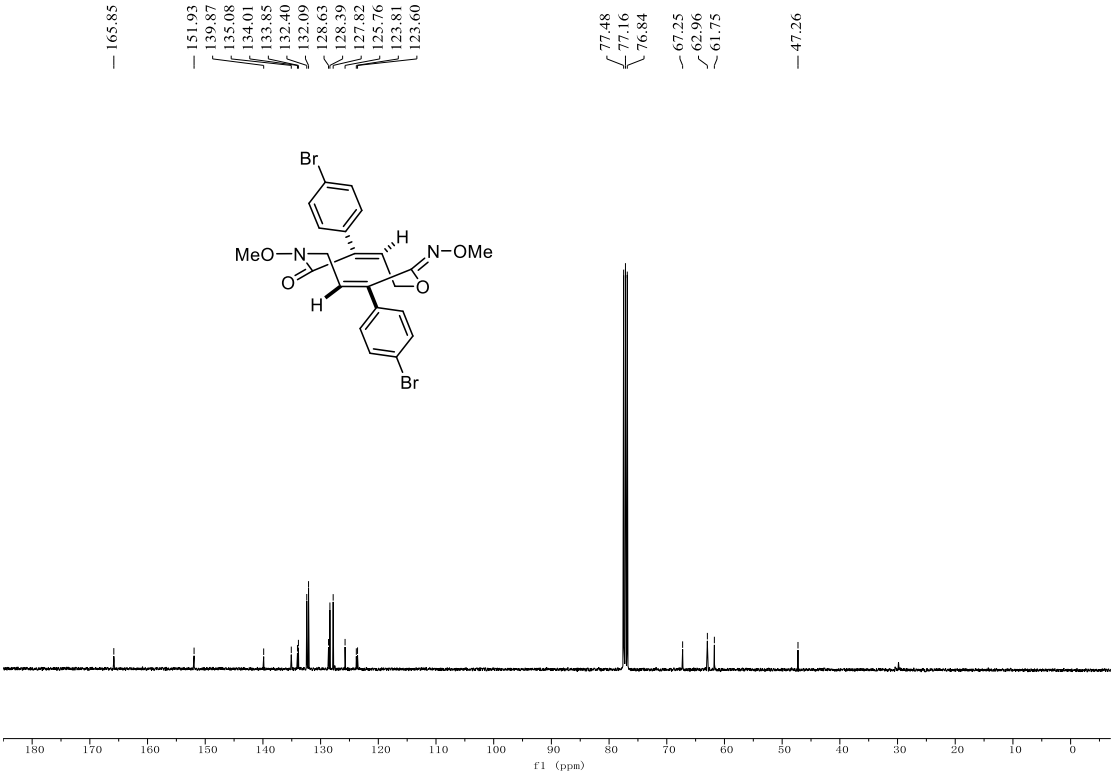
^{13}C NMR (101 MHz, $CDCl_3$) of **2i**



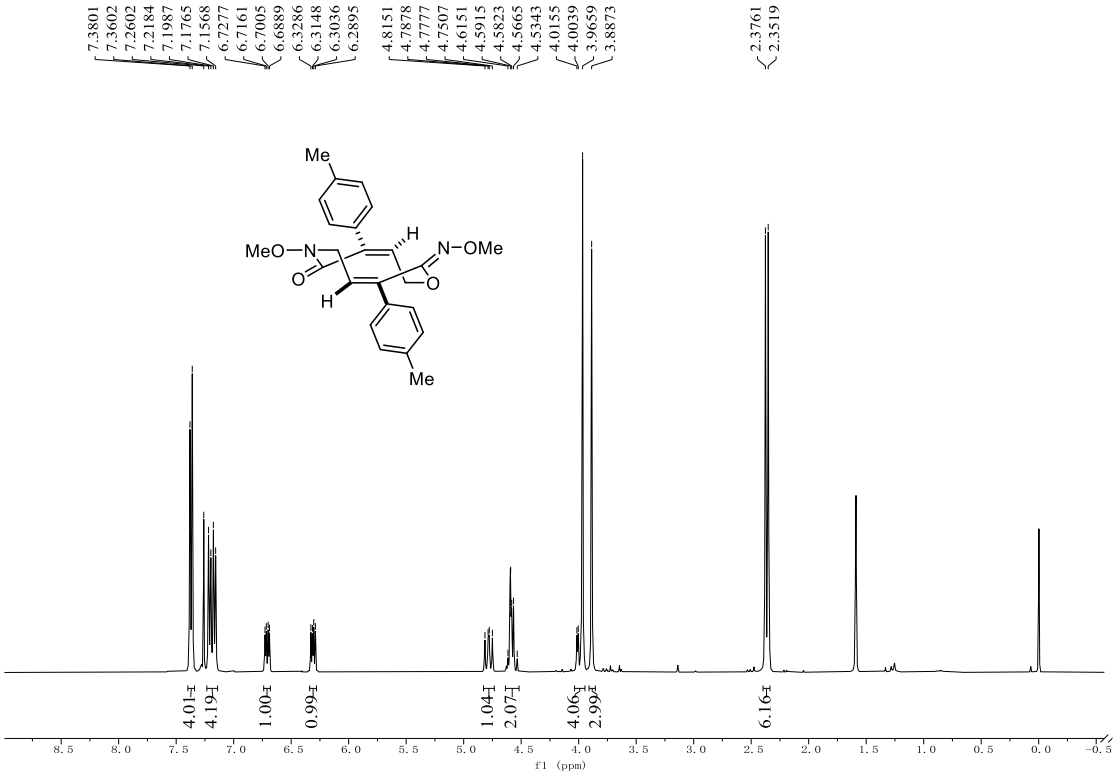
^{1}H NMR (400 MHz, $CDCl_3$) of **2j**



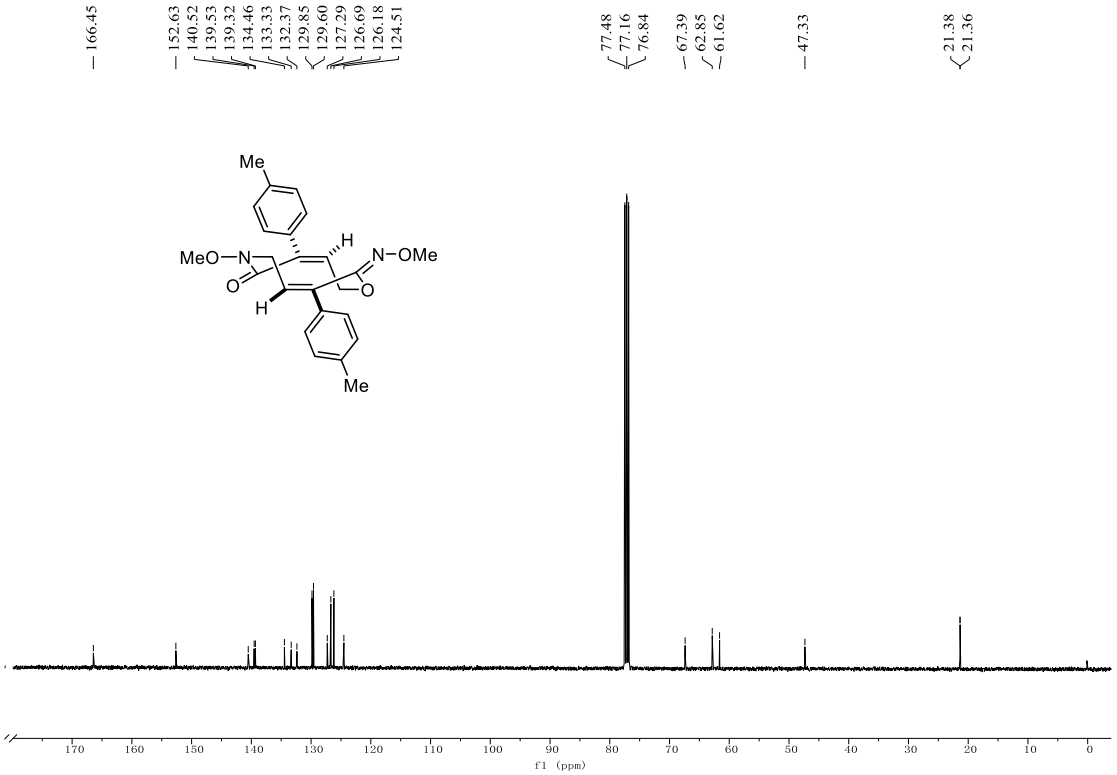
^{13}C NMR (101 MHz, $CDCl_3$) of **2j**



