Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Copper-catalyzed regio and diastereoselective three component C-N, C-C and C-O bond forming reaction: Oxidative sp^3 C-H functionalization of tetrahydroisoquinolines (THIQs) for fused naphtho-1,3-oxazines

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Contents

X-ray Crystallography data

X-ray data for the compounds were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method [1]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data were accomplished using SAINT program [1]. The structure was solved by direct methods using SHELXS [2] and refinement was carried out by full-matrix least-squares technique using SHELXL [2]. Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(c)$ for other H atoms]. The methyl groups were allowed to rotate but not to tip.

Crystal Data for BB34 (**4b**): $C_{27}H_{23}NO$ (M =377.46): monoclinic, space group $P2_1/n$ (no. 14), a = 11.3302(8) Å, b = 10.5415(7) Å, c = 16.9754(12) Å, β = 95.2530(10)°, V = 2019.0(2) Å^3, Z = 4, T = 294.15 K, μ(MoKα) = 0.075 mm^{-1}, *Dcalc* = 1.242 g/mm^3, 23053 reflections measured ($4.152 \leq 2\Theta \leq 56.534$), 4856 unique ($R_{int}$ = 0.0245) which were used in all calculations. The final R_1 was 0.0509 ($I > 2\sigma(I)$) and wR_2 was 0.1405 (all data). CCDC 1434564 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

1. Bruker (2001). SAINT (Version 6.28a) & SMART (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015**)** Acta Crystallogr C71: 3-8.

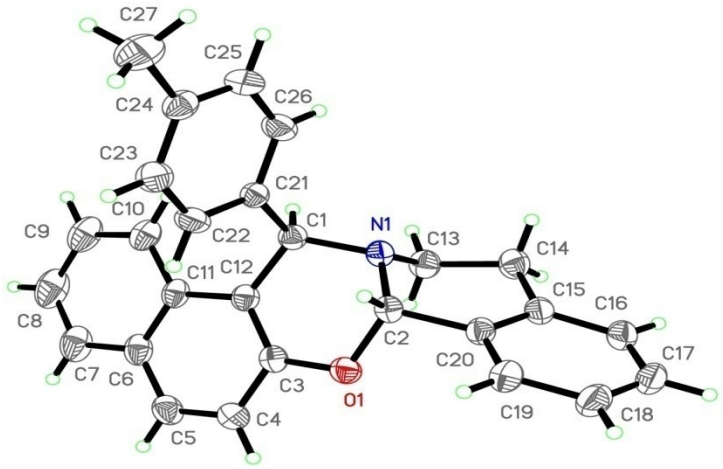


Fig.1. A view of BB34 (**4b**), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

Optical properties

The preliminary photo physical properties of 1, 3-oxazine derivatives were studied for selected compounds (**4a-4c, 4g-4l, 4n-4o, and 4q-4r).** The UV-Vis absorption spectra of these compounds in chloroform are shown in Fig. 2 and the characteristic data are summarized in Table 3. The UV-Vis absorption spectra revealed 1, 3-oxazines (**4a-4c, 4g-4l, 4n-4o, 4q-4r**) had absorption maxima between 288-330 nm. The florescence spectra of **4a-4c, 4g-4l, 4n-4o, and 4q-4r** were measured in chloroform and the corresponding emission wavelengths were in the region 329-348 nm (Fig. 3). Electrochemical band gaps (E_{0-0}) of these compounds are calculated from the intersection of the normalized UV-Vis and PL spectra (Fig. 3) and the corresponding data were shown in (Table 3).

Table 3 Photo physical data of compounds **4a-4c, 4g-4l, 4n-4o, 4q-4r, 6a** and **6b** in $CHCl_3$

Comp.	λ_{abs} (nm)[a]	ε(x 10^4 M^{-1} cm^{-1})[b]	λ_{fluo} (nm)[a]	E_{0-0}[c]
4a	328	0.14	329	4.00
4b	326	0.08	334	4.00
4c	326	0.07	330	4.02
4g	326	0.12	338	3.89
4h	330	0.14	336	3.89
4i	330	0.12	344	3.92
4j	330	0.14	342	3.92
4k	288	0.31	337	3.89
4l	330	0.06	333	3.97
4n	318	0.15	335	3.94
4o	326	0.09	334	3.94
4q	326	0.14	345	3.80
4r	326	0.10	348	3.85

[a]Absorption and emission spectra were recorded in chloroform solutions at 298 K; [b]Molar extension coefficient; [c]The band gap, E_{0-0} was derived from the intersection of normalized absorbance and fluorescence spectra.

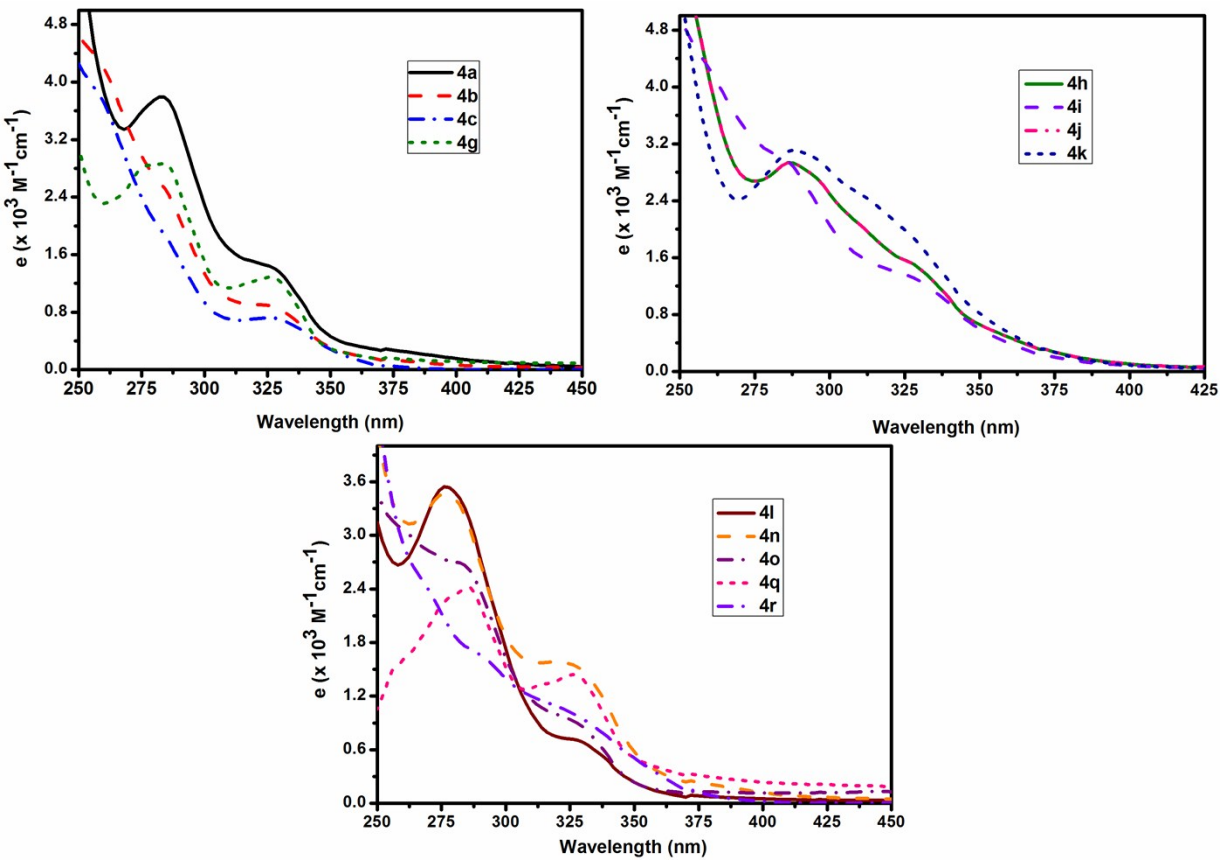


Fig. 2 UV-Vis absorption spectra of **4a-4c, 4g-4l, 4n-4o, 4q-4r** in chloroform.

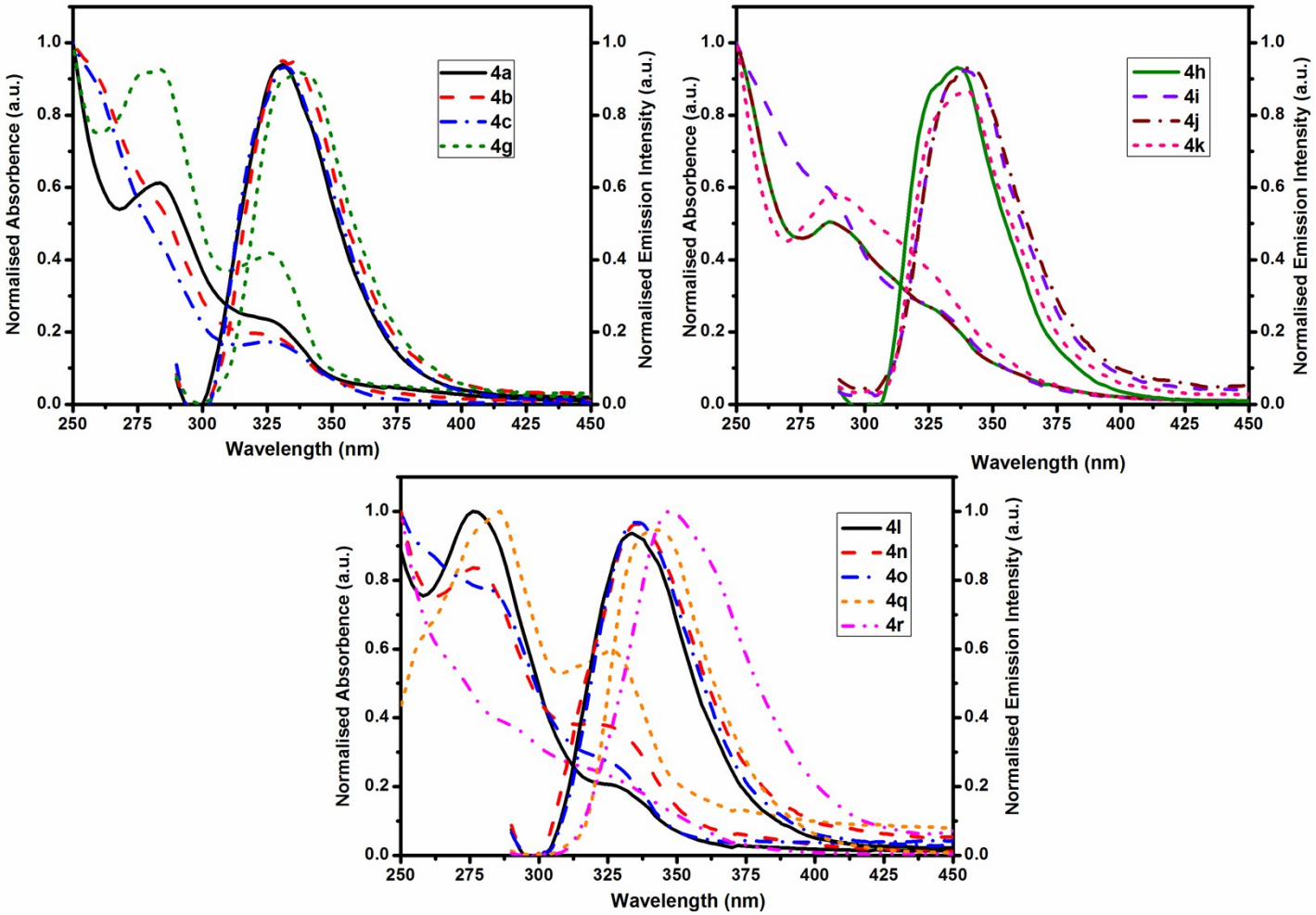


Fig. 3 Electronic absorption & emission spectra of **4a-4c**, **4g-4l**, **4n-4o**, **4q-4r** in chloroform.

General information

All commercially available chemicals were used as received. All solvents were dried and distilled by standard methods. Purification of products was carried out by column chromatography using commercial column chromatography grade silica gel (60-120 mesh) using mixture of ethyl acetate and hexane as eluting agent. The ^{1}H NMR and ^{13}C NMR spectra were obtained as solutions in $CDCl_3$ solvent. ^{1}H spectra were obtained on 300 MHz spectrometers and ^{13}C NMR spectra were obtained on 75 MHz spectrometers with tetramethylsilane and chloroform-d respectively as the internal standard. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Data for ^{1}H NMR are reported as follows: chemical shift (multiplicity, coupling constant, number of hydrogens). Multiplicity is abbreviated as follows: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), m (multiplet). Mass spectra were carried out using Quattro LC triple-quadrupole mass spectrometer (Micromass, Manchester, UK). High-resolution mass spectra were determined using Quadrupole time-of-flight (Q-TOF) mass spectrometer (QSTARXL, Applied Biosystems/MDS Sciex, Foster city, USA).

General procedure

To a flame dried round-bottomed flask (10 mL) was added CuI (10 mol%), freshly activated 4 Å molecular sieves (200 mg), tetrahydroisoquinoline (0.2 mmol, 2 equiv), the aldehyde (0.1 mmol, 1 equiv), naphthalen-2-ol (0.1 mmol, 1 equiv) and toluene (2 mL). The mixture was stirred at 65 °C for 48 h under nitrogen atmosphere. Subsequently, the reaction mixture was allowed to cool to room temperature and extracted with ethyl acetate. The organic layer was washed with brine (10 mL) and dried over anhydrous Na_2SO_4 and then solvent was removed under reduced pressure. Finally, the residue was purified by silica gel chromatography using mixture of ethyl acetate and hexane as the eluent to give the product.

