Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Facile and highly atom-economic approach to biaryl-containing medium-ring bislactones

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Contents

General

Nuclear magnetic resonance spectra were recorded on a Bruker DPX 300 at 300MHz with $CDCl_3$ as solvent. Chemical shifts are reported in δ (ppm) with the solvent resonance as the internal standard (chloroform, H, 7.263 ppm; C, 77.66, 77.23, 76.81 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br s = broad), coupling constant in Hz, integration, and assignment. Mass spectra were recorded with a VG ZAB-HS spectrometer or a LCQ FLEET mass spectrometer (ESI). Elemental analyses were done on a Elementar Vario MICRO analyzer. Reagents: Benzene (AR grade) was dried with sodium and distilled. Acetonitrile (AR grade) was first refluxed with CaH_2 and distilled. Chloroform was also refluxed with CaH_2 and distilled. THF was dried with sodium and distilled.

Optimization for photoreaction

To make the **DOP** type [4+2] cycloadducts as the predominant product with high yields, solvent for the photo-induced reaction of **PQ** and bicyclopropylidene **1a** was optimized. As shown in Table 1, photoinduced reaction of **PQ** with **1a** in benzene gave the corresponding **DOP** type product **2a** with higher yield than the reaction in acetonitrile.

Table 1 Optimization on photocycloaddition conditions of **PQ** with **1a** leading to **DOP 2a**

Entry	Alkene	Solvents	**DOP** product and yields [a]
1	**1a**	PhH	**2a** (95%)
2		CH_3CN	**2a** (81%)

[a] Isolated yield after flash column chromatography.

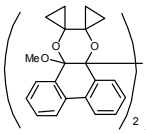
Photo-cycloaddition of 9, 10-phenanthrenedione (PQ) with strained alkenes 1a in anhydrous benzene. A solution of **PQ** (416 mg, 2 mmol) and **1a** (4 mmol) in anhydrous benzene (100 mL) was photolyzed by λ > 400 nm light and monitored by TLC to reach a complete conversion of **PQ**. Flash column chromatograph on 300-400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded pure analytic final **DOP** product **1a**.

2a, colorless oil; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.71 (d, *J* = 8.1 Hz, 2H), 8.27 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.75-7.63 (m, 4H), 1.36-1.31(m, 4H), 0.95-0.90(m, 4H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 134.7 (2C), 132.3 (2C), 126.8 (2C), 126.5 (2C), 125.0 (2C), 122.6 (2C), 120.8 (2C), 62.0 (2C), 11.0 (4C) ppm; MS m/z (% base): 236 (14), 194 (24), 181 (73), 152 (100), 68 (55); **EA** Found: C, 83.27; H, 5.43. Calc. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59%.

Photooxidation of 2a in anhydrous CH_3CN. A solution of **DOP 2a** (0.02M) in anhydrous acetonitrile was photolyzed by λ > 400 nm light and purged with dry O_2. The reactions were monitored by TLC to reach a complete conversion of the **DOP**. Flash column chromatograph on 300-400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded the bislactone products **3a**.

3a, white powder; m.p. 192-194˚C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.58-7.36 (m, 8H), 1.78-1.69 (m, 2H), 1.44-1.35 (m, 2H), 0.99-0.90 (m, 2H), 0.28-0.19 (m,2H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 170.0 (2C), 137.9 (2C), 133.7 (2C), 131.1 (2C), 131.0 (2C), 127.8 (2C), 126.2 (2C), 63.5 (2C), 14.2 (2C), 6.4 (2C) ppm; IR (KBr) ν_{max}/cm^{-1}: 1754, 1443, 1274, 1224, 1069, 756, 748; MS m/z (% base): 236 (2), 180 (100), 152 (55), 68 (16); **EA** Found: C, 75.05; H, 5.05. Calc. for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03%.

Photooxidation of 2a in anhydrous CH_3OH. A solution of **DOP 2a** (0.02M) in anhydrous CH_3OH was photolyzed by λ > 400 nm light and purged with dry O_2. The reactions were monitored by TLC to reach a complete conversion of the **DOP**. Flash column chromatograph on 300-400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded the major product **A** and the minor bislactone product **3a**.

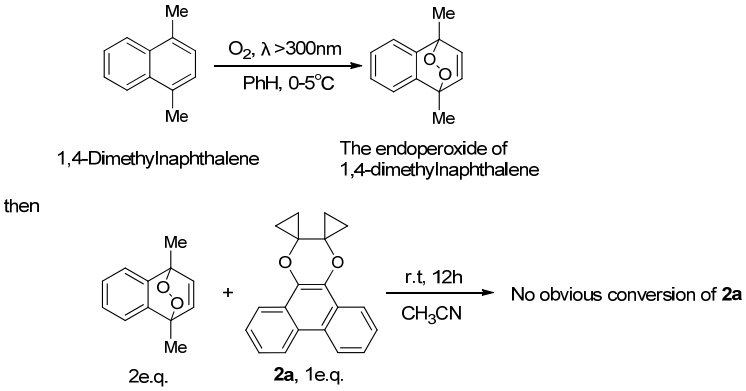


[2] **A**, white powder; m.p. 142-144˚C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.9 Hz, 4H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 7.6, 1.2 Hz, 2H), 7.39-7.32 (m, 6H), 7.29-7.23 (m, 4H), 2.79 (s, 6H), 1.46-1.38 (m, 2H), 1.09-0.76 (m, 10H), 0.16-0.07 (m, 4H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 132.9, 132.6, 132.5, 132.0, 129.2, 129.1, 127.4, 127.3, 126.6, 125.4, 124.1, 123.6, 102.0, 96.5, 77.4, 57.1, 56.9, 50.7, 13.4, 13.2, 6.3, 6.0 ppm; MS m/z (% base): 239 (100), 211 (23), 195 (91), 180 (77), 152 (47).

Investigations on active oxygen species for photooxidation step

TPP sensitized $^1O_2$ generation. A solution of **2a** (0.02M) and tetraphenylporphin (TPP, 0.002M) in anhydrous benzene was photolyzed and purged with dry O_2. The reaction was monitored by TLC and no obvious conversion of **2a** was observed extended the reaction time to 24h.

Thermal decomposition to provide $^1O_2$. A solution of 1,4-dimethylnaphthalene (0.02M) in anhydrous benzene was purged with dry O_2 and photolyzed by $\lambda > 400$ nm light at 0-5℃. The reaction was monitored by TLC to reach a complete conversion of 1,4-dimethylnaphthalene. There was only one major product and the reaction mixture was evaporated at 0-5℃ to get the product which was the endoperoxide of 1,4-dimethylnaphthalene and could release the pure $^1O_2$ at room temperature. Then dissolved the endoperoxide (0.04M) and **1a** (0.02M) in anhydrous CH_3CN and the solution was stirred at 25℃. The reaction was monitored by TLC and no obvious conversion of **2a** was observed extended the reaction time to 12h while the endoperoxide was converted to 1,4-dimethylnaphthalene.



Scheme 1 Thermal decomposition to provide $^1O_2$

Detection of the active oxygen species by ESR. The generation of the active oxygen species under photolysis was evaluated by electron spin resonance spectroscopy (ESR) analysis using 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) as spin-trapping agent. The results were shown in Figure 1.

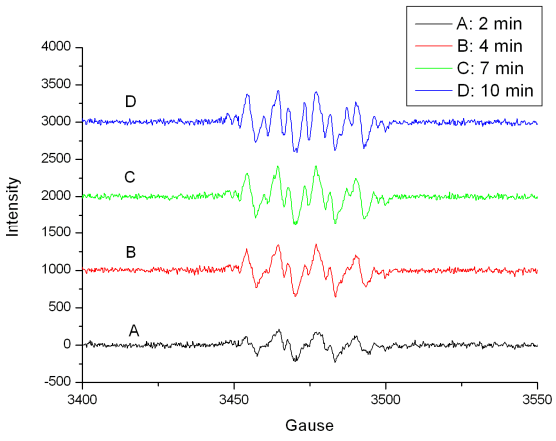


Figure S1. ESR spectrum using DMPO (200 mM) as the spin trapper were measured after photolysis of 2a in O_2-saturated acetonitrile for A, 2min; B, 4min; C, 7min and D, 10min. The sample was oxygen-saturated.

Quenching superoxide anion radical by BQ. A solution of **2a** (0.02M) and benzoquinone (BQ, 0.002M) in anhydrous acetonitrile was photolyzed and purged with dry O_2. The reaction was monitored by TLC and no obvious conversion of **2a** was observed extended the reaction time to 24h.

Detection of CTC complex of 2a by UV spectrum. The absorption changement from the substrate to the ground-state CT complex with molecular oxygen can be measured by direct recording the UV spectrum of oxygen-saturated and oxygen-free solutions of **2a**. The results were shown in Figure 2.

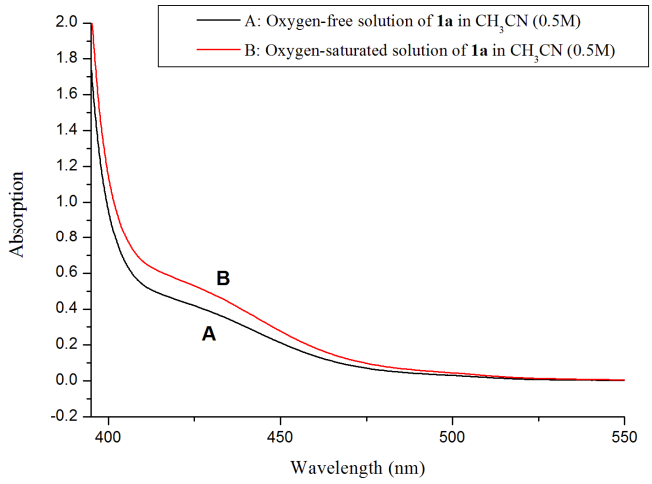


Figure 2. UV spectrum of CTC complex of **2a**.

Synthesis of DOP substrates

Photo-cycloaddition of 9, 10-phenanthrenedione (PQ) with alkenes in anhydrous benzene. A solution of **PQ** (416 mg, 2 mmol) and alkenes (4 mmol) in anhydrous benzene (100 mL) was photolyzed by $\lambda > 400$ nm light and monitored by TLC to reach a complete conversion of **PQ**. Flash column chromatograph on 300-400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded pure analytic final **DOP** products.

Photo-cycloaddition of 1,10-phenanthroline-5,6-dione (PN) with alkenes in anhydrous CH_3CN. A solution of **PN** (204mg, 1 mmol) and alkenes (2mmol) in anhydrous acetonitrile (50 mL) was photolyzed by $\lambda > 400$ nm light and monitored by TLC to reach a complete conversion of **PN**. Flash column chromatograph on 300-400 mesh silica gel with chloroform/methanol as eluents afforded pure analytic final **DOP** products.

2b, colorless oil; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.75 (dd, J = 7.9, 2.1 Hz, 2H), 8.51 (dd, J= 8.1, 0.9 Hz, 1H), 8.30 (dd, J = 8.1, 1.1 Hz, 1H), 7.84-7.65 (m, 4H), 2.65-2.54(m, 2H), 2.38-2.29(m, 2H), 2.20-2.09(m, 1H), 1.89-1.78(m, 1H), 1.36-1.31(m, 2H), 1.16-1.11(m, 2H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 134.1, 132.5, 126.9, 126.7 (2C), 126.5, 126.4, 125.0, 124.8, 122.6 (2C), 121.1, 120.7, 78.7, 61.8, 31.6 (2C), 13.0, 9.0 (2C) ppm; MS m/z (% base): 302 (4), 234 (100); **EA** Found: C, 83.40; H, 5.88. Calc. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00%.

2c, colorless oil; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.64-8.59 (m, 2H), 8.29 (dd, *J* = 8.1, 0.9 Hz, 1H), 8.05-8.02 (m, 1H), 7.66-7.49 (m, 4H), 2.08-2.04 (m, 2H), 1.94-1.79 (m, 3H), 1.68-1.63 (m, 2H), 1.39-1.24 (m, 3H), 1.09-0.96 (m, 4H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 127.2, 127.1, 126.8, 126.7, 125.0, 124.6, 122.7, 122.6, 121.1, 120.6, 76.1, 64.5, 30.9 (2C), 25.9, 21.5 (2C), 9.6 (2C) ppm; MS m/z (% base): 180 (92), 152 (100), 76 (42); **EA** Found: C, 83.70; H, 6.75. Calc. for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71%.

2d, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.62 (d, *J* = 7.8 Hz, 2H), 8.26 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.64-7.51 (m, 4H), 2.00-1.21 (m, 20H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 134.1, 132.5, 126.9, 126.7 (2C), 126.5, 126.4, 125.0, 124.8, 122.6 (2C), 121.1, 120.7, 78.7, 61.8, 31.6 (2C), 13.0, 9.0 (2C) ppm; MS m/z (% base): 208 (82), 180 (100), 152 (97), 104(24), 76 (31); **EA** Found: C, 83.78; H, 7.63. Calc. for $C_{26}H_{28}O_2$: C, 83.83; H, 7.58%.

4a, white powder; m.p. 164-166°C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.03 (d, *J* = 3.2 Hz, 2H), 8.35 (d, *J* = 8.1 Hz, 2H), 7.54 (dd, *J* = 8.0, 4.4 Hz, 2H), 1.21-1.15 (m, 4H), 0.83-0.78 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 148.4, 142.5, 133.8, 128.8, 123.2, 122.8, 62.5, 11.0 ppm; MS m/z (% base): 290 (100), 262 (24), 233 (16), 182 (16), 79 (17); **EA** Found: C, 74.55; H, 4.89; N, 9.50. Calc. for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65%.

4d, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.04 (dd, *J* = 4.3, 1.7 Hz, 2H), 8.54 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.60 (dd, *J* = 8.3, 4.4 Hz, 1H), 1.96-1.22 (m, 20H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 148.0, 142.5, 130.7, 128.7, 123.8, 122.9, 79.4, 25.9, 21.6 ppm; MS m/z (% base): 374 (57.1), 212 (100), 81 (37.8); **EA** Found: C, 77.03; H, 7.11; N, 7.29. Calc. for $C_{24}H_{26}N_2O_2$: C, 76.98; H, 7.00; N, 7.48%.

6, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.66-8.60 (m, 2H), 8.29-8.25 (m, 1H), 8.22-8.18 (m, 1H), 8.03 (d, *J* = 7.5 Hz, 2H), 7.69-7.50 (m, 5H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.05 (s, 1H), 4.74 (dd *J* = 11.5, 1.5 Hz, 1H), 4.49 (d, *J* = 11.6 Hz, 1H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 133.8, 130.3, 128.6, 127.1, 127.0, 125.7, 125.5, 122.7, 122.6, 121.2, 121.0, 88.2, 85.6, 32.2, 29.9, 29.6, 22.9, 14.3 ppm; **EA** Found: C, 77.48; H, 4.60. Calc. for $C_{23}H_{16}O_4$: C, 77.52; H, 4.53%.

8, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.66-8.61 (m, 2H), 8.29-8.23 (m, 2H), 7.70-7.56 (m, 4H), 5.49 (dd, *J* = 3.0, 1.7 Hz, 1H), 4.45 (dd, *J* = 11.0, 2.9 Hz, 1H), 4.36 (dd, *J* = 11.0, 1.8 Hz, 1H), 4.07-3.98 (m, 1H), 3.82-3.73 (m, 1H), 1.70-1.60 (m, 2H), 1.43-1.30 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 133.4, 130.8, 127.1, 126.9, 126.8, 126.5, 126.2, 125.2, 125.1, 122.7, 122.6, 121.2, 120.7, 69.1, 66.6, 31.7, 19.3, 13.9 ppm; **EA** Found: C, 78.03; H, 6.55. Calc. for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54%.

10, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.64-8.60 (m, 2H), 8.23-8.14 (m, 2H), 7.67-7.55 (m, 4H), 6.78 (t, 1H, *J* = 1.5 Hz), 4.59 (dd, 1H, *J* = 11.6, 1.9 Hz), 4.49 (dd, 1H, *J* = 11.7, 1.4 Hz), 2.11 (s, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.8, 133.3, 130.7, 127.1, 127.0, 126.9, 125.9, 125.6, 125.4, 122.7, 122.6, 121.0, 120.8, 87.5, 65.3, 21.1 ppm; **EA** Found: C, 73.55; H, 4.81. Calcd. for: $C_{18}H_{14}O_4$ C, 73.46; H, 4.79%.

Substrate **12** was prepared according to reported method.

Photooxidation of DOPs in anhydrous CH_3CN

A solution of **DOP** (0.02M) in anhydrous acetonitrile was photolyzed by λ > 400 nm light (used λ > 300 nm light for the photooxidation of substrate **4a** and **4d**) and purged with dry O_2. The reactions were monitored by TLC to reach a complete conversion of the **DOPs**. Flash column chromatograph on 300-400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded the bislactone products.

3b, white powder; m.p. 145-147˚C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.5 Hz, 1H), 7.58-7.35 (m, 7H), 3.10-2.99 (m, 1H), 2.79-2.69 (m, 1H), 2.63-2.51 (m, 1H), 2.05-1.57 (m, 4H), 1.54-1.45 (m, 1H), 1.18-1.09 (m, 1H), 1.03-0.91 (m, 1H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 170.9, 168.7, 138.8, 138.7, 134.0, 132.5, 131.4, 131.3, 130.9, 130.8, 127.7, 127.6, 127.3, 125.9, 87.1, 66.0, 33.0, 30.4, 15.6, 11.2, 6.1 ppm; IR (KBr) ν_{max}/cm^{-1}: 1742, 1727, 1478, 1279, 1233, 1125, 1063, 746; MS m/z (% base): 224 (1), 180 (100), 152 (60), 76 (5), 54 (11); **EA** Found: C, 75.44; H, 5.32. Calc. for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43%.

3c, white powder; m.p. 171-172˚C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.60-7.39 (m, 8H), 3.43-3.38 (d, *J* = 13.8 Hz, 1H), 1.99-1.94 (d, *J* = 12.9 Hz, 1H), 1.74-0.54(m, 12H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 170.3, 169.4, 138.5, 137.6, 135.3, 134.0, 130.8, 130.7, 130.6, 130.5, 127.7, 127.4, 126.5, 126.0, 89.9, 67.3, 33.2, 33.0, 25.1, 22.5, 22.1, 11.5, 8.2 ppm; IR (KBr) ν_{max}/cm^{-1}: 1743, 1726, 1445, 1288, 1234, 1125, 1070, 747; MS m/z (% base) 225 (1), 180 (100), 152 (26), 81 (20), 67 (19). **EA** Found: C, 76.13; H, 6.15. Calc. for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12%.

3d, white powder; m.p. 176-180˚C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.72-7.68 (dd, *J* = 7.5, 0.8 Hz, 2H), 7.56-7.50 (td, *J* = 7.5, 1.3 Hz, 2H), 7.45-7.36 (m, 4H), 2.76-2.71 (d, *J* = 13.1 Hz, 2H), 2.76-2.71 (d, *J* = 12.2 Hz, 2H), 1.77-1.18 (m, 16H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.5 (2C), 139.6 (2C), 134.6 (2C), 130.9 (4C), 127.4 (2C), 127.2 (2C), 94.5 (2C), 33.6 (2C), 31.1 (2C), 25.3 (2C), 23.0 (4C) ppm; IR (KBr) ν_{max}/cm^{-1}: 1732, 1450, 1275, 1236, 1074, 749; MS m/z (% base): 180 (100), 162 (28), 152 (14), 91 (59), 79 (71); **EA** Found: C, 77.24; H, 7.00. Calc. for $C_{26}H_{28}O_4$: C, 77.20; H, 6.98%.

5a, white powder; m.p. 254-256˚C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.93 (d, *J* = 3.6 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.41 (dd, *J* = 7.5, 4.8 Hz, 2H), 1.78-1.65 (m, 2H), 1.45-1.33 (m, 2H), 1.03-0.94 (m, 2H), 0.33-0.24 (m, 2H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.6, 153.6, 152.0, 134.4, 130.3, 123.0, 64.5, 14.1, 6.7 ppm; IR (KBr) ν_{max}/cm^{-1}: 1759, 1741, 1417, 1278, 1236, 1131, 1079, 768; MS m/z (% base): 322 (0.14, M^+), 266 (2), 210 (48), 182 (100), 154 (65), 127 (31); **EA** Found: C, 67.09; H, 4.27; N, 8.74. Calc. for $C_{18}H_{14}N_2O_4$: C, 67.07; H, 4.38; N, 8.69%.

5d, white powder; m.p. 180-183˚C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.90 (dd, *J* = 4.8, 1.4 Hz, 2H), 8.13 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.40 (dd, *J* = 7.8, 4.8 Hz, 2H), 2.44-2.34 (m, 4H), 1.72-1.14 (m, 16H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.9, 155.0, 151.7, 136.2, 130.0, 123.0, 96.3, 32.8, 31.1, 25.0, 22.7, 22.3 ppm; IR (KBr) ν_{max}/cm^{-1}: 1730, 1557, 1416, 1305, 1274, 1080, 763; MS m/z (% base): 210 (13), 182 (100), 162 (42), 154 (32), 91 (74), 79 (73); **EA** Found: C, 71.11; H, 6.58; N, 6.69. Calc. for $C_{24}H_{26}N_2O_4$: C, 70.92; H, 6.45; N, 6.89%.

7, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$) of the predominant diastereoisomer: δ 8.14 (d, *J* = 7.5 Hz, 2H), 7.68-7.38 (m, 12H), 5.46 (t, *J* = 10.1 Hz, 1H), 4.30 (dd, *J* = 11.1, 2.7 Hz, 1H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.2, 166.8, 163.9, 137.4, 137.2, 134.4, 134.3, 133.3, 133.2, 133.1, 132.9, 132.3, 131.7, 131.5, 131.2, 131.1, 130.4, 128.8, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 126.6, 126.3, 126.2,

90.8, 89.8, 64.7, 64.4 ppm; IR (KBr) ν_{max}/cm^{-1}: 1754, 1733, 1438, 1235, 1015, 750, 707; MS m/z (% base): 180 (70), 152 (8), 105 (100), 77 (15); **EA** Found: C, 71.05; H, 4.40. Calc. for $C_{23}H_{16}O_6$: C, 71.13; H, 4.15%.

9, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$) of the predominant diastereoisomer: δ 7.59-7.39 (m, 8H), 6.29 (dd, *J* = 8.8, 2.7 Hz, 1H), 5.16 (t, *J* = 10.0 Hz, 1H), 4.12 (dd, *J* = 11.2, 2.5 Hz, 1H), 3.96-3.87 (m, 1H), 3.75-3.67 (m, 1H), 1.72-1.62 (m, 2H), 1.50-1.42 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.3, 169.0, 137.5, 137.0, 133.9, 133.4, 133.3, 133.0, 132.6, 131.5, 131.3, 131.2, 130.9, 130.8, 128.0, 127.8, 127.7, 127.4, 126.2, 126.0, 99.6, 98.9, 70.4, 70.3, 67.6, 65.7, 31.5, 31.4, 19.2, 19.1, 13.9 ppm; IR (KBr) ν_{max}/cm^{-1}: 1755, 1733, 1438, 1257, 1235, 1014, 751, 707; MS m/z (% base): 196 (100), 180 (58), 168 (43), 152 (18), 139 (43); **EA** Found: C, 70.66; H, 6.05. Calc. for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92%.

11, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$) of the predominant diastereoisomer: δ 7.57-7.40 (m, 8H), 7.27 (dd, 1H, *J* = 9.2, 2.9 Hz), 5.26 (dd, 1H, *J* = 11.1, 9.4 Hz), 4.15 (dd, 1H, *J* = 11.0, 2.8 Hz), 2.20 (s, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.2, 168.3, 166.8, 137.4, 137.3, 133.3, 133.2, 132.9, 132.3, 131.7, 131.5, 131.3, 131.1, 130.9, 130.6, 128.2, 127.9, 127.8, 127.7, 126.7, 126.3, 126.1, 90.3, 89.3, 64.5, 64.3, 20.8, 20.7 ppm; IR (KBr) cm^{-1}: 1758, 1277, 1204, 1024, 755; MS m/z (% base); **EA** Found: C, 66.29; H, 4.19. Calcd. for: $C_{18}H_{14}O_6$ C, 66.26; H, 4.32%.

13, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.73 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.60 (tt, *J* = 7.6, 1.6 Hz, 2H), 7.47 (tt, *J* = 7.6, 1.2 Hz, 2H), 7.38-7.32 (m, 2H), 5.89 (q, *J* = 5.7 Hz, 1H), 1.72 (d, *J* = 5.9 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.0, 167.9, 140.6, 140.5, 132.7, 132.4, 132.3, 131.7, 129.9, 129.2, 129.1, 127.9, 127.8, 127.7, 98.2, 29.8, 20.7 ppm; MS m/z (% base): 224 (3), 180 (100), 152 (37), 76 (2); **EA** Found: C, 71.56; H, 4.61. Calc. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51%.

Substrate **14** was also prepared according to reported method, but only PQ obtained for **14** under photooxidation.

Sequential photocycloadditions and photooxidations of PQ or PN with aryl substituted alkenes

One-pot photoreaction of PQ with styrene. A solution of **PQ** (416 mg, 2 mmol) and styrene (4 mmol) in anhydrous acetonitrile (100 mL) was photolyzed by λ > 400 nm light and purged with dry O_2. The reactions were monitored by TLC to reach a complete conversion of **PQ** and **DOP** product. Flash column chromatograph on 300-400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded the bislactone with a yield of 67%.

Sequential photocycloadditions and photooxidations of PQ or PN with aryl substituted alkenes. A solution of **PQ** (416 mg, 2 mmol) and aryl substituted alkenes (4 mmol) in 100 mL anhydrous benzene (**PN** (420 mg, 2 mmol) and **1e** (4 mmol) in 100 mL anhydrous acetonitrile) was photolyzed by λ > 400 nm light and monitored by TLC to reach a complete conversion of **PQ** (or **PN**). Then evaporation to remove benzene and the residue were dissolved by 100 mL anhydrous CH_3CN. The solution was photolyzed and purged with dry O_2. The reactions were monitored by TLC to reach a complete conversion of **DOP** products. Flash column chromatograph on 300-400 mesh silica gel with

petroleum ether/ethyl acetate as eluents afforded the bislactone products as a mixture of diastereoisomers.

3e, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$) of the predominant diastereoisomer: δ 7.66-7.33 (m, 13H), 6.48 (dd, *J* = 10.7, 2.9 Hz, 1H), 5.33 (t, *J* = 11.1 Hz, 1H), 4.14 (dd, *J* = 12.5, 3.0 Hz, 1H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.5, 169.0, 137.4, 137.3, 133.8, 133.7, 131.3, 131.2, 130.9, 129.3, 129.1, 127.8, 127.3, 126.8, 126.4, 126.2, 77.2, 69.1 ppm; IR (KBr) ν_{max}/cm^{-1}: 1742, 1599, 1280, 1238, 1128, 754; MS m/z (% base): 238 (35), 180 (100), 152 (49), 91 (4), 76 (4); **EA** Found: C, 76.70; H, 4.66. Calc. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68%.

5e, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$) of the predominant diastereoisomer: δ 8.97 (s, 2H), 7.86-7.83 (m, 2H), 7.58-7.40 (m, 7H), 6.50 (d, *J* = 9.5 Hz, 1H), 5.37 (t, *J* = 11.1 Hz, 1H), 4.19 (d, *J* = 10.6 Hz, 1H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.9, 167.5, 155.6, 152.9, 152.8, 151.9, 134.3, 134.2, 133.2, 133.1, 130.2, 130.1, 129.7, 129.2 (2C), 128.4, 127.3, 123.1, 77.9, 69.3 ppm; IR (KBr) ν_{max}/cm^{-1}: 1754, 1741, 1562, 1413, 1271, 1235, 1082, 769, 704; MS m/z (% base): 240 (16), 210 (56), 182 (100), 154 (55), 127 (26); **EA** Found: C, 69.32; H, 4.18; N, 7.94. Calc. for $C_{20}H_{14}N_2O_4$: C, 69.36; H, 4.07; N, 8.09%.

3f, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$) of the predominant diastereoisomer: δ 7.66-7.39 (m, 10H), 7.00-6.94 (m, 2H), 6.42 (dd, *J* = 10.7, 2.9 Hz, 1H), 5.32 (t, *J* = 11.6 Hz, 1H), 4.09 (dd, *J* = 11.5, 3.1 Hz, 1H), 3.85 (s, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.5, 169.0, 160.4, 137.4, 137.2, 133.8, 133.7, 131.3, 131.1, 130.9, 130.8, 128.8, 128.4, 127.8, 126.4, 126.2, 125.7, 114.4, 77.0, 69.0, 55.5 ppm; IR (KBr) ν_{max}/cm^{-1}: 1742, 1516, 1276, 1237, 1133, 752; MS m/z (% base): 180 (100), 152 (55), 135 (23), 121 (15); **EA** Found: C, 73.77; H, 4.63. Calc. for $C_{23}H_{18}O_5$: C, 73.79; H, 4.85%.

3g, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$) of the predominant diastereoisomer: δ 7.80-7.20 (m, 12H), 6.82 (d, *J* = 9.4 Hz, 1H), 5.14 (t, *J* = 10.7 Hz, 1H), 4.33 (d, *J* = 10.6 Hz, 1H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.7, 168.4, 137.5, 137.4, 133.7, 133.6, 133.3, 131.4, 131.3, 131.1, 131.0, 130.6, 128.8, 128.3, 128.0, 127.9, 126.3, 126.2, 122.5, 76.3, 67.6 ppm; IR (KBr) ν_{max}/cm^{-1}: 1746, 1476, 1274, 1232, 1068, 748; MS m/z (% base): 224 (4), 180 (100), 152 (76), 76 (3); **EA** Found: C, 62.39; H, 3.62; Br, 18.77. Calc. for $C_{22}H_{15}BrO_4$: C, 62.43; H, 3.57; Br, 18.88%.

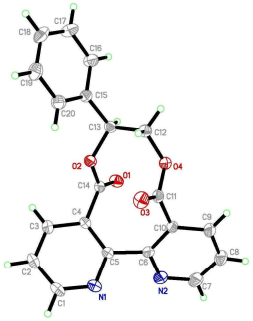
3h, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$) of the predominant diastereoisomer: δ 8.67 (br s, 2H), 7.62-7.34 (m, 10H), 6.47 (dd, *J* = 10.5, 2.3 Hz, 1H), 5.22 (t, *J* = 12.2 Hz, 1H), 4.15 (dd, *J* = 11.5, 2.7 Hz, 1H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.2, 168.5, 150.4, 142.6, 137.2, 133.3, 133.1, 131.2, 131.1, 131.0, 127.9, 126.2, 126.1, 121.5, 75.4, 68.2 ppm; IR (KBr) ν_{max}/cm^{-1}: 1745, 1440, 1285 1240, 1133, 753; MS m/z (% base): 315 (2), 238 (5), 208 (72), 180 (68), 152 (100), 76 (14); **EA** Found: C, 72.97; H, 4.44; N, 4.09. Calc. for $C_{21}H_{15}NO_4$: C, 73.03; H, 4.38; N, 4.06%.

3i, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.3 Hz, 1H), 7.63-7.26 (m, 17H), 5.48 (d, *J* = 12.3 Hz, 1H), 4.95 (d, *J* = 12.5 Hz, 1H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 170.0, 167.1, 142.0, 141.1, 138.3, 138.2, 133.9, 133.4, 131.3, 131.0, 130.9, 130.8, 128.5, 128.3, 127.9, 127.8, 127.6, 126.9, 126.5, 125.9, 89.5, 69.7 ppm; IR (KBr) ν_{max}/cm^{-1}: 1732, 1721, 1451, 1278, 1269, 1135, 758, 700; MS m/z (% base): 196 (5), 180 (100), 167 (96), 152 (64), 76 (4); **EA** Found: C, 80.06; H, 4.75. Calc. for $C_{28}H_{20}O_4$: C, 79.98; H, 4.79%.

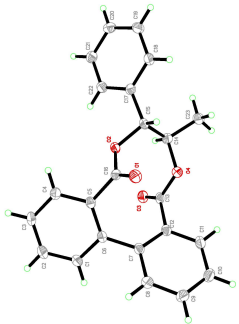
3j, white powder; **^{1}H NMR** (300 MHz, $CDCl_3$) of the predominant diastereoisomer: δ 7.65-7.33 (m, 13H), 6.06 (d, *J* = 9.3 Hz, 1H), 5.64-5.53 (m, 1H), 1.27 (d, *J* = 6.3 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.7, 169.0, 137.3, 137.2, 134.7, 134.2, 133.9, 131.3, 131.2, 130.8, 130.7, 129.5, 129.1, 128.3, 127.9, 127.8, 126.4, 126.3, 82.1, 76.0, 15.8 ppm; IR (KBr) ν_{max}/cm^{-1}: 1754, 1734, 1445, 1275, 1234, 1121, 1062, 746; MS m/z (% base): 208 (100), 180 (15), 152 (75), 76 (10); **EA** Found: C, 76.91; H, 4.96. Calc. for: $C_{23}H_{18}O_4$: C, 77.08; H, 5.06%.

3l, white powder; all the characterization data below are of the mixture of diastereoisomers; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.16 (d, *J* = 7.2 Hz, 1H), 7.70-7.32 (m, 15H), 6.43 (d, *J* = 1.9 Hz, 1H), 6.03 (d, *J* = 3.7 Hz, 1H), 5.63 (t, *J* = 9.6 Hz, 1H), 5.26-5.07 (m, 5H), 4.46-4.09 (m, 6H), 2.12 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.86 (s, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ 170.8, 170.7, 169.8 (2C), 169.5 (2C), 168.3, 168.2, 166.3, 166.0, 140.8, 140.4, 139.7, 137.4, 134.0, 133.8, 133.1, 132.7, 132.5, 132.4, 132.2, 131.7, 131.6, 131.0, 130.7, 130.4, 128.4, 128.3, 128.0 (2C), 126.8, 126.5, 125.9, 125.1 97.2, 95.0, 73.8, 72.3, 71.2, 70.9, 70.1, 69.2, 67.6, 67.4, 61.6, 61.3, 20.9, 20.8 (2C), 20.7, 20.6 (2C) ppm; IR (KBr) ν_{max}/cm^{-1}: 1752, 1370, 1285, 1226, 1017; MS m/z (% base): 224 (0.5), 180 (100), 152 (31), 43 (85); **EA** Found: C, 60.74; H, 4.80. Calc. for $C_{26}H_{24}O_{11}$: C, 60.94; H, 4.72%.

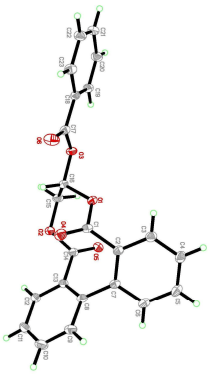
Crystal structure of compound 5e:



Crystal structure of compound 3j:

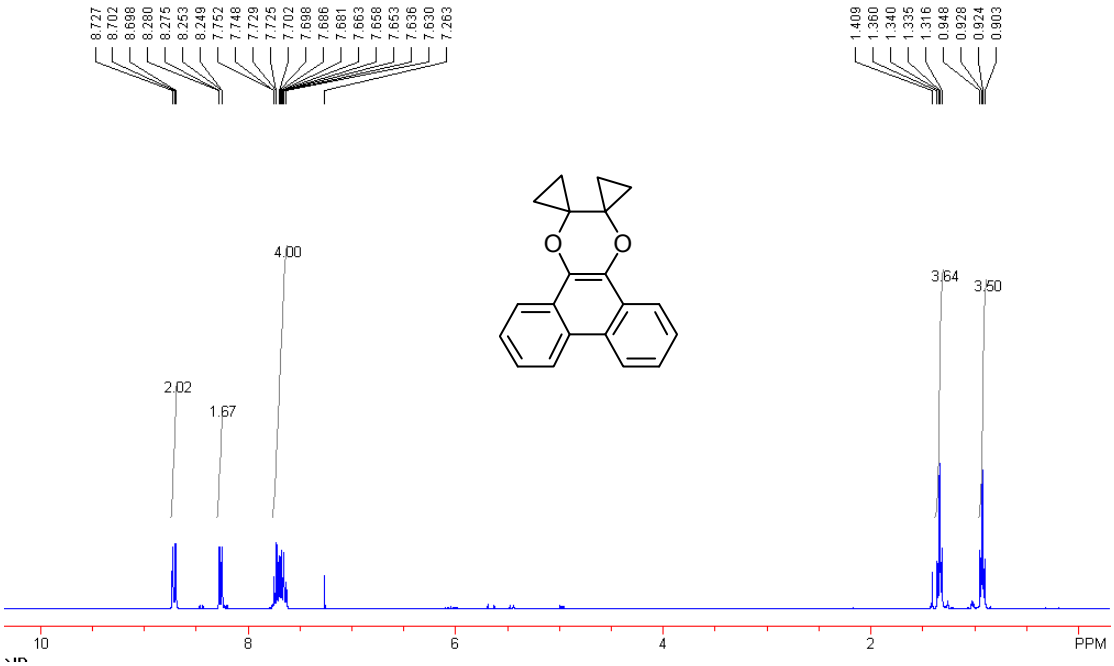


Crystal structure of compound 7:

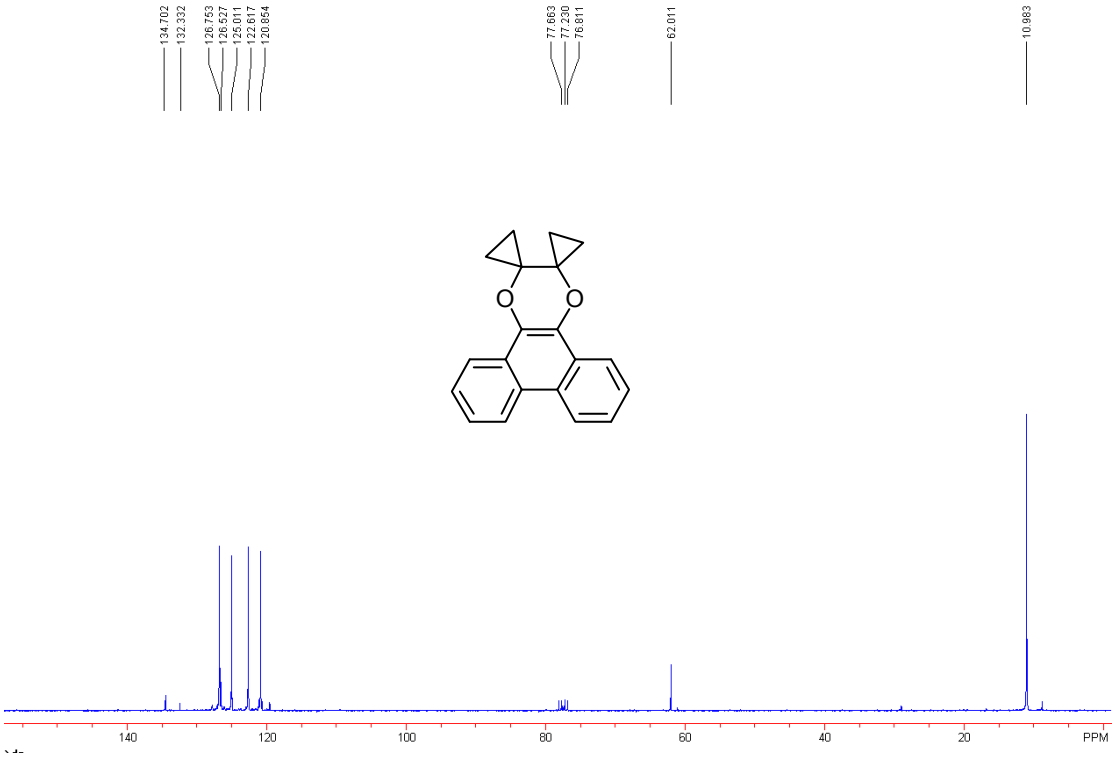


Copies of ^{1}H NMR and ^{13}C NMR spectra of all the new compounds

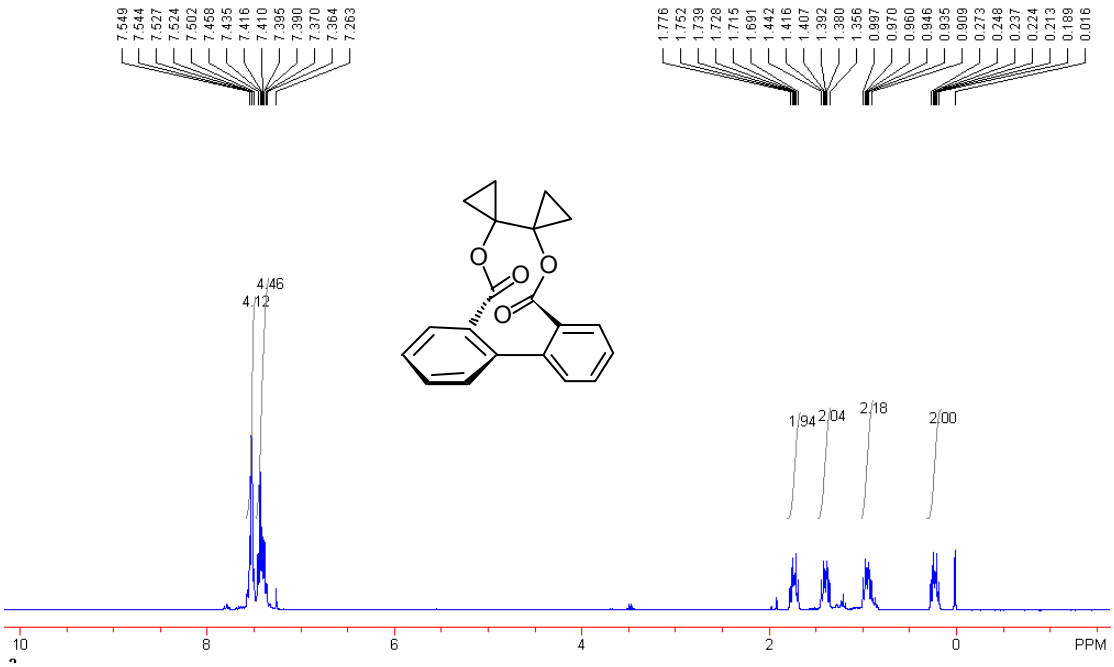
2a-^{1}H NMR($CDCl_3$)



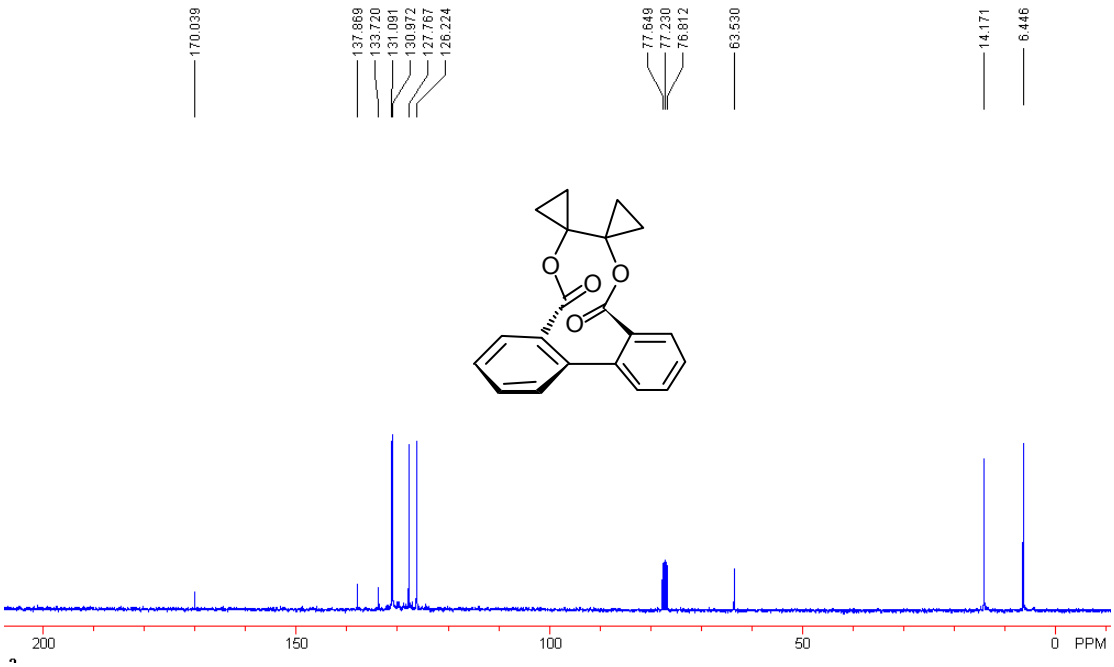
2a-^{13}C NMR($CDCl_3$)



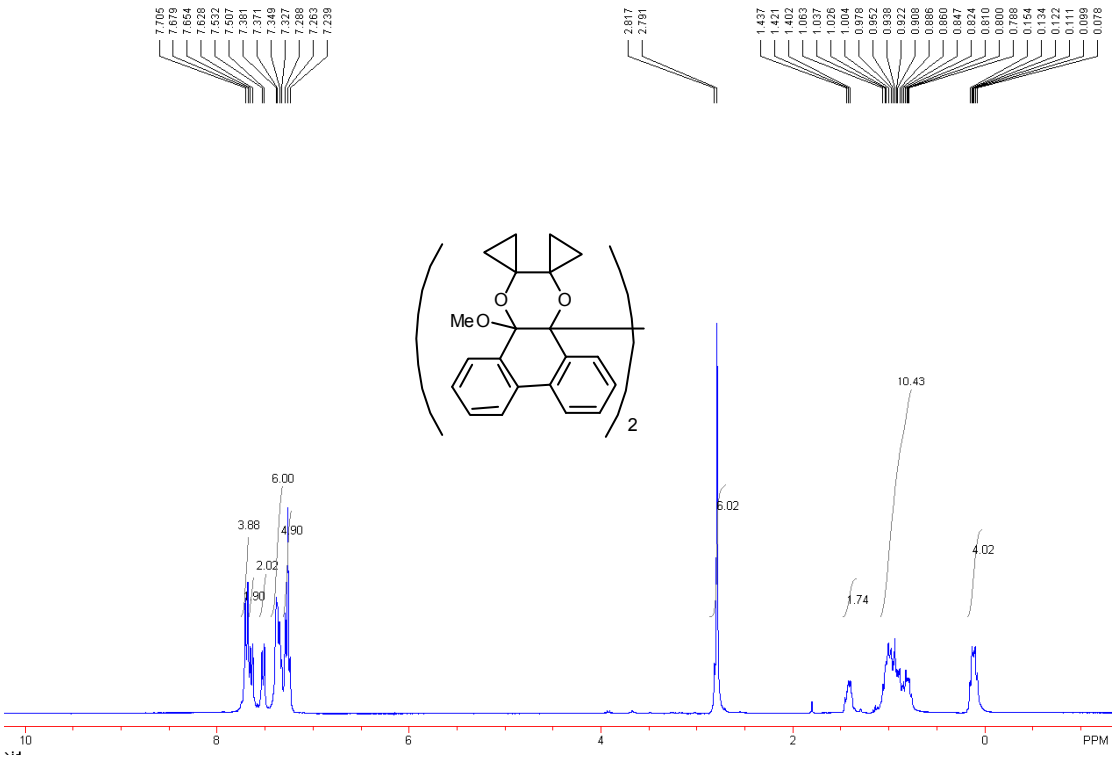
3a-^{1}H NMR($CDCl_3$)