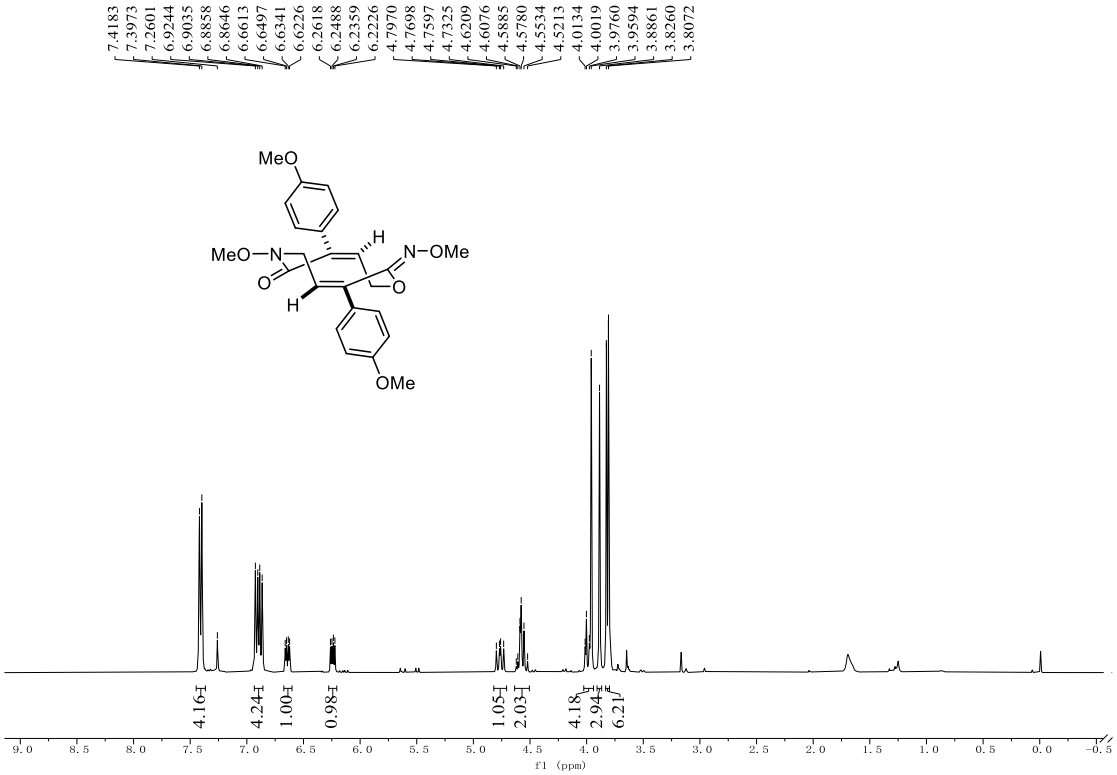
^{1}H NMR (400 MHz, $CDCl_3$) of **2k**



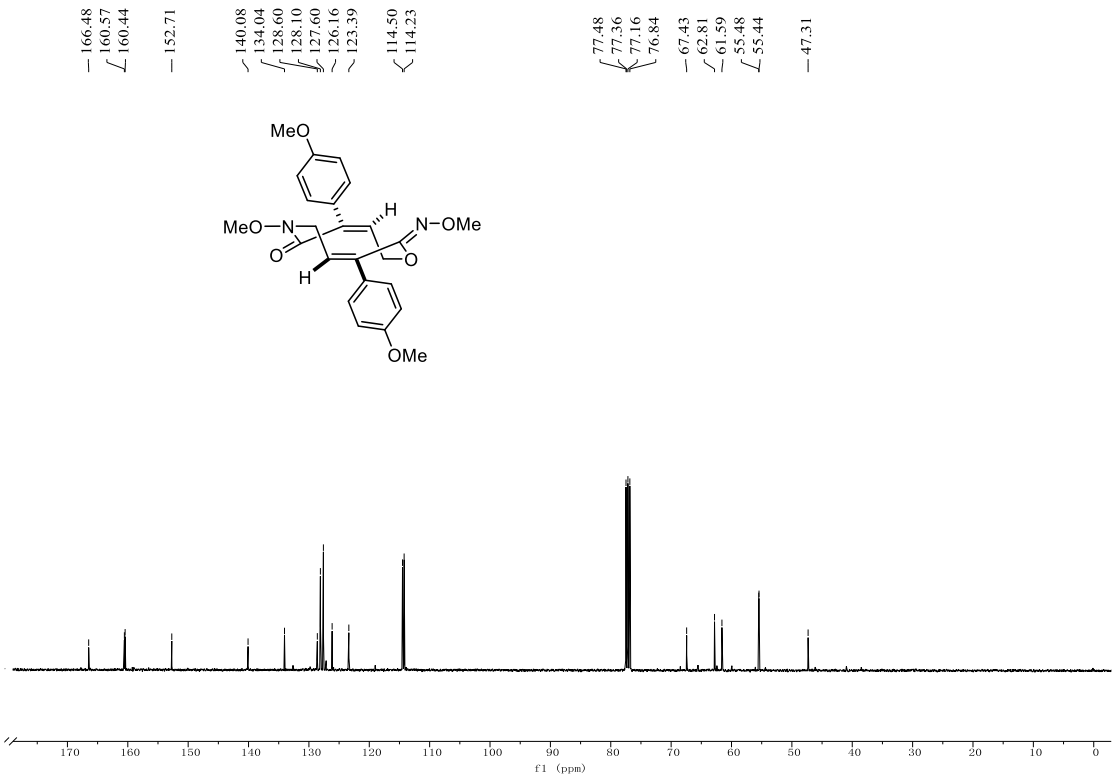
^{13}C NMR (101 MHz, $CDCl_3$) of **2k**