Spectral data of all compounds

4-phenyl-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4a

White solid (76%). See the ref. 10 for spectral data.

4-(p-tolyl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4b

White solid (81%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.81-7.70 (m, 2H), 7.46-7.40 (d, *J* = 7.5 Hz, 1H), 7.33-7.15 (m, 9H), 7.12-7.04 (m, 2H), 5.65 (s, 1H), 5.40 (s, 1H), 3.40-3.22 (m, 2H), 3.13-3.06 (m, 1H), 2.91-2.83 (d, *J* = 13.6 Hz, H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 151.8, 139.4, 136.9, 134.9, 133.1, 132.4, 129.1, 129, 128.9, 128.8, 128.7, 128.5, 126.5, 126.1, 123.1, 122.7, 118.9, 111.1, 122.4, 82.2, 62.3, 45.3, 29.3; HRMS (ESI) calcd for $C_{27}H_{24}ON$: 378.18524 Found: 378.18656.

4-(4-isopropylphenyl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3 a]isoquinoline 4c

White solid (79%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.79-7.76 (d, *J* = 9.1 Hz, 1H), 7.73-7.71 (d, *J* = 9 Hz, 1H), 7.46-7.44 (d, *J* = 8.2 Hz, 1H), 7.34-7.27 (m, 4H), 7.24-7.18 (m, 4H), 7.13-7.09 (m, 3H), 5.67 (s, 1H), 5.41 (s, 1H), 3.36-3.23 (m, 2H), 3.11-3.07 (m, 1H), 2.89-2.83 (m, 2H), 1.21-1.18 (dd, *J* = 3.9, 6.9 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 151.8, 147.8, 139.7, 135.0, 133.1, 132.4, 130.0, 129.1, 128.9, 128.8, 128.7, 128.5, 127.1, 126.4, 126.3, 126.1, 123.0, 122.8, 118.9, 111.2, 82.1, 62.3, 45.2, 33.7, 29.3; HRMS (ESI) calcd for $C_{29}H_{28}ON$: 406.21654 Found: 406.21808.

4-(4-methoxyphenyl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4d

White solid (77%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.80-7.71 (m, 2H), 7.47-7.40 (d, *J* = 7.7 Hz, 1H), 7.35-7.18 (m, 8H), 7.13-7.07 (d, *J* = 8.8 Hz, 1H), 6.83-6.77 (d, *J* = 8.4 Hz, 2H), 5.65 (s, 1H), 5.39 (s, 1H), 3.75 (s, 3H), 3.39-3.23 (m, 2H), 3.12-3.04 (m, 1H), 2.91-2.83 (d, *J* = 13.2 Hz, H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 158.7, 151.8, 134.9, 134.5, 133.1, 132.3, 130.4, 129, 128.8, 128.7, 128.5, 126.5, 126.1, 123.1, 122.6, 118.8, 113.5, 111.2, 82.1, 62.1, 55.1, 45.1, 29.3.

4-(3,4,5-trimethoxyphenyl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4e

White solid (75%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.79-7.76 (d, *J* = 7.8 Hz, 1H), 7.74-7.72 (d, *J* = 9.1 Hz, 1H), 7.48-7.44 (d, *J* = 8.2 Hz, 1H), 7.38-7.34 (m, 2H), 7.33-7.29 (m, 2H), 7.27-7.25 (m, 1H), 7.22-7.20 (d, *J* = 7.5 Hz, 1H), 7.11-7.09 (d, *J* = 9.1 Hz, 1H), 6.57-6.51 (s, 2H), 5.72 (s, 1H), 5.35 (s, 1H), 3.81 (s, 3H), 3.68 (s, 6H), 3.35-3.26 (m, 2H), 3.10-3.05 (m, 1H), 2.90-2.86 (d, *J* = 12.5 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 152.9, 151.7, 137.9, 137.2, 134.9, 132.9, 132.4, 129.2, 128.8, 128.7, 128.5, 126.5, 126.1,123.1, 122.6, 118.7, 110.7, 106.6, 82.3, 62.7, 60.7, 56.1, 45.2, 29.3; HRMS (ESI) calcd for $C_{29}H_{28}O_4N$: 454.20128 Found: 454.20326.

4-(2,3,4-trimethoxyphenyl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4f

White solid (70%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.76-7.73 (d, *J* = 7.5 Hz, 1H), 7.71-7.69 (d, *J* = 9.1 Hz, 1H), 7.39-7.33 (m, 2H), 7.31-7.22 (m, 6H), 7.19-7.16 (d, *J* = 7.4 Hz, 1H), 7.12-7.09 (d, *J* = 9.1 Hz, 1H), 6.54-6.51 (d, *J* = 8.5 Hz, 1H), 6.44-6.41 (d, *J* = 8.5 Hz, 1H), 5.82 (s, 1H), 5.76 (s, 1H), 4.09 (s, 3H), 3.97 (s, 3H), 3.77 (s, 3H), 3.41-3.35 (m, 2H), 3.26-3.15 (m, 1H), 2.89-2.84 (dd, *J* = 4.6, 16.3 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 153.2, 152.3, 151.9, 142.6, 134.9, 133.1, 131.9, 129.5, 128.9, 128.8, 128.7, 128.4, 126.4, 126.1, 124.4, 123.1, 122.7, 118.7, 111.0, 106.1, 81.9, 61.3, 60.8, 57.1, 55.8 45, 29.3; HRMS (ESI) calcd for $C_{29}H_{28}O_4N$: 454.20128 Found: 454.20304.

4-(4-bromophenyl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4g

White solid (84%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.81-7.72 (m, 2H), 7.41-7.17 (m, 11H), 7.13-7.08 (d, *J* = 8.9 Hz, 1H), 5.58 (s, 1H), 5.37 (s, 1H), 3.39-3.22 (m, 2H), 3.12-3.06 (m, 1H), 2.91-2.84 (d, *J* = 13.9 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 155.2, 151.9, 141.3, 134.7, 132.7, 132.2, 131.3, 131, 129.3, 128.9, 128.8, 128.7, 126.7, 126.2, 123.2, 122.4, 121.4, 118.9, 110.2, 82.2, 61.9, 45.3, 29.3; HRMS (ESI) calcd for $C_{26}H_{21}ONBr$: 442.08010 Found: 442.08208.

4-(2-bromophenyl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4h

White solid (82%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.80-7.73 (m, 2H), 7.70-7.66 (m, 1H), 7.37-7.08 (m, 10H), 6.96-6.91 (m, 1H), 5.69 (s, 1H), 5.64 (s, 1H), 3.41-3.23 (m, 3H), 2.87-2.81 (d, *J* = 15.5 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 152.5, 141.2, 135.3, 133.5, 132.7, 131.8, 131.0,

129.4, 129.1, 129.0, 128.8, 128.7, 128.6, 128.6, 126.8, 126.7, 126.1, 125.5, 123.2, 122.6, 118.9, 110.3, 82.0, 62.1, 45.2, 29.2; HRMS (ESI) calcd for $C_{26}H_{21}ONBr$: 442.08010 Found: 442.08187.

4-(4-chlorophenyl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4i

White solid (83%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.81-7.78 (d, *J* = 8.8 Hz, 1H), 7.75-7.73 (d, *J* = 9.1 Hz, 1H), 7.39-7.28 (m, 5H), 7.26-7.19 (m, 6H), 7.11-7.09 (d, *J* = 8.85 Hz, 1H), 5.58 (s, 1H), 5.38 (s, 1H), 3.39-3.24 (m, 2H), 3.10-3.07 (m, 1H), 2.90-2.85 (d, *J* = 13.1 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 151.9, 140.8, 134.8, 133.2, 132.8, 132.2, 130.6, 129.3, 128.9, 128.8, 128.7, 128.6, 128.6, 128.4, 126.7, 126.2, 123.2, 122.4, 118.9, 110.4, 82.1, 62.0, 45.3, 29.3; HRMS (ESI) calcd for $C_{26}H_{21}ONCl$: 398.13062 Found: 398.13219.

4-(3-chlorophenyl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4j

White solid (73%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.82-7.72 (m, 2H), 7.37-7.27 (m, 7H), 7.22-7.08 (m, 5H), 5.60 (s, 1H), 5.38 (s, 1H), 3.40-3.23 (m, 2H), 3.13-3.04 (m, 1H), 2.91-2.83 (d, *J* = 12.4 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 151.6, 144.4, 134.8, 134.2, 132.8, 132.2, 129.5, 129.4, 129.3, 128.9, 128.8, 128.7, 128.6, 127.7, 127.6, 126.7, 126.2, 123.3, 122.4, 118.9, 110.1, 82.1, 62.2, 45.3, 29.3; HRMS (ESI) calcd for $C_{26}H_{21}ONCl$: 398.13062 Found: 398.13239.

4-(2-bromo-5-fluorophenyl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4k

White solid (86%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.81-7.74 (m, 2H), 7.66-7.60 (m, 1H), 7.40-7.26 (m, 5H), 7.22-7.12 (m, 3H), 6.92-6.82 (m, 2H), 6.70-6.65 (dd, *J* = 2.8, 9.2 Hz,1H) 5.67 (s, 1H), 5.59 (s, 1H), 3.41-3.22 (m, 3H), 2.88-2.80 (d, *J* = 15.6 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 162.5, 160.5, 152.5, 143.5, 143.5, 135.1, 134.5, 134.5, 132.5, 131.6, 129.7, 129.1, 128.9, 128.7, 126.8, 126.1, 123.4, 122.3, 119.5, 119.4, 118.8, 118.4, 118.3, 116.1, 115.9, 109.5, 81.9, 61.9, 45.3, 29.2; HRMS (ESI) calcd for $C_{26}H_{20}ONBrF$: 460.07068 Found: 460.07271.

4-(3-bromo-4-methoxyphenyl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4l

White solid (85%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.81-7.78 (d, *J* = 8.85 Hz, 1H), 7.75-7.73 (d, *J* = 9.1 Hz, 1H), 7.39-7.28 (m, 5H), 7.26-7.19 (m, 6H), 7.11-7.09 (d, *J* = 8.85 Hz, 1H), 5.58 (s,

1H), 5.38 (s, 1H), 3.39-3.24 (m, 2H), 3.10-3.07 (m, 1H), 2.90-2.85 (d, *J* = 13.1 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 151.9, 140.8, 134.8, 133.2, 132.8, 132.2, 130.6, 129.3, 128.9, 128.8, 128.7, 128.6, 128.5, 126.7, 126.2, 123.2, 122.4, 118.9, 111.6, 111.1, 110.4, 82.1, 62.0, 56.1, 45.1, 29.2; HRMS (ESI) calcd for $C_{27}H_{23}O_2NBr$: 472.09067 Found: 472.09277.

4-(3-nitrophenyl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4m

Yellow solid (89%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.12-8.09 (d, *J* = 7 Hz, 1H), 7.84-7.76 (m, 2H), 7.58-7.52 (d, *J* = 7.7 Hz, 1H), 7.42-7.23 (m, 8H), 7.15-7.11 (d, *J* = 8.9 Hz, 1H), 5.53 (s, 1H), 5.47 (s, 1H), 3.43-3.26 (m, 2H), 3.19-3.11 (m, 1H), 2.95-2.88 (d, *J* = 13.4 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 152.1, 148.4, 144.6, 135.4, 134.7, 132.4, 132, 129.9, 129.1, 129, 128.9, 128.8, 128.7, 127, 126.2, 124.3, 123.4, 122.6, 122.0, 119.0, 109.3, 82.1, 61.9, 45.4, 29.3; HRMS (ESI) calcd for $C_{26}H_{21}O_3N_2$: 409.15467 Found: 409.15668.

4-(furan-2-yl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4n

White solid (74%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.80-7.68 (m, 2H), 7.49-6.93 (m, 9H), 6.40-6.23 (m, 1H), 5.94-5.91 (d, *J* = 3.2 Hz, 1H), 5.88 (s, 1H), 5.47 (s, 1H), 3.65-3.27 (m, 2H), 3.07-3.01 (m, 1H), 2.92-2.85 (d, *J* = 13.4 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 154.5, 151.7, 142.5, 142.4, 134.9, 132.7, 129.4, 128.9, 128.8, 128.7, 128.5, 126.6, 126.1, 123.2, 122.1, 118.8, 110.7, 110.6, 110.1, 109.4, 82.4, 57.1, 44.5, 29.1; HRMS (ESI) calcd for $C_{24}H_{22}O_2N$: 356.16451 Found: 356.16570.

4-(thiophen-2-yl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4o

White solid (81%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.80-7.77 (d, *J* = 8.1 Hz, 1H), 7.74-7.71 (d, *J* = 8.8 Hz, 1H), 7.65-7.63 (d, *J* = 8.4 Hz, 1H), 7.43-7.30 (m, 4H), 7.27-7.20 (m, 3H), 7.10-7.05 (d, *J* = 9.1 Hz, 1H), 6.83-6.81 (t, *J* = 3.9 Hz, 1H), 6.64-6.61 (d, *J* = 3.5 Hz, 1H), 5.87 (s, 1H), 5.60 (s, 1H), 3.34-3.26 (m, 2H), 3.09-3.05 (m, 1H), 2.89-2.85 (d, *J* = 11.9 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 151.3, 147.2, 135.0, 133.2, 132.8, 132.1, 129.3, 128.9, 128.8, 128.7, 128.7, 128.5, 127.6, 126.6, 126.4, 126.2, 125.7, 123.2, 122.5, 118.9, 110.5, 82.2, 58.6, 44.6, 29.3; HRMS (ESI) calcd for $C_{24}H_{20}ONS$: 370.12601 Found: 370.12765.

