Supplementary Material (ESI) for Chemical Communications

Nitrones as Dipoles for Rapid Strain-Promoted 1,3-Dipolar Cycloadditions with Cyclooctynes

Supplementary Material

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Materials and Methods

All chemical reagents were purchased from Sigma-Aldrich and were used without further purification. Deuterated solvents were purchased from Cambridge Isotope laboratories. Thin layer chromatography (TLC) was carried out on Analtech Uniplate® silica gel plates (60 Å F254, layer thickness 250μm) using UV light to visualize the course of the reaction. Flash column chromatography was performed using silica gel (60 Å, particle size 40–63 μm). ^{1}H NMR and ^{13}C NMR spectra were obtained using a 400 MHz Bruker NMR spectrometer. Chemical shifts are reported as δ referenced to solvent and coupling constants (*J*) are reported in Hz. Acyclic nitrones, *N*-methyl-α-phenylnitrone, *N*-benzyl-α-phenylnitrone and *N*-phenyl-α-phenylnitrone were prepared by micelle catalysis[1]. Cyclic nitrones, 1-pyrroline *N*-oxide[2], 3,4-dihydroisoquinoline *N*-oxide[2], and (±)-4-(tert-butoxycarbonylamino)-3,4-dihydro-2H-pyrrole 1-oxide[3,4] were prepared according to literature procedure.

Synthesis of 5,6-didehydro-11,12-dihydrodibenzo[a,e]cyclooctene (2).

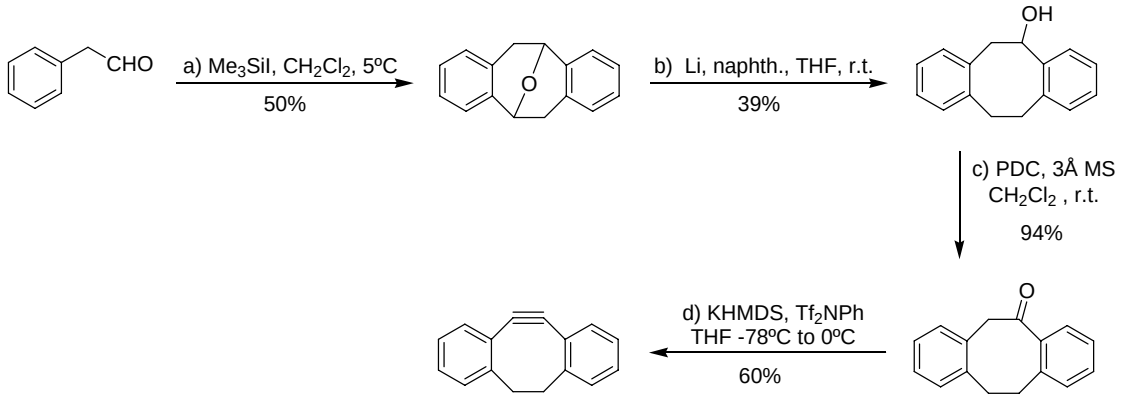
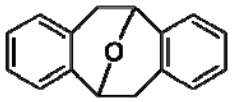
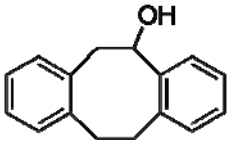


Figure S1. Reagents and conditions for synthesis of 5,6-didehydro-11,12-dihydrodibenzo[a,e]cyclooctene.

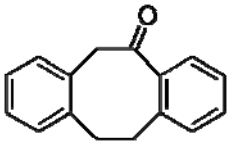


2,3:6,7-Dibenzo-9-oxabicyclo[3.3.l]nona-2,6-diene[5]. An oven dried 100 mL Erlenmeyer flask was charged with phenylacetaldehyde (12.5 g, 104 mmol) and freshly distilled dichloromethane (52 mL). The flask was stoppered under an atmosphere of nitrogen and cooled in an ice bath. To this solution was added iodotrimethylsilane (17.5 mL, 125 mmol) and the reaction was allowed to stand at 5 ºC for 7 days. Upon completion, sodium thiosulfate solution (1 M, 100 mL) and dichloromethane (100 mL) were added, and the mixture was stirred until the iodine color had been discharged. The organic phase was separated, and dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo* yielding a dark brown oil that was purified by flash column chromatography (dichloromethane:hexanes 6:4 to 100% dichloromethane); R_f = 0.72. The ether (5.78 g, 50%) was obtained as a brittle brown solid. 'H NMR (400 MHz, CDC1$_3$) δ 7.17-6.99 (m, 8H), 5.32 (d, *J* = 6Hz, 2H), 3.58 (dd, *J* = 16.2, 6.2 Hz), 2.70 (d, *J* = 16.2 Hz, 2H,); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 131.6, 129.0, 126.8, 125.9, 125.1, 69.5, 36.1.

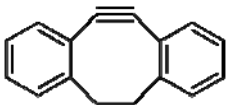


5,6,11,12-Tetrahydro-dibenzo[a,e]cycloocten-5-ol[5,6,7]: Li metal (300mg, ~10mmol, from a 25% wt. dispersion in mineral oil) was placed under Ar in a 15mL pear shaped flask. The Li metal was washed with THF (3x1mL). The resultant metal was suspended in THF (6 mL) and a catalytic amount of naphthalene (15 mg, 0.1 mmol) was added and the mixture was stirred until it turned a dark green colour. A solution of 2,3,6,7-dibenzo-9-oxabicyclo[3.3.l]nona-2,6-diene (225 mg, 1 mmol) in THF (0.4mL) was added dropwise over 5 min. After stirring the reaction mixture for 2 h, a solution of water (23 μL, 1.3mmol) in THF (1 mL) was carefully added. After stirring for 15 min, the mixture was quenched by slow dropwise addition of H_2O (2 mL) and the resulting mixture extracted with Et_2O (3x10 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous magnesium sulfate, filtered and concentrated to give a crude yellow oil. Purification by column chromatography, eluting dichloromethane:hexanes/8:2 (R_f=0.3) to 100% dichloromethane, yielded the title compound as a crystalline white solid (87 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-6.93 (m, 8H), 5.26 (t, *J* = 8.0 Hz, 1H), 3.54 (dd, *J* = 14.1, 7.7Hz, 1H), 3.43-3.38 (m, 1H), 3.21-3.01 (m, 4H), 2.25 (br, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 139.3, 138.0, 137.5, 130.1, 130.0, 129.8, 127.5, 126.9, 126.5, 126.4, 126.0, 74.8, 43.7, 35.1, 33.6.