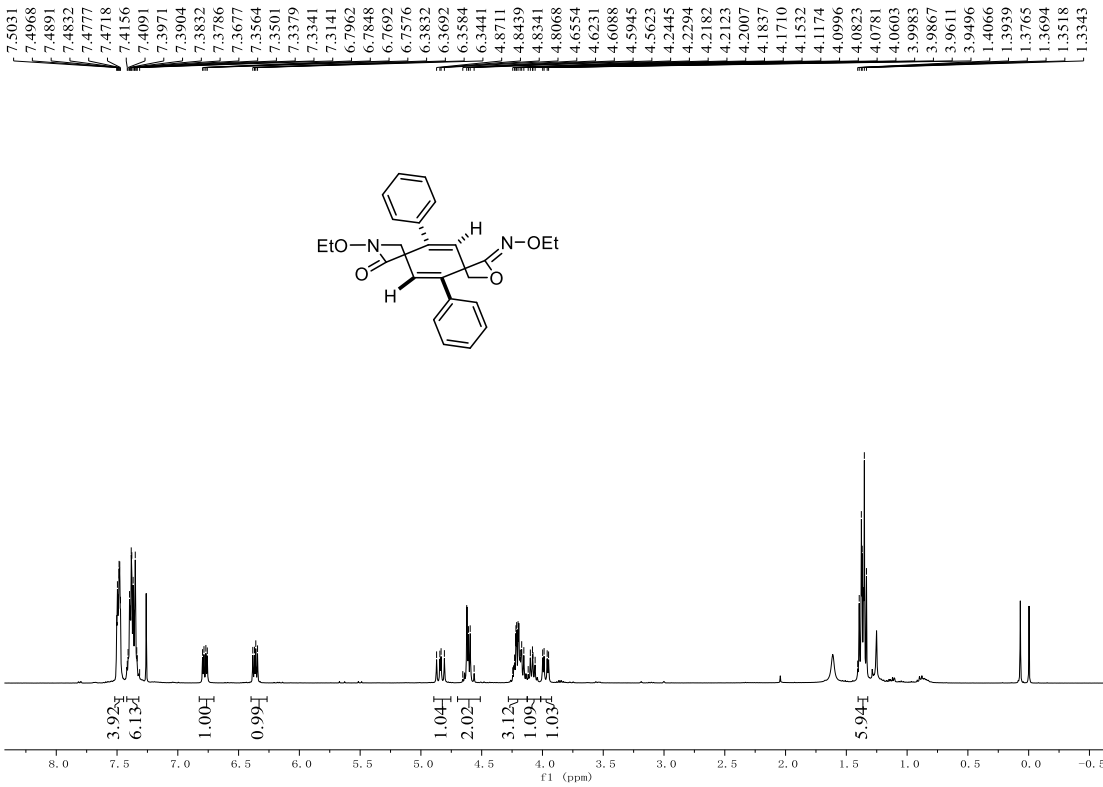
^{1}H NMR (400 MHz, $CDCl_3$) of **2l**



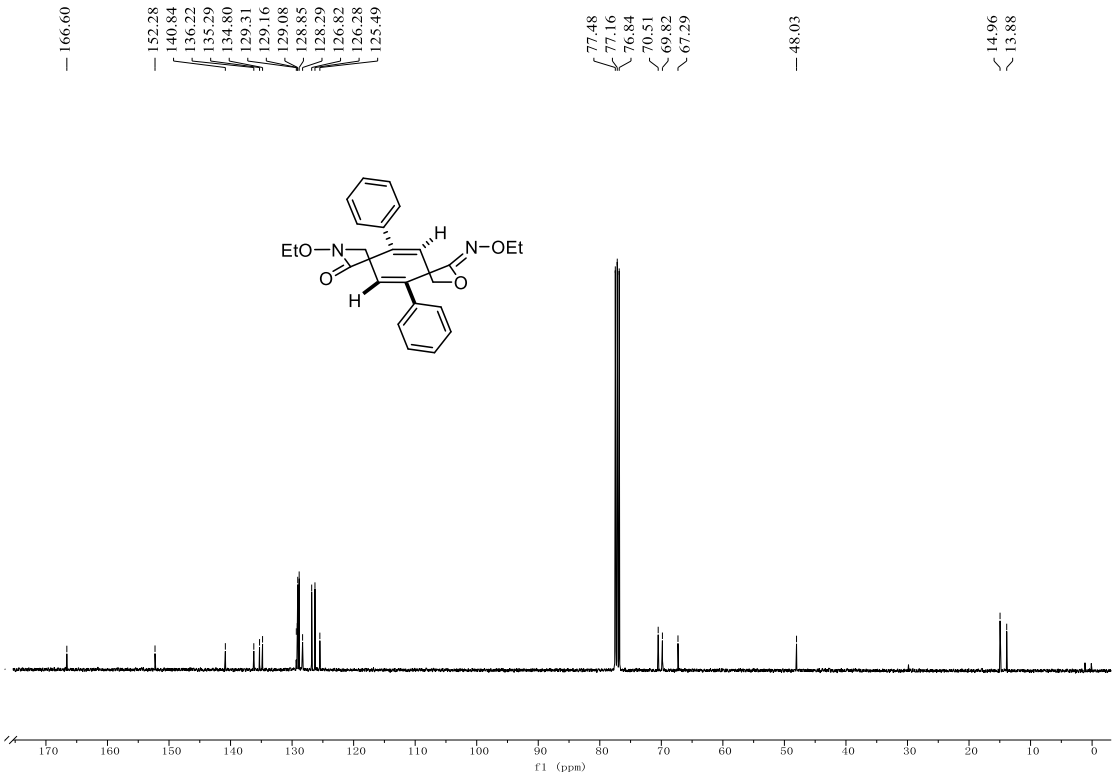
^{13}C NMR (101 MHz, $CDCl_3$) of **2l**



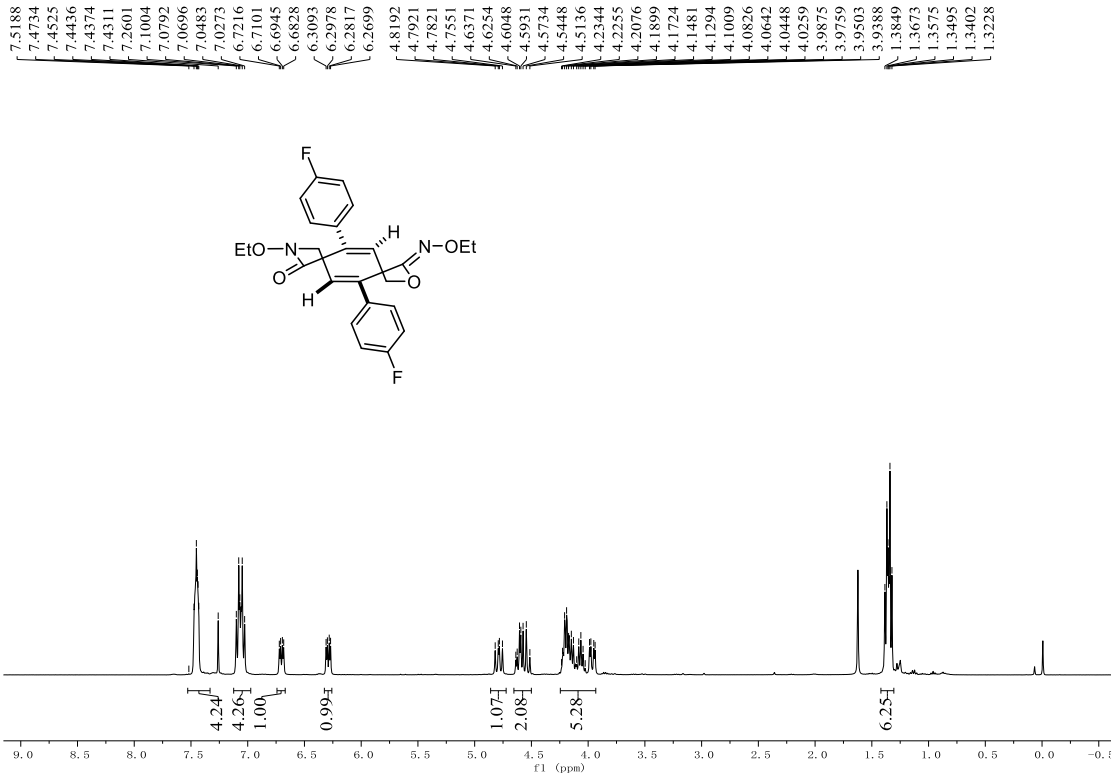
^{1}H NMR (400 MHz, $CDCl_3$) of **2m**



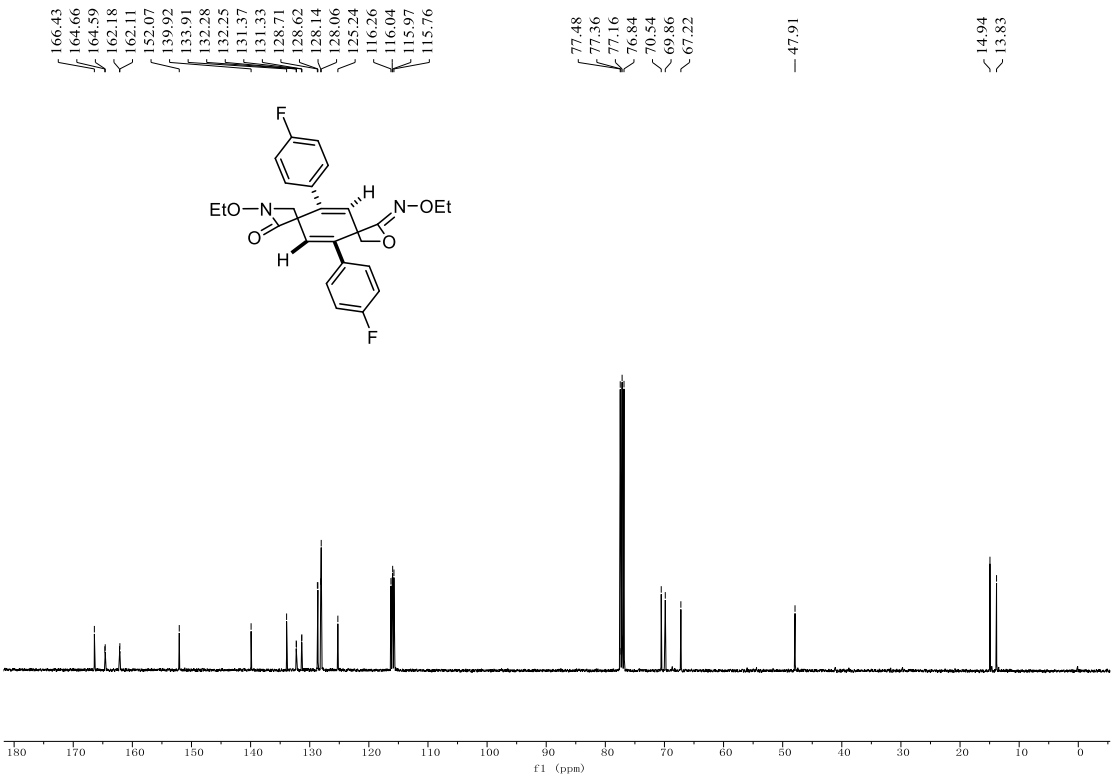
^{13}C NMR (101 MHz, $CDCl_3$) of **2m**