4-propyl-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4p

White solid (47%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.77-7.72 (m, 2H), 7.62-7.60 (d, *J* = 8.8 Hz, 1H), 7.51-7.47 (m, 2H), 7.35-7.31 (m, 3H), 7.23-7.20 (d, *J* = 6.6 Hz, 1H), 7.23-7.20 (d, *J* = 8.6 Hz, 1H), 6.02 (s, 1H), 4.19-4.16 (dd, *J* = 2.6, 11 Hz, 1H), 3.33-3.18 (m, 2H), 2.83-2.76 (m, 2H), 2.11-2.04 (m, 1H), 1.94-1.76 (m, 2H), 1.7-1.62 (m, 2H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 150.7, 135.4, 133.2, 131.6, 129.1, 128.9, 128.8, 128.7, 128.1, 126.3, 126.2, 122.9, 121.6, 118.9, 115.1, 81.9, 59.3, 45.5, 38.2, 29.3, 19.9, 13.9; HRMS (ESI) calcd for $C_{23}H_{24}ON$: 330.18540 Found: 330.18524.

7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3]oxazino[2,3-a]isoquinoline 4q

White solid (61%). See the ref. 10 for spectral data.

4-(6-methoxynaphthalen-2-yl)-4,6,7,11b-tetrahydronaphtho[1',2':5,6][1,3]oxazino[4,3-a]isoquinoline 4r

White solid (82%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.82-7.80 (m, 1H), 7.79-7.76 (d, *J* = 8.8 Hz, 1H), 7.72-7.70 (d, *J* = 8.4 Hz, 1H), 7.67-7.62 (d, *J* = 6.7 Hz, 1H), 7.53-7.51 (d, *J* = 9 Hz, 1H), 7.4 (s, 1H), 7.31-7.26 (m, 4H), 7.22-7.18 (t, *J* = 7.1 Hz, 2H), 7.16-7.13 (d, *J* = 9 Hz, 1H), 7.11-7.09 (d, *J* = 2.4 Hz, 1H), 7.07-7.04 (dd, *J* = 2.6, 9 Hz, 1H), 5.69 (s, 1H), 5.55 (s, 1H), 3.89 (s, 3H) 3.44-3.28 (m, 2H), 3.17-3.12 (m, 1H), 2.92-2.87 (dd, *J* = 3.1, 16.3 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 157.7, 152.0, 137.5, 135, 133.9, 133.0, 132.4, 129.6, 129.1, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 127.9, 127.0, 126.5, 126.1, 123.1, 122.7, 118.9, 118.5, 110.9, 105.5, 82.2, 62.7, 55.2, 45.3, 29.3; HRMS (ESI) calcd for $C_{31}H_{25}O_2N$: 444.19616 Found: 444.19518.

15-(6-bromobenzo[d][1,3]dioxol-5-yl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3]oxazino[2,3-a]isoquinoline 4s

White solid (78%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 7.81-7.71 (m, 2H), 7.40-7.09 (m, 9H), 6.44 (s, 1H), 5.89 (s, 2H), 5.73 (s, 1H), 5.55 (s, 1H), 3.40-3.20 (m, 3H), 2.86-2.80 (d, *J* = 13.4 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 152.4, 147.5, 146.7, 135.2, 135.0, 132.7, 131.7, 129.4, 129.1, 128.9, 128.8, 128.7, 128.6, 126.8, 126.1, 123.3, 122.5, 118.8, 116.1, 113.6, 111.1, 110.4, 101.7, 82.1, 62.0, 45.2, 29.2; HRMS (ESI) calcd for $C_{27}H_{21}O_3NBr$: 486.06993 Found: 486.07215.

6-(4-methoxyphenyl)-6,8,9,13b-tetrahydronaphtho[2',1':5,6][1,3]oxazino[4,3-a]isoquinoline 6a

Yellow solid (87%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 8.17-8.14 (d, *J* = 8.2 Hz, 1H), 7.81-7.77 (d, *J* = 7.7 Hz, 1H), 7.48-7.29 (m, 6H), 7.27-7.10 (m, 4H), 6.83-6.81 (d, *J* = 8.7 Hz, 2H), 5.7 (s, 1H), 4.99 (s, 1H), 3.77 (s, 3H), 3.40-3.23 (m, 2H), 3.10-3.04 (m, 1H), 2.90-2.85 (dd, *J* = 2.9,16.3 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 158.7, 149.3, 135.5, 135.1, 133.6, 133.3, 130.3, 128.9, 128.6, 127.4, 126.8, 126.2, 126.0, 125.9, 125.1, 121.9, 119.1, 113.8, 113.4, 113.1, 82.6, 64.4, 55.2, 45.1, 29.4; HRMS (ESI) calcd for $C_{27}H_{26}O_2N$: 396.19581 Found: 396.19741.

6-(4-bromophenyl)-6,8,9,13b-tetrahydronaphtho[2',1':5,6][1,3]oxazino[4,3-a]isoquinoline 6b

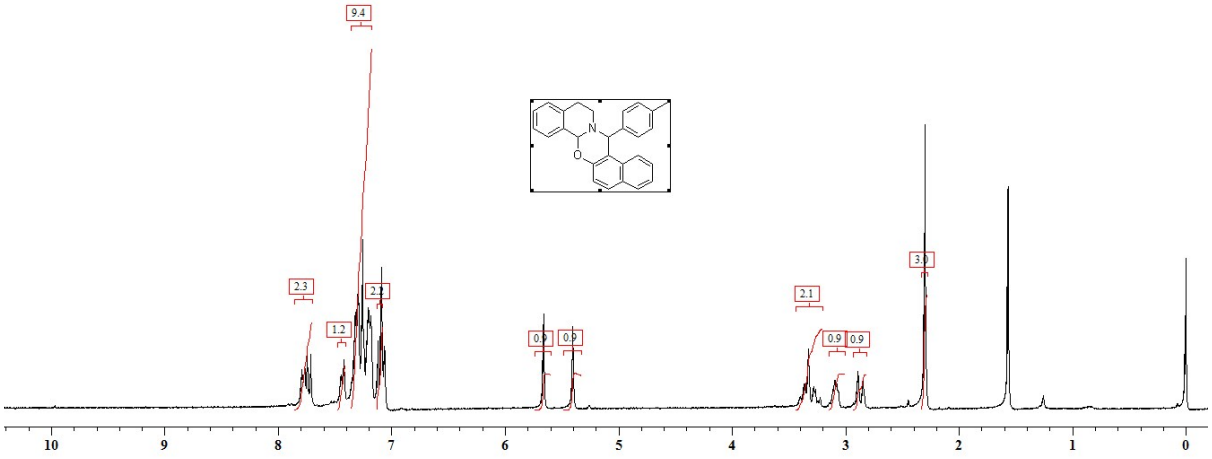
Yellow solid (83%); **^{1}H** NMR (300 MHz, $CDCl_3$) δ 8.18-8.14 (d, *J* = 8.2 Hz, 1H), 7.81-7.77 (d, *J* = 8.1 Hz, 1H), 7.51-7.29 (m, 9H), 7.26-7.17 (m, 2H), 7.12-7.08 (d, *J* = 8.4 Hz, 1H), 5.62 (s, 1H), 4.98 (s, 1H), 3.42-3.23 (m, 2H), 3.11-3.02 (m, 1H), 2.90-2.84 (d, *J* = 16.5 Hz, 1H); **^{13}C** NMR (75 MHz, $CDCl_3$) δ 149.4, 142.3, 135.0, 133.7, 133, 131.7, 131.2, 130.1, 128.9, 128.7, 128.6, 128.3, 127.4, 126.6, 126.3, 126.1, 125.2, 124.8, 121.9, 121.4, 119.3, 112.1, 82.6, 64.3, 45.3, 29.4; HRMS (ESI) calcd for $C_{26}H_{21}ONBr$: 442.08010 Found: 442.08188.

1-((3,4-dihydroisoquinolin-2(1H)-yl)(p-tolyl)methyl)naphthalen-2-ol A

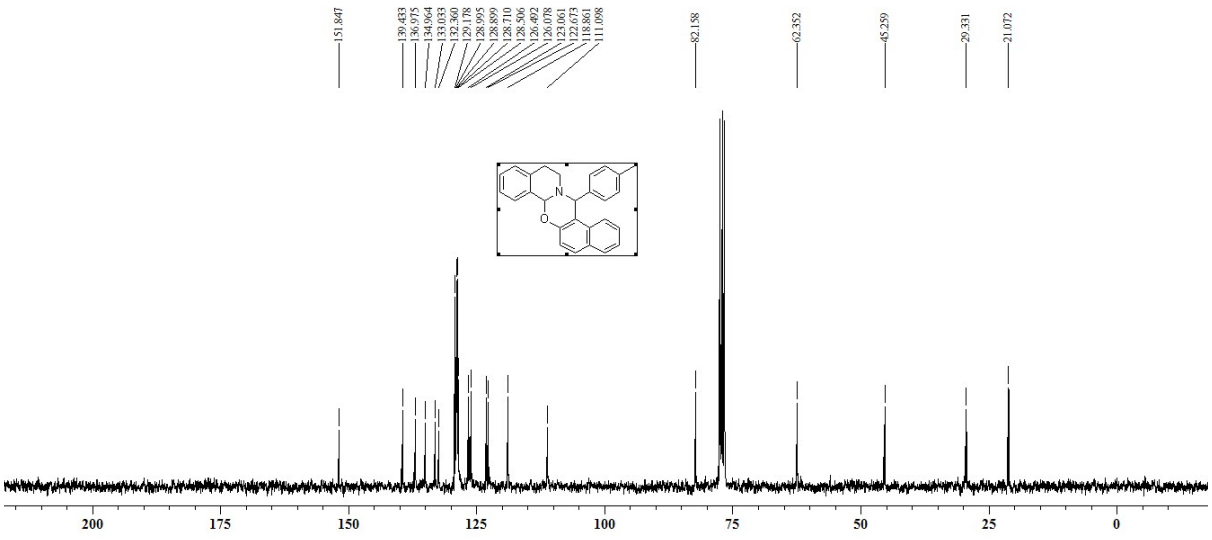
It was synthesized by the literature procedure of *Tetrahedron,* 2015**, 71,** 7216-7221.

White solid; **^{1}H** NMR (400 MHz, $CDCl_3$) δ 13.3 (s, 1H), 7.95-7.85 (d, *J* = 8.5 Hz, 1H), 7.73-7.63 (m, 2H), 7.56-7.46 (d, *J* = 7.8 Hz, 2H), 7.42-7.33 (m, 1H), 7.26-7.19 (m, 1H), 7.18-7.06 (m, 6H), 6.93-6.85 (d, *J* = 7.3 Hz, 1H), 5.25 (s, 1H), 3.71-3.57 (d, *J* = 14.5 Hz, 1H), 3.18-3.10 (t, *J* = 5.8 Hz, 1H), 2.97-2.74 (m, 2H), 2.27 (s, 3H).