11,12-Dihydro-dibenzo[a,e]cycloocten-5(6H)-one[7,8]: To a stirring solution of 5,6,11,12-tetrahydro-dibenzo[a,e]cycloocten-5-ol (87 mg, 0.39 mmol) in freshly distilled dichloromethane (4 mL), was added crushed 3Å molecular sieves (150 mg) and the resultant mixture was stirred at room temperature under a stream of nitrogen gas for 5 min. Then pyridinium dichromate (293 mg, 0.78mmol) was added and the reaction was stirred at room temperature for 8 h until the reaction was complete as evident by thin layer chromatography. The reaction was diluted with dichloromethane (25 mL) and was filtered through a plug of celite. The solvent was removed by rotary evaporation providing a brown crude orange solid. Purification by flash column chromatography eluting dichloromethane: hexanes (6:4) (R_f = 0.38) yielded the title compound (81.2 mg, 94%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-6.99 (m, 8H), 4.16 (s, 2H), 3.40-3.25(m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 138.7, 138.4, 137.8, 133.5, 131.5, 130.8, 130.5, 129.6, 128.0, 127.4, 126.7, 126.5, 51.5, 34.7, 33.7.



5,6-Didehydro-11,12-dihydrodibenzo[a,e]cyclooctene (2)[9,10]: A stirred solution of 11,12-dihydro-dibenzo[a,e]-cycloocten-5(6H)-one (991 mg, 4.46 mmol) in freshly distilled THF (44 mL) was cooled to −78˚C and *N*-phenyl-trifluoromethanesulfonimide (1.911 g, 5.35 mmol) was added, followed by the slow addition of a potassium bis(trimethylsilyl)amide solution (10.7 mL, 5.35 mmol of a 0.5 M solution in toluene). The resulting mixture was stirred at −78 °C and was allowed to warm to 0 ºC. Potassium bis(trimethylsilyl)amide solution (10.7 mL, 5.35 mmol) was then added dropwise over 45 minutes at 0 ºC. The reaction was allowed to warm to room temperature over 30 minutes and was concentrated *in vacuo*. Purification by flash column chromatography, eluting Hexanes: Dichloromethane (97:3 to 95:5), yielded 5,6-dihydro-11,12-didehydrodibenzo[a,e]cyclooctyne (544 mg, 60%) as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 8H), 3.38-3.29 (m, 2H),

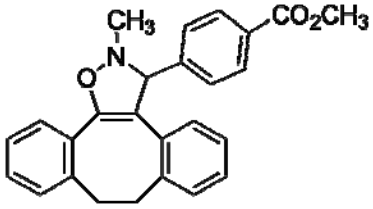
2.51-2.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 129.35, 127.6, 126.5, 126.1, 123.9, 111.5, 36.4.

General procedure for strain-promoted 1,3-dipolar cycloadditions of nitrones with alkynes.

To a stirring solution of dibenzocyclooctyne, **2** (10.2 mg, 0.05 mmol) in toluene (500 μL) was added nitrone, **1a-n** (0.05 mmol). Reactions were stirred open to air and were monitored by thin layer chromatography for disappearance of the nitrone. Upon completion, the solvent was removed under reduced pressure and the crudes were purified by flash column chromatography to afford pure isoxazoline products.

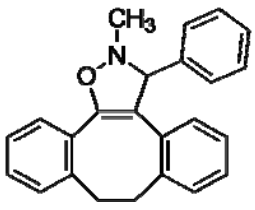
Characterization Data for New Compounds

Compound 3a



Purified by eluting hexanes:EtOAc (9:1, R_f = 0.34) and was obtained as a white solid (19.0 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.96 (d, *J* = 8.3Hz, 2H), 7.52-7.50 (m, 1H), 7.45 (d, *J* = 8.3Hz, 2H), 7.18-7.04 (m, 7H), 5.09 (s, 1H), 3.89 (s, 3H), 3.41-3.33 (m, 1H), 3.15 (s, 3H), 3.19-2.98 (m, 2H), 2.88-2.81 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 147.3, 146.2, 141.1, 139.1, 131.9, 131.0, 129.9, 129.8, 129.7, 129.3, 128.8, 127.9, 127.5, 127.2, 126.5, 125.8, 125.5, 109.8, 80.3, 52.0, 47.0, 36.7, 35.7, 32.8. HRMS calcd. for $C_{26}H_{23}NO_3$ $[M+1]^+$ 398.1756, found 398.1744.

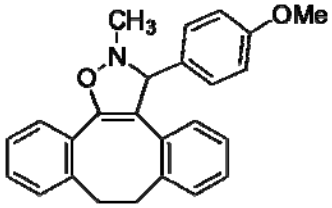
Compound 3b



Purified by eluting hexanes:EtOAc (96:4, R_f = 0.41) and was obtained as a white solid (15.2 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-6.98 (m, 13H), 5.03 (m, 1H), 3.45-3.38 (m, 1H), 3.23-3.08 (m, 2H), 3.13 (s, 3H), 3.00-2.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 141.1, 138.9, 132.4, 131.0, 129.8, 129.6,

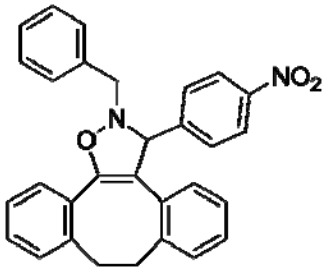
128.6, 128.6, 127.9, 127.8, 127.6, 127.0, 126.8, 125.7, 125.5, 110.2, 80.9, 47.1, 36.9, 32.9. HRMS calcd. for $C_{24}H_{21}NO$ $[M+1]^+$ 340.1701, found 340.1660.

Compound 3c



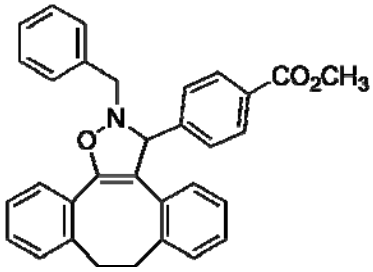
Purified by eluting hexanes:EtOAc (95:5, R_f = 0.43) and was obtained as a white solid (19.0 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 1H), 7.32 (d, *J* = 8.7Hz, 2H), 7.18-6.94 (m, 7H), 6.84 (d, *J* = 8.7Hz, 2H), 4.99 (s, 1H), 3.78 (s, 3H), 3.46-3.39 (m, 1H), 3.26-3.08 (m, 2H), 3.10 (s, 3H), 3.05-2.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 147.3, 141.0, 138.8, 132.5, 131.0, 129.8, 129.6, 128.5, 128.2, 128.0, 127.7, 126.9, 125.7, 125.5, 114.0, 110.3, 80.5, 55.2, 37.0, 32.9. HRMS calcd. for $C_{25}H_{23}NO_2$ $[M+1]^+$ 370.1807, found 370.1721.