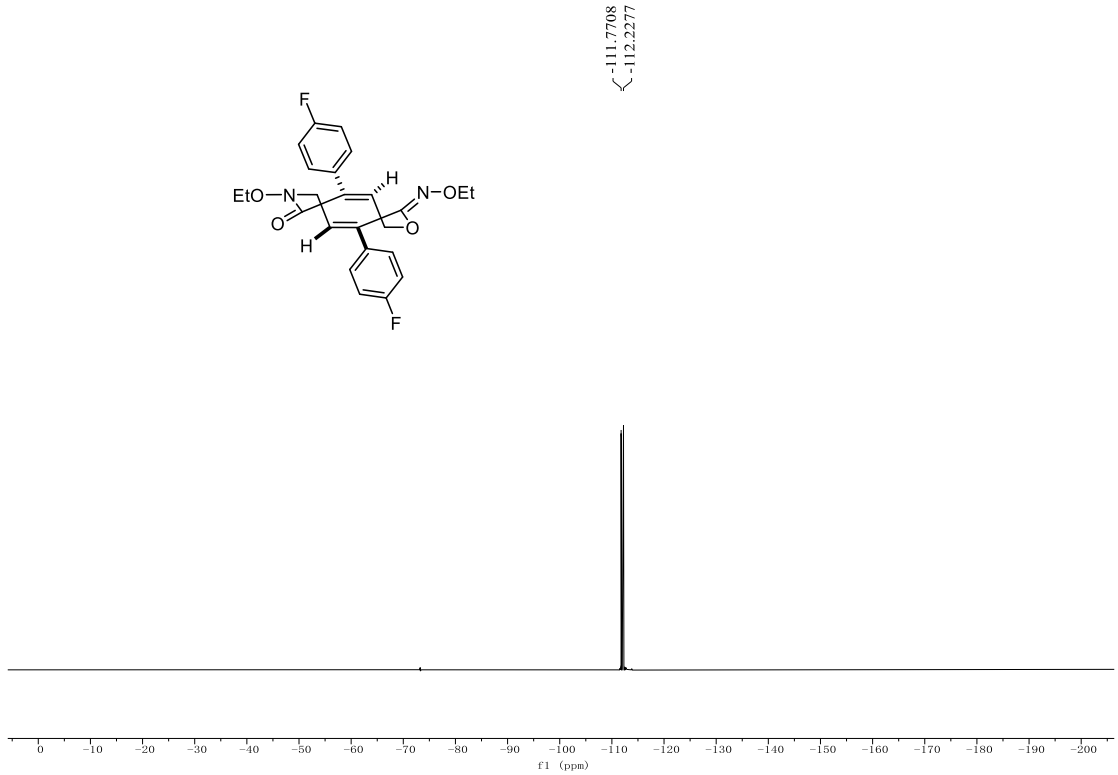
^{1}H NMR (400 MHz, $CDCl_3$) of **2n**



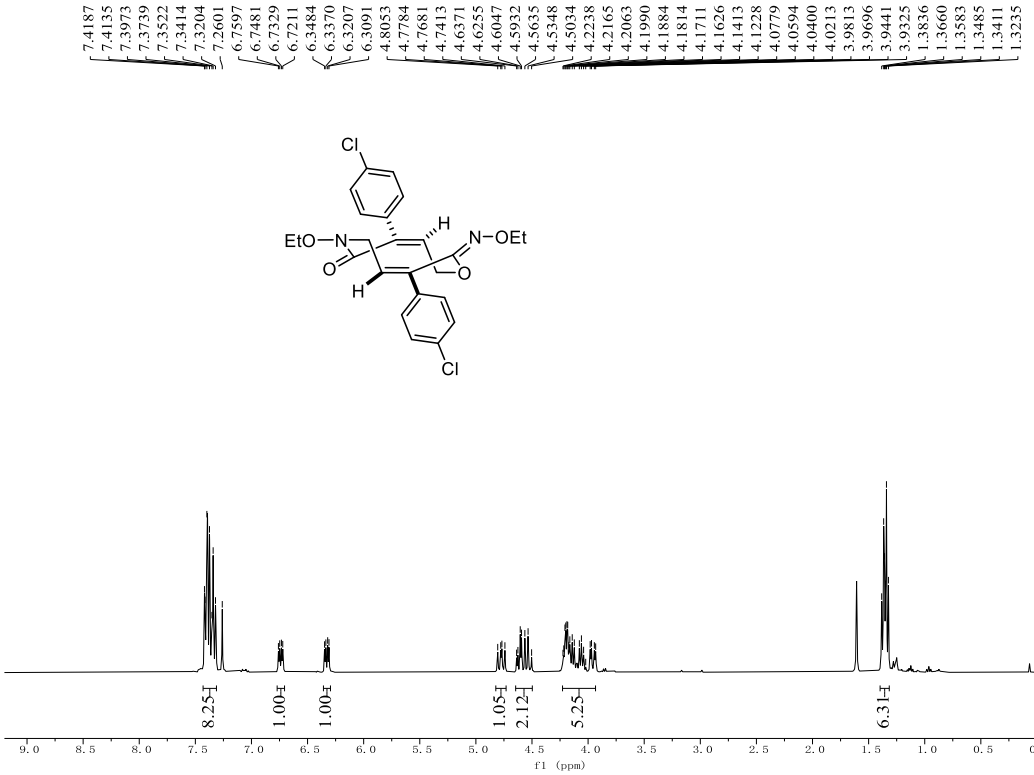
^{13}C NMR (101 MHz, $CDCl_3$) of **2n**



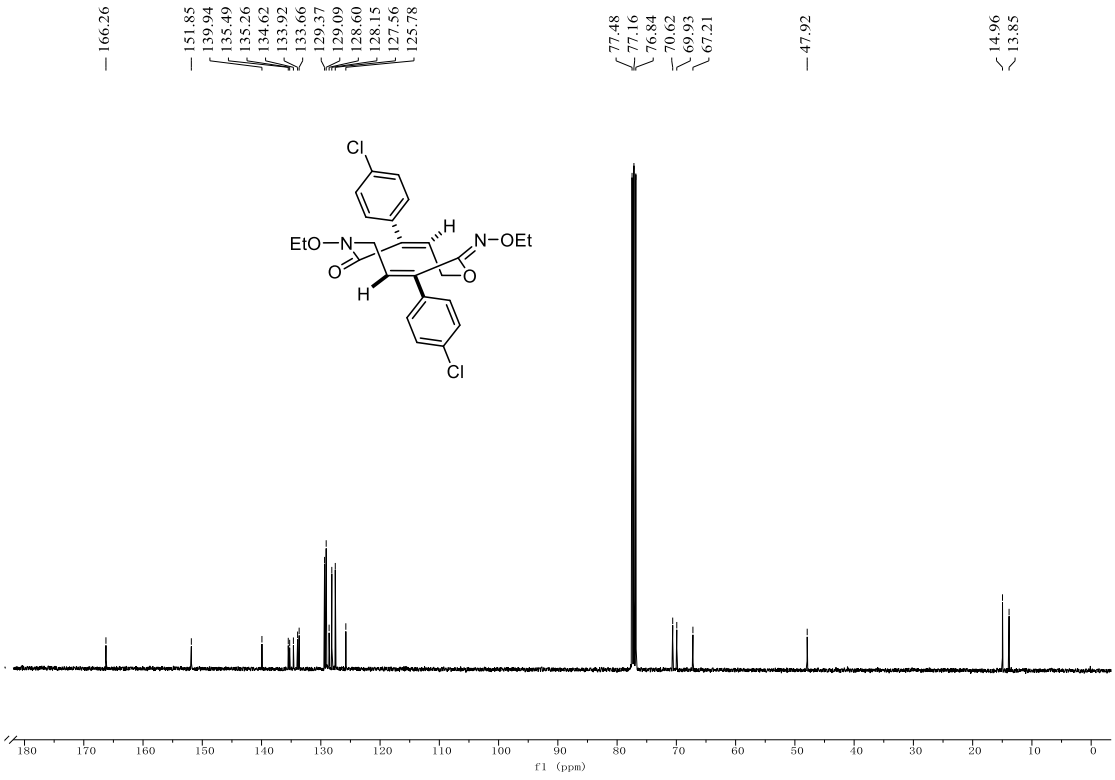
^{19}F NMR (376 MHz, $CDCl_3$) of **2n**