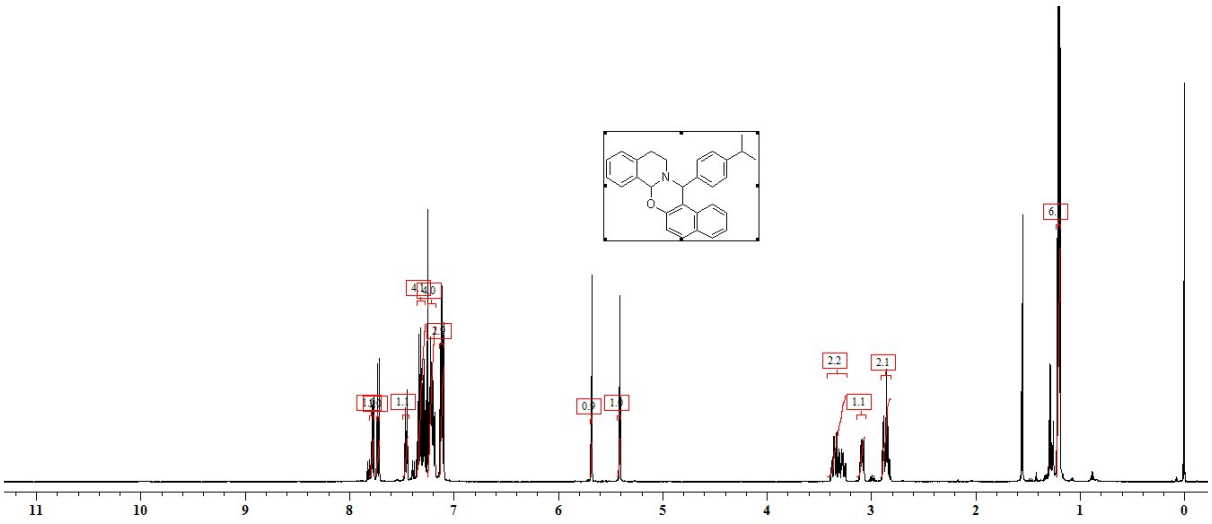
[1]H NMR spectra of **4b**



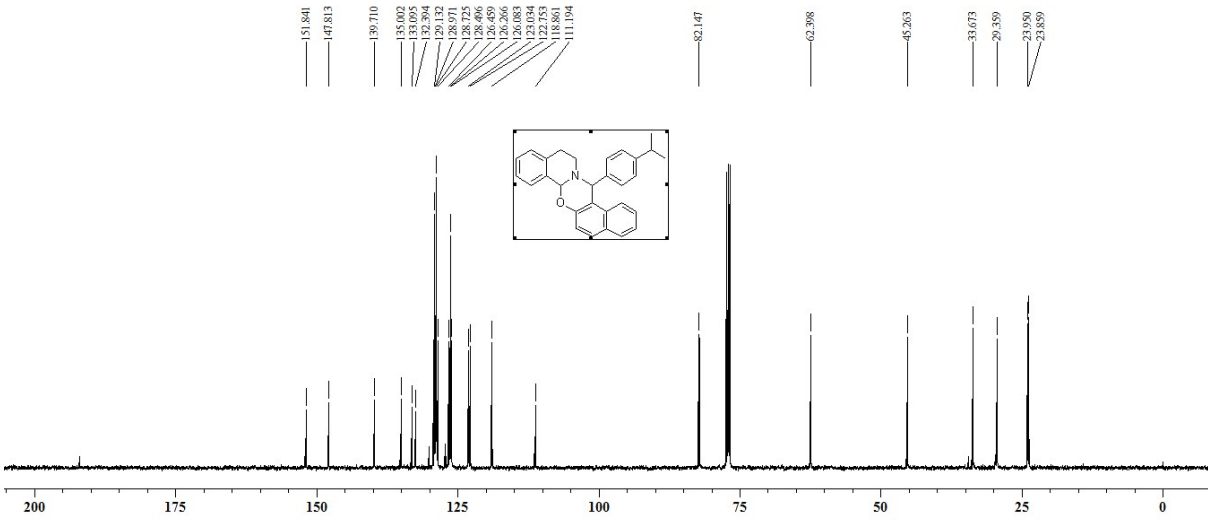
[13]C NMR spectra of **4b**



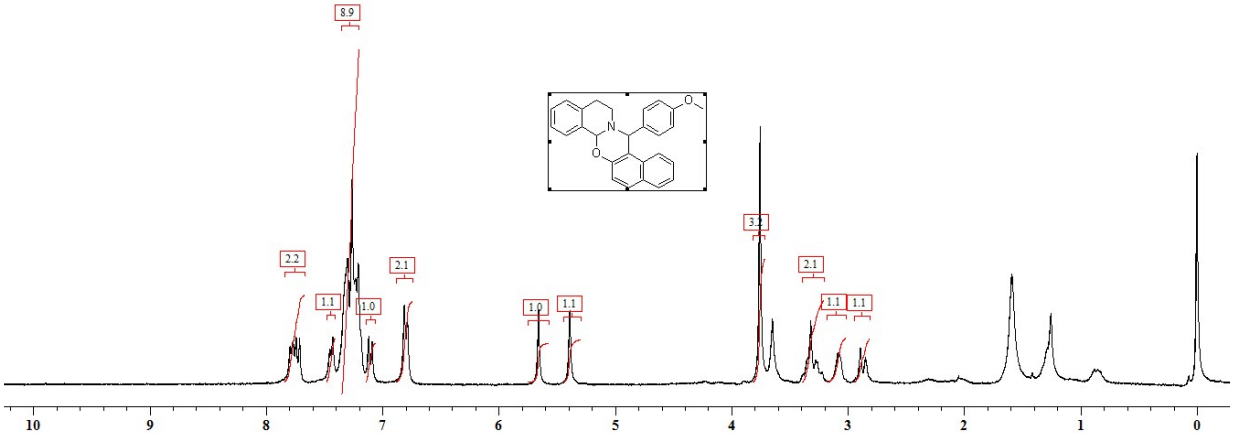
^{1}H NMR spectra of **4c**



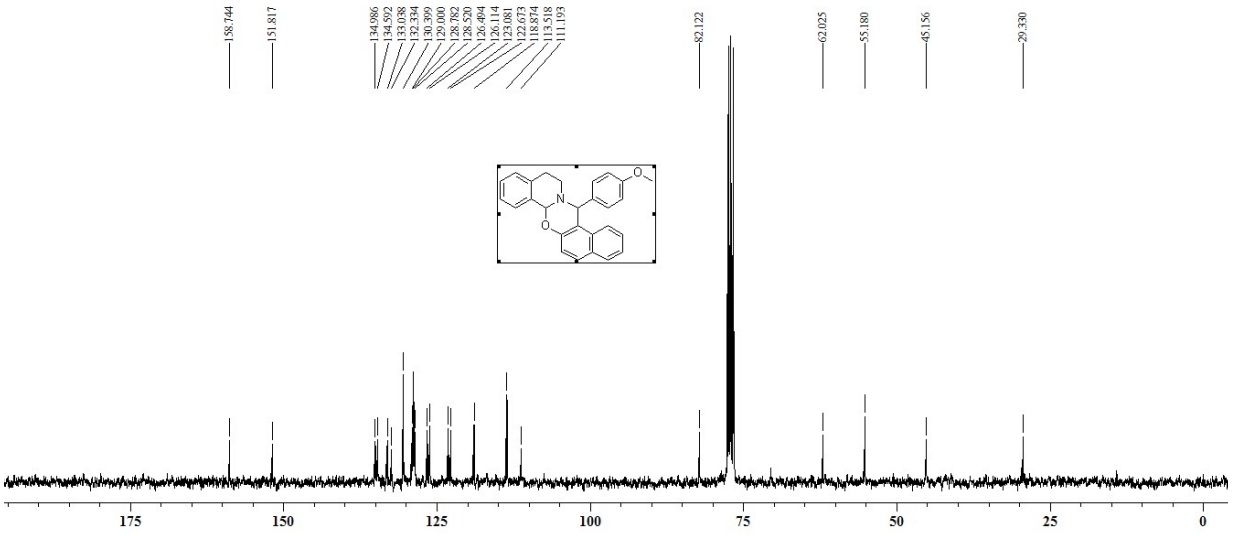
^{13}C NMR spectra of **4c**



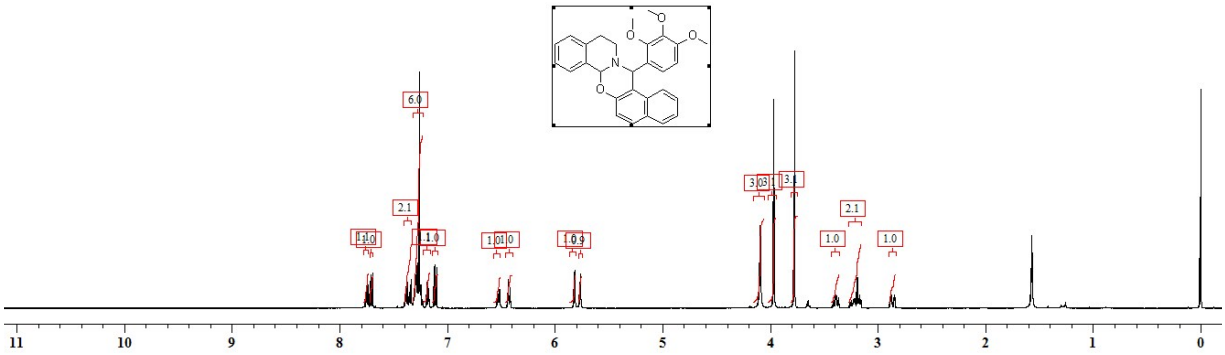
^{1}H NMR spectra of **4d**



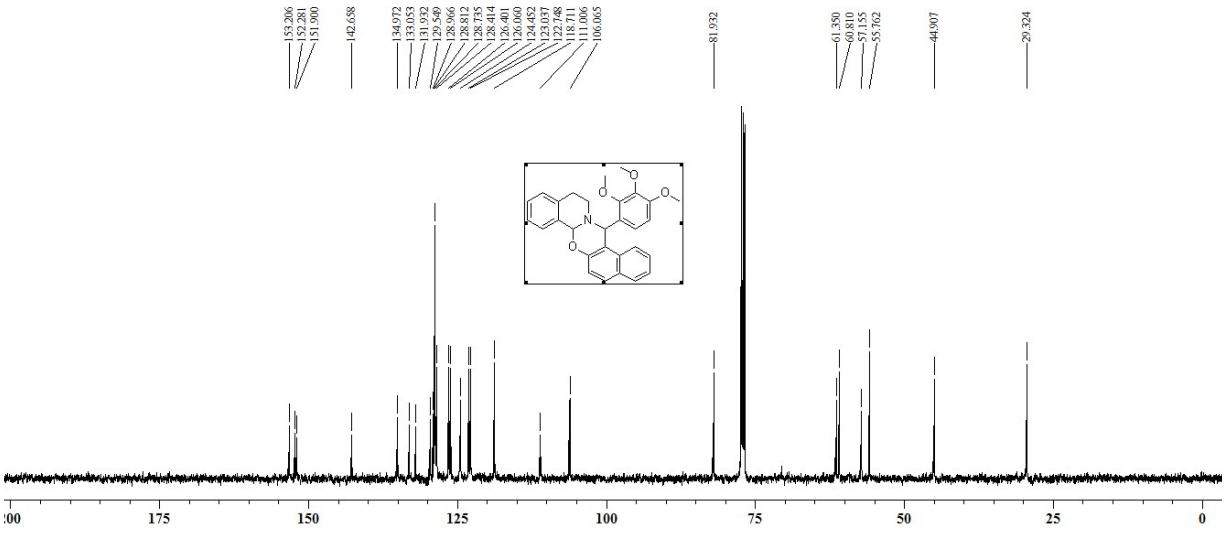
^{13}C NMR spectra of **4d**



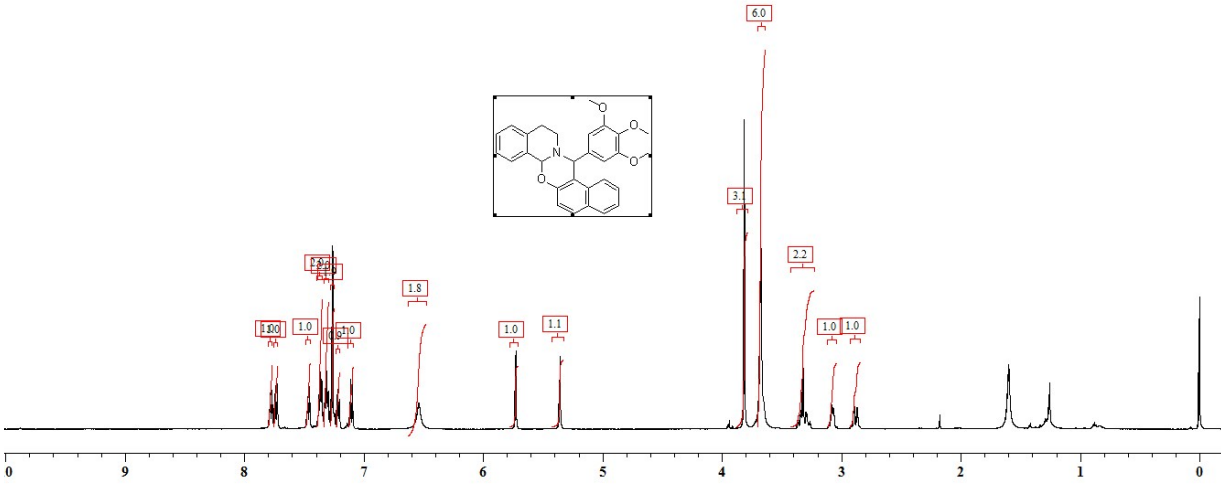
^{1}H NMR spectra of **4e**



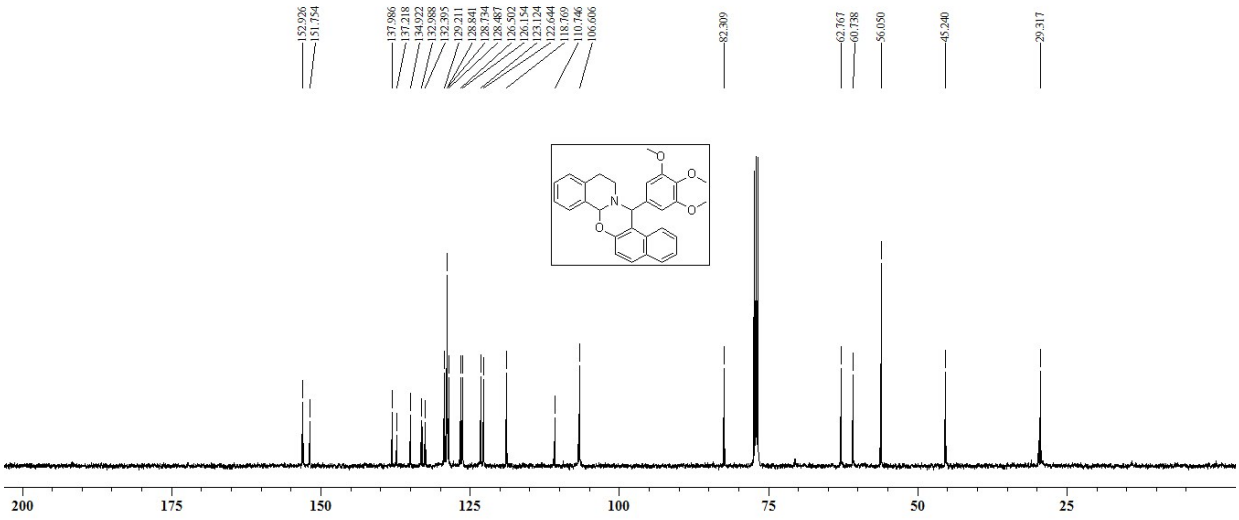