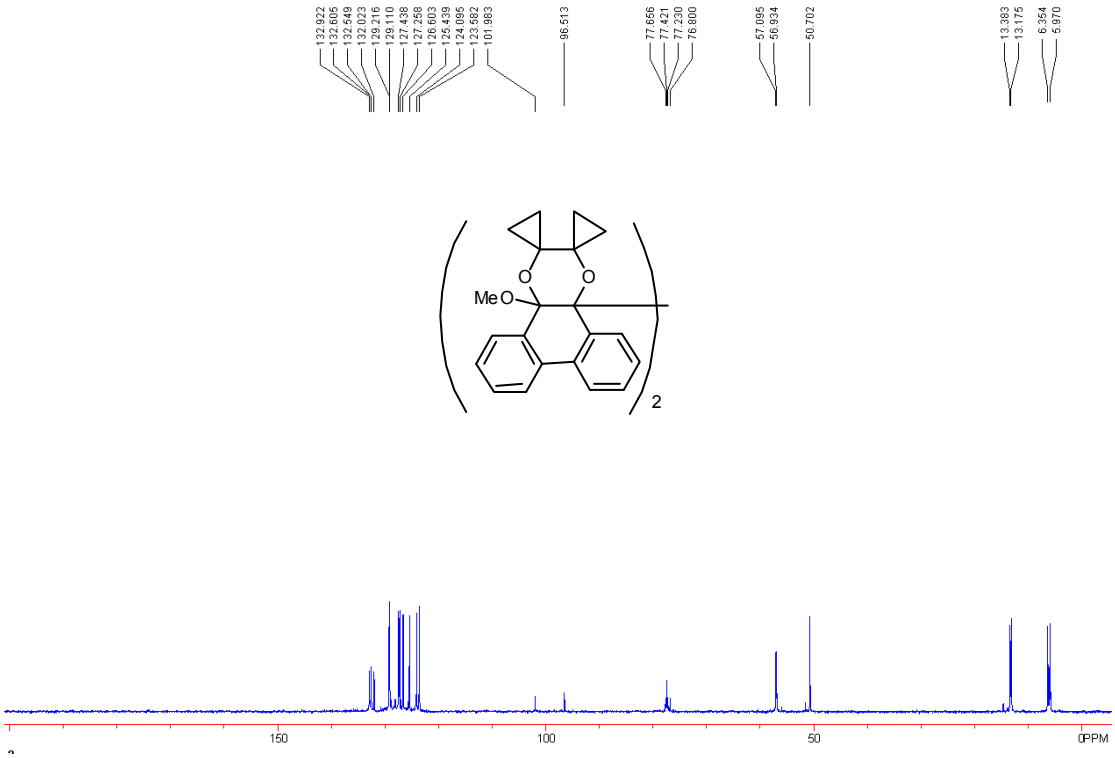
3a-^{13}C NMR($CDCl_3$)



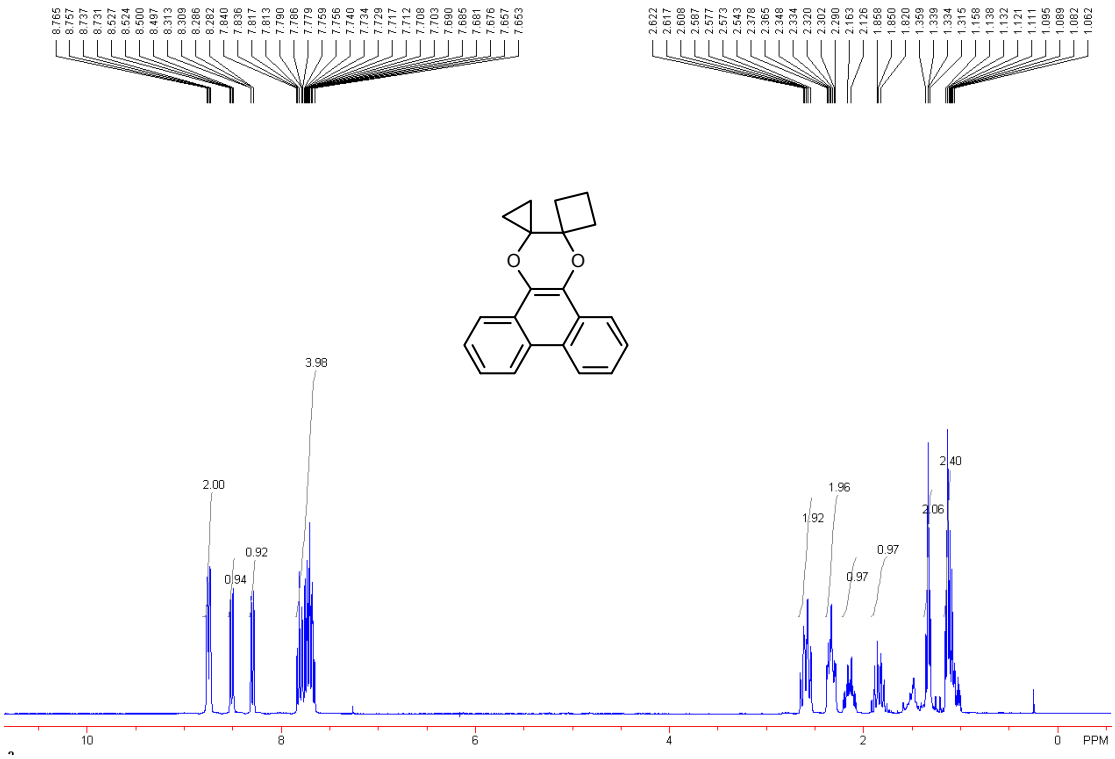
A-^{1}H NMR($CDCl_3$)



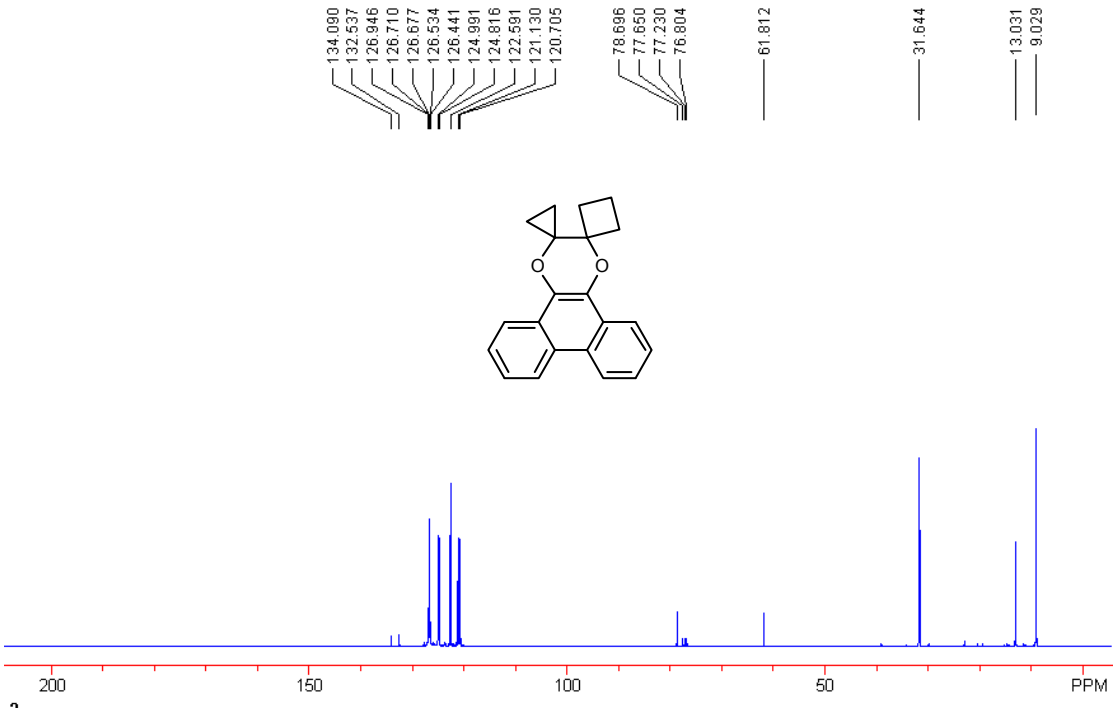
A-^{13}C NMR($CDCl_3$)



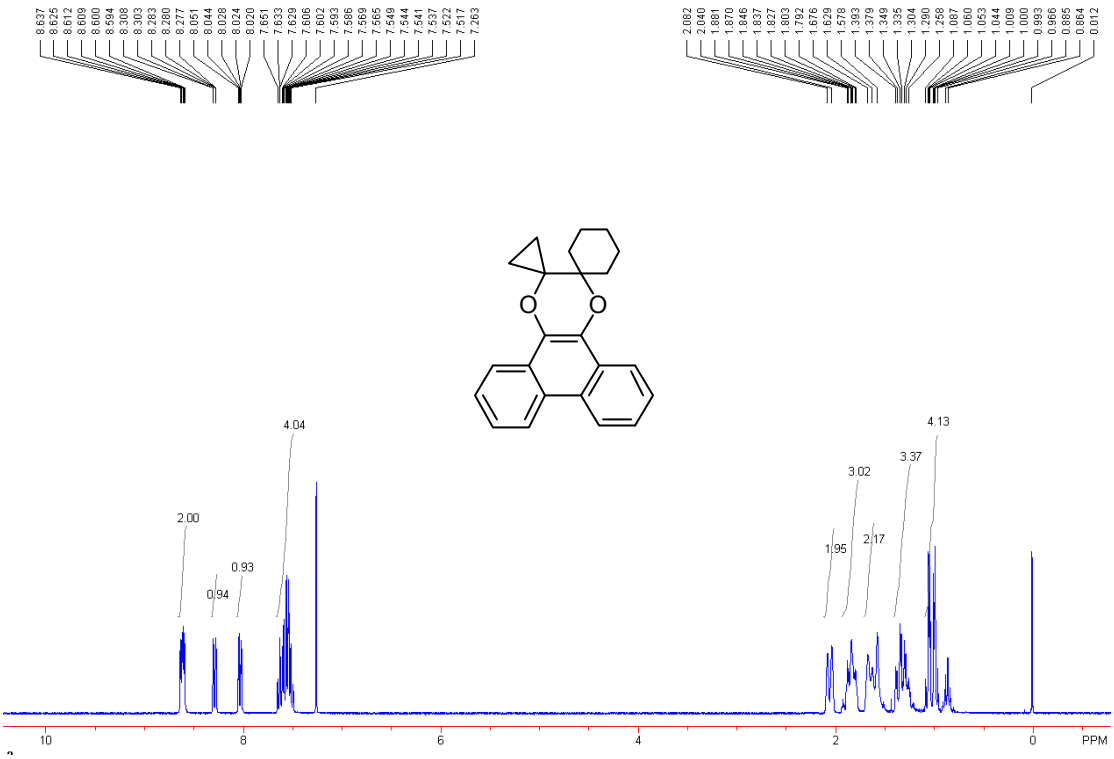
2b-^{1}H NMR($CDCl_3$)



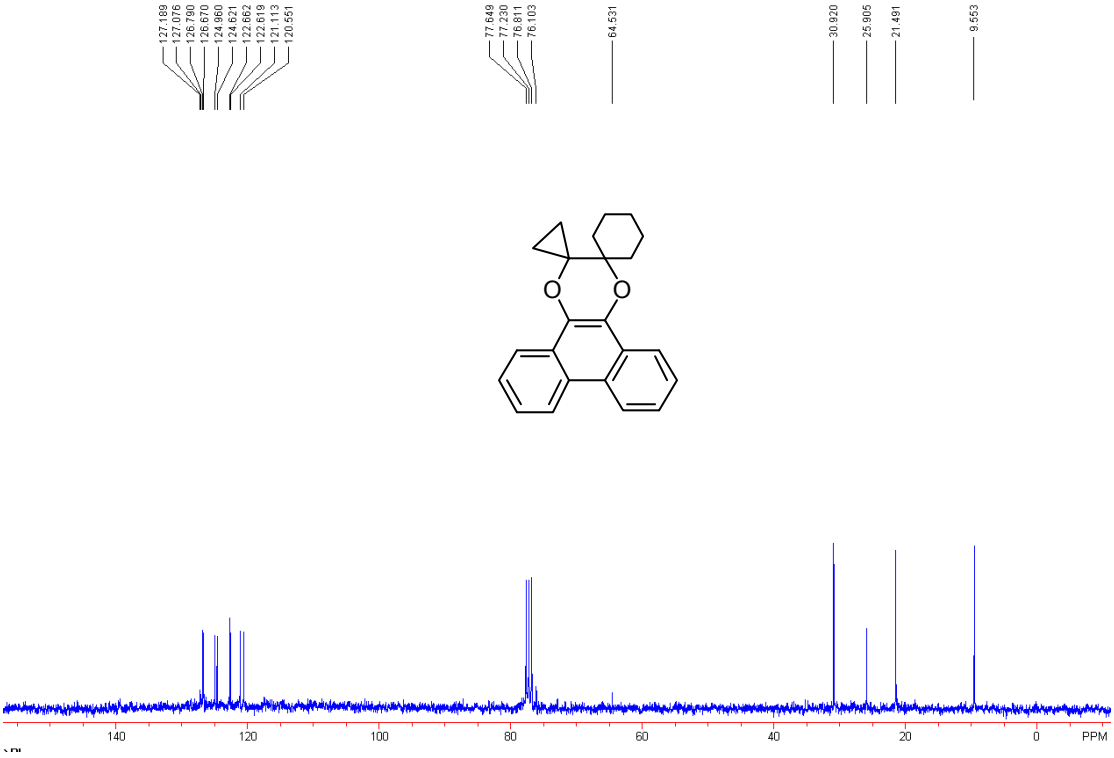
2b-^{13}C NMR($CDCl_3$)



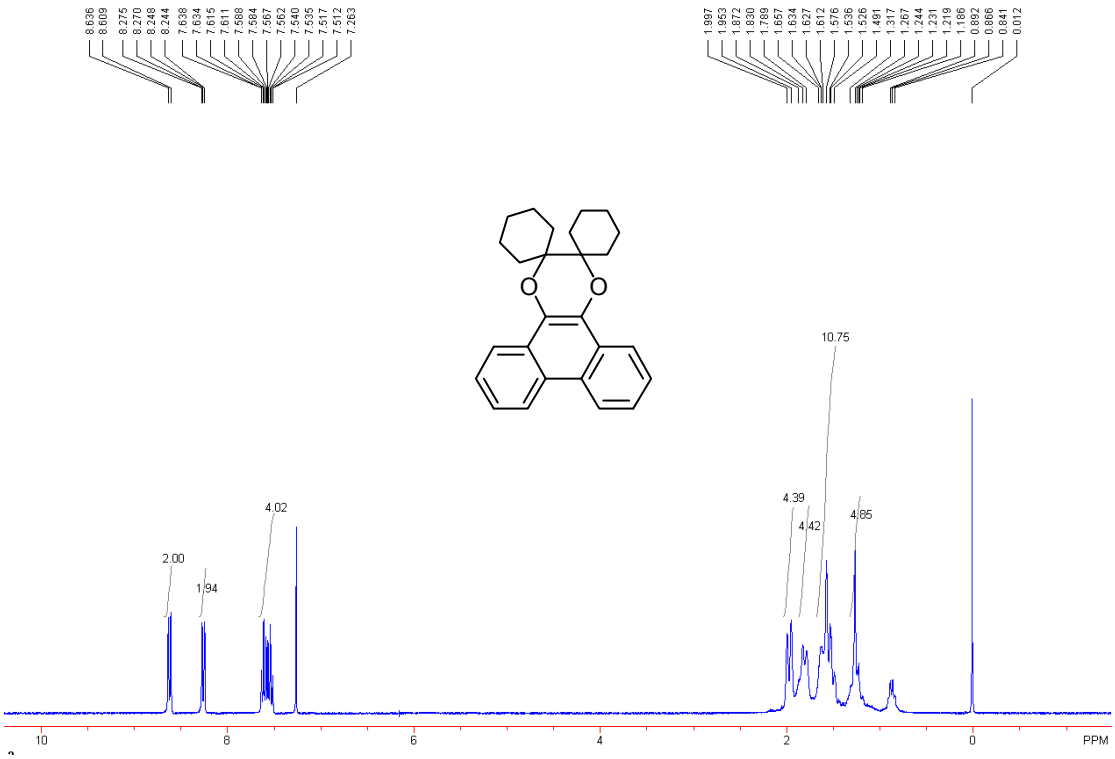
2c-^{1}H NMR($CDCl_3$)



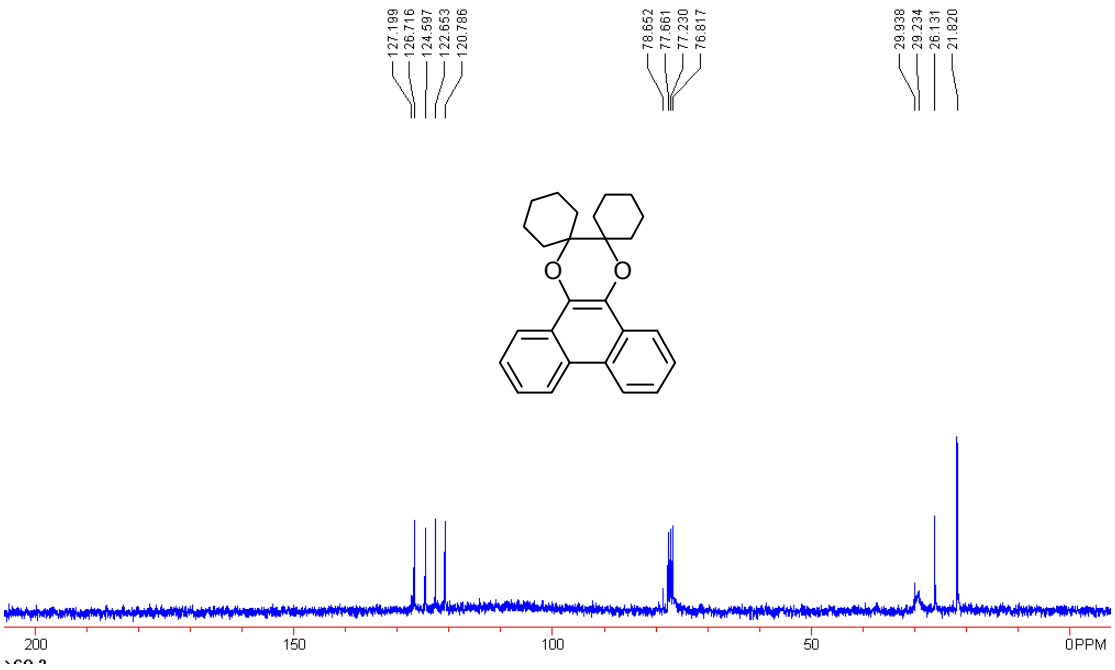
2c-^{13}C NMR($CDCl_3$)



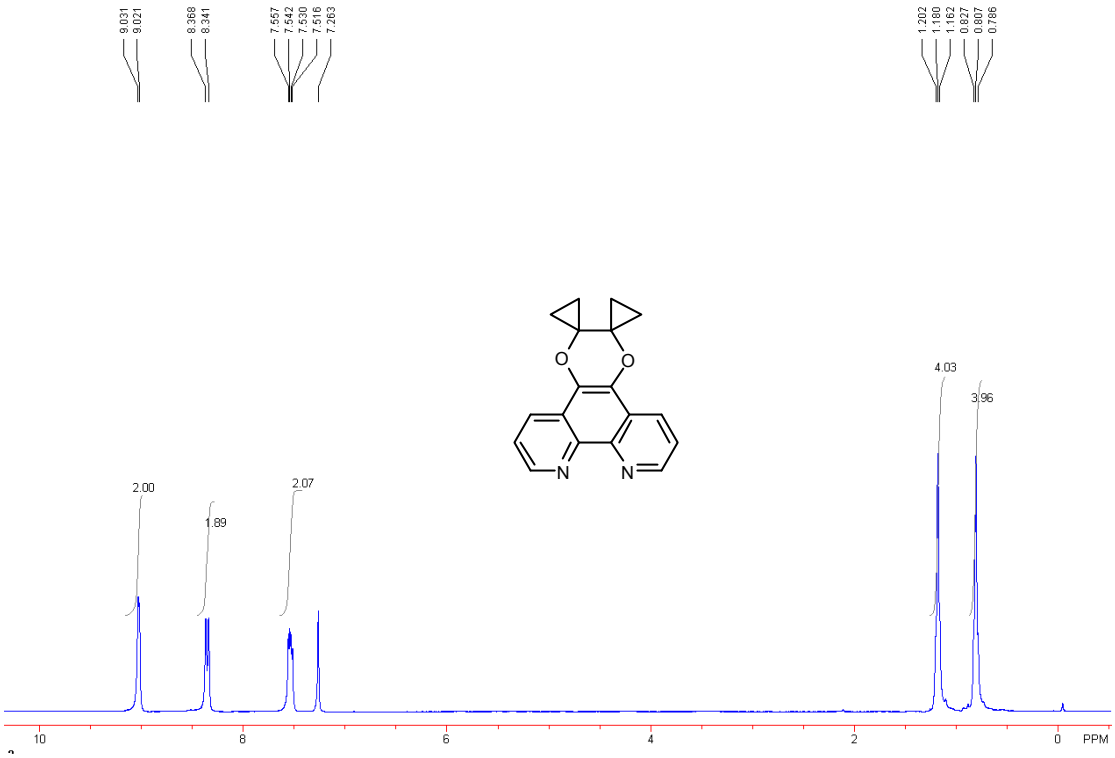
2d-^{1}H NMR($CDCl_3$)