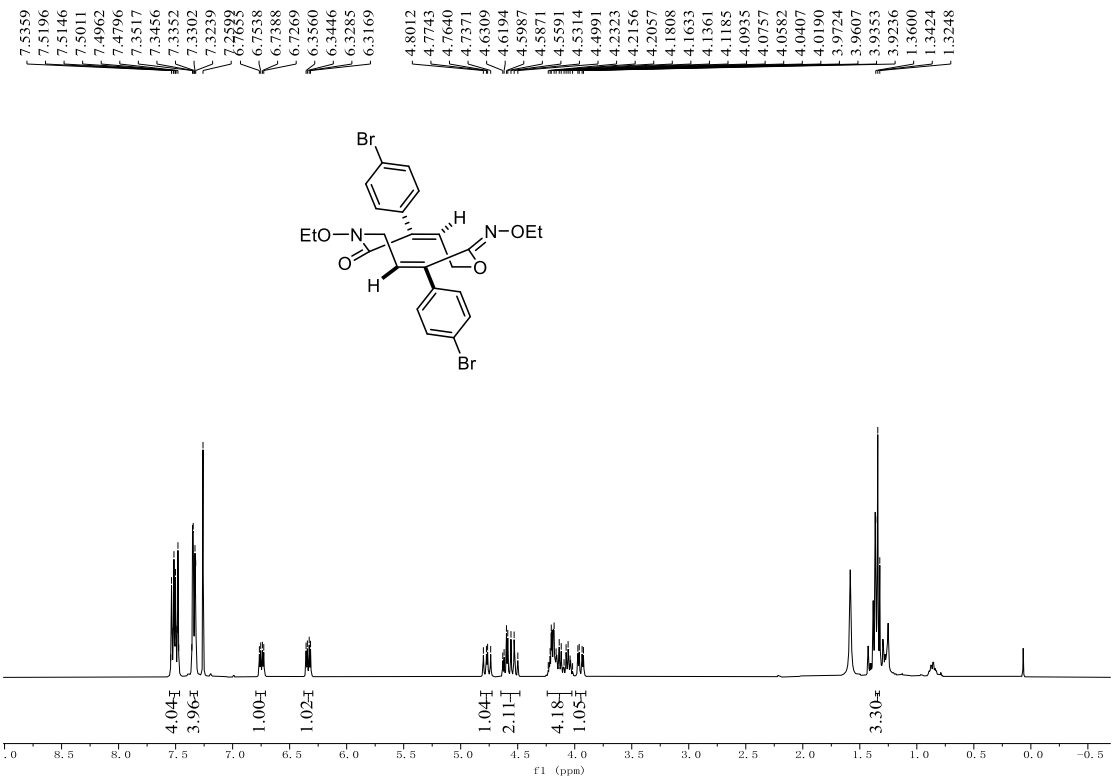
^{1}H NMR (400 MHz, $CDCl_3$) of **2o**



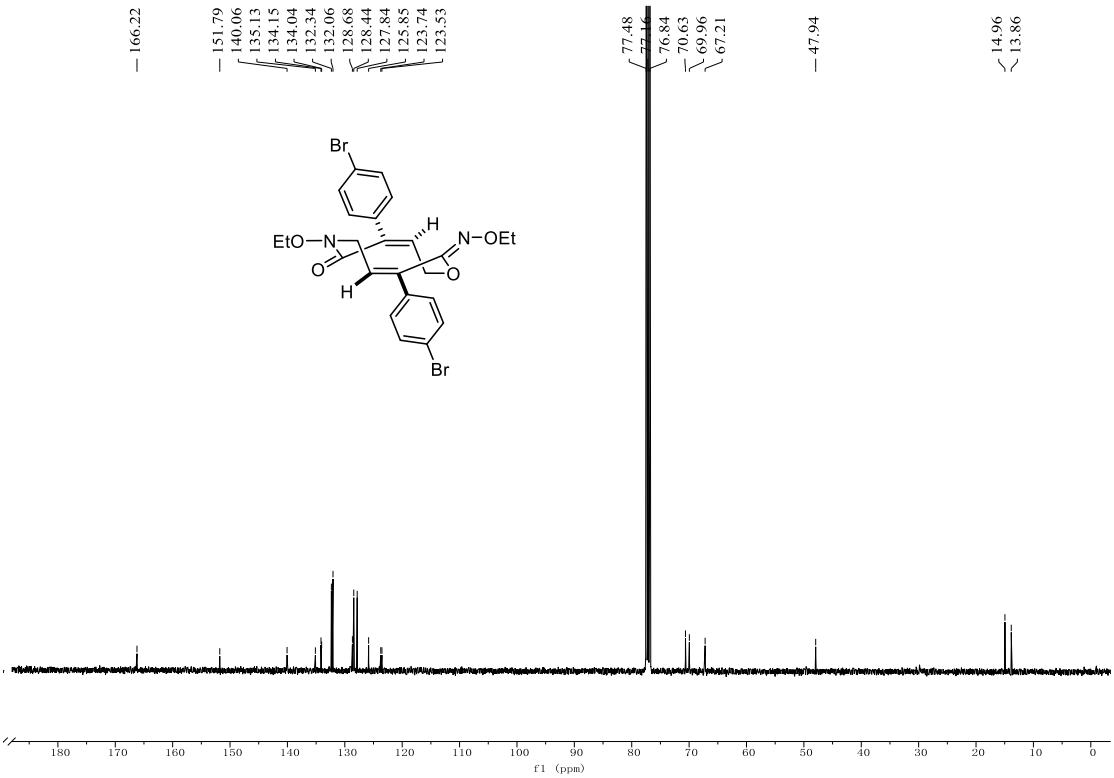
^{13}C NMR (101 MHz, $CDCl_3$) of **2o**