Compound 3d



Purified eluting hexanes:EtOAc (9:1, R_f = 0.18) and was obtained as a yellow solid (22.3 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.8 Hz, 2H), 7.55-7.09 (m, 15H), 5.36 (s, 1H), 4.72 (d, *J* = 12.7 Hz, 1H), 4.33 (d, *J* = 12.7 Hz, 1H), 3.39-3.32 (m, 1H), 3.14-2.85 (m, 2H), 2.84-2.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 148.3, 147.2, 141.1, 139.2, 135.7, 131.6, 131.0, 130.0, 129.3, 129.3, 129.1, 128.7, 127.9, 127.4, 127.3, 127.2, 126.0, 125.6, 123.7, 109.5, 76.3, 62.9, 36.5, 33.0. HRMS calcd. for $C_{30}H_{24}N_2O_3$ $[M+1]^+$ 461.1865, found 461.1866.

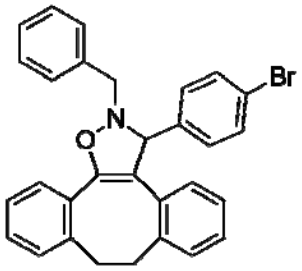
Compound 3e



Purified eluting hexanes:EtOAc (9:1, R_f = 0.31) and was obtained as a white solid (19.2 mg, 96%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3Hz, 2H), 7.53-7.02 (m, 15H), 5.30 (s, 1H), 4.67 (d, *J* = 12.8 Hz, 1H), 4.32 (d, *J* = 12.8 Hz, 1H), 3.89 (s, 3H), 3.39-3.32 (m, 1H), 3.15-2.98 (m, 2H), 2.87-2.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$)

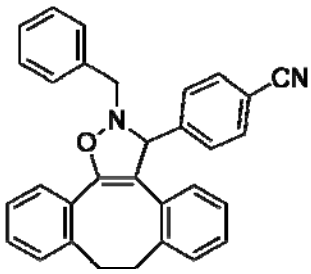
δ 167.0, 148.0, 146.4, 141.1, 139.2, 136.0, 132.0, 131.0, 130.0, 129.8, 129.3, 129.2, 128.8, 128.6, 128.0, 127.8, 127.6, 127.2, 126.6, 125.8, 125.6, 110.0, 76.9, 63.0, 52.0, 36.6, 33.0. HRMS calcd. for $C_{32}H_{27}NO_3$ $[M+1]^+$ 474.2069, found 474.2080.

Compound 3f.



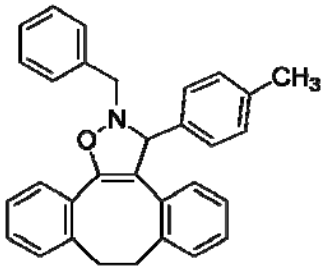
Purified eluting hexanes:EtOAc (9:1, R_f = 0.55) and was obtained as an off white solid (24.2 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.52-7.00 (m, 17H), 5.21 (s, 1H), 4.65 (d, *J* = 12.8 Hz, 1H), 4.30 (d, *J* = 12.8 Hz, 1H), 3.42-3.35 (m, 1H), 3.20-3.04 (m, 2H), 2.95-2.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 141.1, 140.5, 139.1, 136.0, 132.1, 131.6, 131.0, 130.0, 129.8, 129.3, 128.8, 128.6, 128.5, 127.9, 127.8, 127.7, 127.1, 125.8, 125.6, 121.3, 110.0, 63.0, 36.7, 33.0. HRMS calcd. For $C_{30}H_{24}NOBr$ $[M+1]^+$ 494.1120, found 494.1098.

Compound 3g



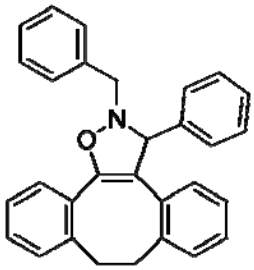
Purified eluting hexanes:EtOAc (9:1, R_f = 0.26) and was obtained as a off white solid (21.7 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.05 (m, 17H), 5.30 (s, 1H), 4.70 (d, *J* = 12.7 Hz, 1H), 4.30 (d, *J* = 12.7Hz, 1H), 3.39-3.32 (m, 1H), 3.15-2.96 (m, 2H), 2.87-2.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 146.5, 141.0, 139.2, 135.7, 132.3, 131.6, 131.0, 129.9, 129.3, 129.0, 128.6, 127.9, 127.9, 127.3, 127.3, 127.1, 125.9, 125.6, 118.9, 111.1, 109.5, 76.5, 62.8, 36.5, 32.9. LRMS calcd. for $C_{31}H_{24}N_2O$ $[M+1]^+$ 455.4, found 455.4.

Compound 3h



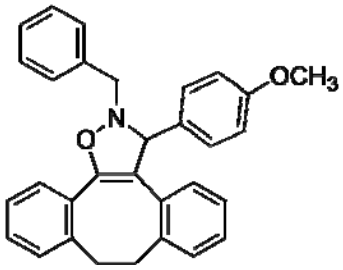
Purified eluting hexanes:EtOAc (9:1, R_f = 0.43) and was obtained as a slow crystallizing white solid (23.2 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-6.96 (m, 17H), 5.22 (s, 1H), 4.62 (d, *J* = 12.9Hz, 1H), 4.31 (d, *J* = 12.9Hz, 1H), 3.45-3.38 (m, 1H), 3.25-3.09 (m, 2H), 3.01-2.94 (m, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 141.0, 138.9, 138.4, 137.1, 136.3, 132.6, 131.0, 129.9, 129.6, 129.4, 129.2, 128.5, 128.5, 128.1, 127.9, 127.6, 126.9, 126.9, 125.7, 125.5, 110.5, 63.1, 36.9, 33.0, 21.1. HRMS calcd. for $C_{31}H_{27}NO$ $[M+1]^+$ 430.2171, found 430.2108.

Compound 3i



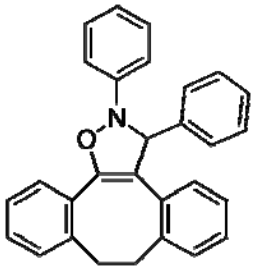
Purified eluting hexanes:EtOAc (9:1, R_f = 0.33) and was obtained as a white solid (19.2 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-6.96 (m, 18H), 5.24 (s, 1H), 4.63 (d, *J* = 12.9 Hz, 1H), 4.31 (d, *J* = 12.9 Hz, 1H), 3.43-3.35 (m, 1H), 3.22-3.05 (m, 2H), 2.97-2.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 141.4, 141.0, 139.0, 136.3, 132.5, 131.0, 130.0, 129.7, 129.4, 128.6, 128.5, 128.5, 127.9, 127.6, 127.4, 127.0, 125.7 ,125.5, 110.4, 63.1, 36.8, 33.0. HRMS calcd. for $C_{30}H_{25}NO$ $[M+1]^+$ 416.2014, found 416.1977.