^{13}C NMR spectra of **4e**



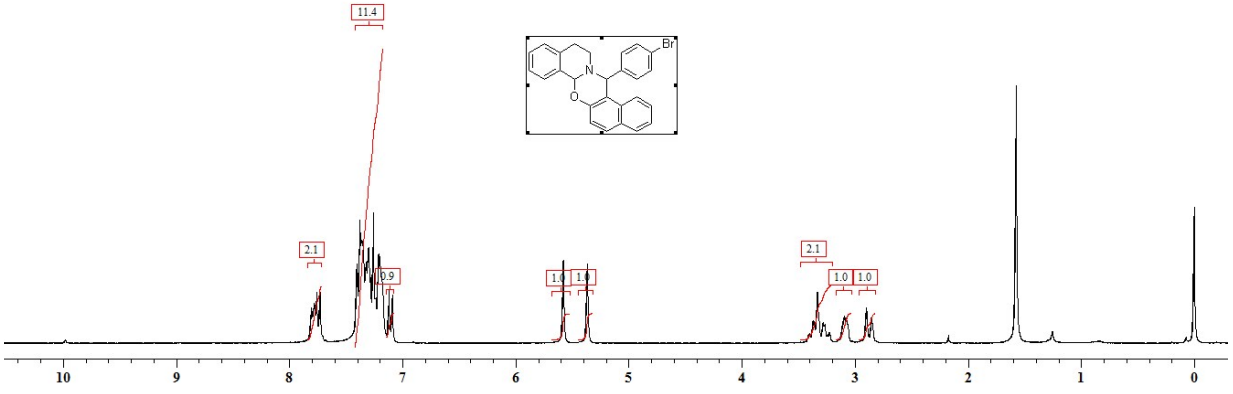
^{1}H NMR spectra of **4f**



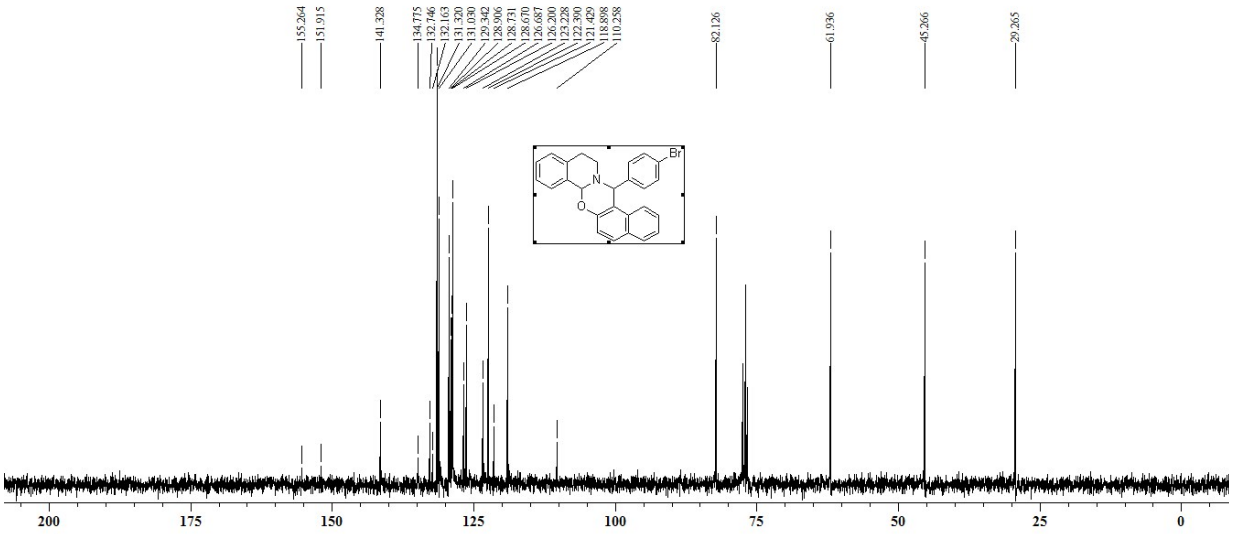
^{13}C NMR spectra of **4f**



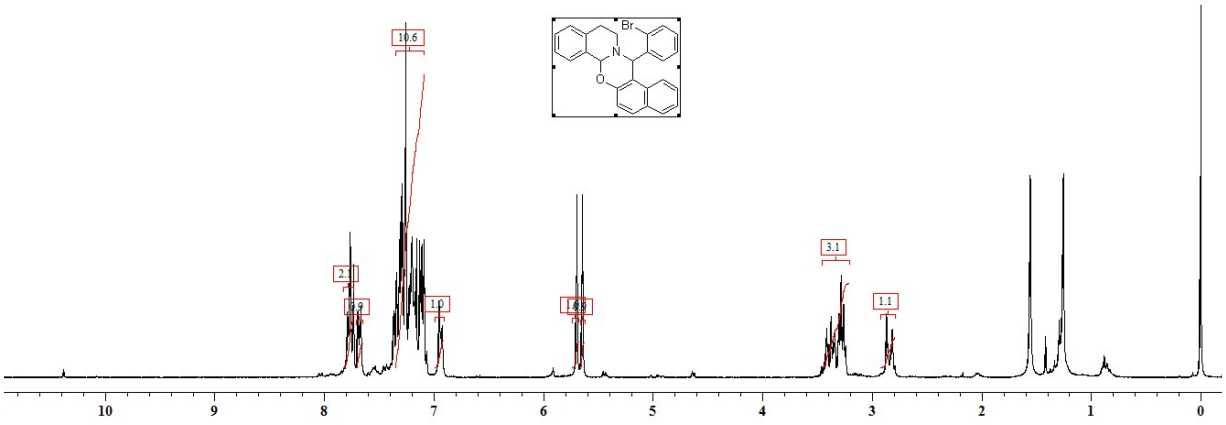
^{1}H NMR spectra of **4g**



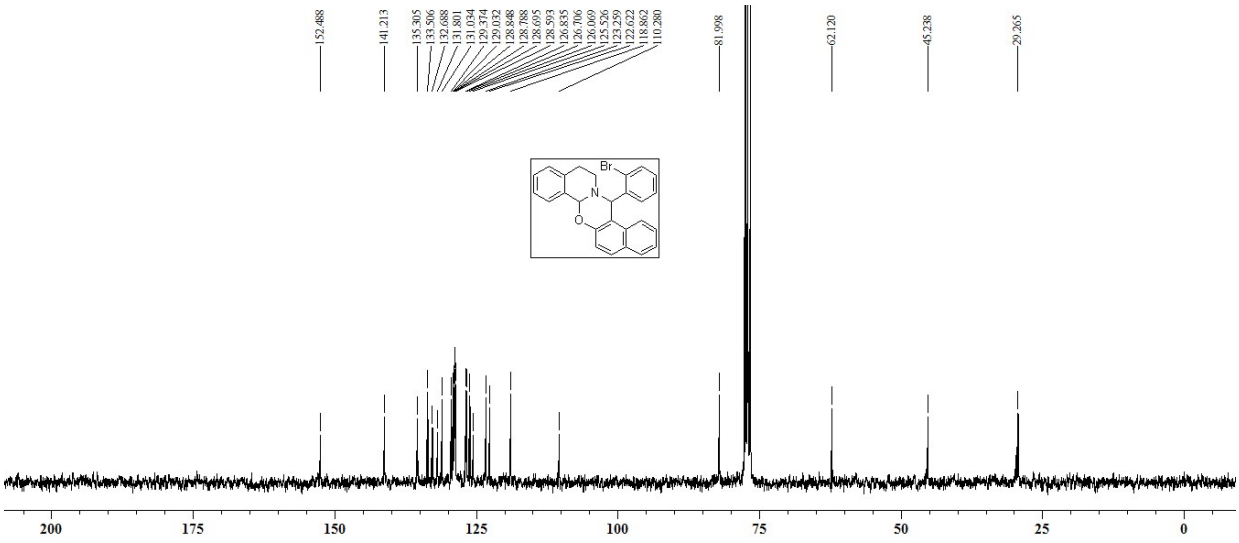
^{13}C NMR spectra of **4g**



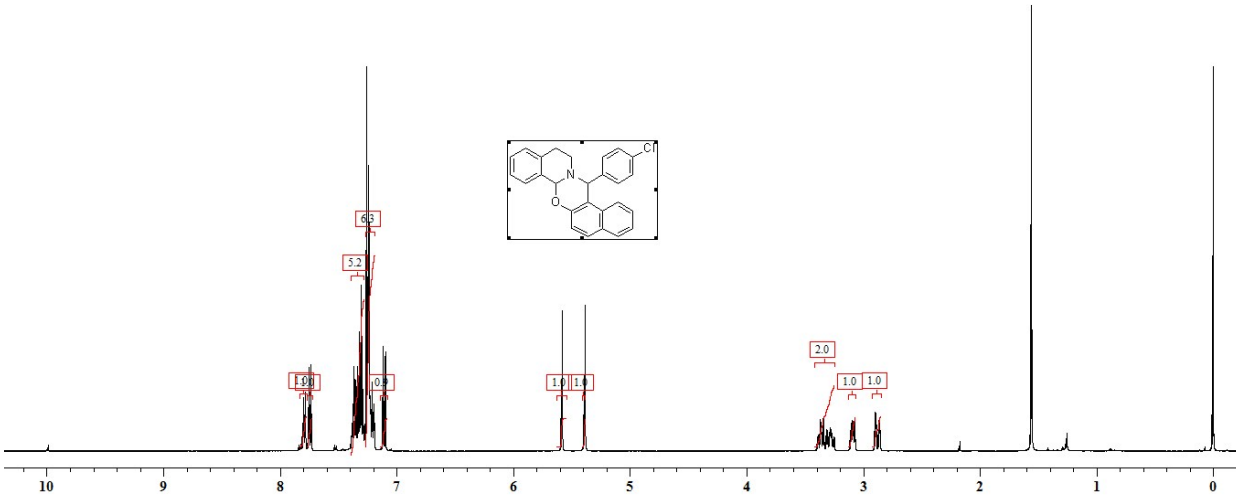
[1]H NMR spectra of **4h**



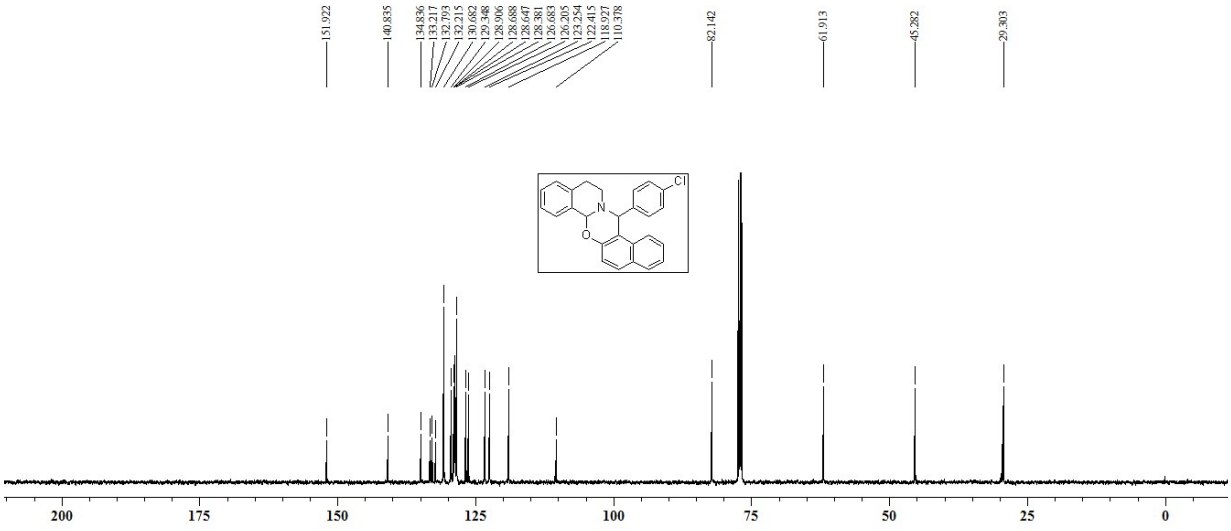
[13]C NMR spectra of **4h**



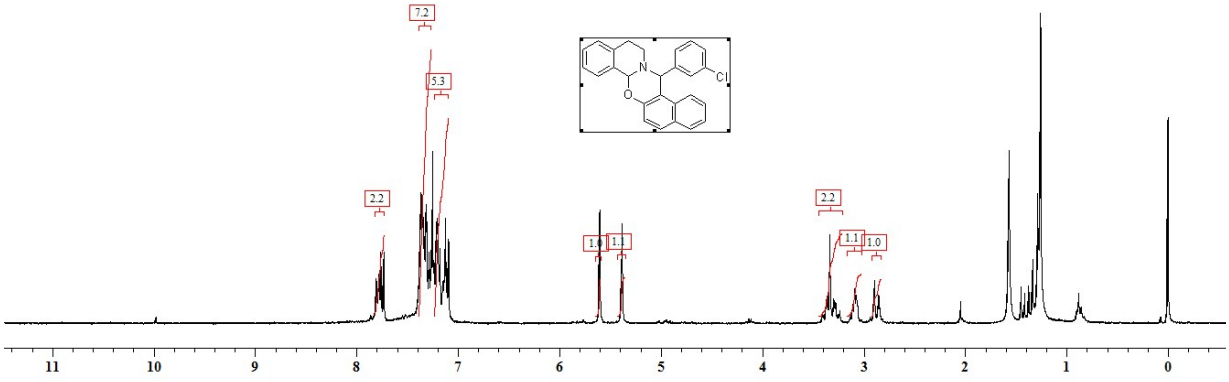
^{1}H NMR spectra of **4i**