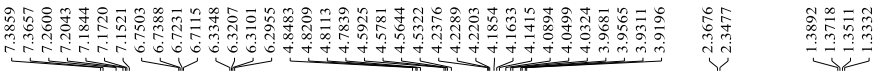
^{1}H NMR (400 MHz, $CDCl_3$) of **2p**

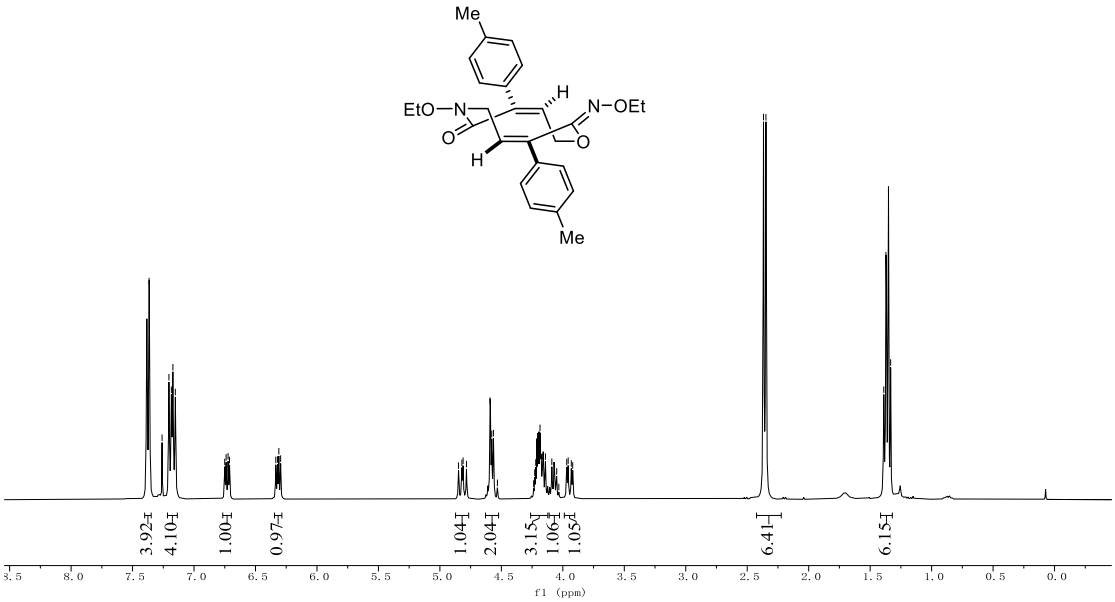


^{13}C NMR (101 MHz, $CDCl_3$) of **2p**

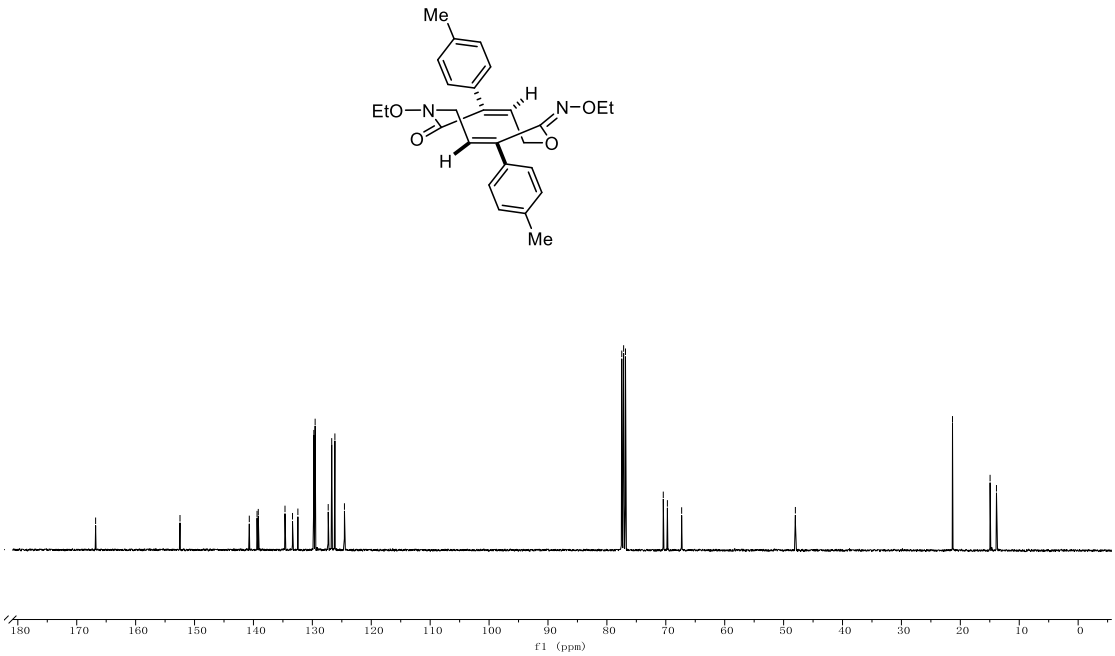


^{1}H NMR (400 MHz, $CDCl_3$) of **2q**

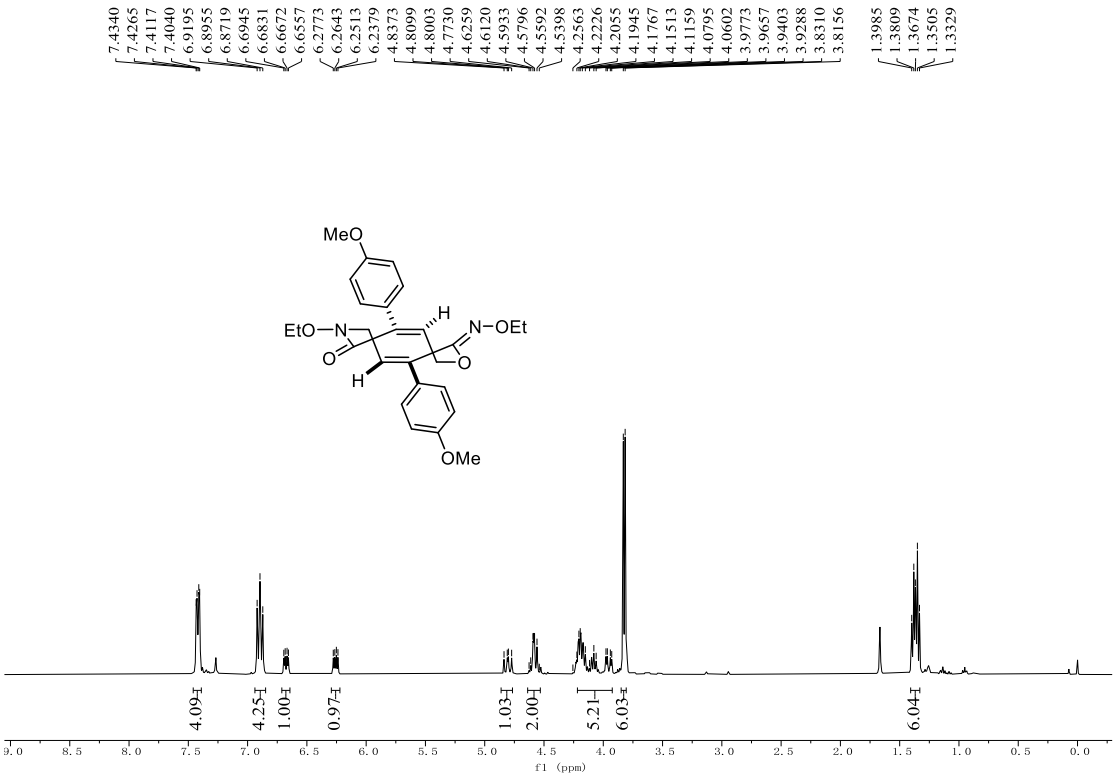




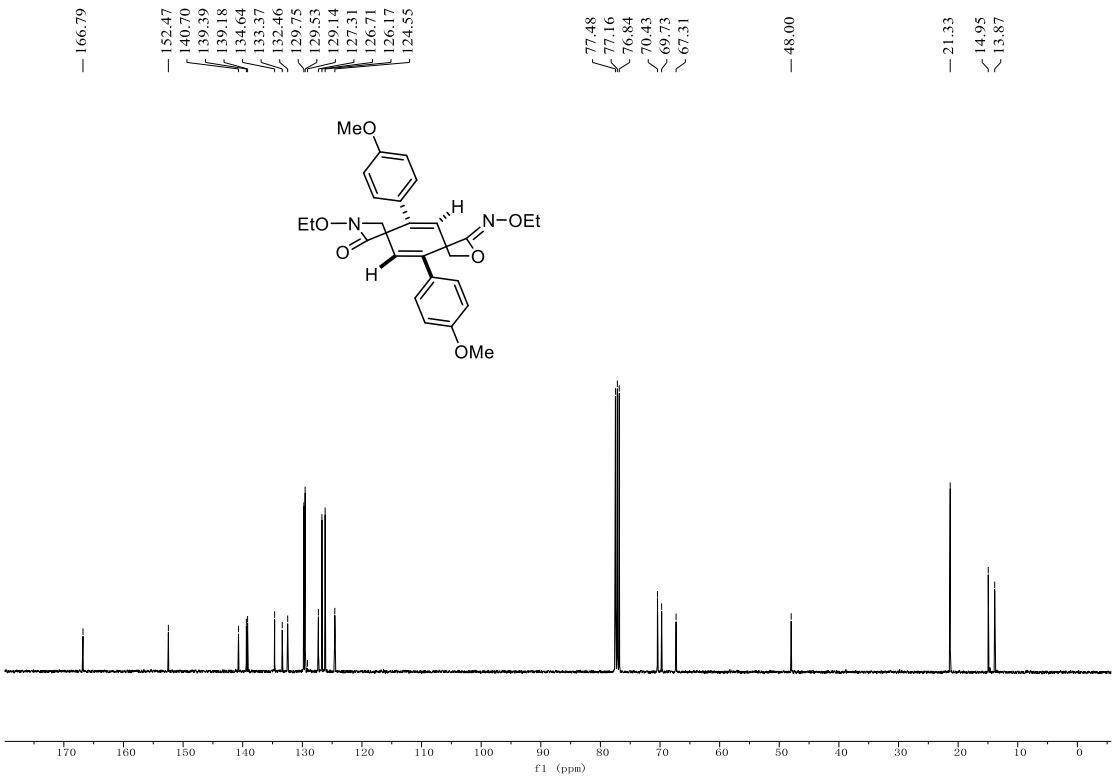
^{13}C NMR (101 MHz, $CDCl_3$) of **2q**



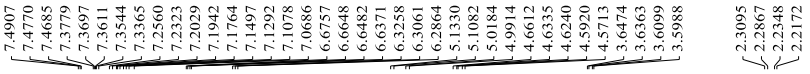
^{1}H NMR (400 MHz, $CDCl_3$) of **2r**

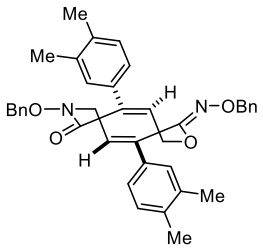


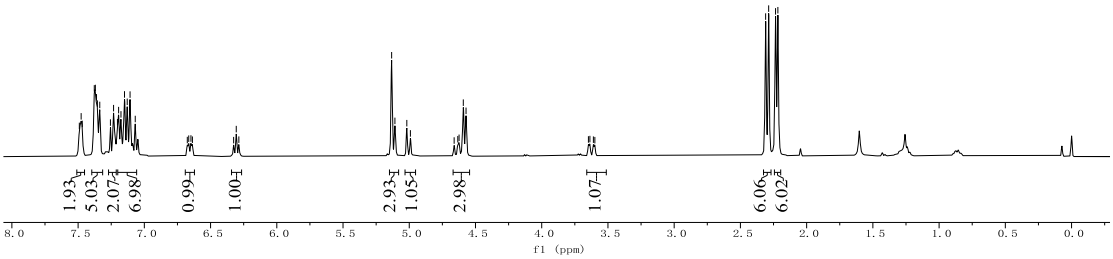
^{13}C NMR (101 MHz, $CDCl_3$) of **2r**



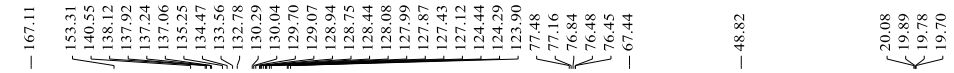
^{1}H NMR (400 MHz, $CDCl_3$) of **2s**

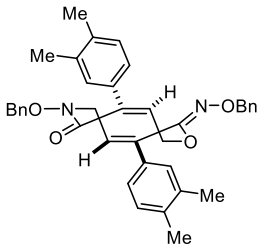


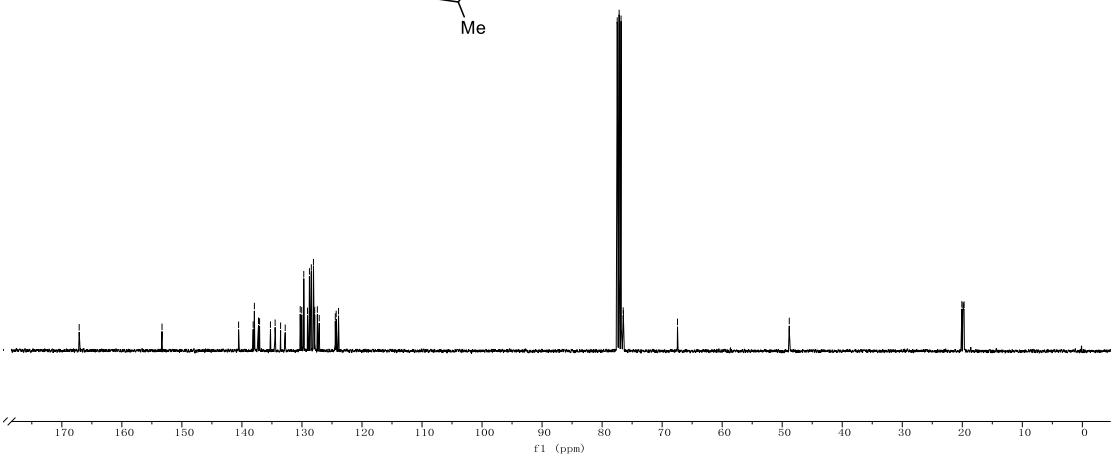




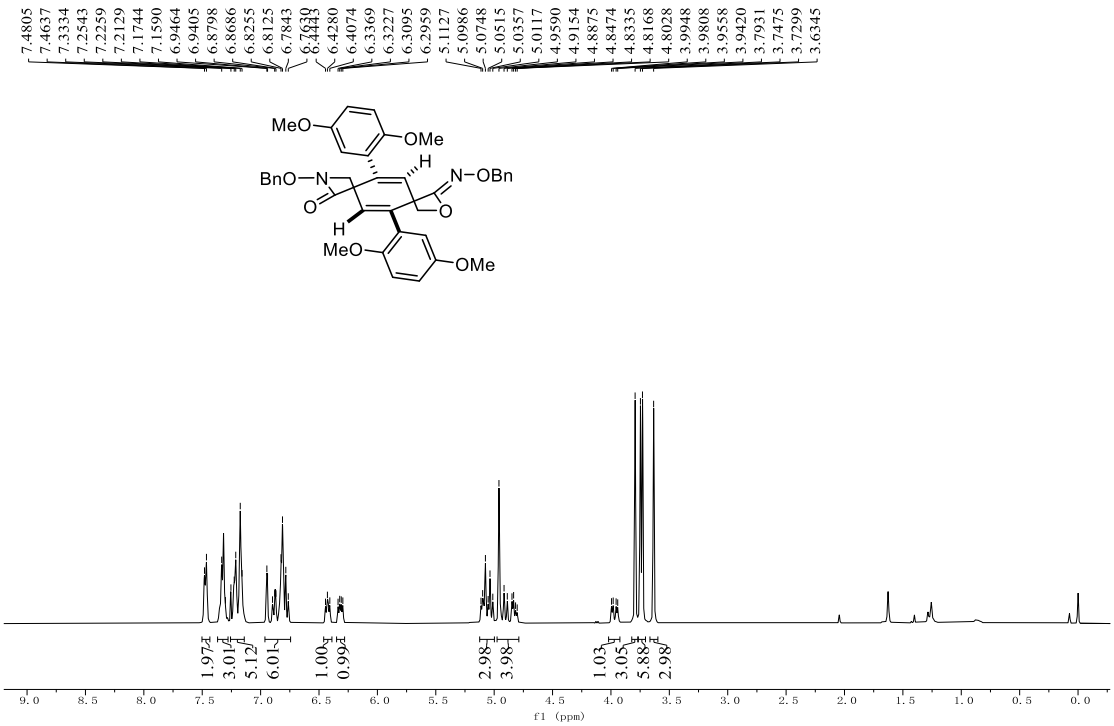
^{13}C NMR (101 MHz, $CDCl_3$) of **2s**