Compound 3j



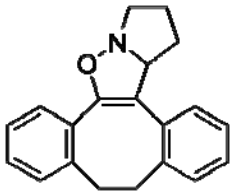
Purified eluting hexanes:EtOAc (9:1, R_f = 0.44) and was obtained as a white solid (21.0 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-6.81 (m, 17H), 5.21 (s, 1H), 4.61 (d, *J* = 12.9 Hz, 1H), 4.30 (d, *J* = 12.9 Hz, 1H), 3.78 (s, 3H), 3.45-3.37 (m, 1H), 3.26-3.09 (m, 2H), 3.03-2.96 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 147.9, 141.0, 138.9, 136.3, 133.6, 132.6, 131.0, 129.9, 129.6, 129.4, 128.5, 128.5, 128.2, 128.0, 127.8, 127.6, 126.9, 125.7, 125.5, 113.9, 110.4, 63.0, 55.2, 36.9, 33.0. HRMS calcd. for $C_{31}H_{27}NO_2$ $[M+1]^+$ 446.1946, found 446.1952.

Compound 3k



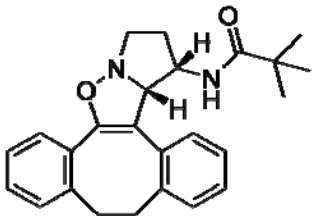
Purified eluting hexanes:EtOAc / 95:5 (R_f = 0.52) and was obtained as an off white solid (19.3 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-6.80 (m, 18H), 6.73 (s, 1H), 3.94-3.83 (m, 2H), 3.25-3.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 141.5, 139.6, 139.5, 138.5, 131.0, 130.8, 130.1,129.7, 129.1, 128.9, 128.8, 128.3, 127.0, 126.3, 126.1, 125.7, 121.0, 119.6, 117.8, 97.9, 35.6, 35.3. LRMS calcd. for $C_{29}H_{23}NO$ $[M+H]^+$ 402.4, found 402.4.

Compound 3l



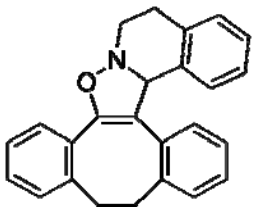
Purified eluting hexanes:EtOAc (7:3, R_f = 0.33) and was obtained as a white solid (14.4 mg, 100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.08 (m, 8H), 5.21 (dd, *J* = 7.3 Hz, 2.2 Hz, 1H), 3.62-3.49 (m, 2H), 3.47-3.40 (m, 1H), 3.32-3.25 (m, 1H), 3.17-3.09 (m, 1H), 2.99-2.92 (m, 1H). 2.07-1.82 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 140.8, 138.2, 132.6, 130.9, 129.7, 129.5, 128.4, 128.0, 127.0, 126.0, 125.6, 109.1, 74.9, 59.9, 36.9, 33.3, 31.3, 22.9. LRMS calcd. for $C_{20}H_{19}NO$ $[M+1]^+$ 290.3, found 290.3.

(±)-Compound 3m



Purified eluting hexanes:EtOAc (6:4, R_f = 0.56) and was obtained as a white crystalline solid (20.2 mg, 100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.08 (m, 8H), 4.94 (s, 1H), 4.76 (d, *J* = 1.9Hz, 1H), 4.07 (m, 1H), 3.65-3.56 (m, 1H), 3.55-3.47 (m, 2H), 3.43-3.36 (m, 1H), 3.17-3.09 (m, 1H), 3.00-2.94 (m, 1H), 2.37-2.32 (m, 1H), 1.91-1.88 (m, 1H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 149.0, 140.5, 138.4, 131.6, 130.9, 129.9, 129.4, 128.7, 128.1, 127.5, 127.2, 126.1, 125.6, 57.8, 36.7, 33.3, 30.6, 28.3. LRMS calcd. for $C_{25}H_{28}N_2O_3$ $[M+1]^+$ 405.4, found 405.4.