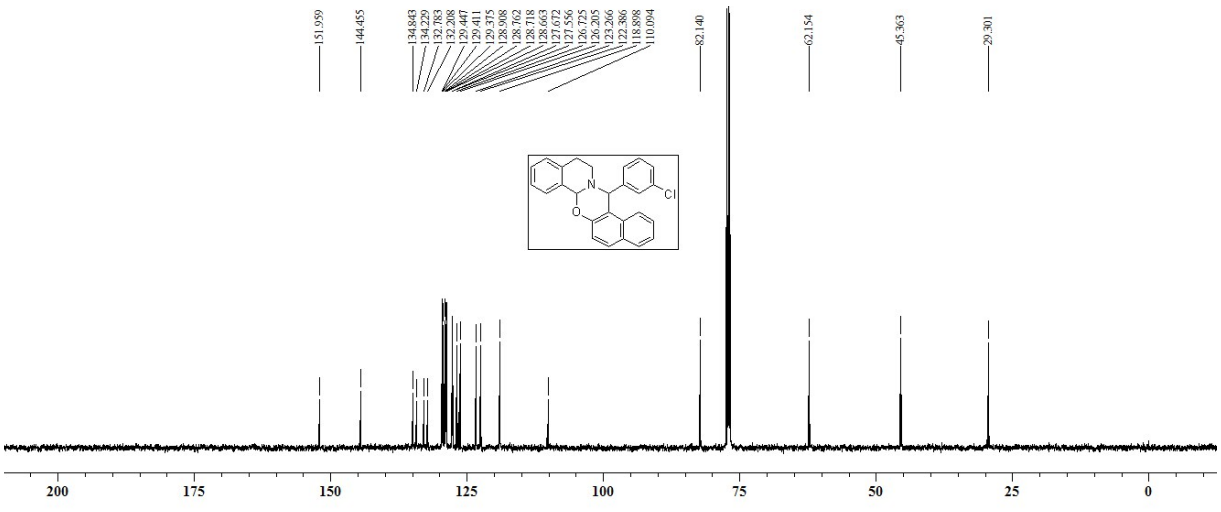
^{13}C NMR spectra of **4i**



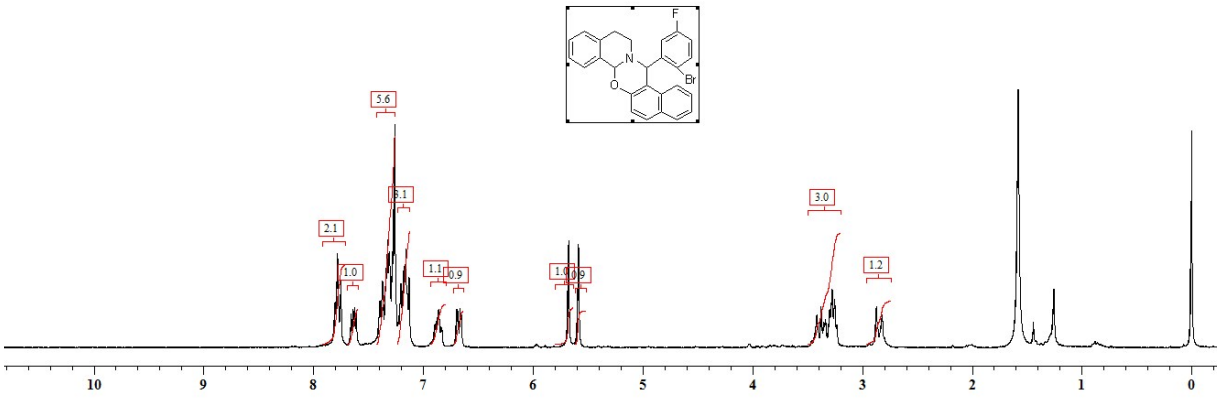
^{1}H NMR spectra of **4j**



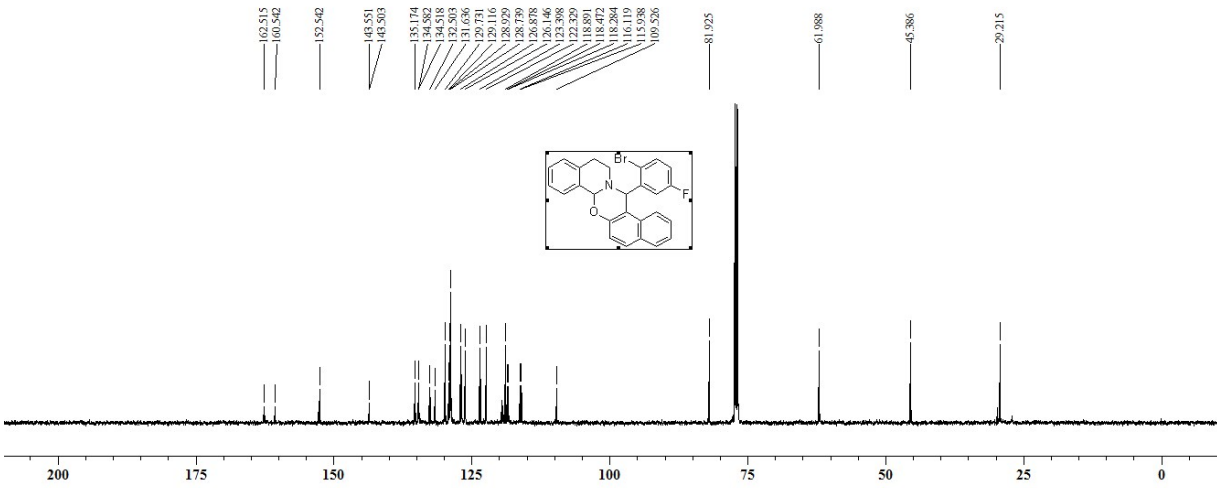
^{13}C NMR spectra of **4j**



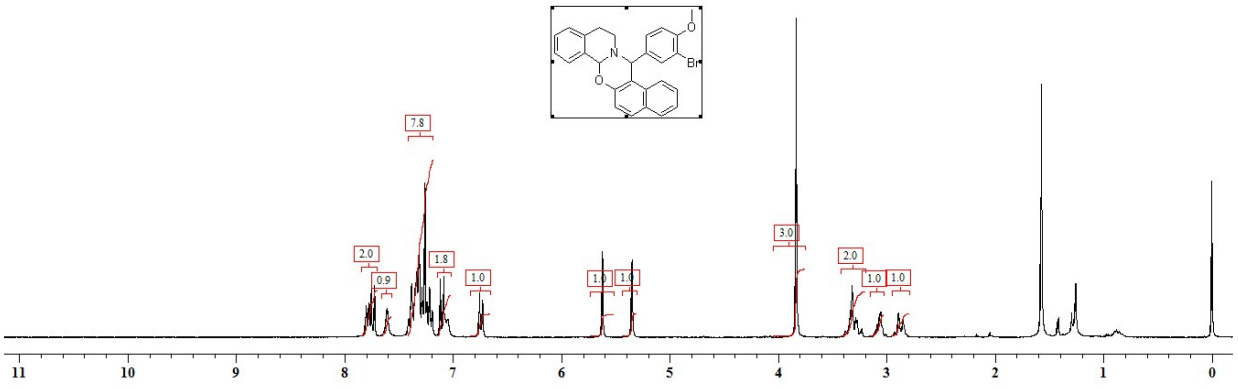
[1]H NMR spectra of **4k**



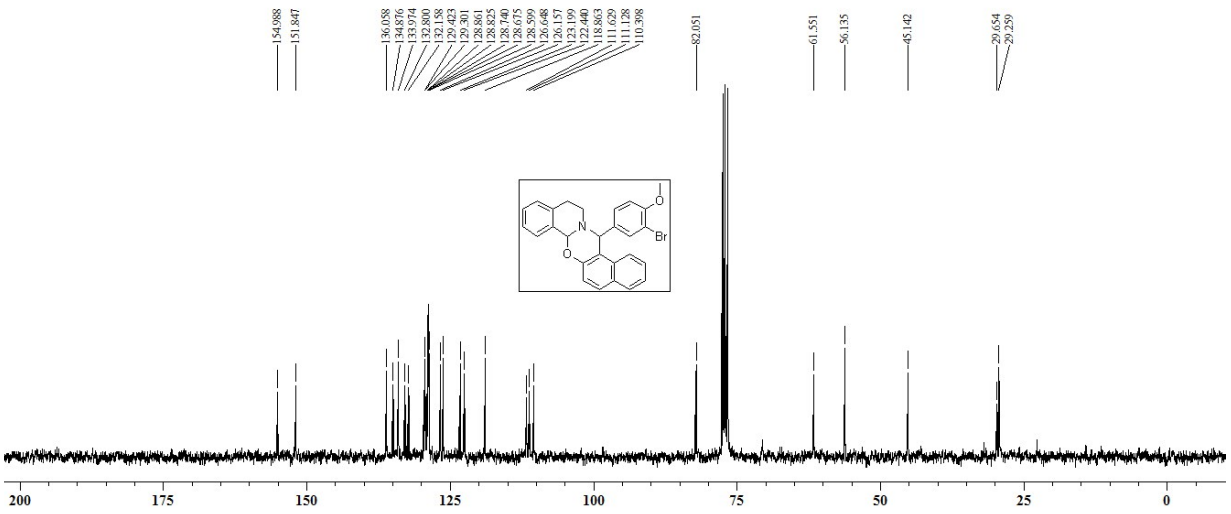
[13]C NMR spectra of **4k**



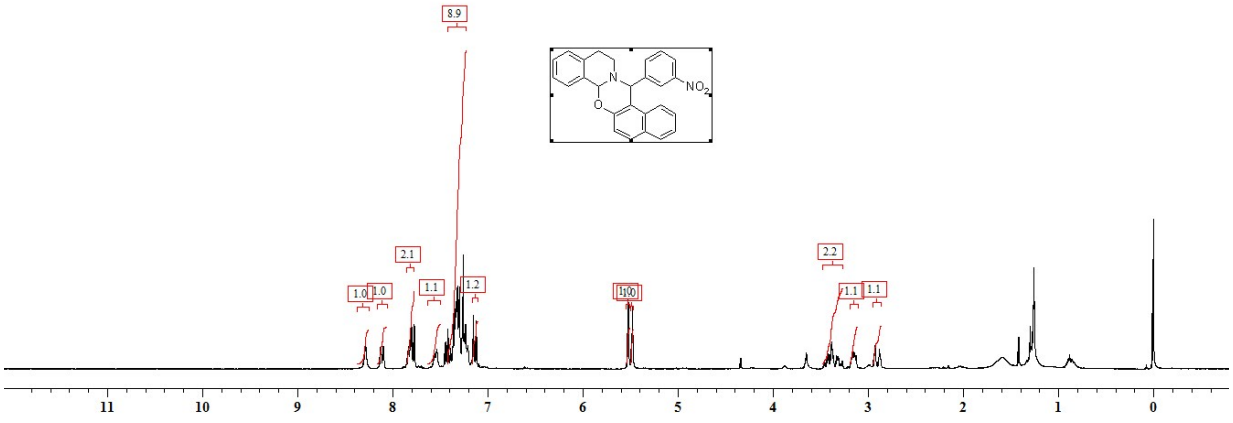
^{1}H NMR spectra of **4l**



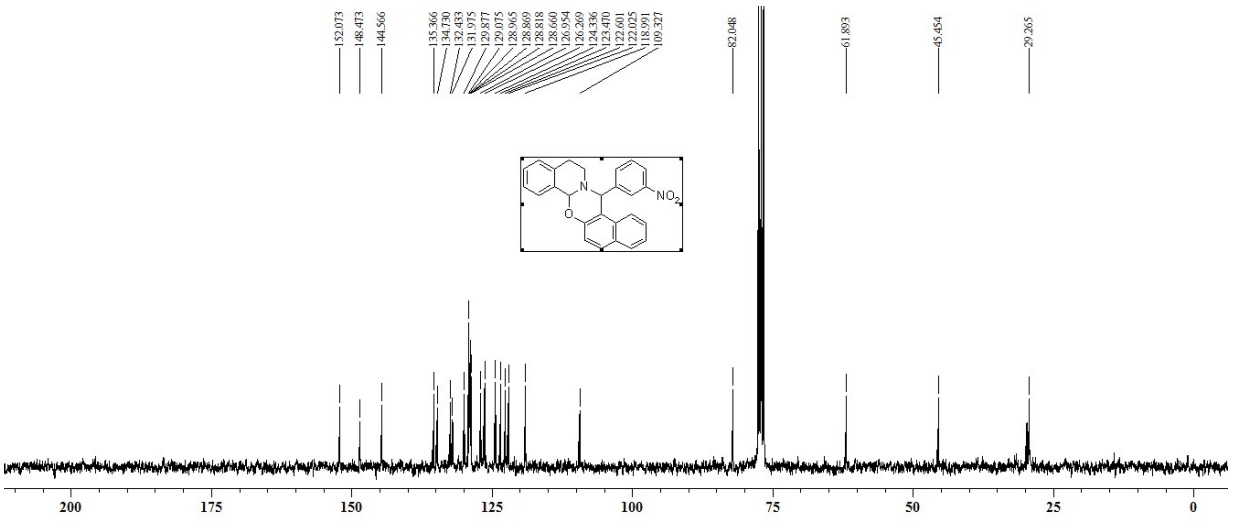
^{13}C NMR spectra of **4l**



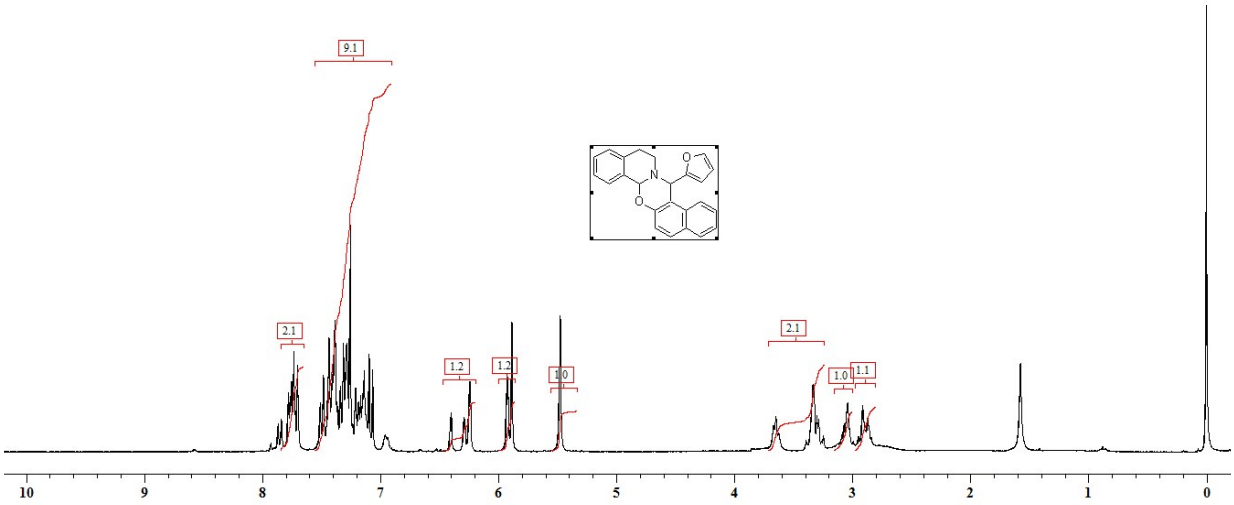