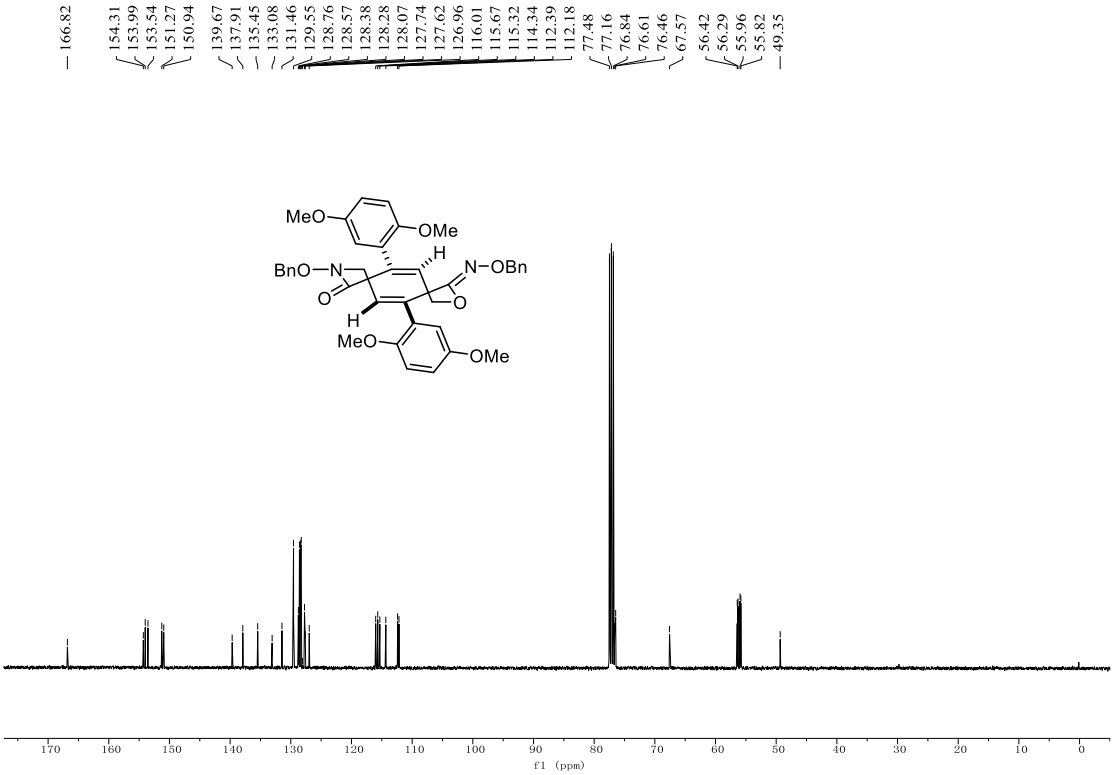




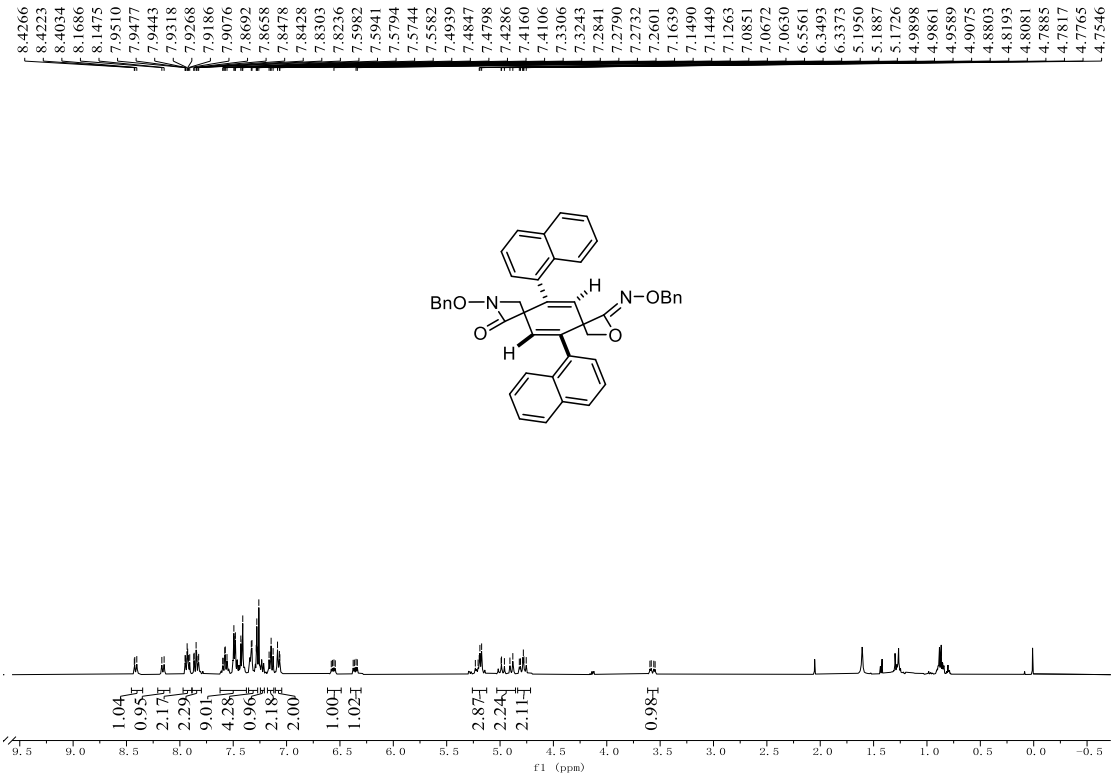
^{1}H NMR (400 MHz, $CDCl_3$) of **2t**



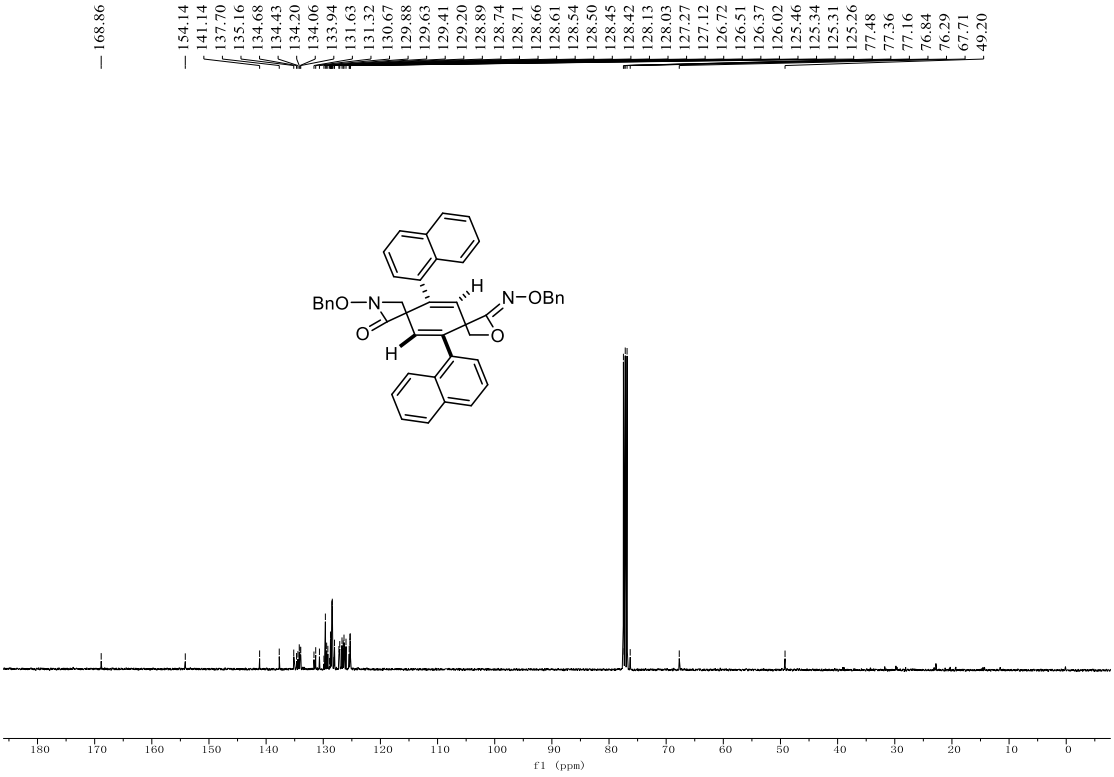
^{13}C NMR (101 MHz, $CDCl_3$) of **2t**