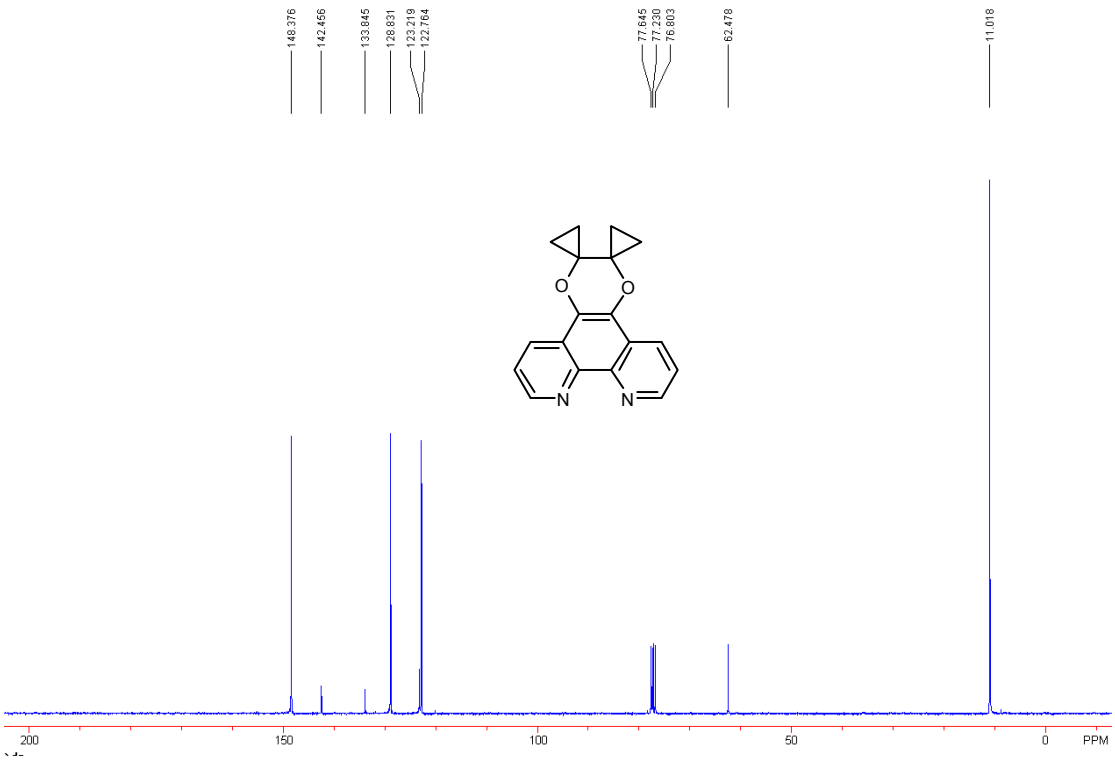
2d-^{13}C NMR($CDCl_3$)



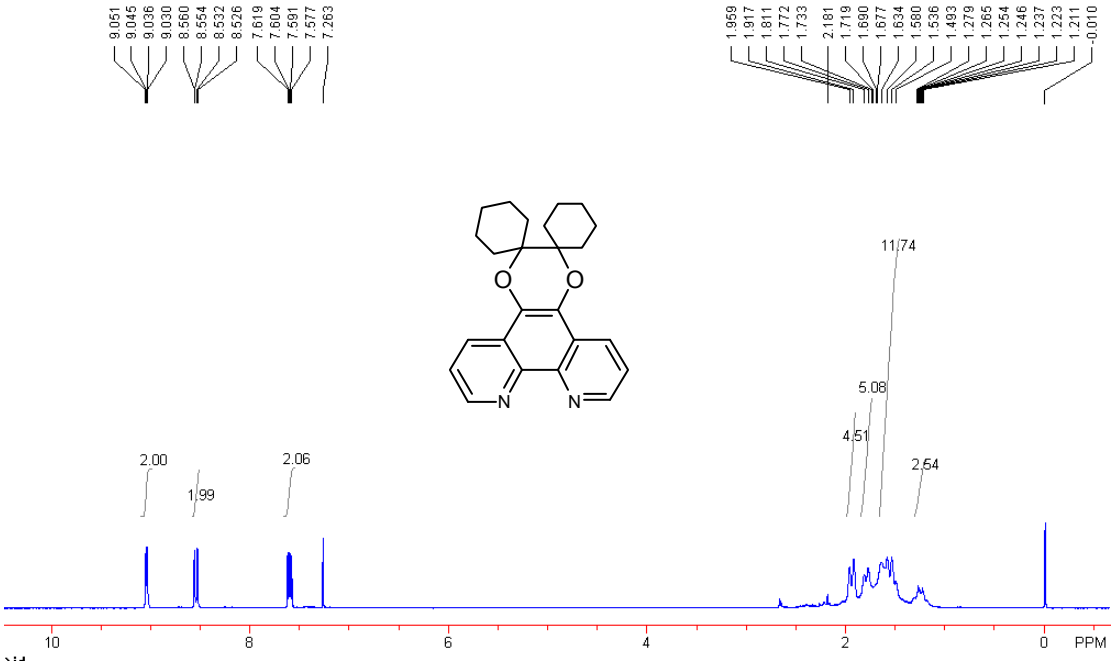
4a-^{1}H NMR($CDCl_3$)



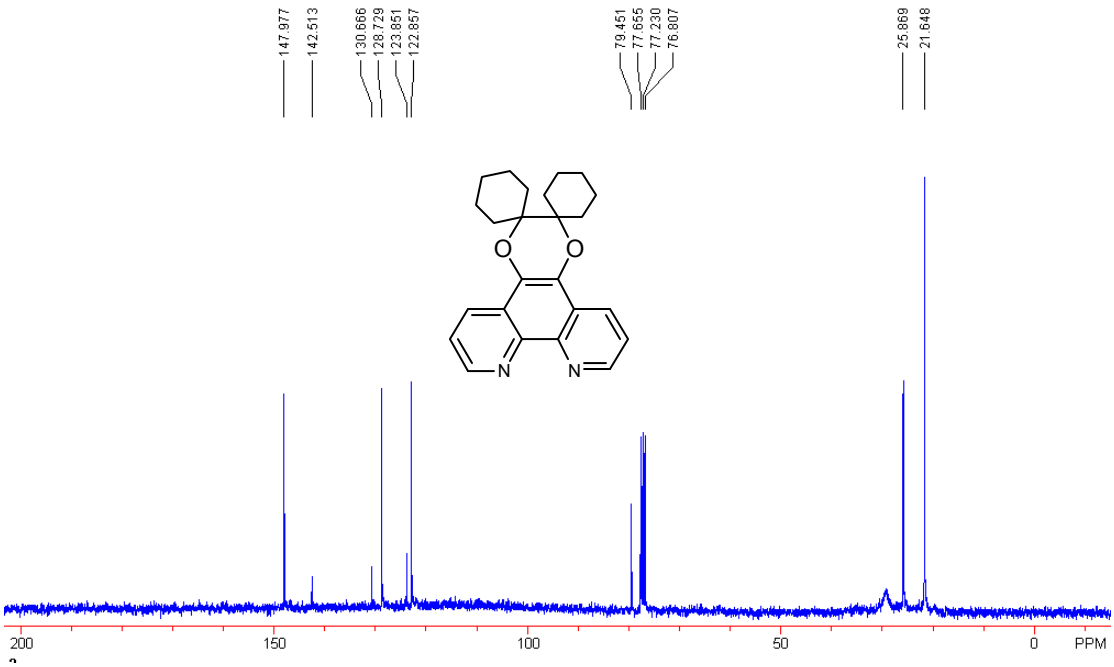
4a-^{13}C NMR($CDCl_3$)



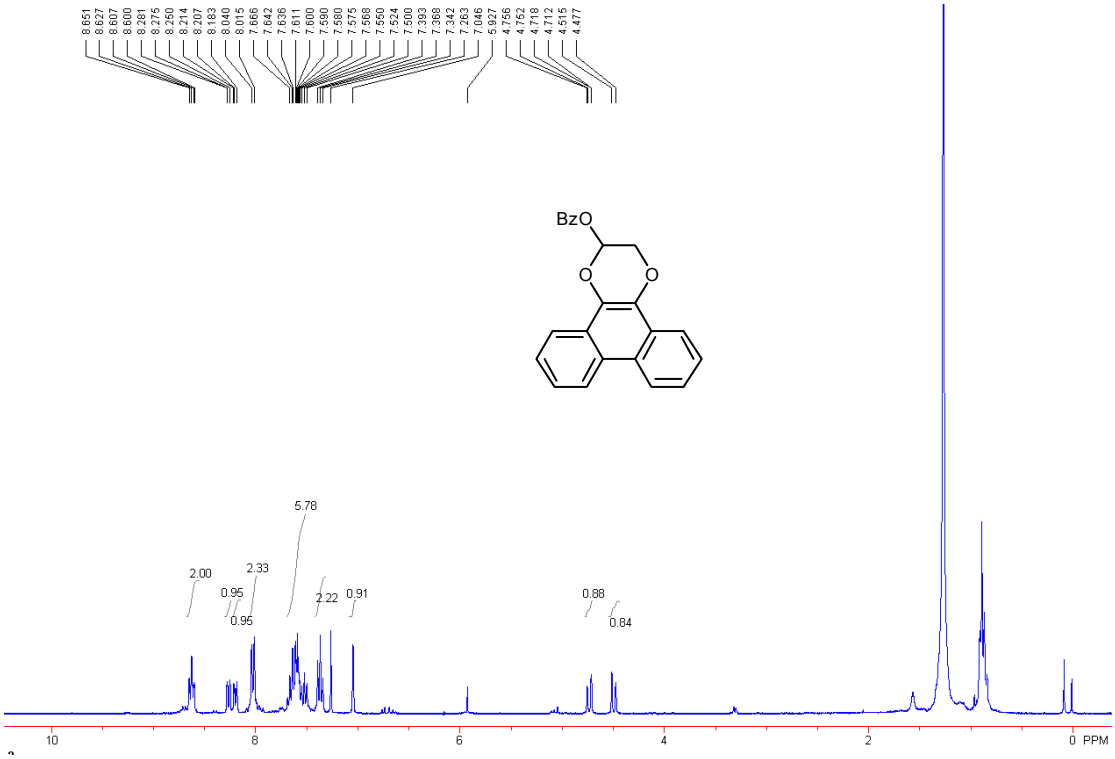
4d-^{1}H NMR($CDCl_3$)



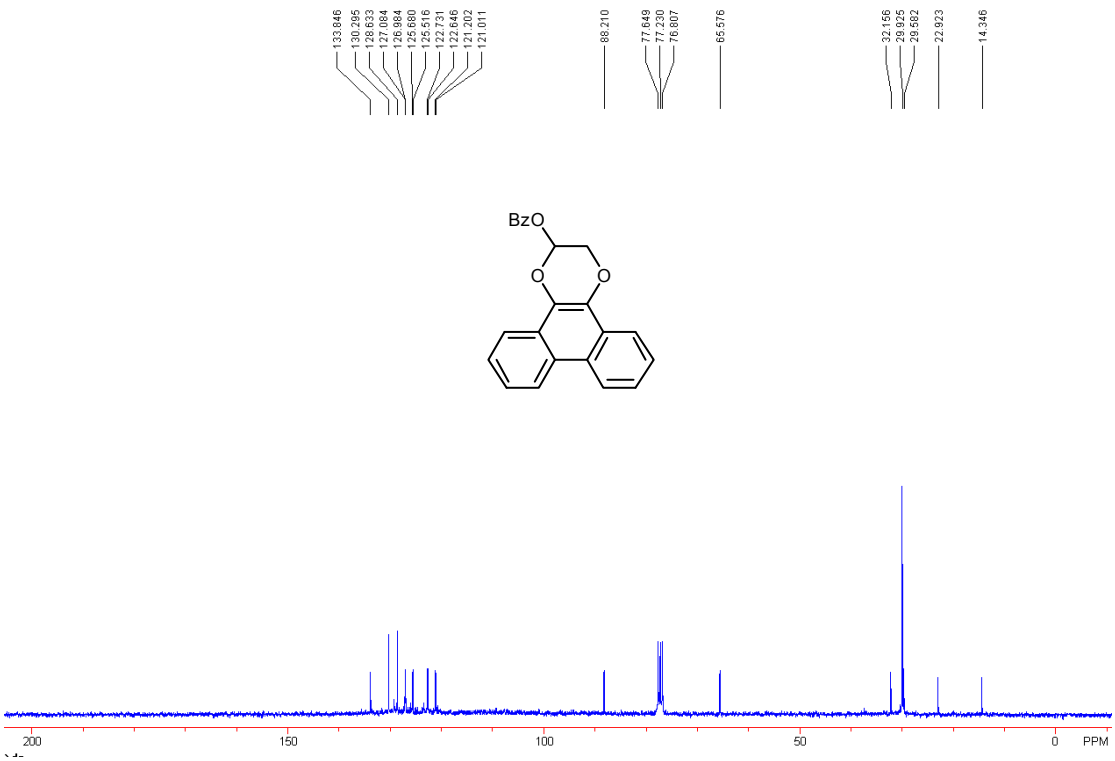
4d-^{13}C NMR($CDCl_3$)



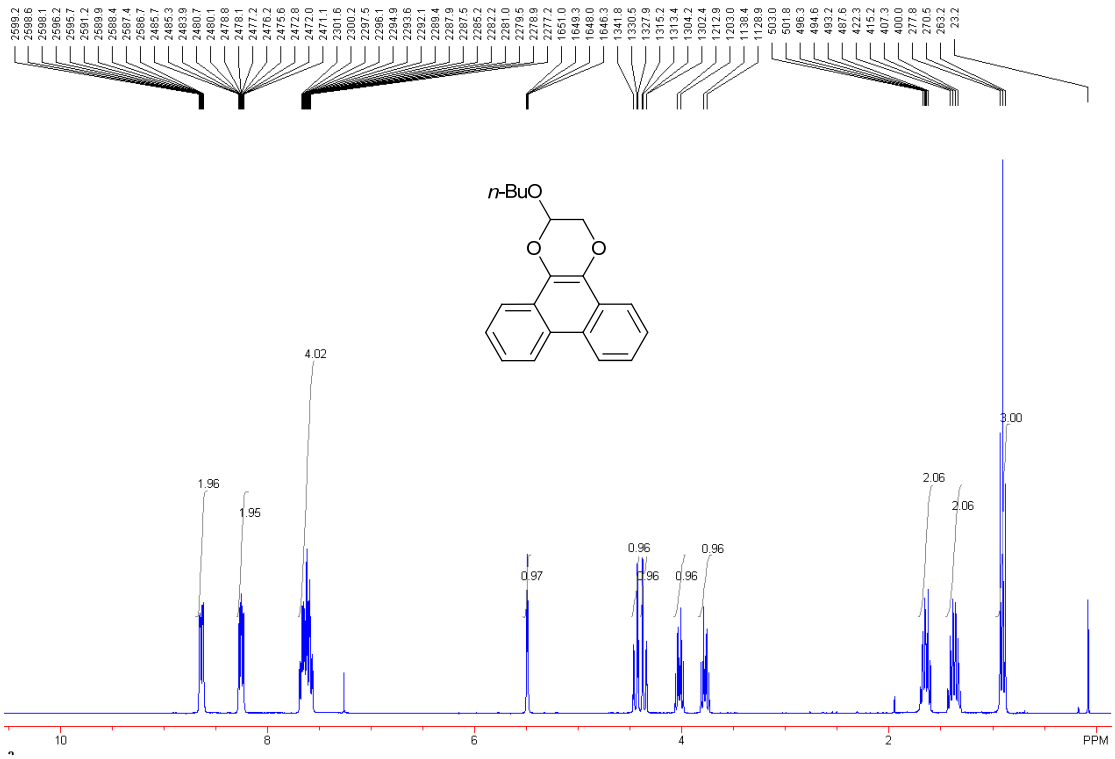
6-^{1}H NMR($CDCl_3$)



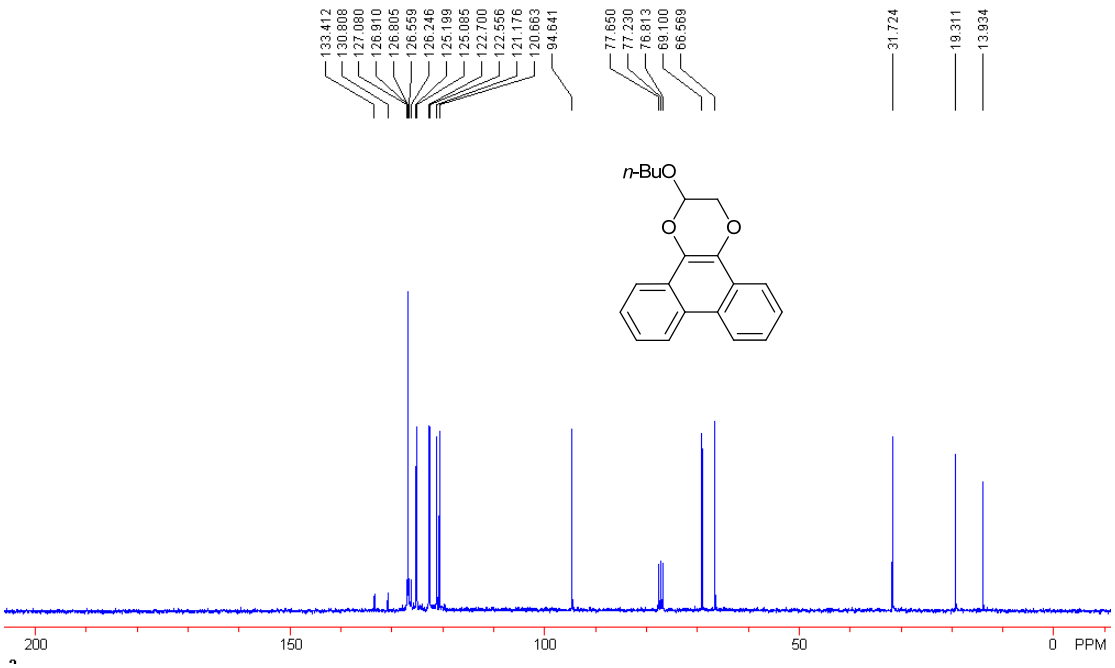
6-^{13}C NMR($CDCl_3$)



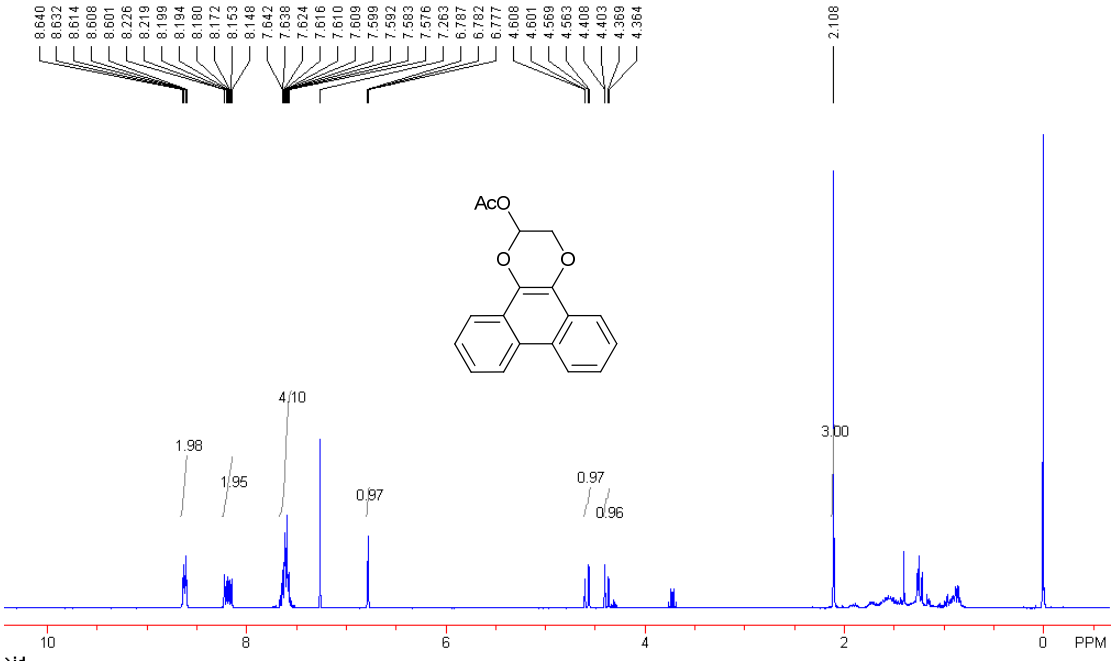
8-^{1}H NMR($CDCl_3$)



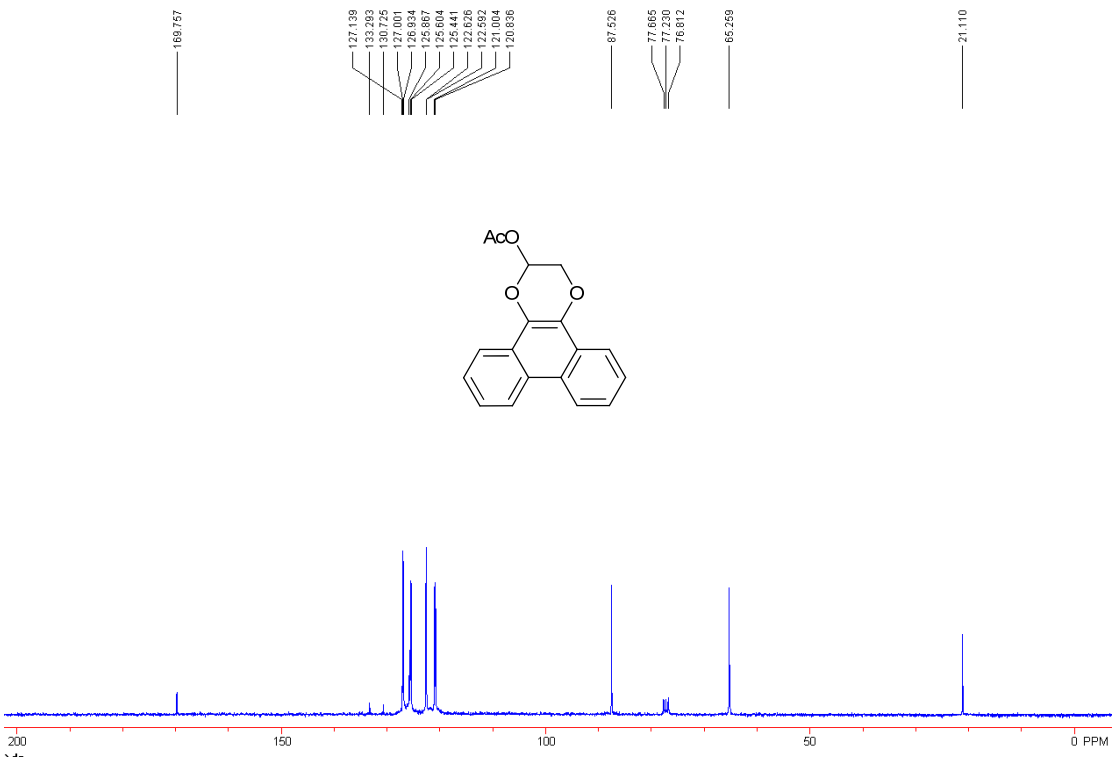
8-^{13}C NMR($CDCl_3$)