Compound 3n

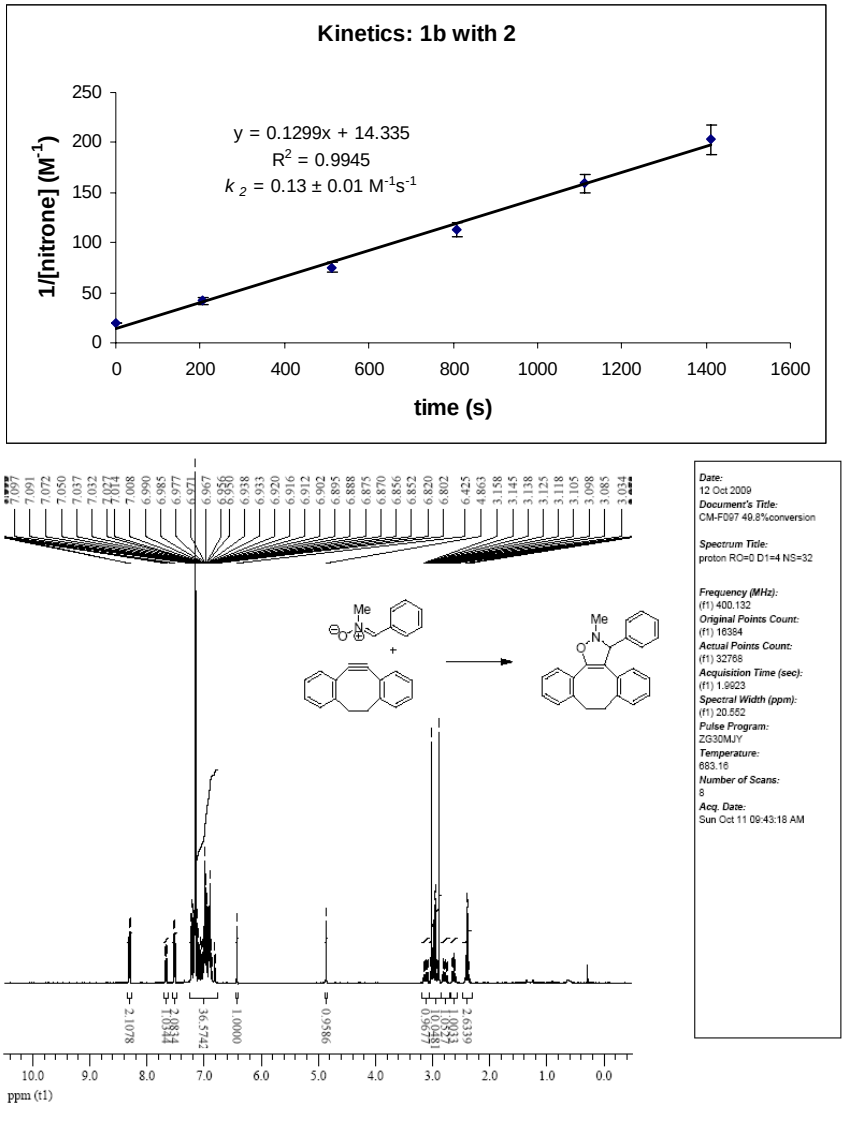


Purified eluting hexanes:EtOAc (9:1, R_f = 0.23) and was obtained as a white crystalline solid (17.3 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 1H), 7.17-7.06 (m, 9H), 6.96-6.92 (m, 1H), 6.58 (d, *J* = 7.7 Hz, 1H), 5.97 (s, 1H), 3.93-3.89 (m, 1H), 3.36-3.22 (m, 3H), 3.10-3.03 (m, 1H), 2.85-2.75 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 141.3, 138.9, 135.1, 133.6, 132.1, 131.0, 130.0, 129.4, 129.3, 128.8, 128.3, 127.8, 127.2, 126.6, 126.4, 126.0, 125.6, 125.5, 111.3, 71.1, 50.8, 36.7, 32.7, 24.5. HRMS calcd. for $C_{25}H_{21}NO$ $[M+1]^+$ 352.1701, found 352.1683.

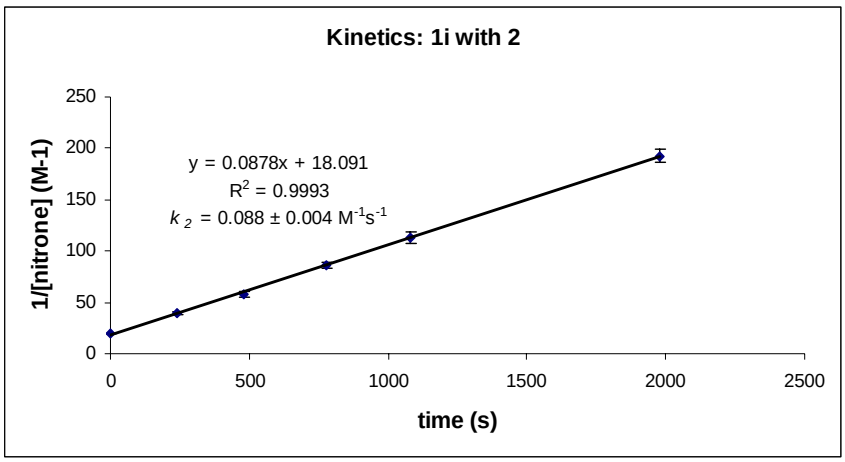
Kinetics measurements of 1b, 1i and 1n with 2

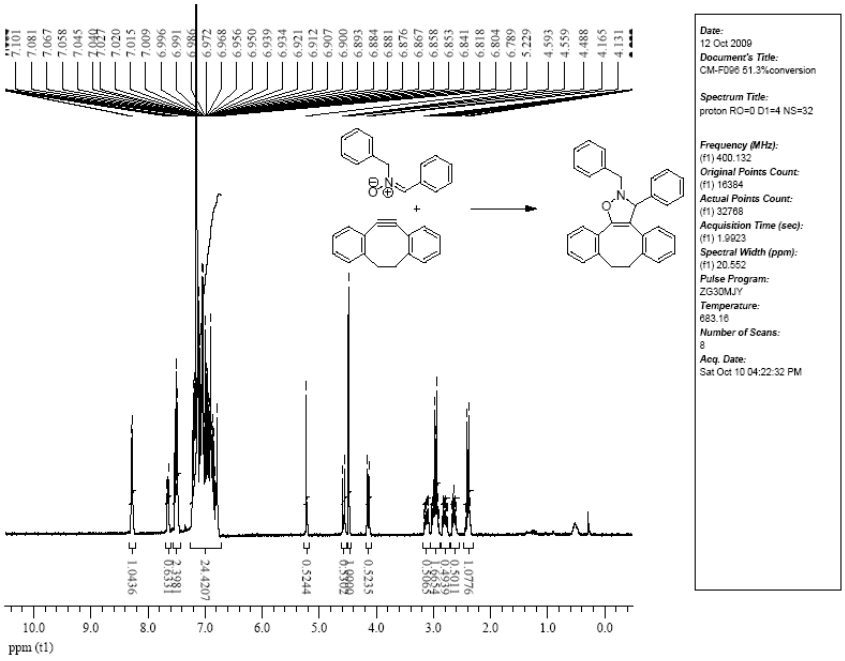
Figure S2 (A, B, C and D). The appropriate nitrone or benzyl azide and **2** were pre-dissolved in C_6D_6 and mixed at equimolar concentrations of ~50mM. Percent conversion was monitored both by disappearance of starting materials and by appearance of product as determined by integration at multiple chemical shifts in the ^{1}H NMR spectrum. No other products were detected by ^{1}H NMR and all reactions were performed in triplicate. Second order rate constants in units of $M^{-1}s^{-1}$ were determined by plotting 1/[nitrone] or 1/[azide] versus time and subsequently using analysis by linear regression. The second order rate constant k_2 ($M^{-1}s^{-1}$) corresponds to the determined slope. A representative ^{1}H NMR spectrum at ~50 to 75% conversion is included.