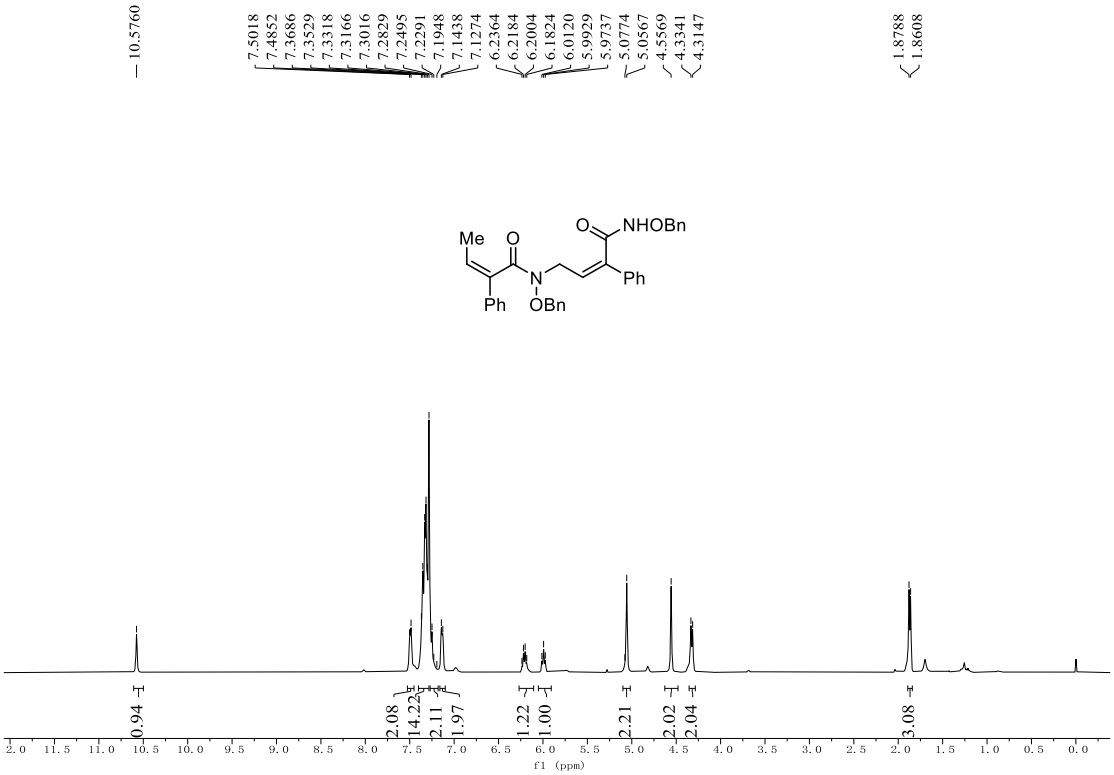
^{1}H NMR (400 MHz, $CDCl_3$) of **2u**



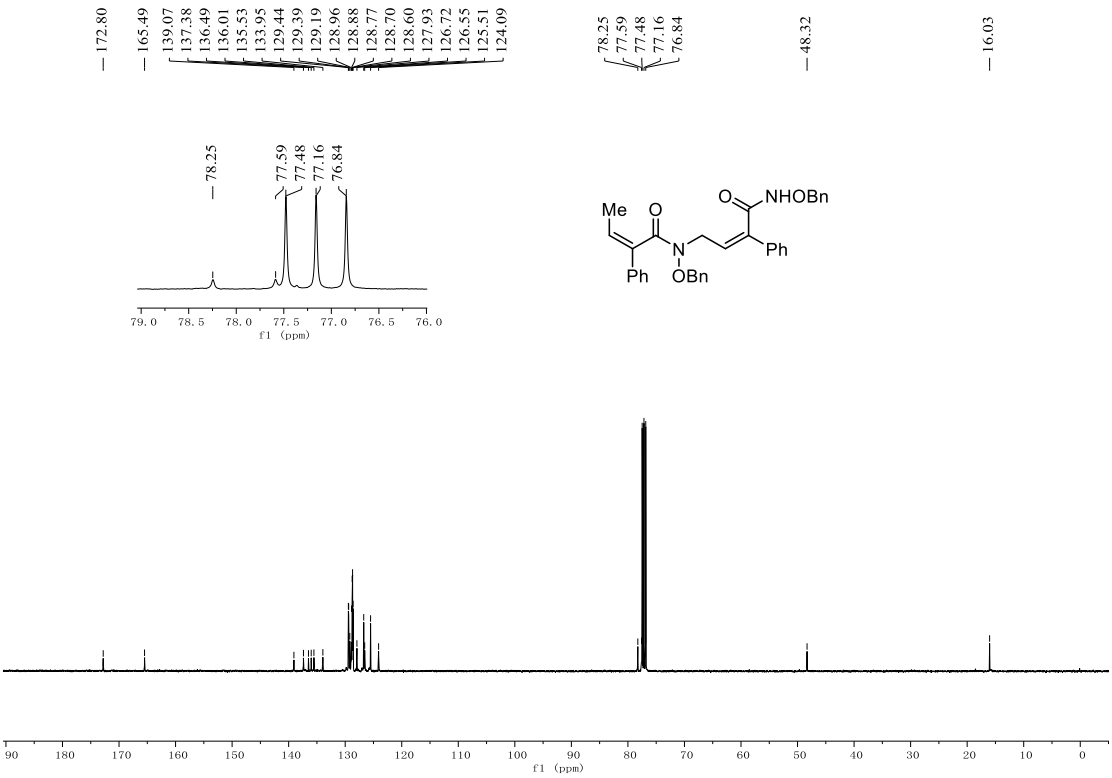
^{13}C NMR (101 MHz, $CDCl_3$) of **2u**



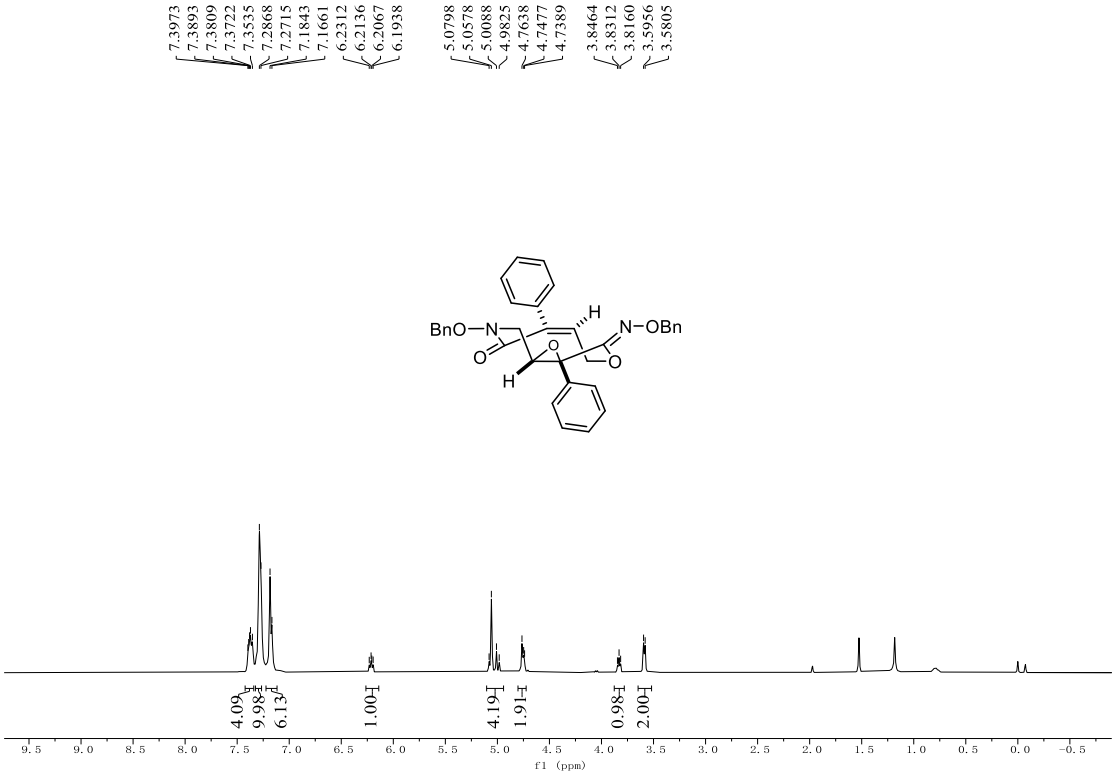
^{1}H NMR (400 MHz, $CDCl_3$) **3**



^{13}C NMR (101 MHz, $CDCl_3$) of **3**



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



^{13}C NMR (101 MHz, $CDCl_3$) of **4**