^{1}H NMR spectra of **4m**



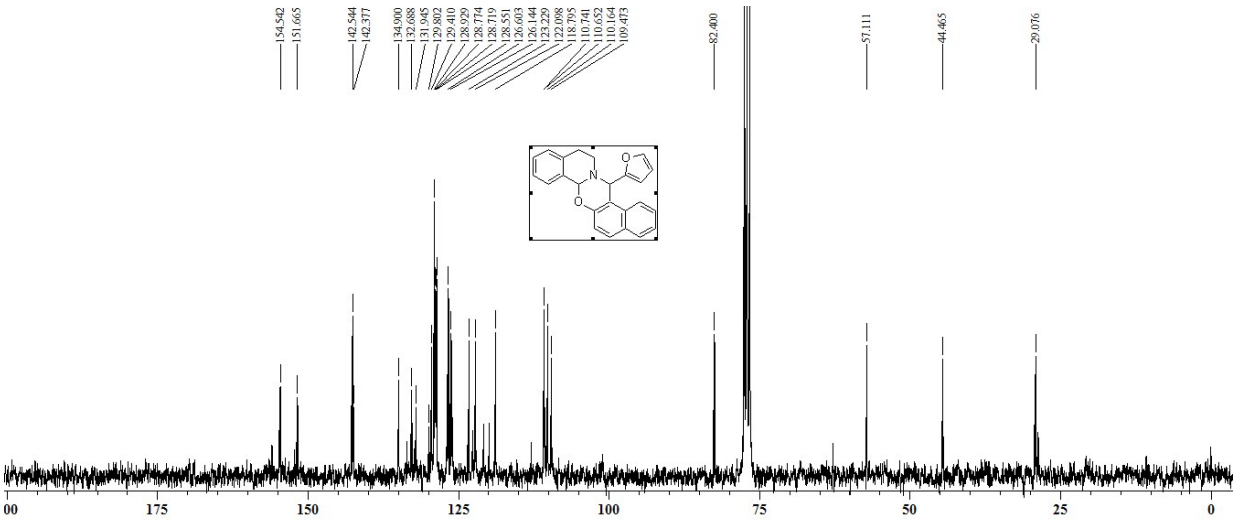
^{13}C NMR spectra of **4m**



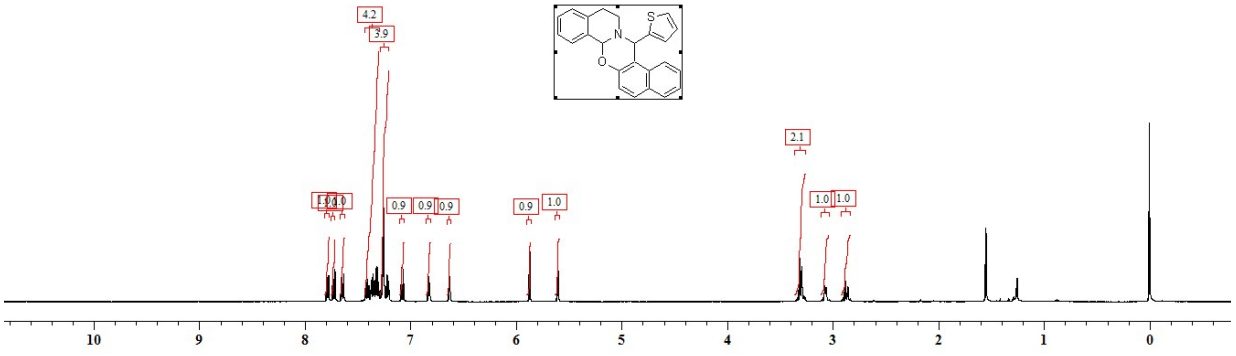
[1]H NMR spectra of **4n**



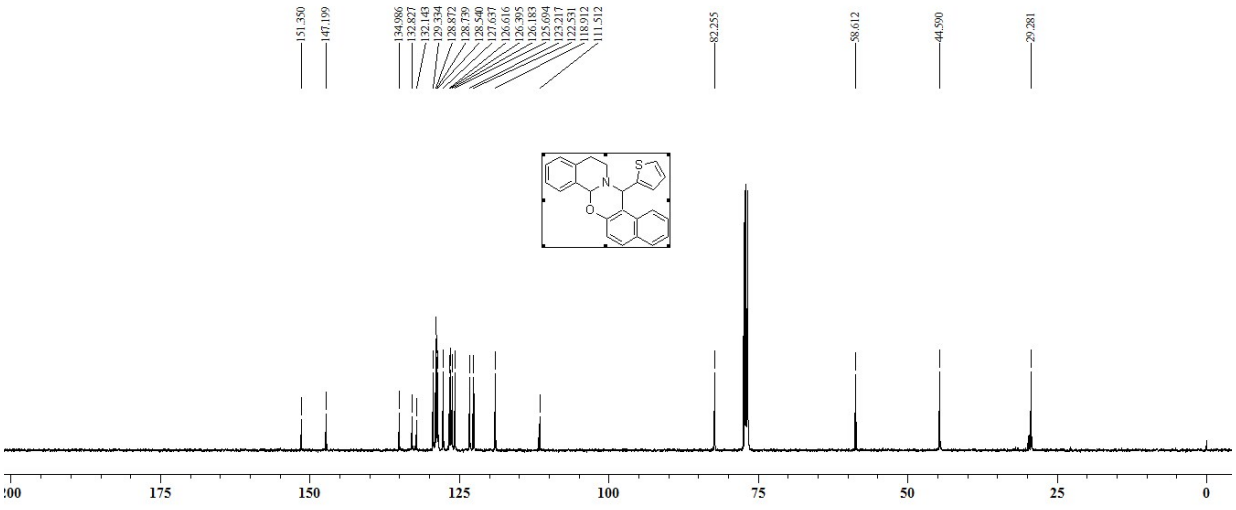
[13]C NMR spectra of **4n**



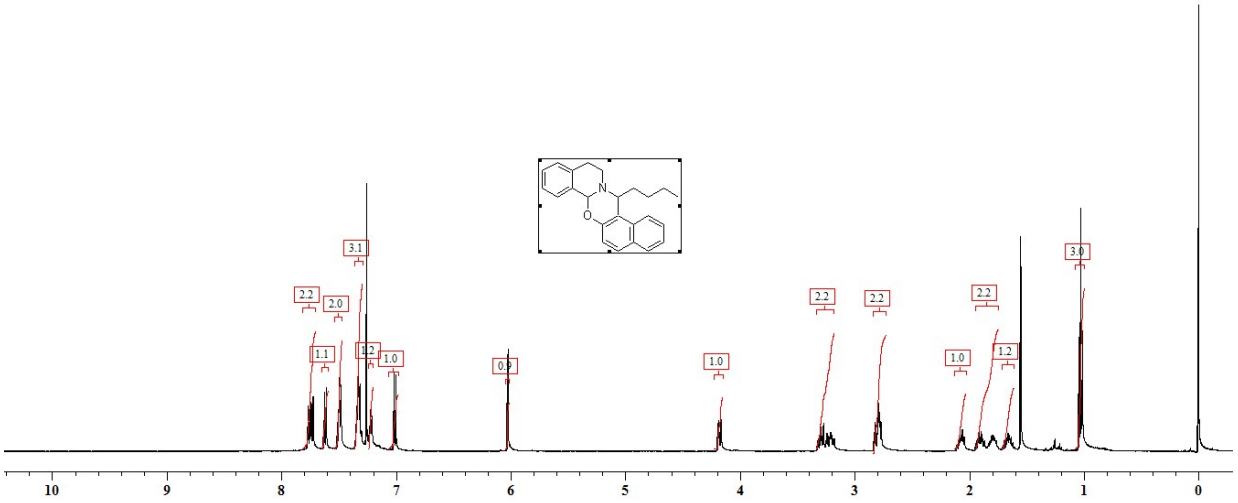
^{1}H NMR spectra of **4o**



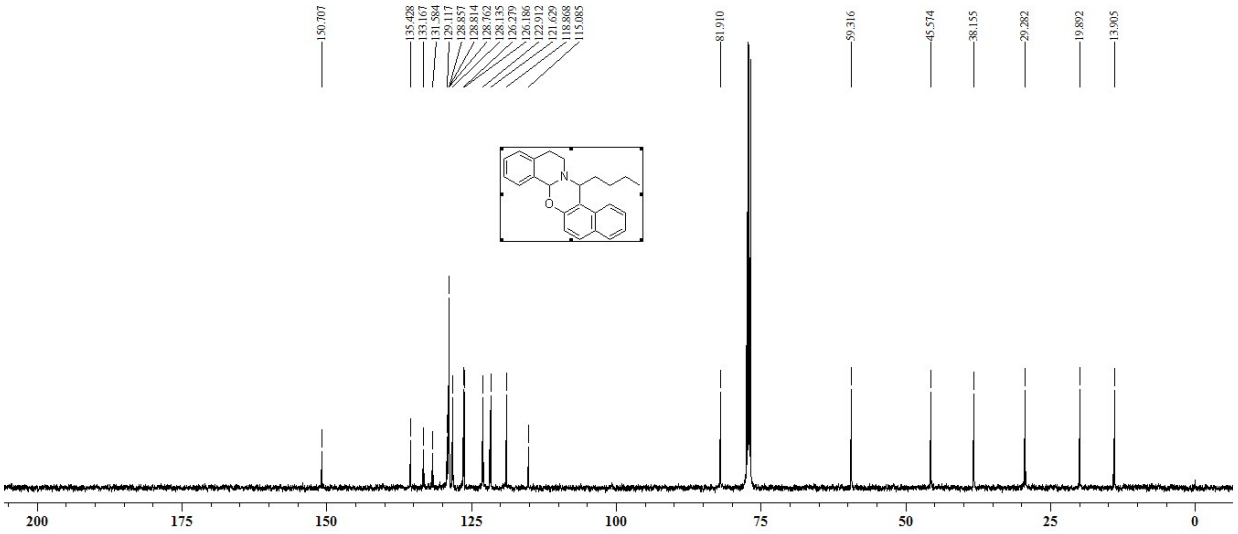
^{13}C NMR spectra of **4o**



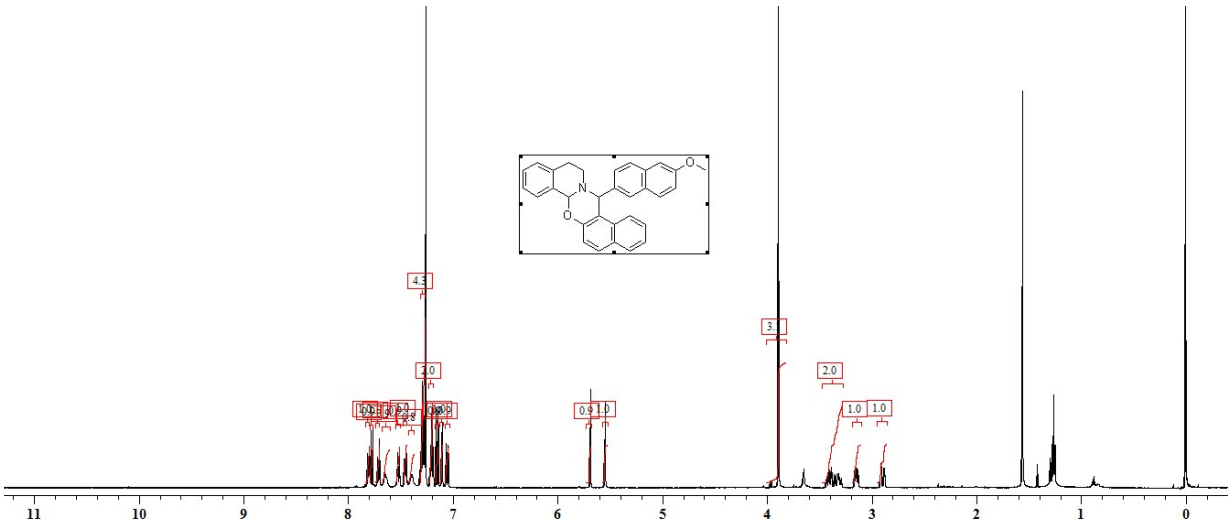
^{1}H NMR spectra of **4p**



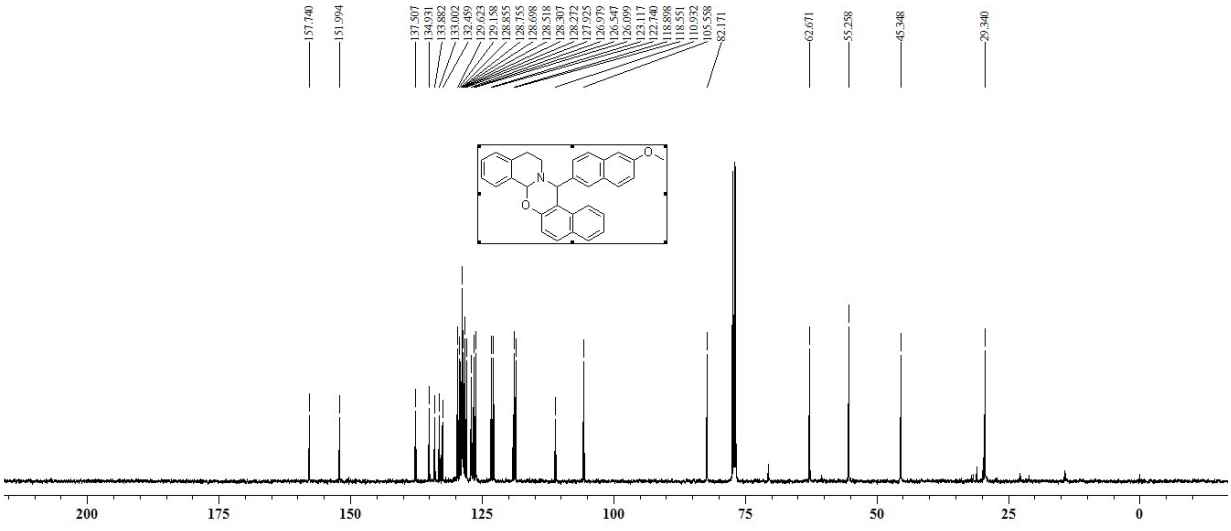
^{13}C NMR spectra of **4p**