A) **1b** with **2**

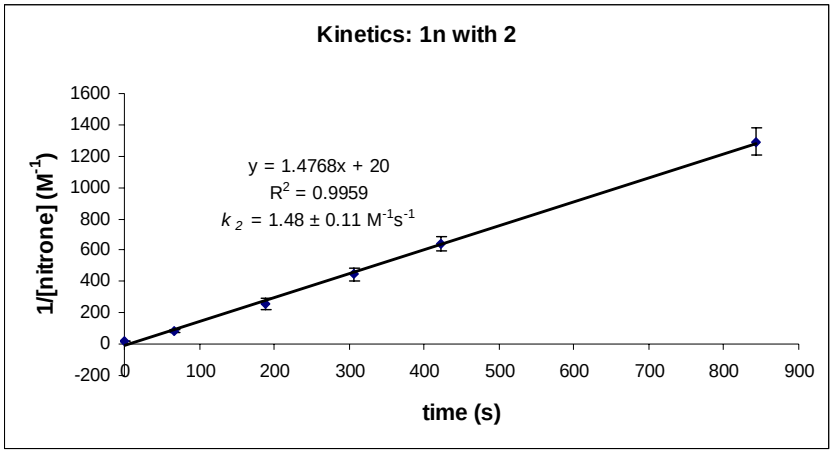


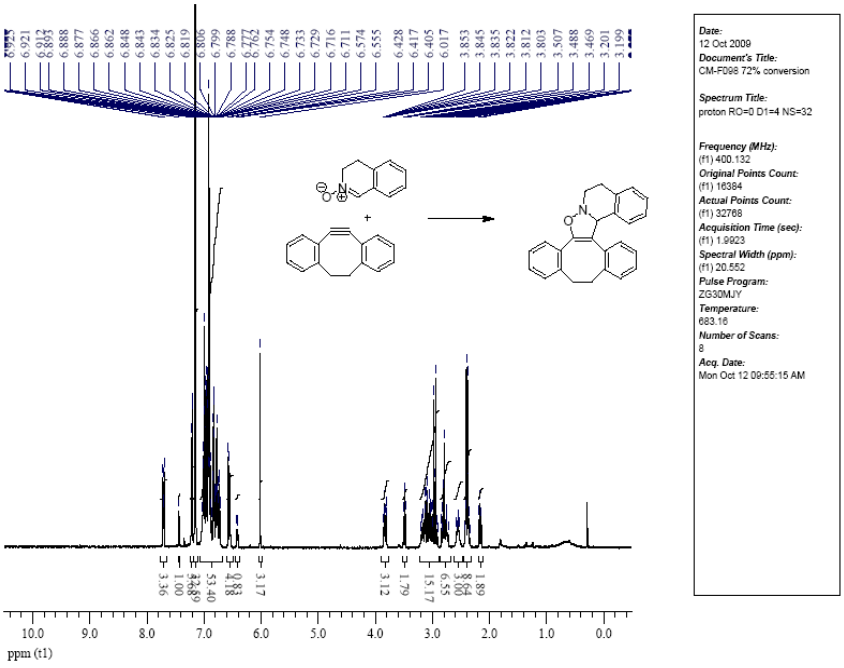
B) **1i** with **2**


Kinetics: 1i with 2
y = 0.0878x + 18.091
R2 = 0.9993
k 2 = 0.088 ± 0.004 M-1s-1
1/[nitrone] (M-1)
time (s)
0
50
100
150
200
250
0
500
1000
1500
2000
2500


ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.0436
2.3981
0.8331
24.4207
0.5244
0.5235
1.0776
Date:
12 Oct 2009
Document's Title:
CM-FD96 51.3%conversion
Spectrum Title:
proton RO=0 D1=4 NS=32
Frequency (MHz):
(f1) 400.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.9923
Spectral Width (ppm):
(f1) 20.552
Pulse Program:
ZG30MJY
Temperature:
683.16
Number of Scans:
8
Acq. Date:
Sat Oct 10 04:22:32 PM

C) **1n** with **2**


Kinetics: 1n with 2
y = 1.4768x + 20
R2 = 0.9959
k 2 = 1.48 ± 0.11 M-1s-1
1/[nitrone] (M-1)
time (s)


ppm (t1)
Date:
12 Oct 2009
Document's Title:
CM-F098 72% conversion
Spectrum Title:
proton RO=0 D1=4 NS=32
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Original Points Count:
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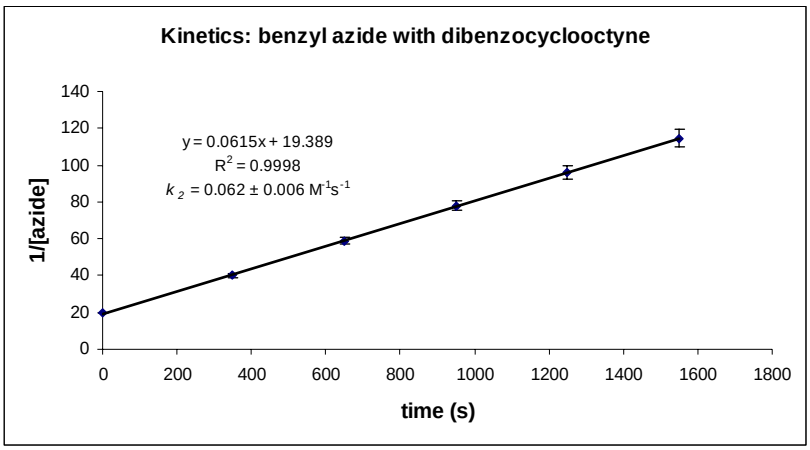
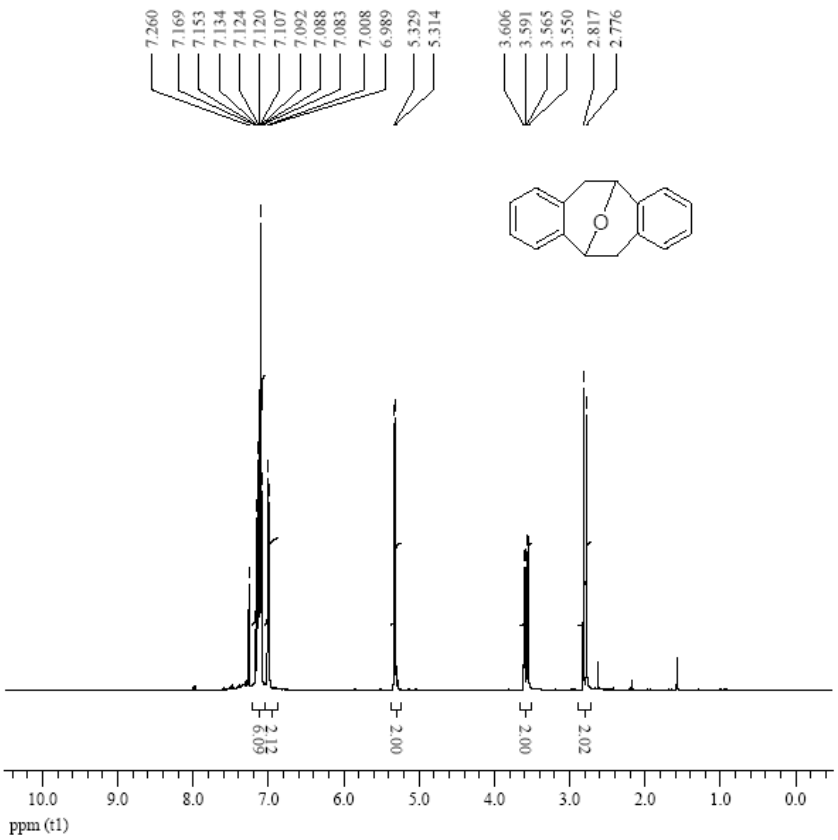
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.9923
Spectral Width (ppm):
(f1) 20.552
Pulse Program:
ZG30MJY
Temperature:
683.16
Number of Scans:
8
Acq. Date:
Mon Oct 12 09:55:15 AM