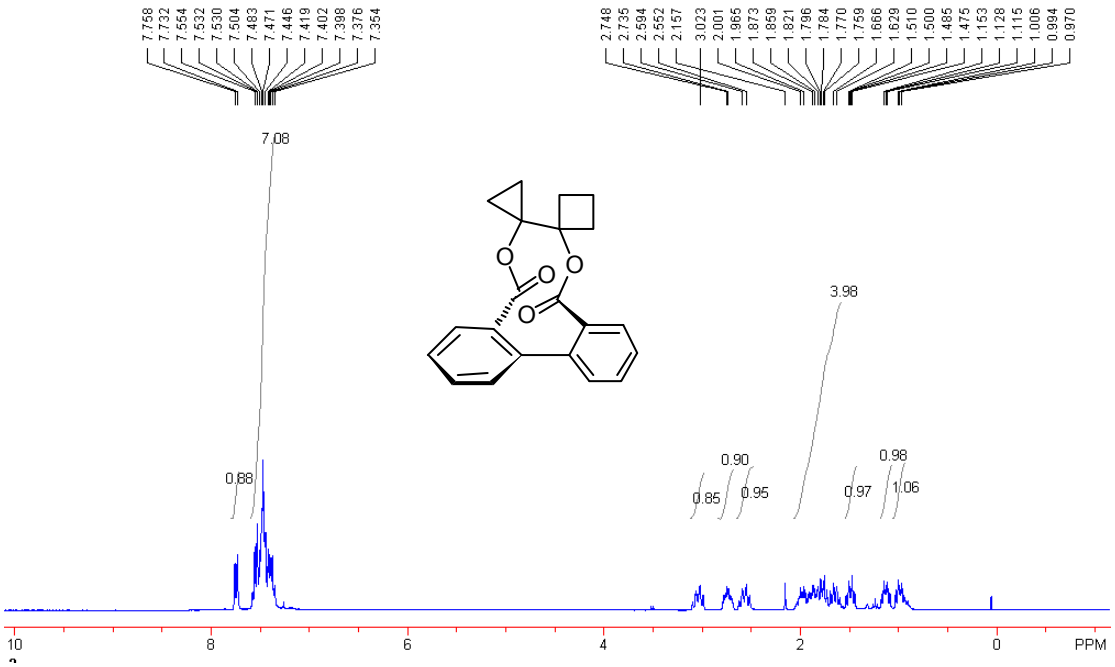
10-^{1}H NMR($CDCl_3$)



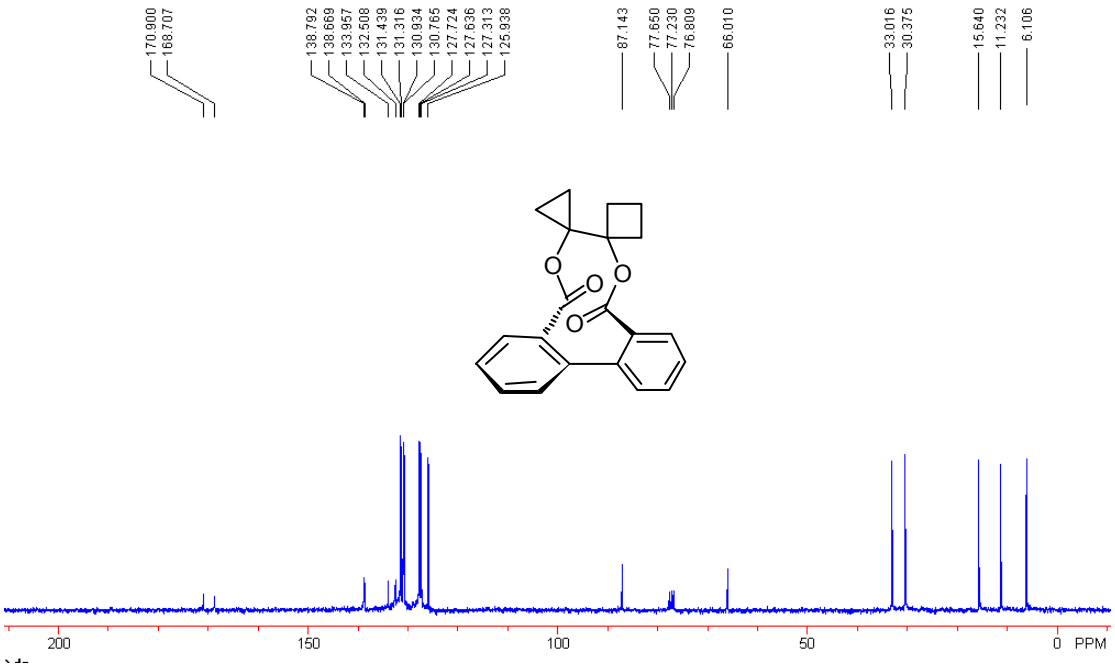
10-^{13}C NMR($CDCl_3$)



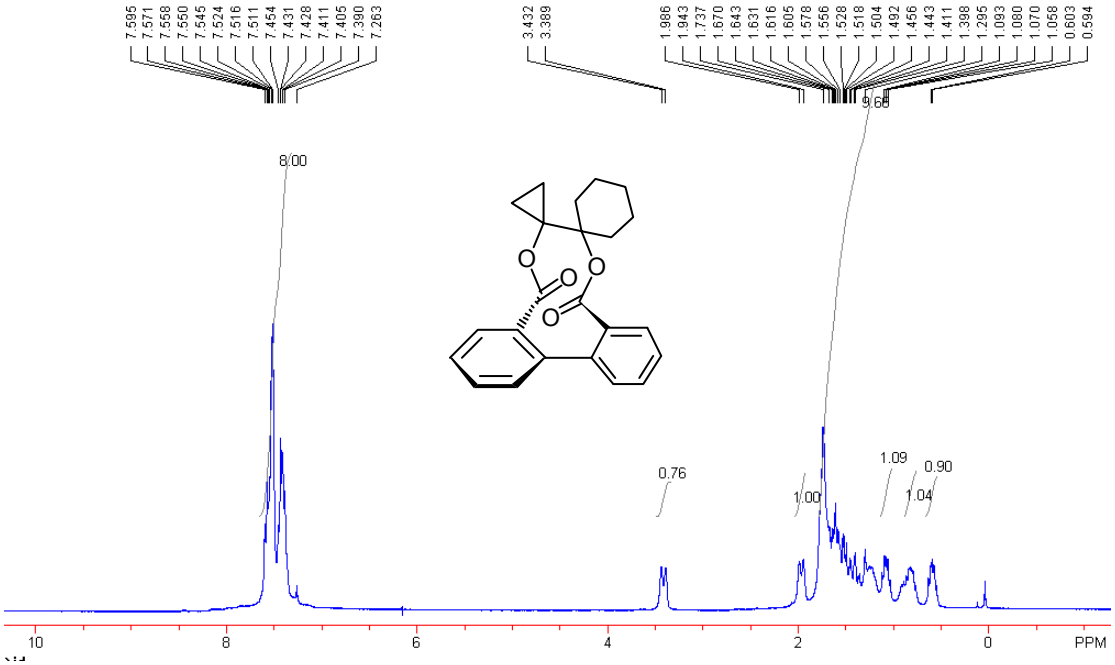
3b-^{1}H NMR($CDCl_3$)



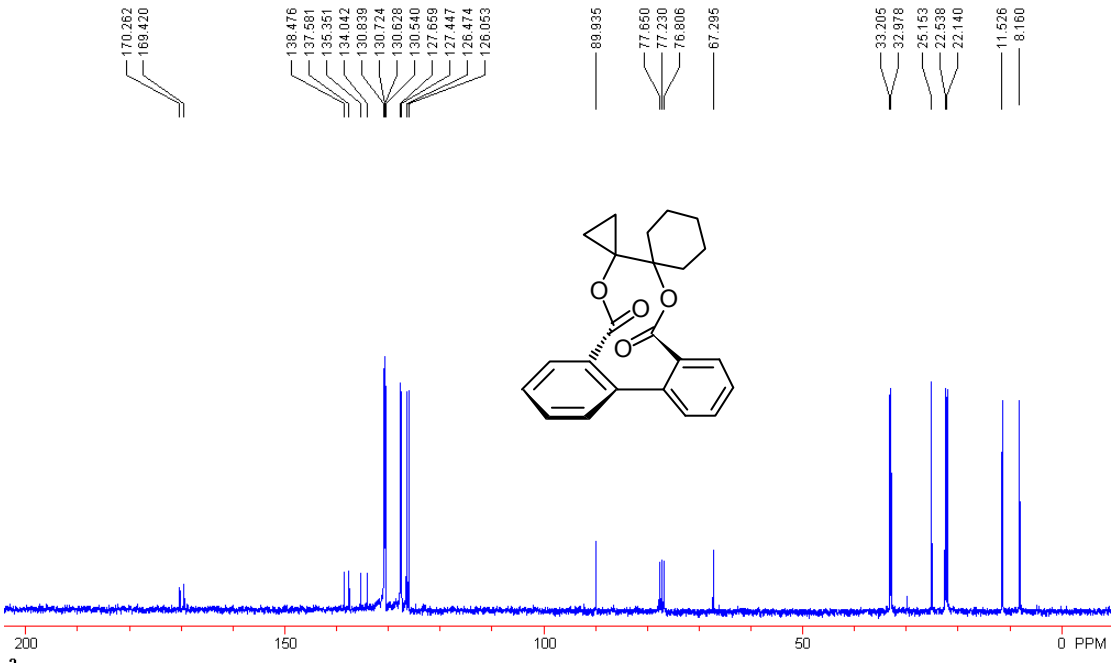
3b-^{13}C NMR($CDCl_3$)



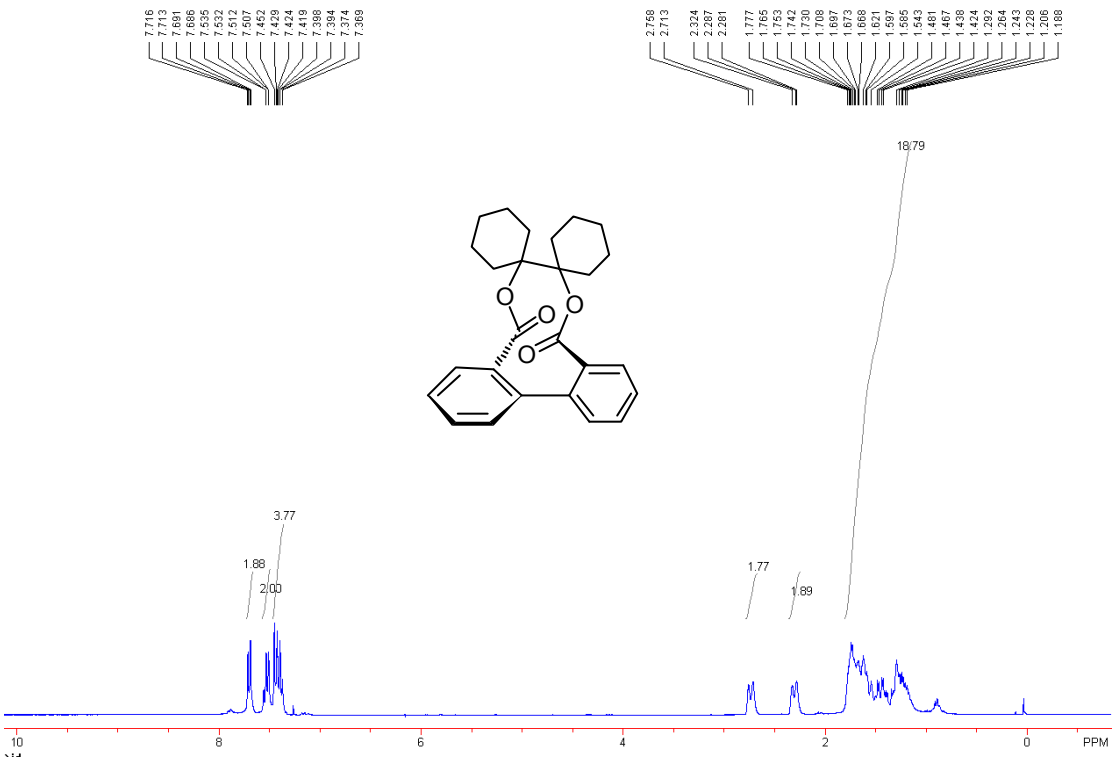
3c-^{1}H NMR($CDCl_3$)



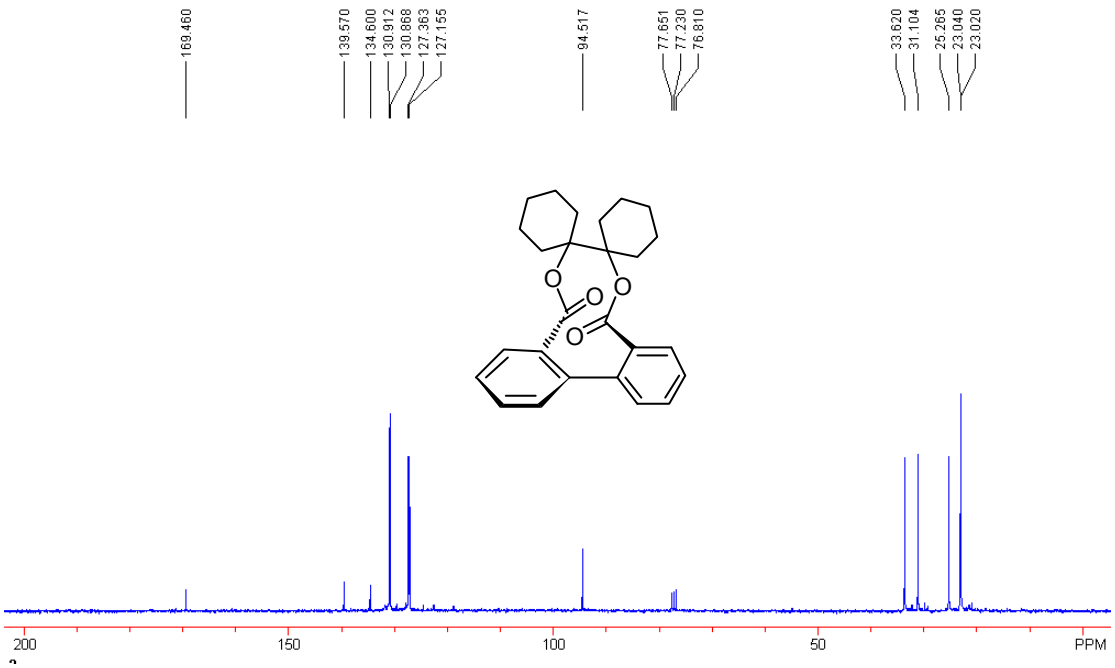
3c-^{13}C NMR($CDCl_3$)



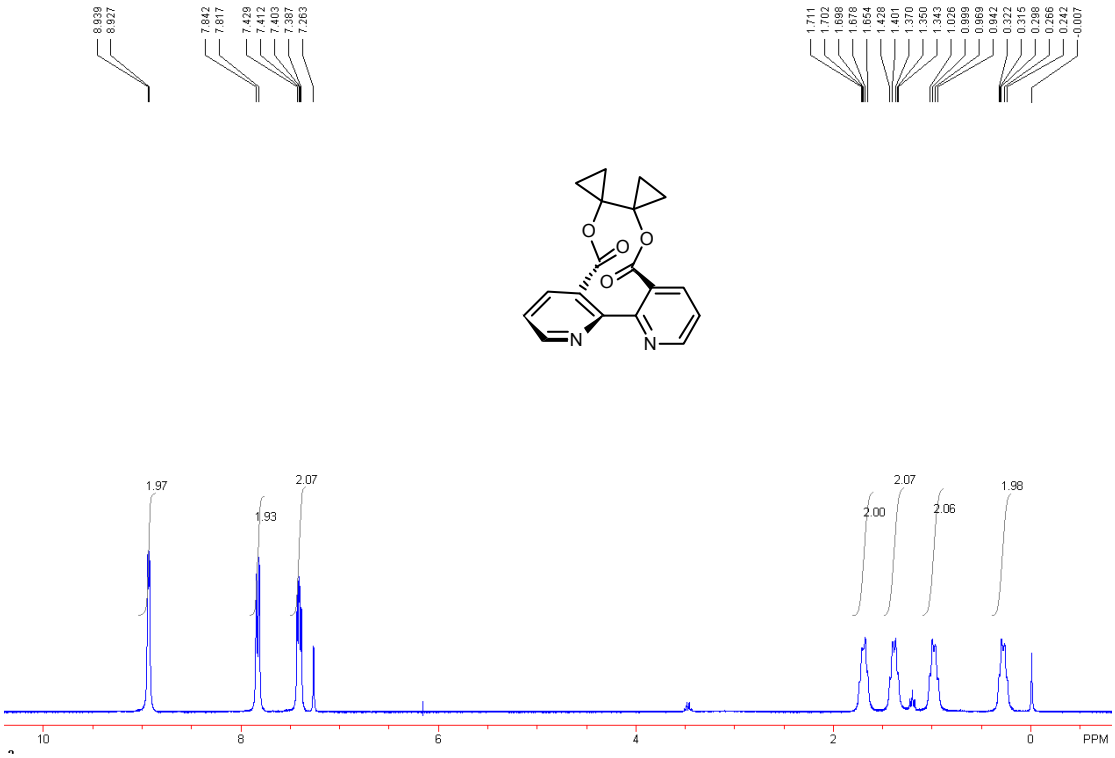
3d-^{1}H NMR($CDCl_3$)



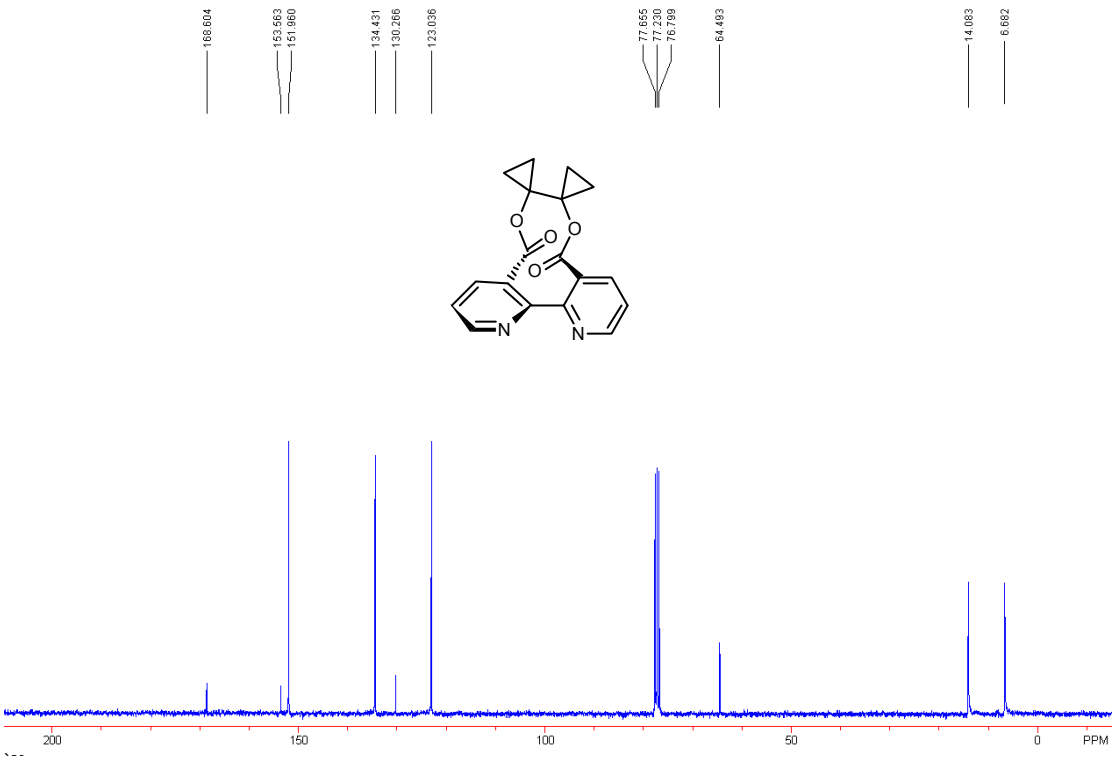
3d-^{13}C NMR($CDCl_3$)



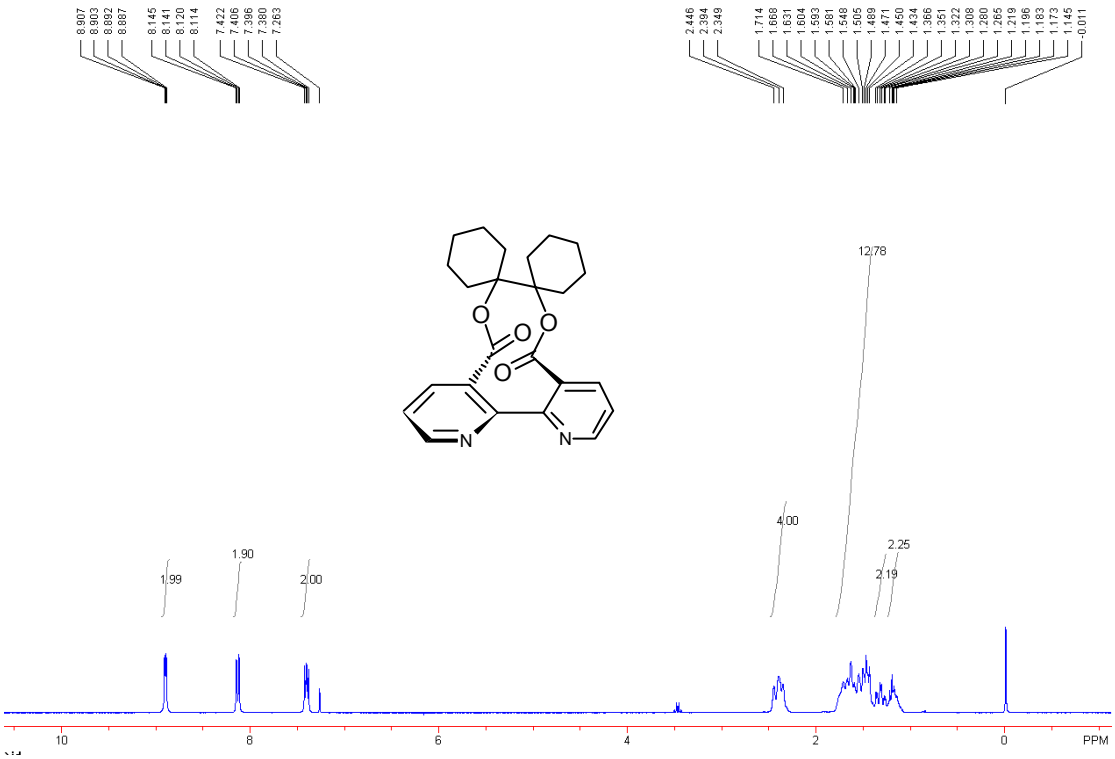
5a-^{1}H NMR($CDCl_3$)



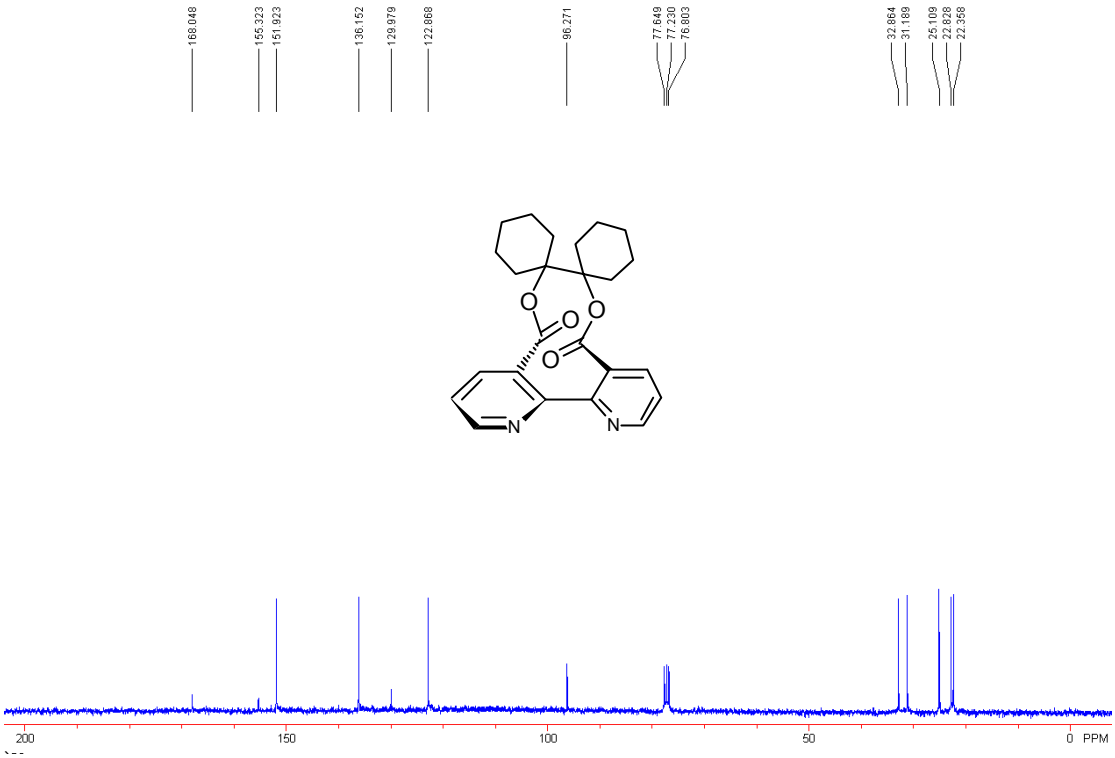
5a-^{13}C NMR($CDCl_3$)