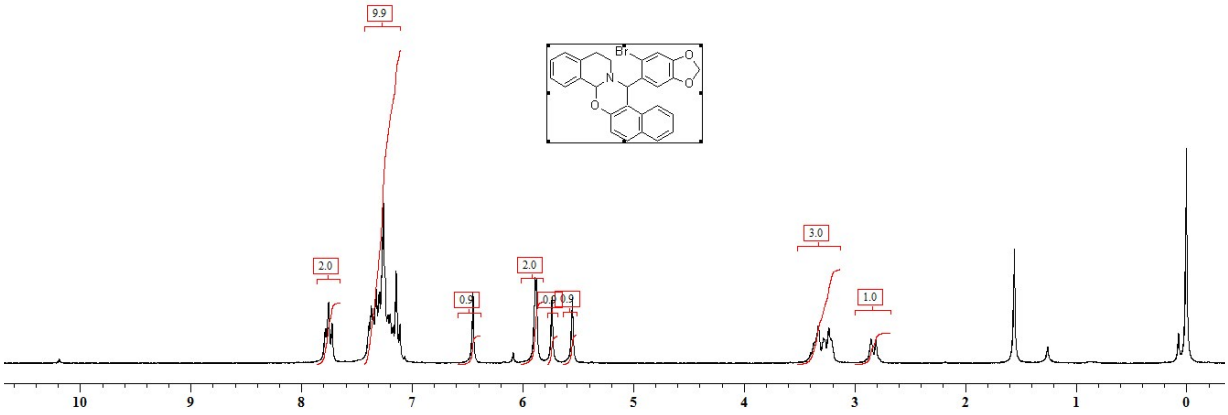
^{1}H NMR spectra of **4r**



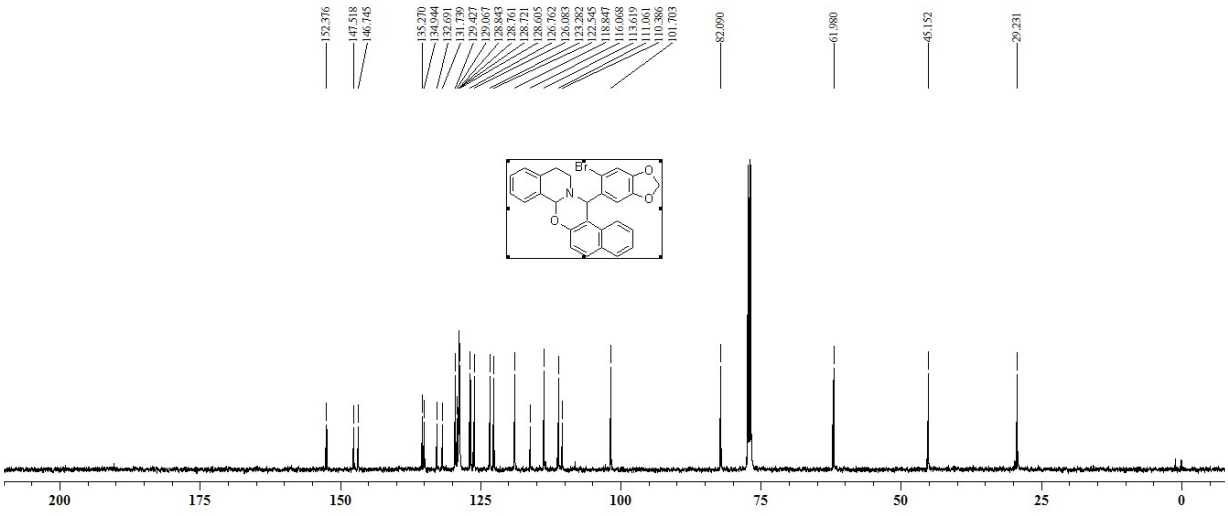
^{13}C NMR spectra of **4r**



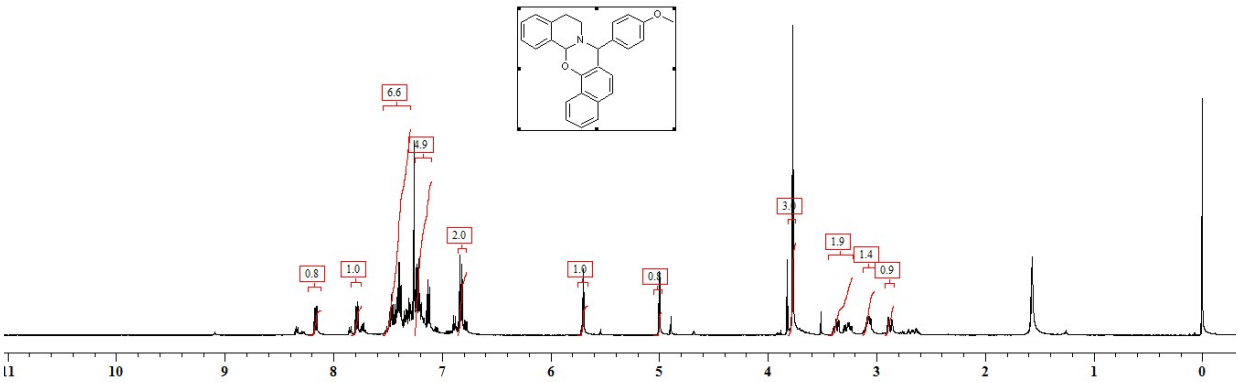
^{1}H NMR spectra of **4s**



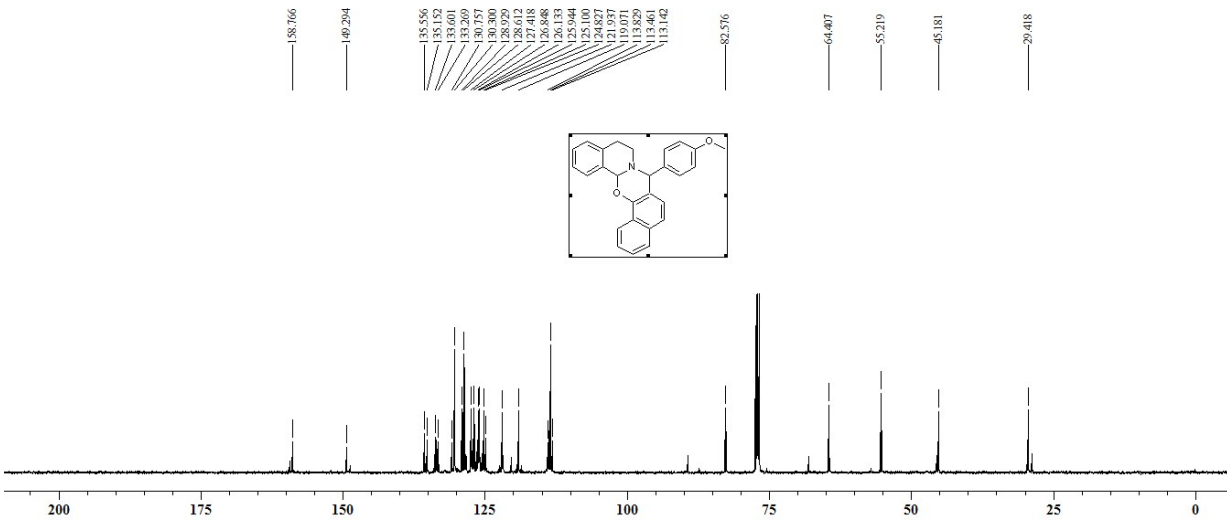
^{13}C NMR spectra of **4s**



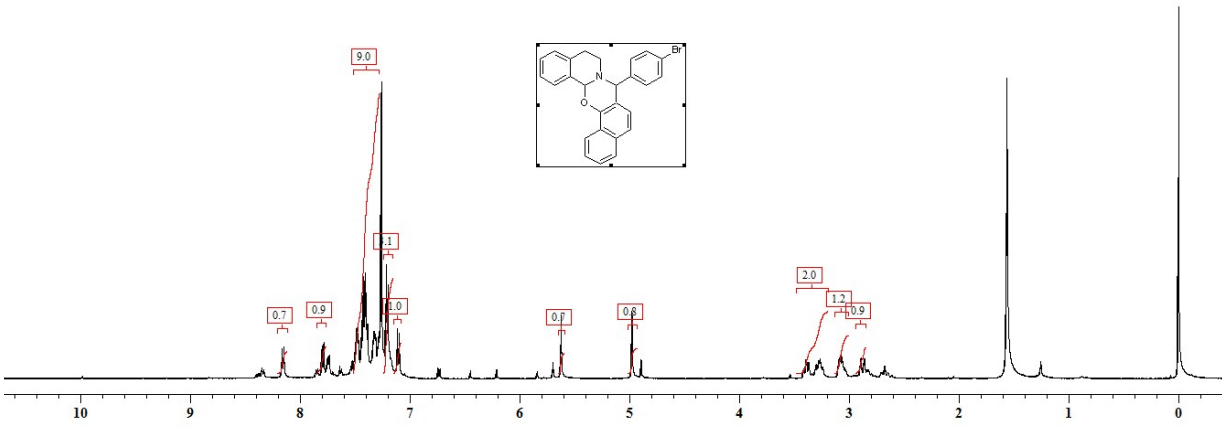
^{1}H NMR spectra of **6a**



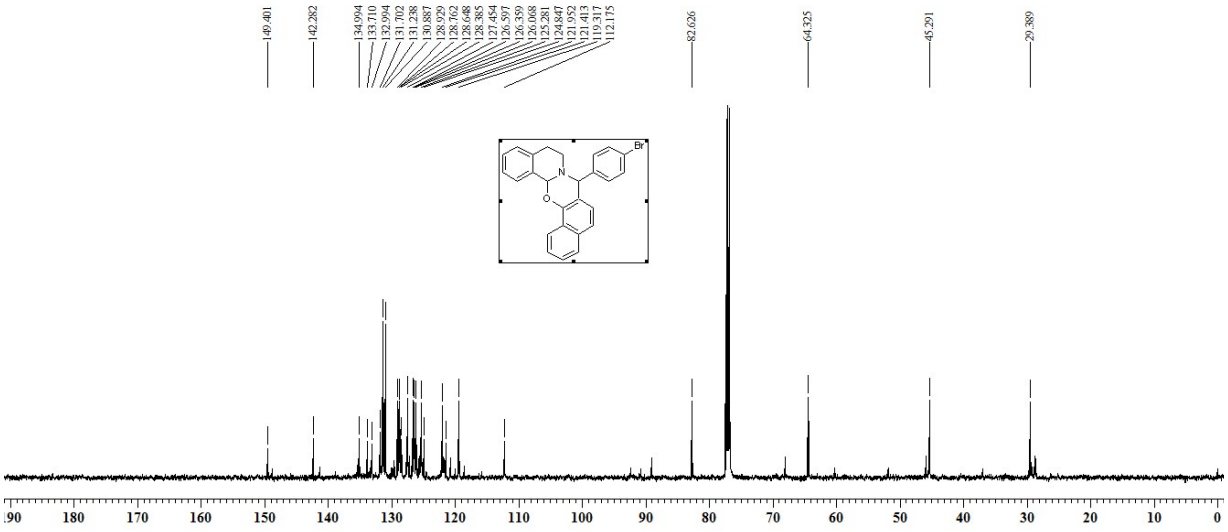
^{13}C NMR spectra of **6a**



[1]H NMR spectra of **6b**



[13]C NMR spectra of **6b**



^{1}H NMR spectra of **A**