D) Benzyl azide with dibenzocyclooctyne



^{1}H and ^{13}C Spectra



Date:
28 Sep 2009
Document's Title:
1H-cm-e138

Spectrum Title:
cm-e138-Imostpure
proton RO=0 D1=4 NS=32

Frequency (MHz):
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Actual Points Count:
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Acquisition Time (sec):
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Spectral Width (ppm):
(f1) 20.552
Pulse Program:
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Temperature:
683.16
Number of Scans:
32
Acq. Date:
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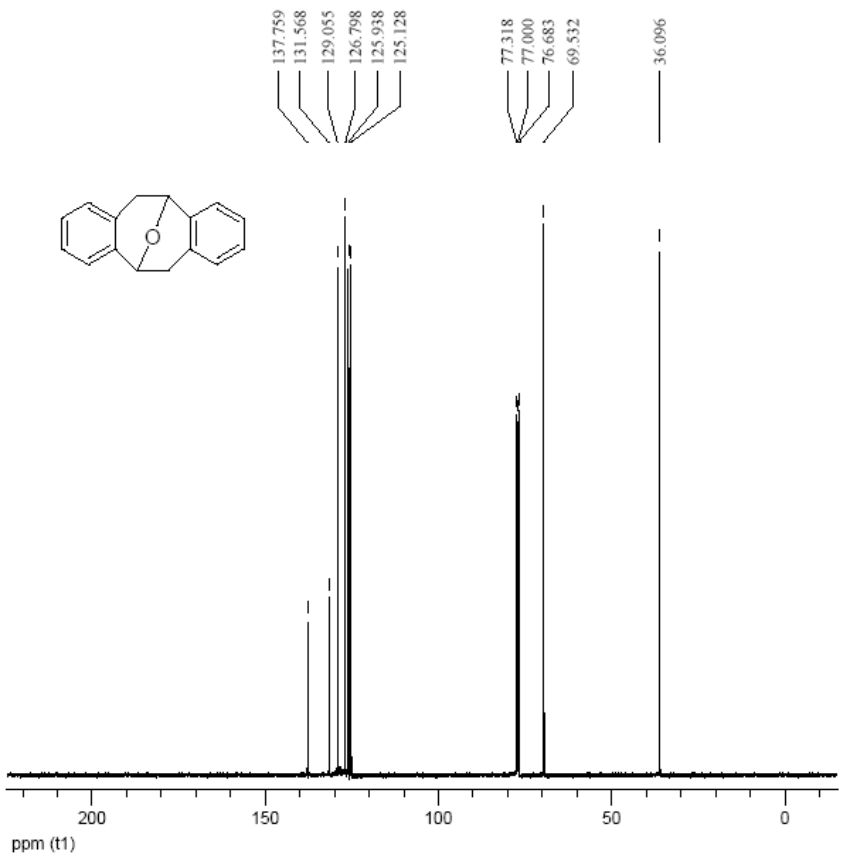

Date:
28 Sep 2009
Document's Title:
13C NMR CM-E138

Spectrum Title:
CM-E138-Imostpure
13C CPD SW=240

Frequency (MHz):
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Actual Points Count:
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Spectral Width (ppm):
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Temperature:
683.16
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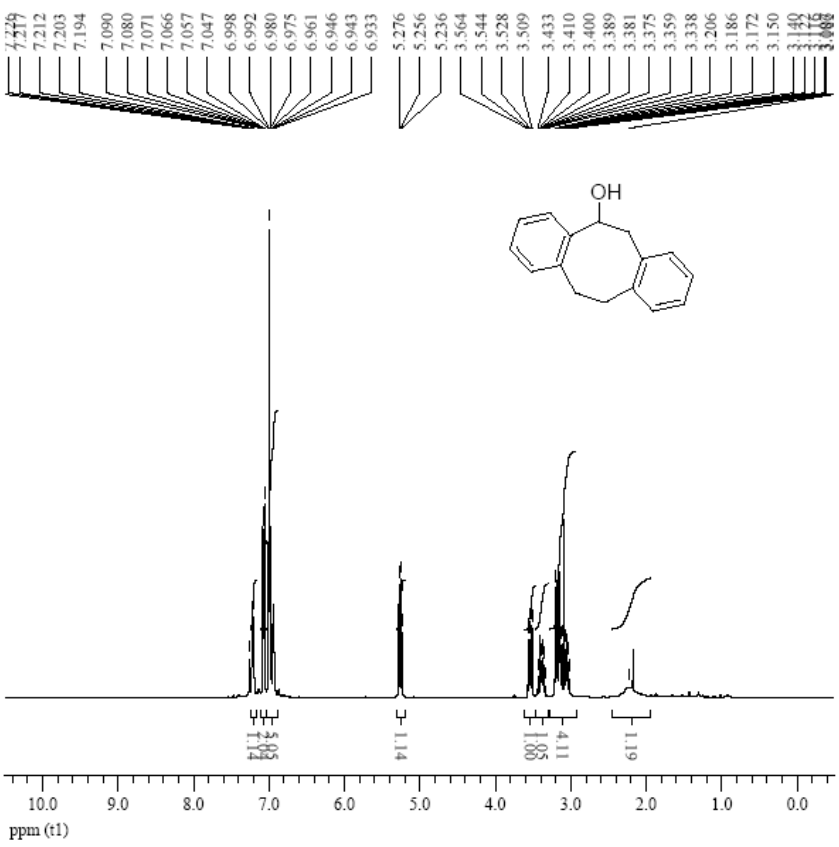
Sun Jun 07 09:35:13 PM