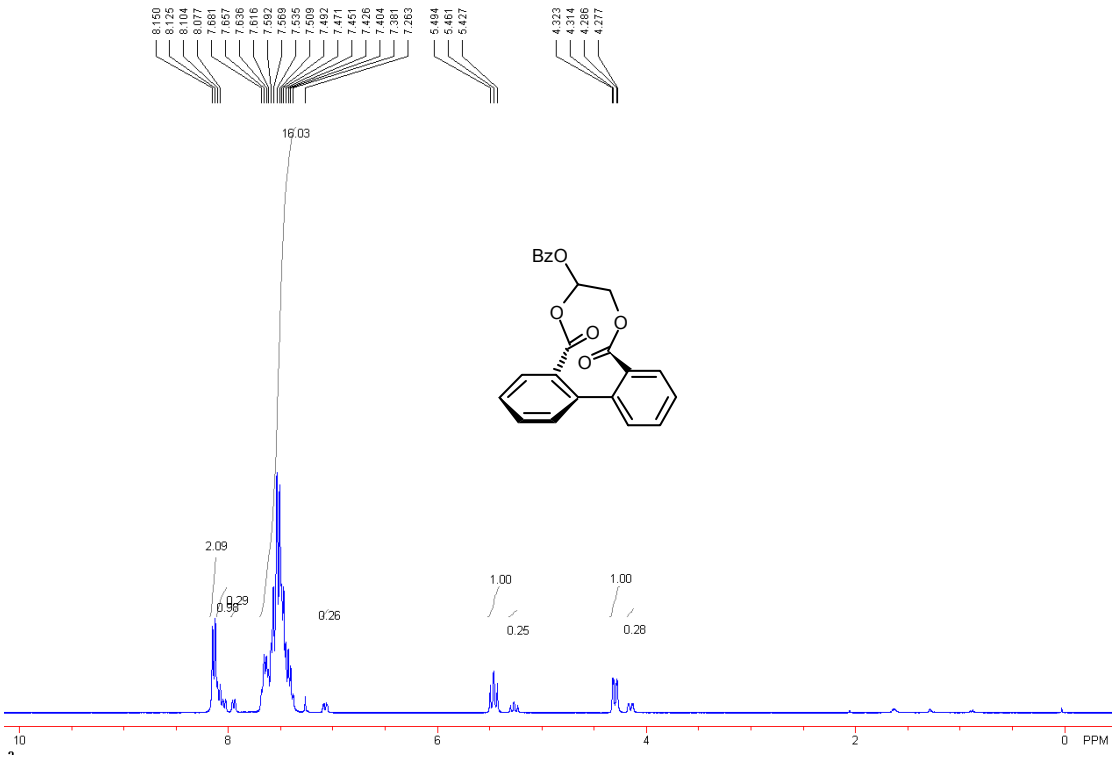
5d-^{1}H NMR($CDCl_3$)



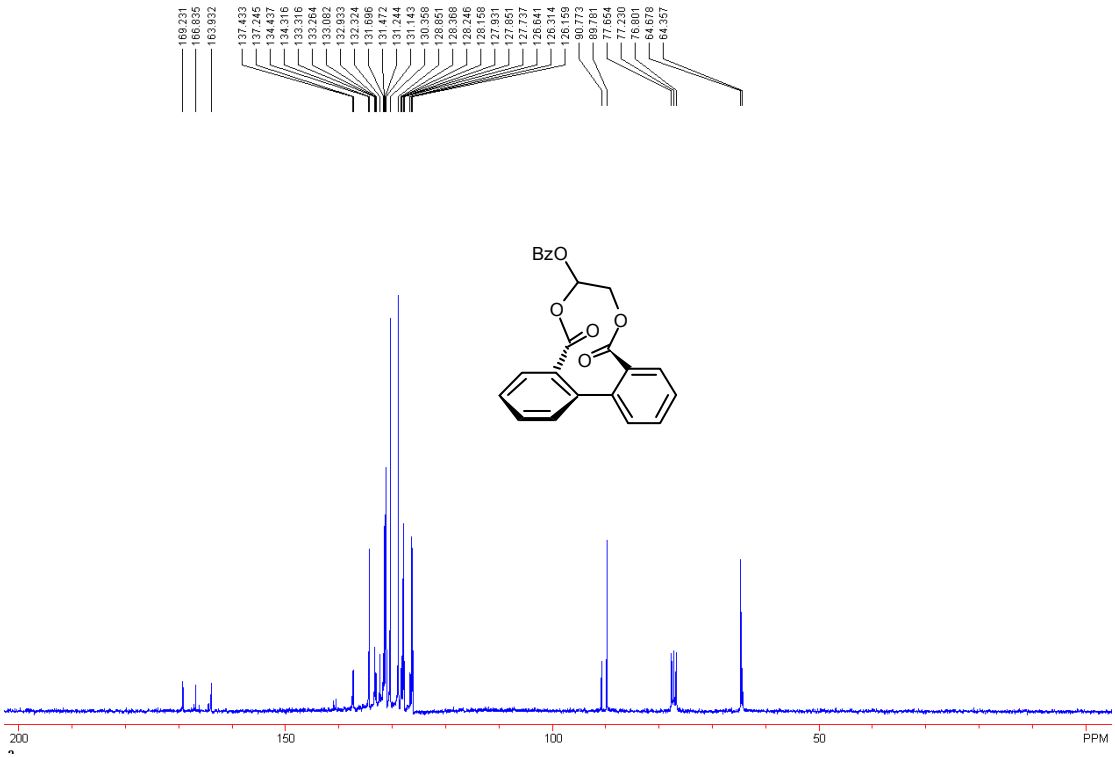
5d-^{13}C NMR($CDCl_3$)



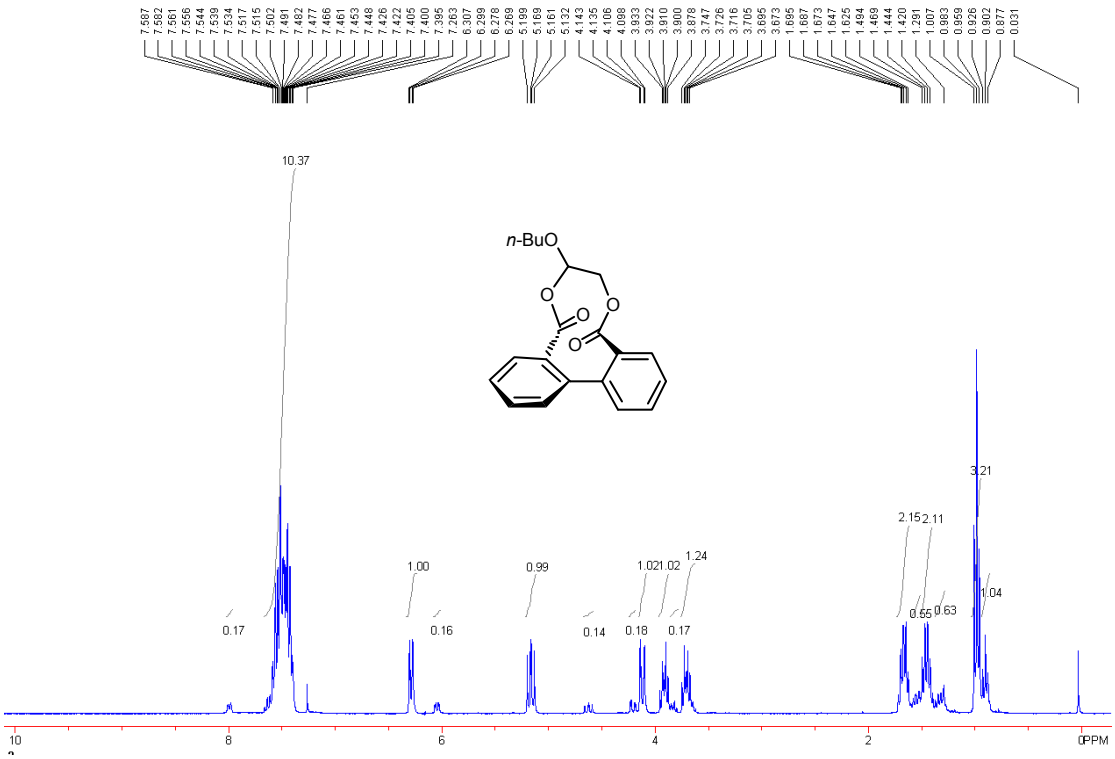
7-^{1}H NMR($CDCl_3$)



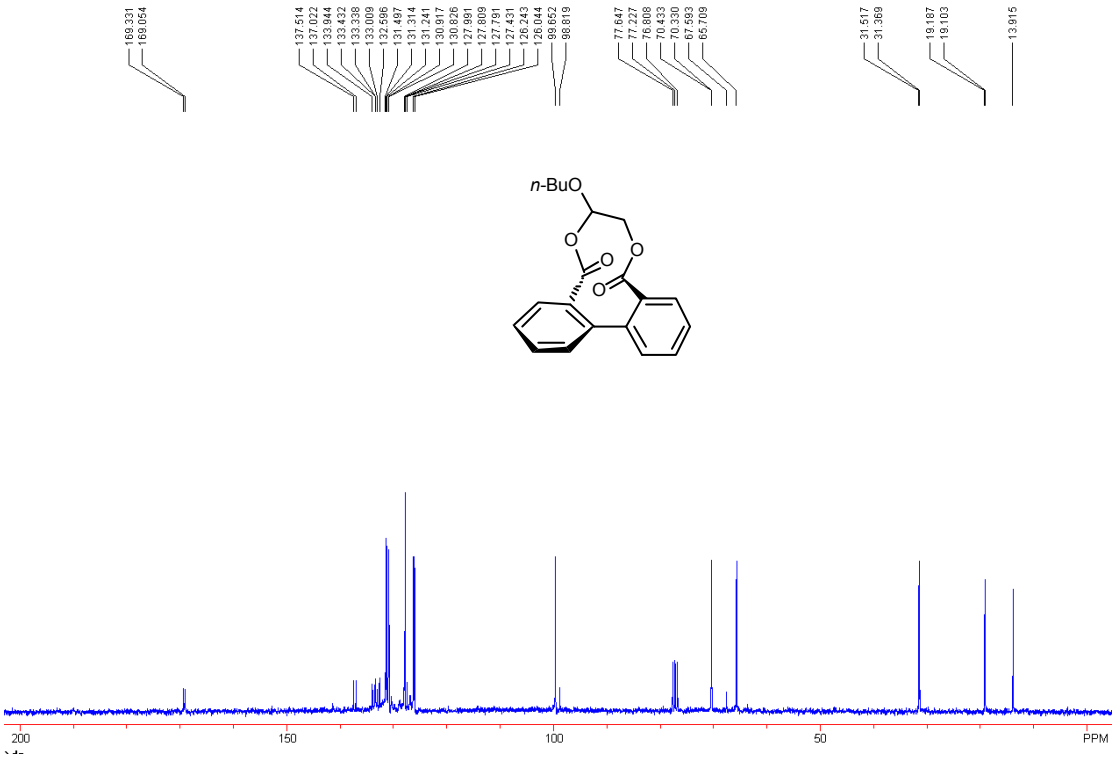
7-^{13}C NMR($CDCl_3$)



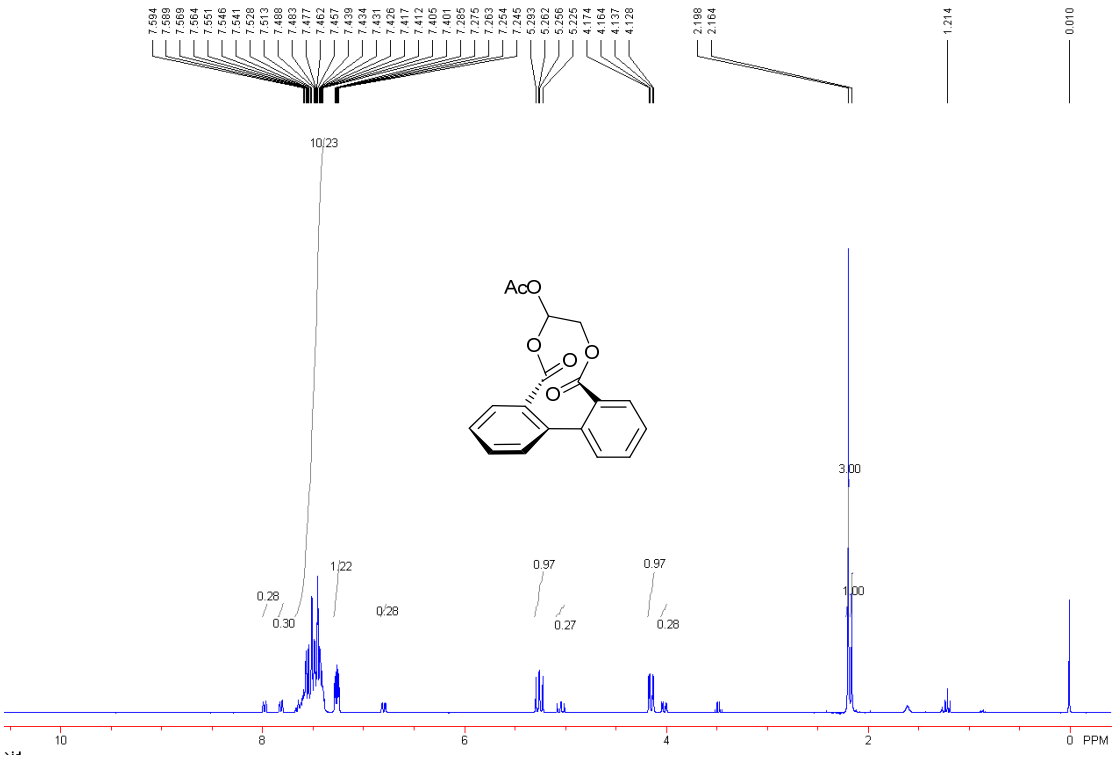
9-^{1}H NMR($CDCl_3$)



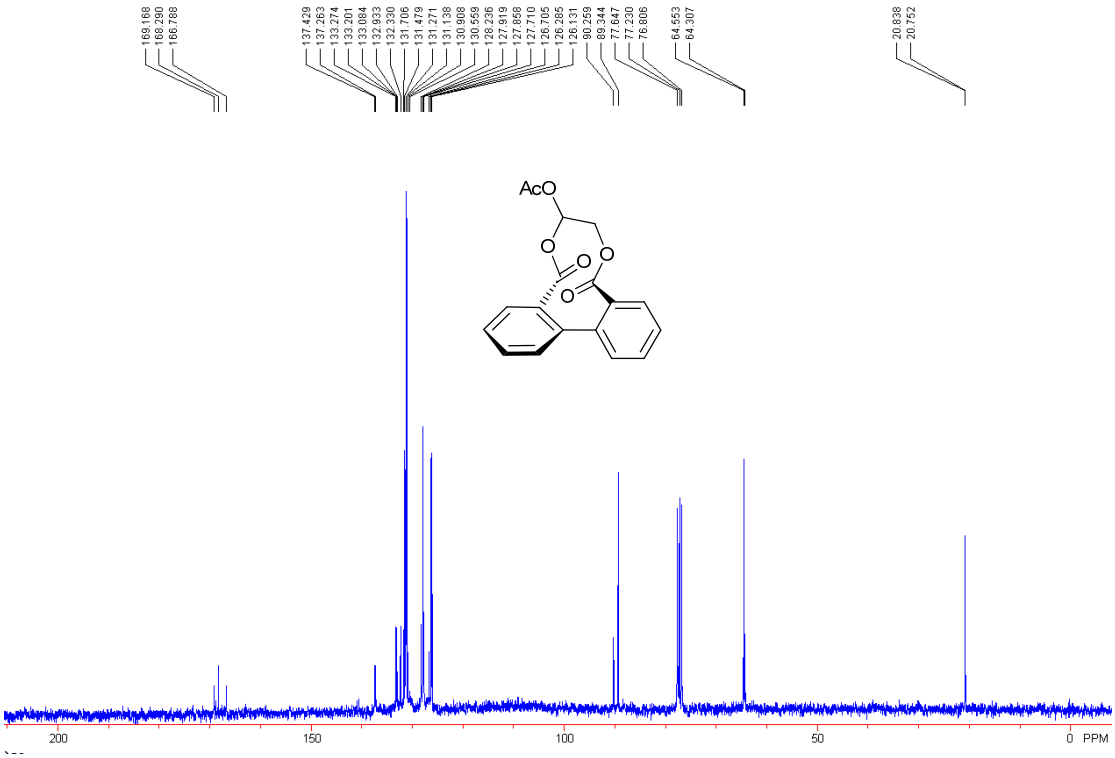
9-^{13}C NMR($CDCl_3$)



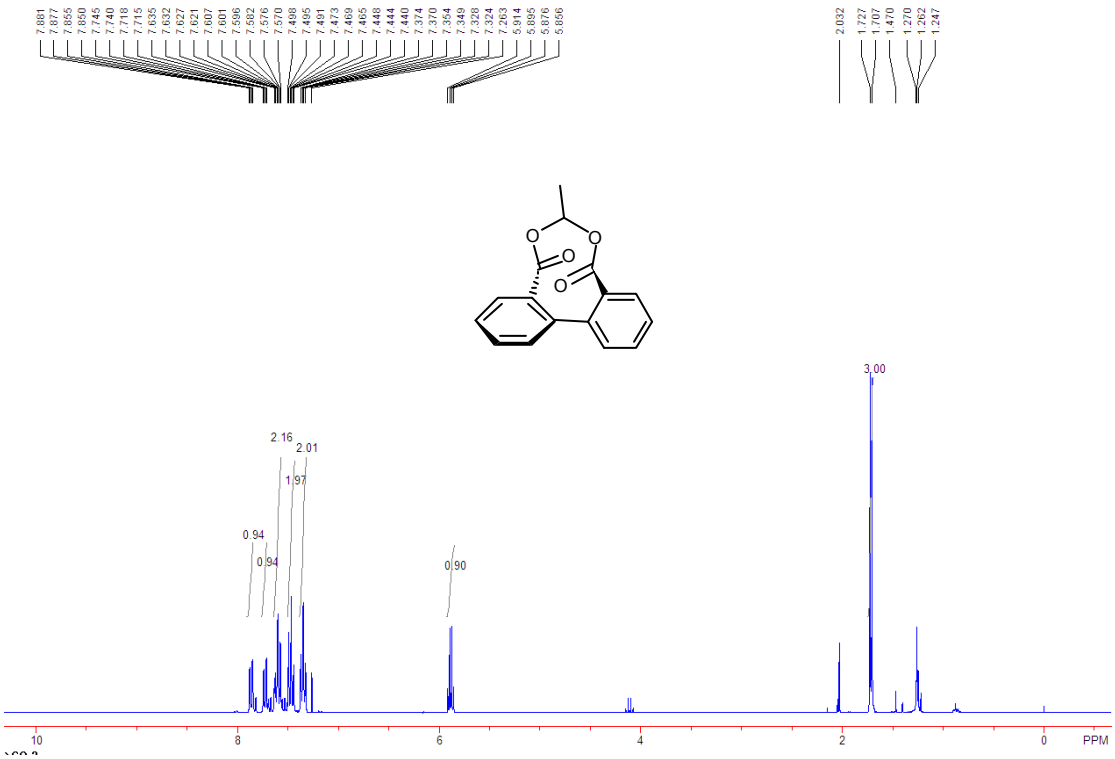
11-^{1}H NMR($CDCl_3$)



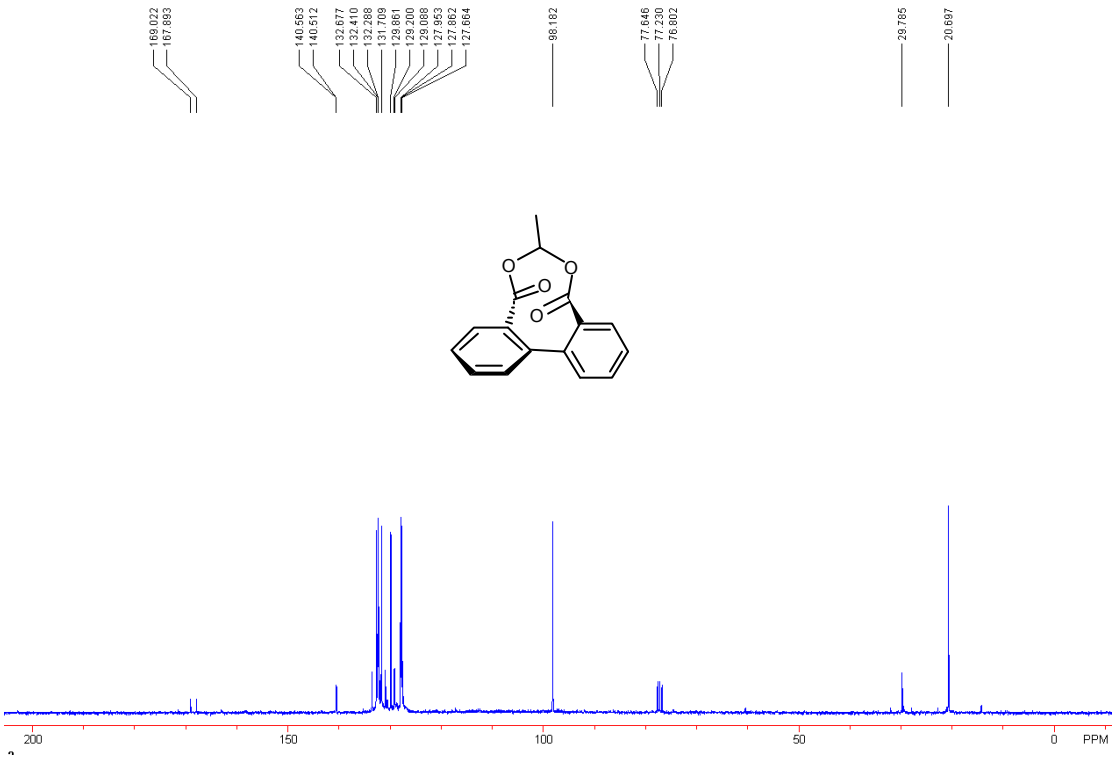
11-^{13}C NMR($CDCl_3$)



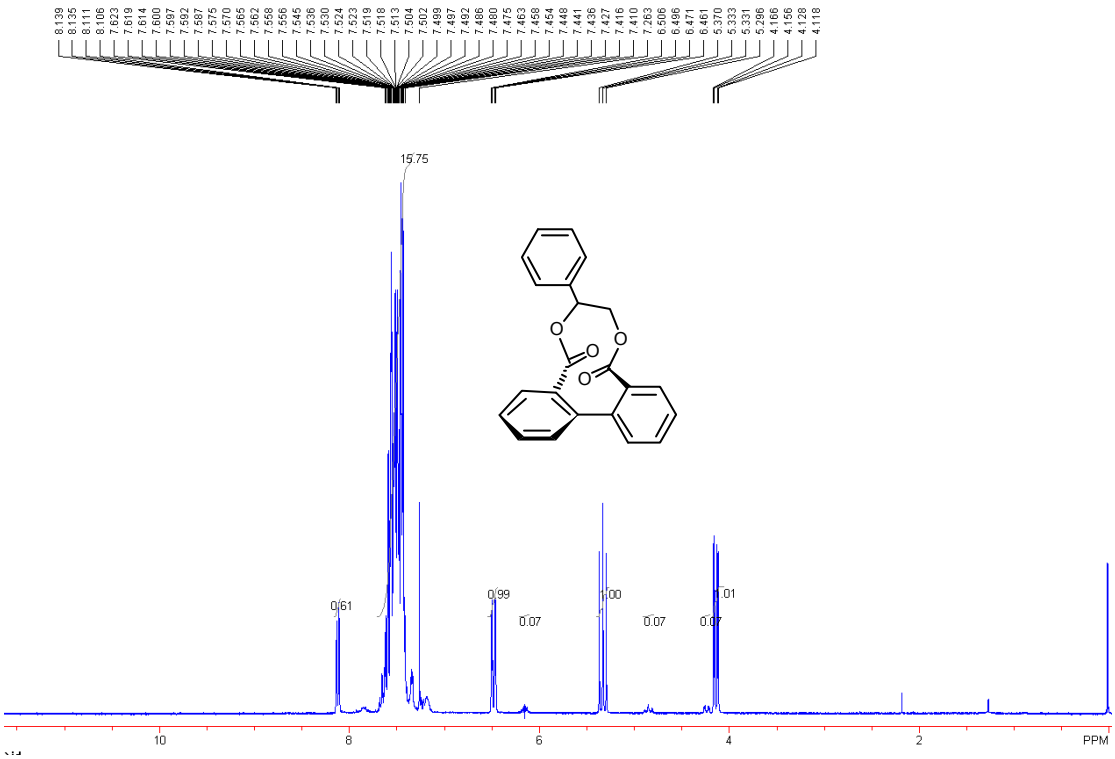
13-^{1}H NMR($CDCl_3$)



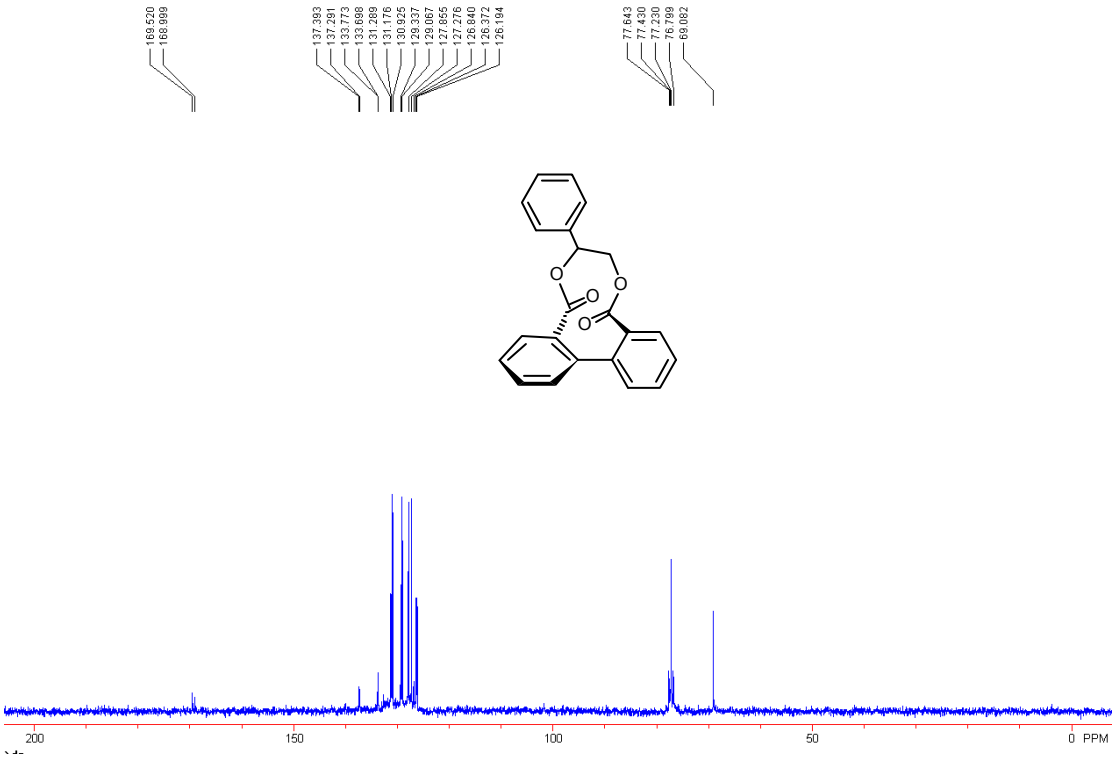
13-^{13}C NMR($CDCl_3$)



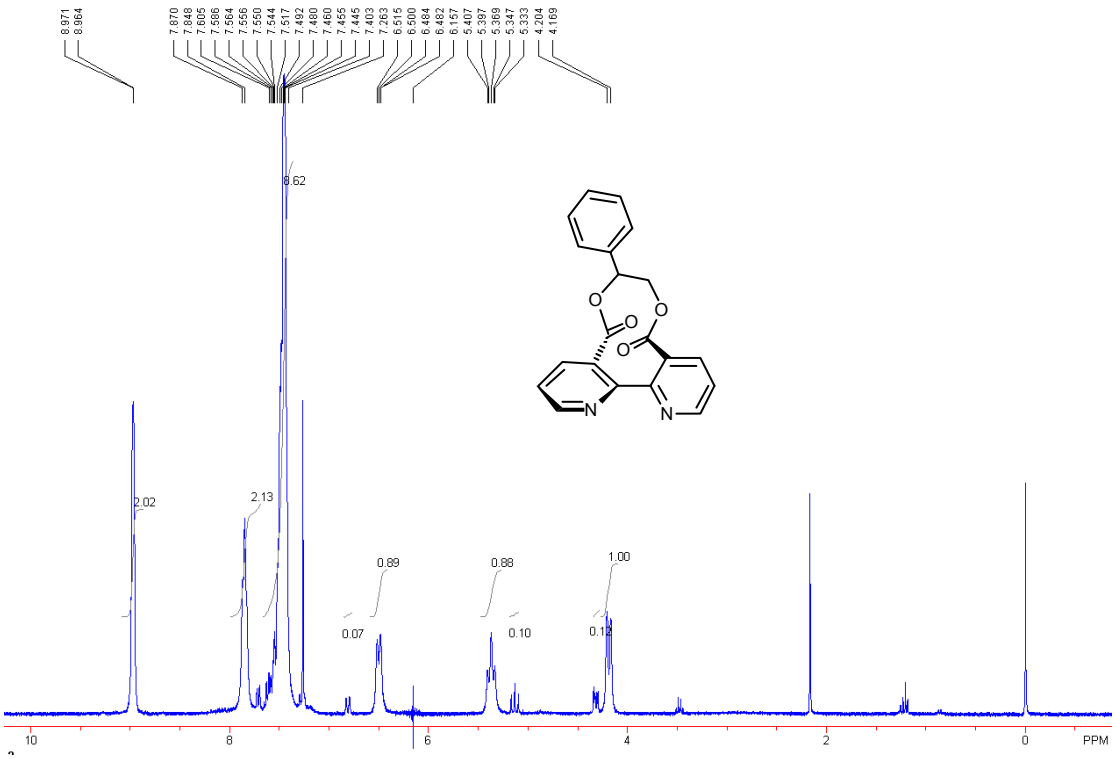
3e-^{1}H NMR($CDCl_3$)



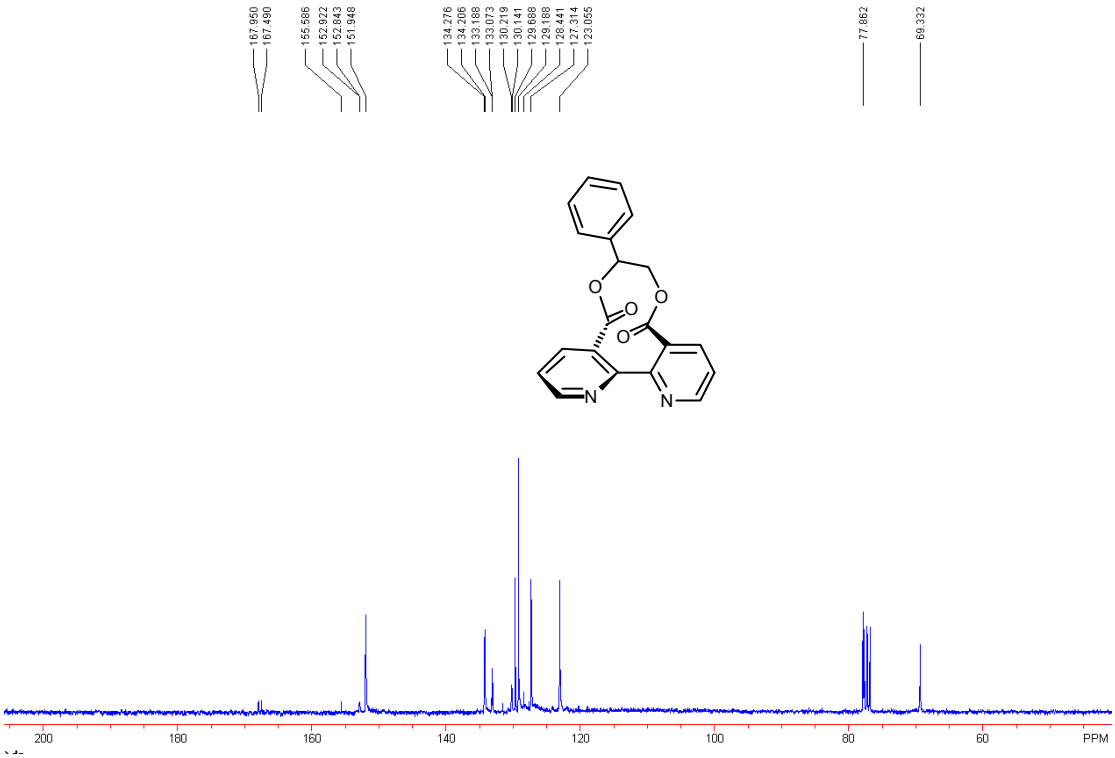
3e-^{13}C NMR($CDCl_3$)



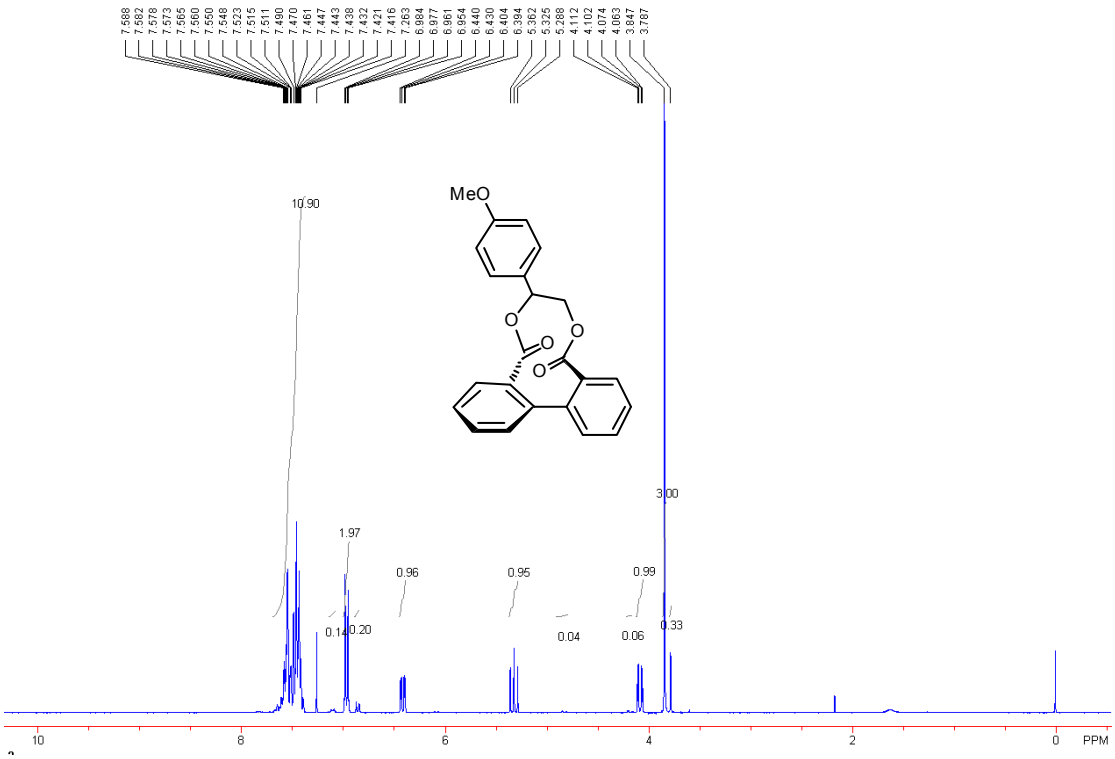
5e-^{1}H NMR($CDCl_3$)



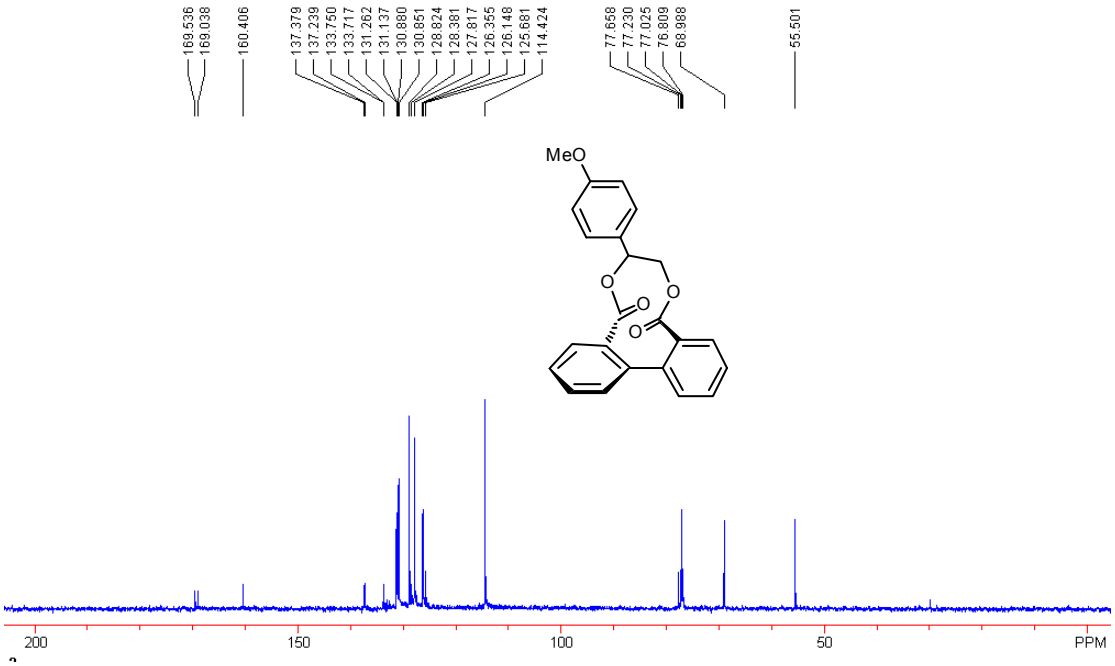
5e-^{13}C NMR($CDCl_3$)



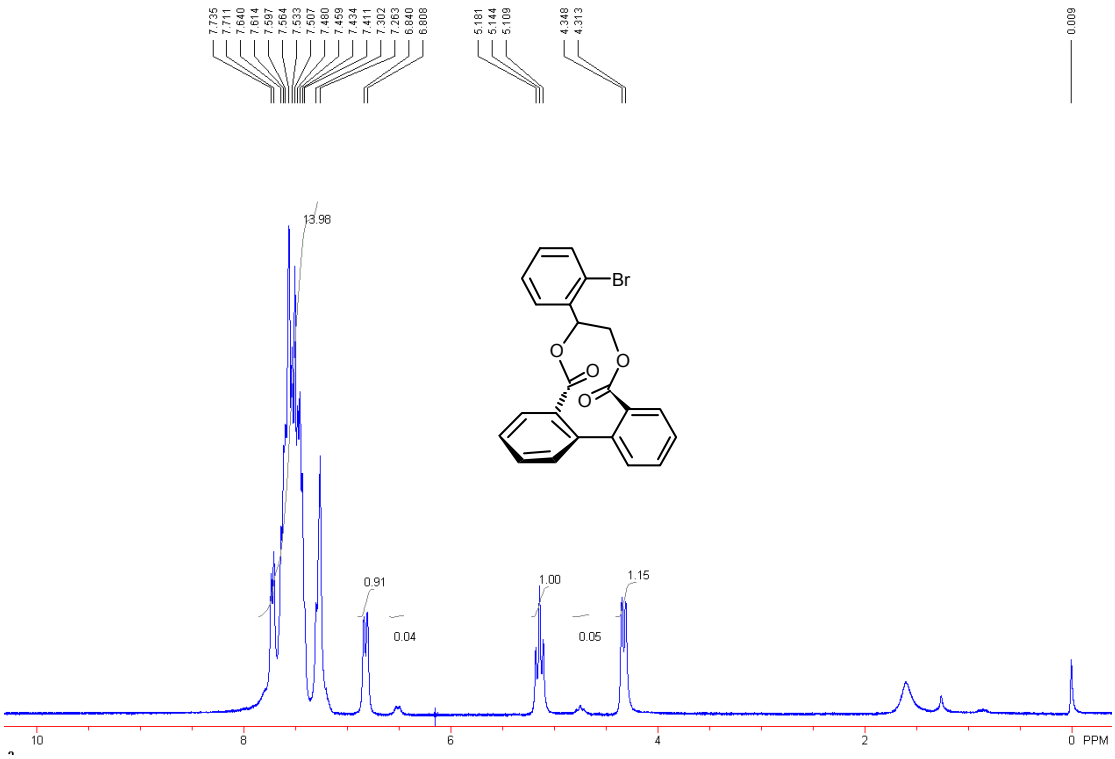
3f-^{1}H NMR($CDCl_3$)



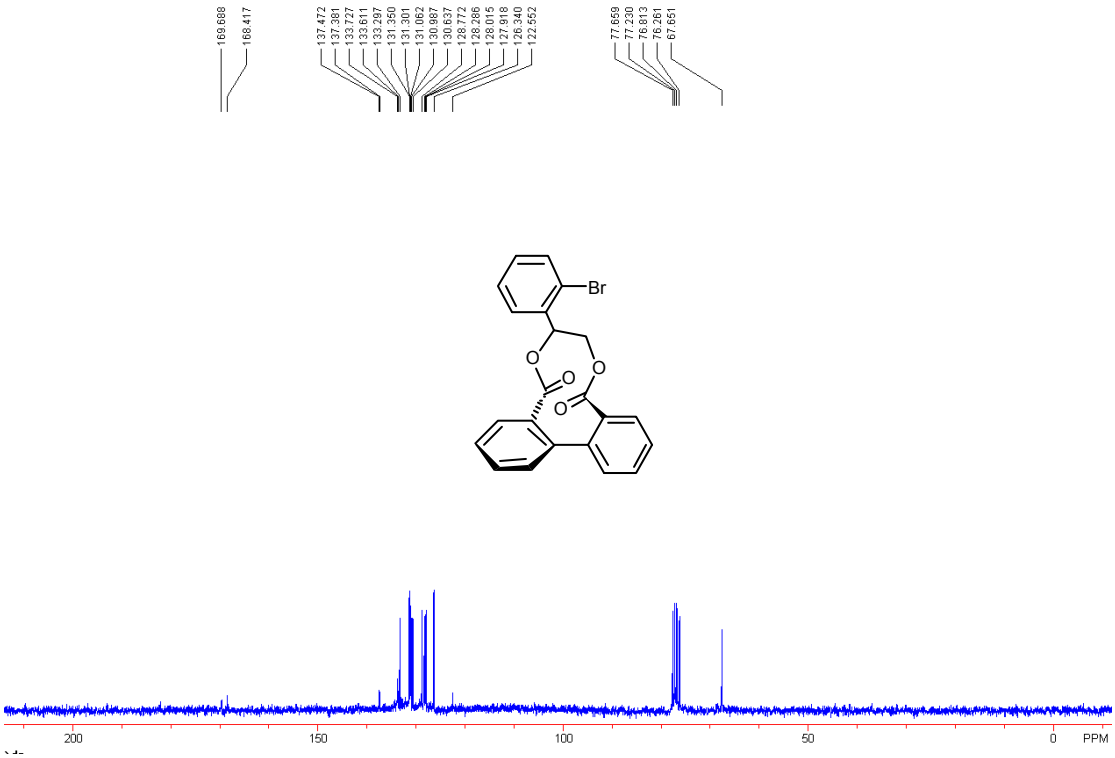
3f-^{13}C NMR($CDCl_3$)



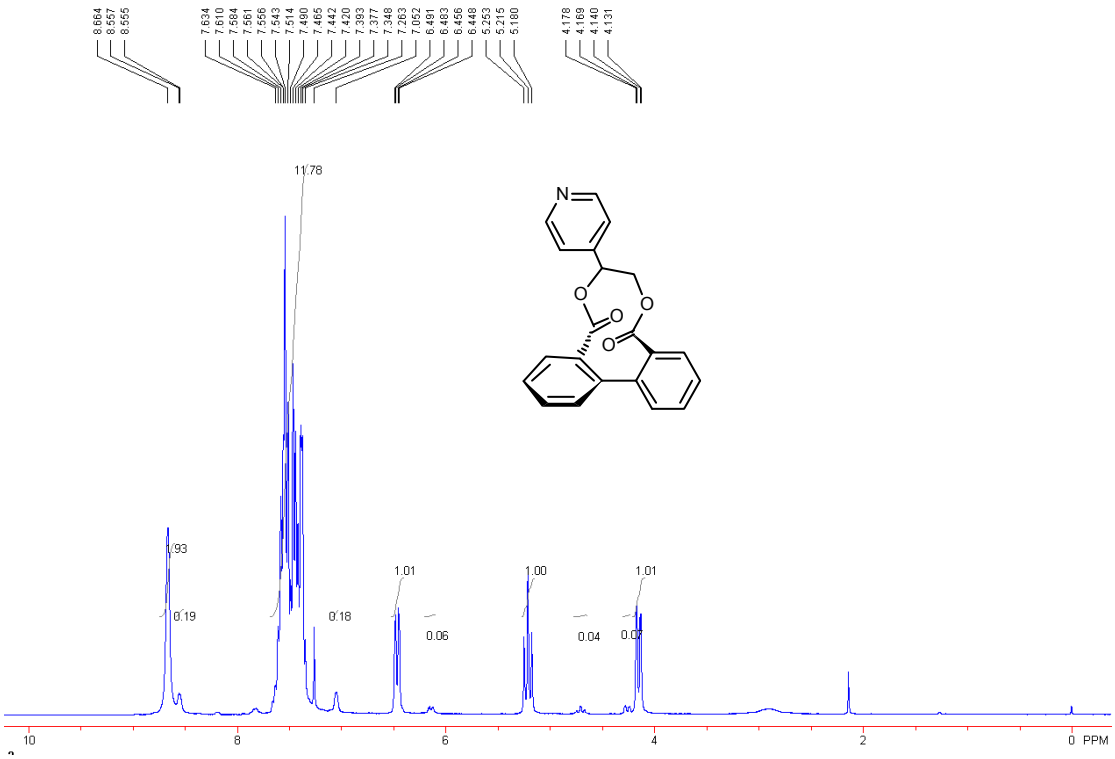
3g-^{1}H NMR($CDCl_3$)



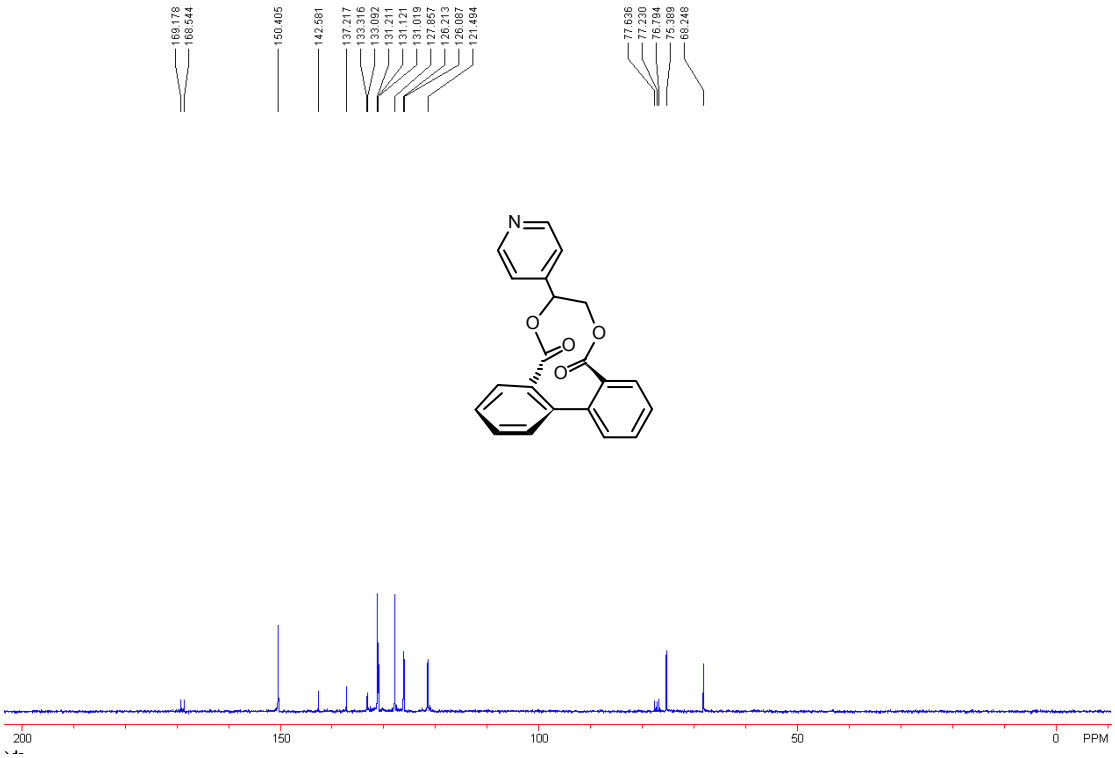
3g-^{13}C NMR($CDCl_3$)



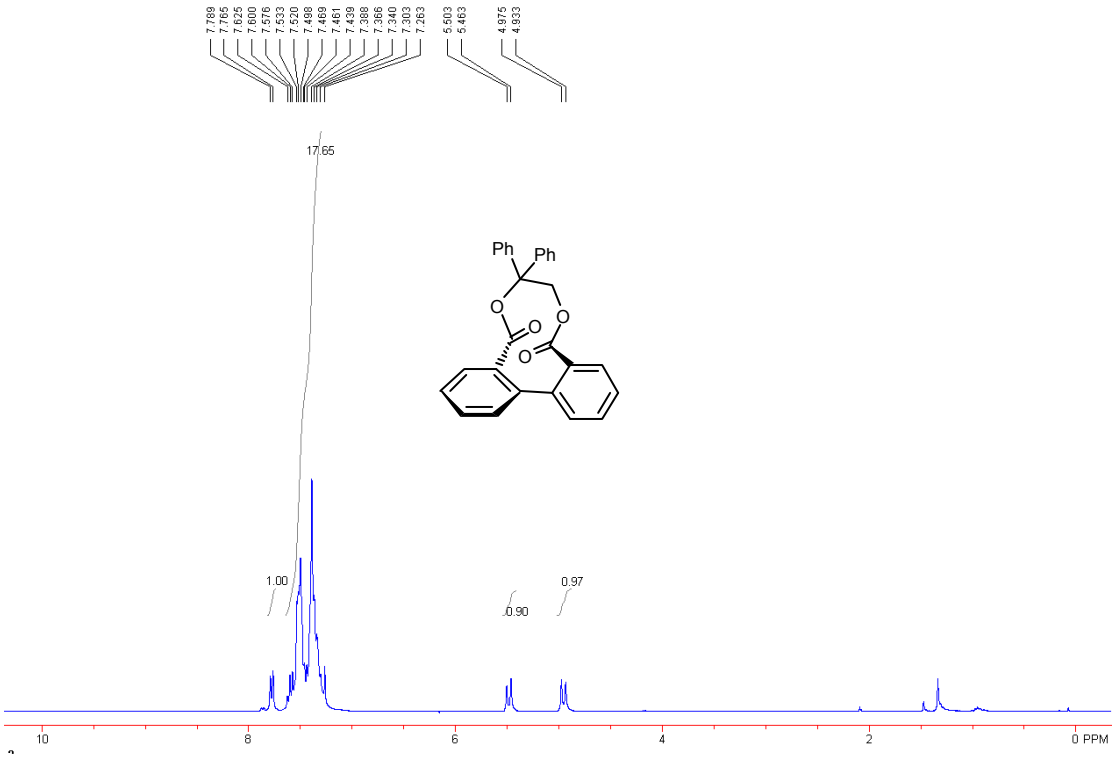
3h-^{1}H NMR($CDCl_3$)



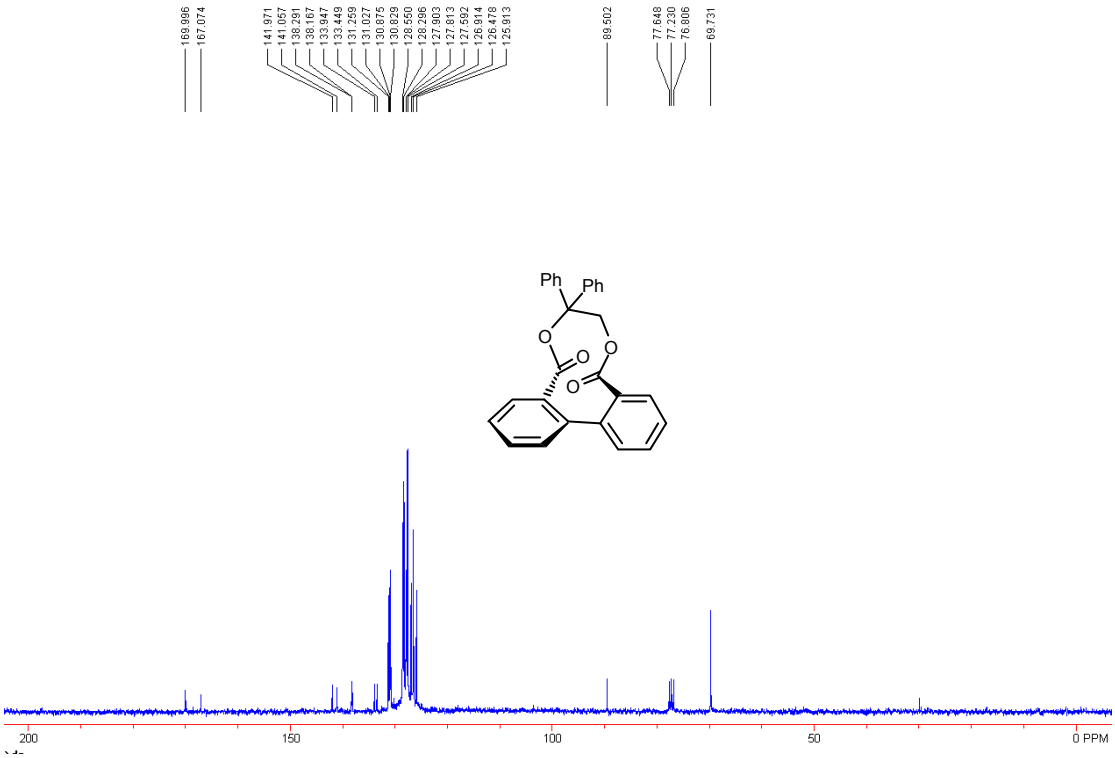
3h-^{13}C NMR($CDCl_3$)



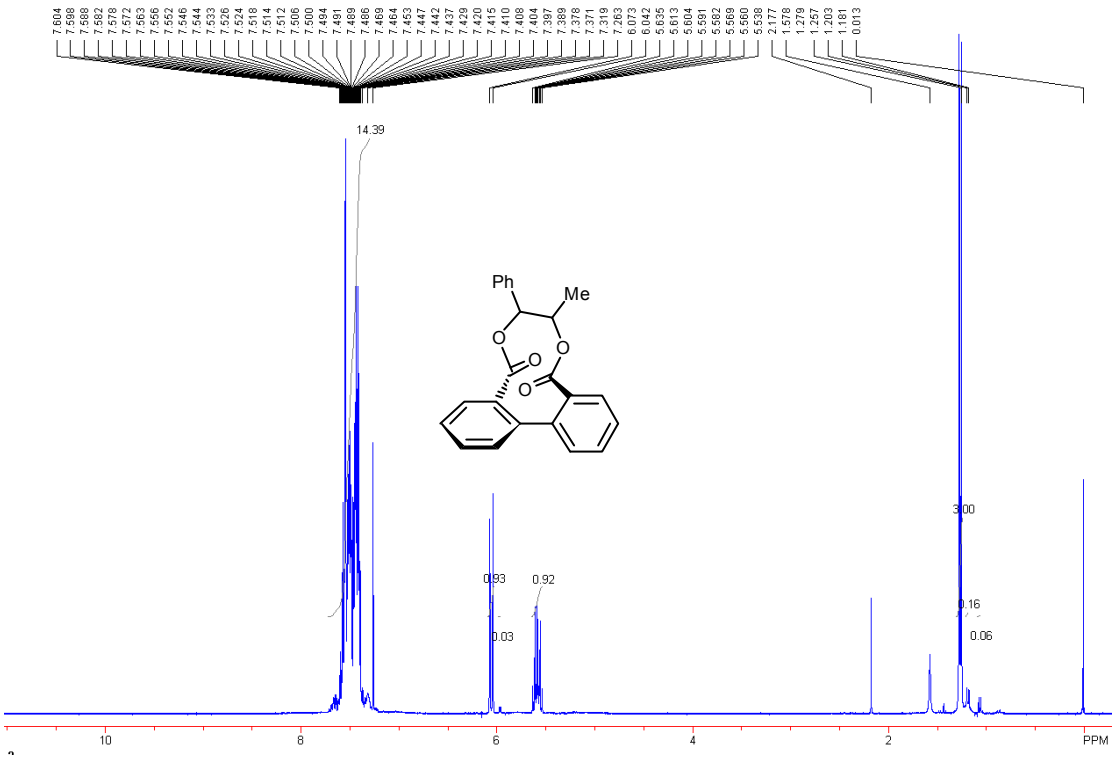
3i-^{1}H NMR($CDCl_3$)



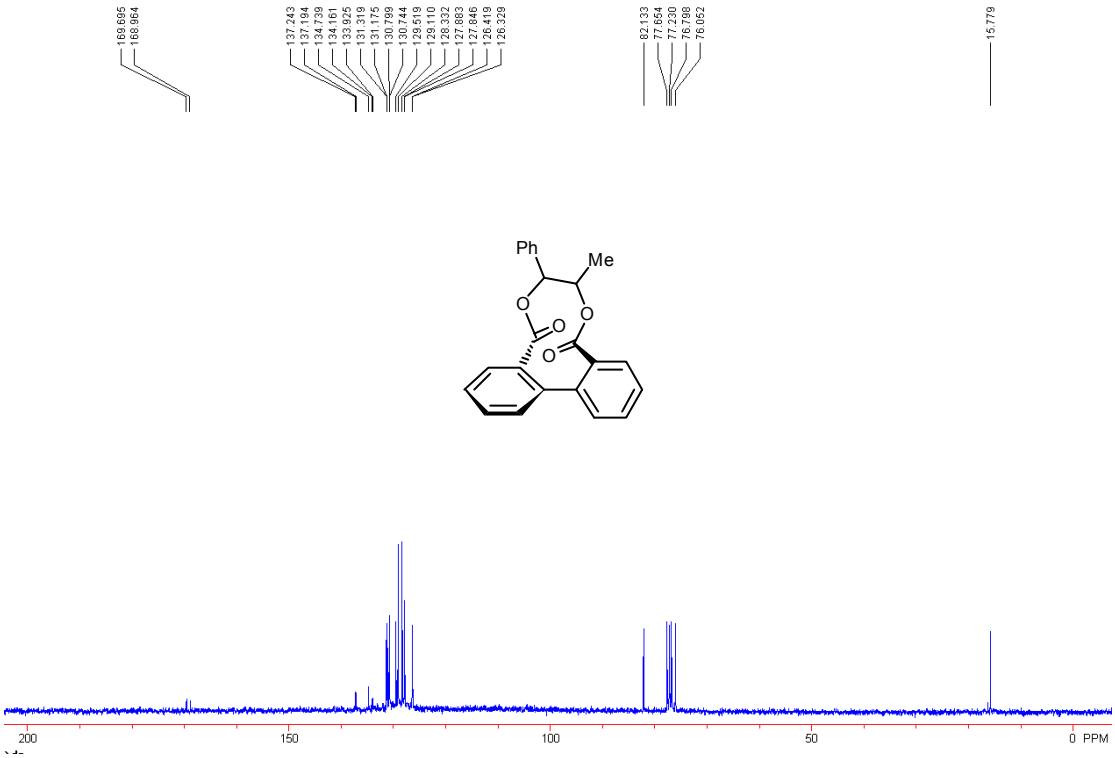
3i-^{13}C NMR($CDCl_3$)



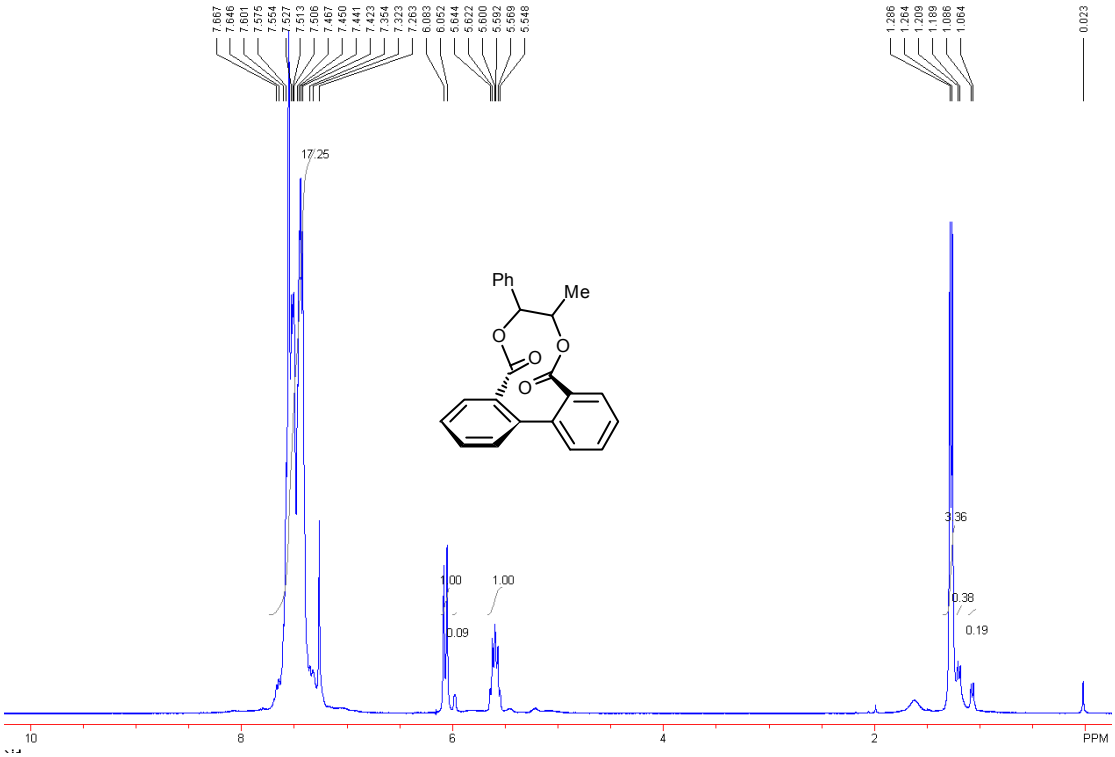
3j from photoreaction of PQ with 1j -^{1}H NMR($CDCl_3$)



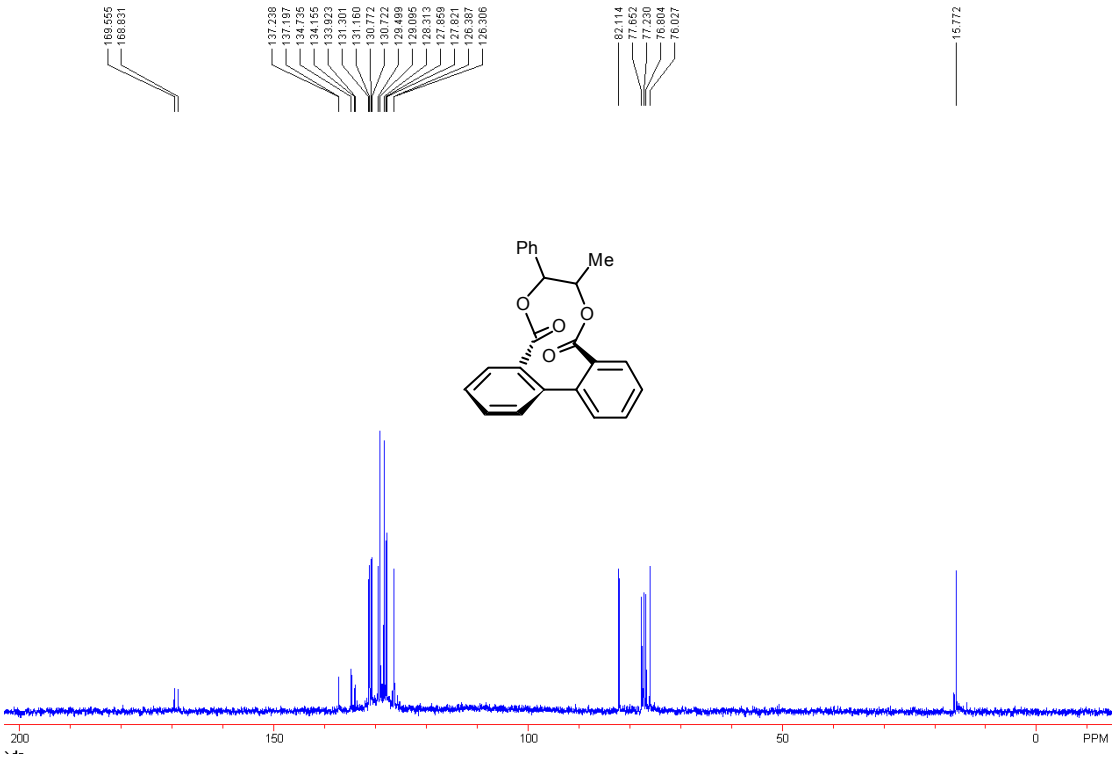
3j from photoreaction of PQ with 1j -^{13}C NMR($CDCl_3$)



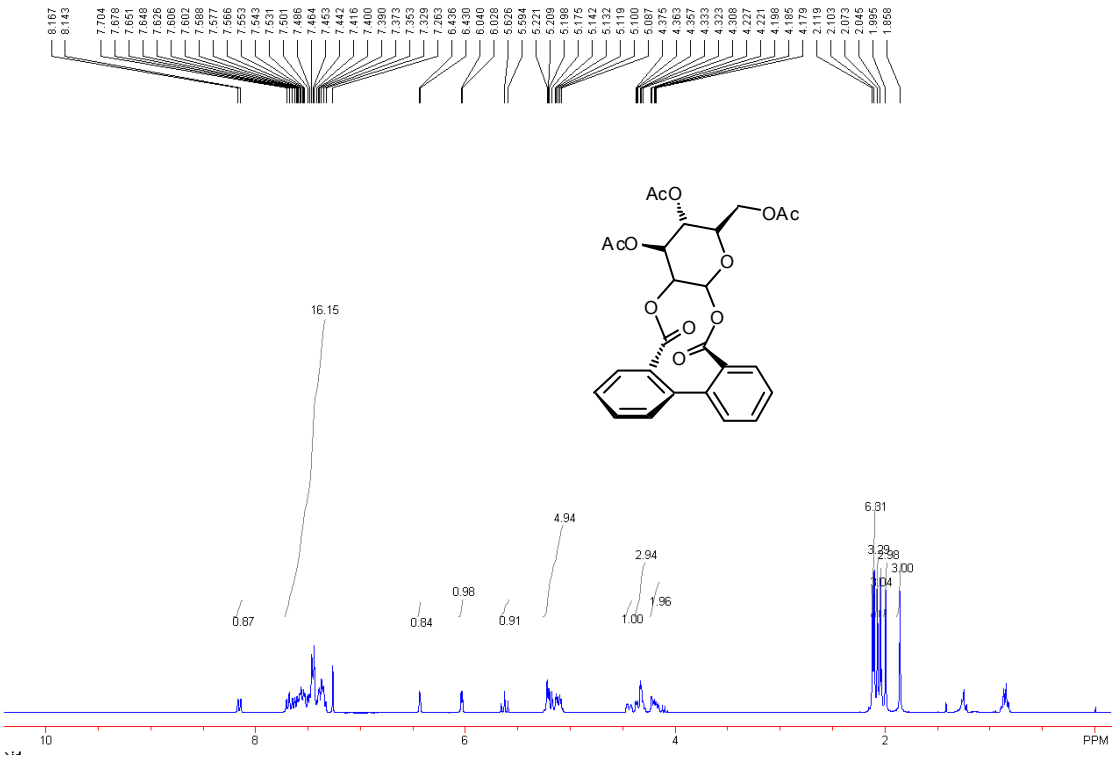
3j from photoreaction of PQ with 1k -^{1}H NMR($CDCl_3$)



3j from photoreaction of PQ with 1k -^{13}C NMR($CDCl_3$)



3l-^{1}H NMR($CDCl_3$)



3l-^{13}C NMR($CDCl_3$)