Date:
28 Sep 2009
Document's Title:
1H-cm e166 dbcyclooctanol

Spectrum Title:
cm-e166
proton RO=0 D1=4 NS=32

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Actual Points Count:
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Spectral Width (ppm):
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Temperature:
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Acq. Date:
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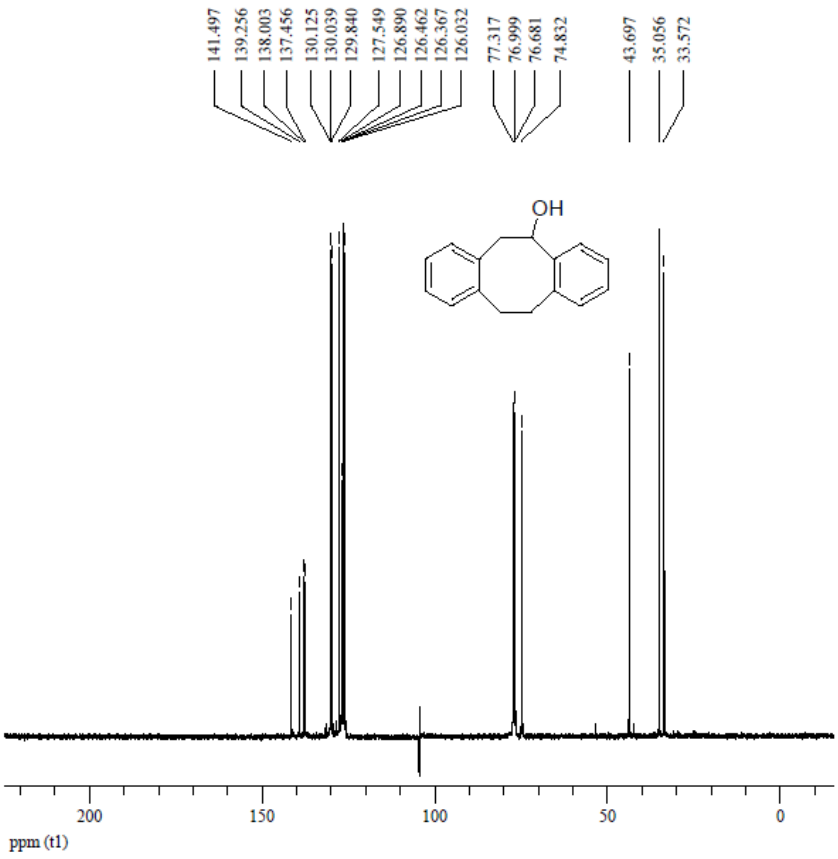

Date:
13 Oct 2009
Document's Title:
1H-CM-E166.mrc

Spectrum Title:
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13C CPD SW=240

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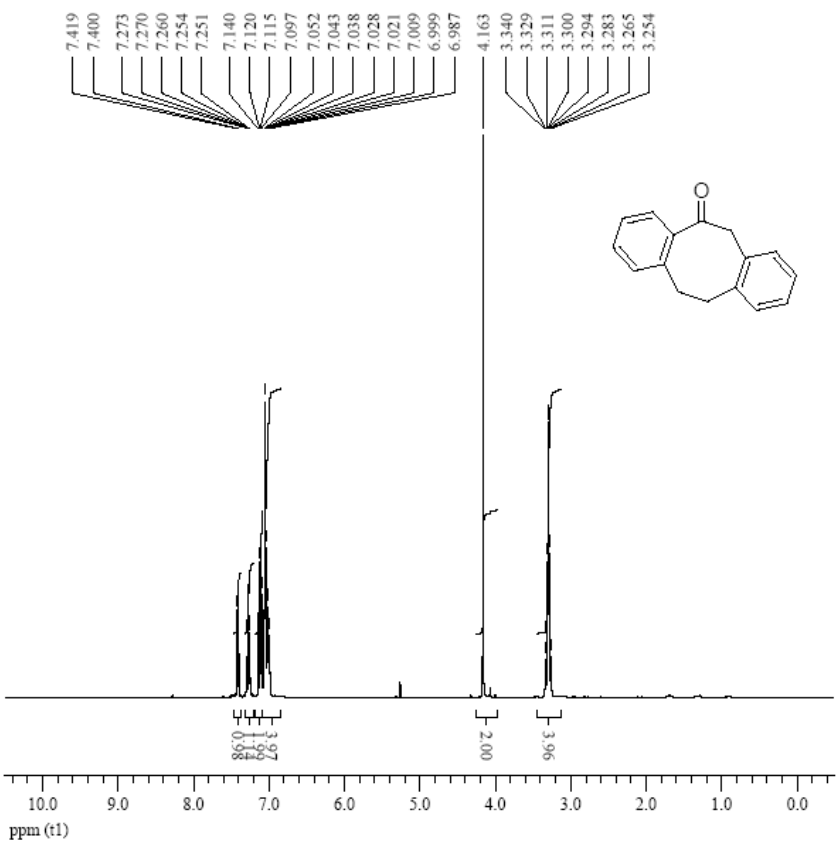

Date:
28 Sep 2009
Document's Title:
1H cm-e172 dbcyclooctanone

Spectrum Title:
cm-e172
proton RO=0 D1=4 NS=32

Frequency (MHz):
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Original Points Count:
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Actual Points Count:
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Spectral Width (ppm):
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Pulse Program:
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Temperature:
683.16
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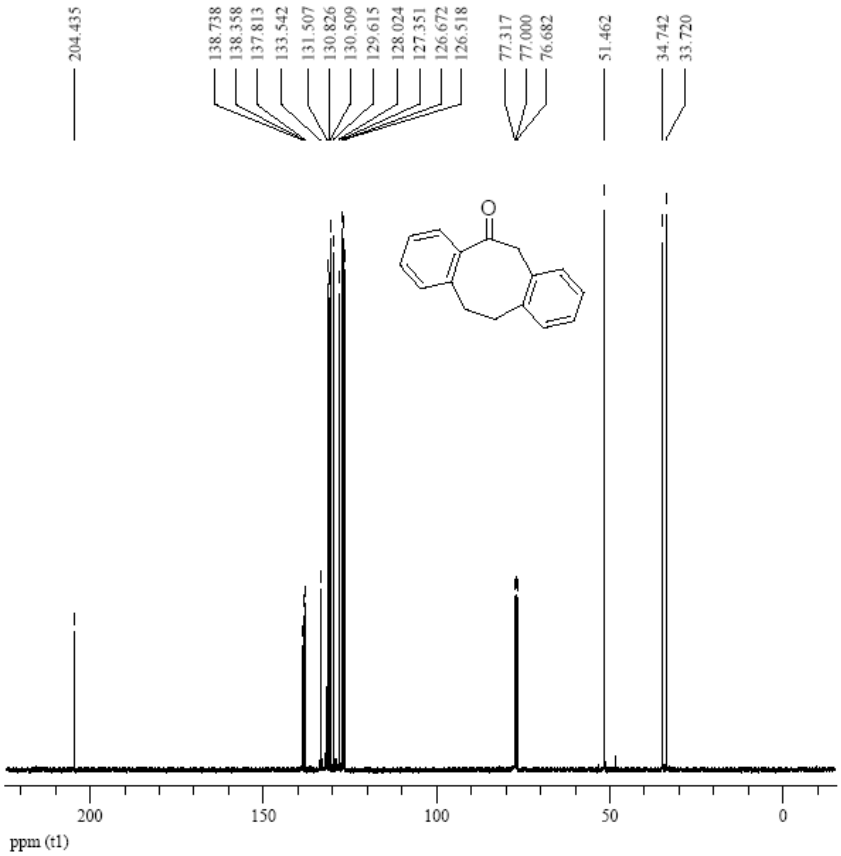
Acq. Date:
Tue Jun 23 02:09:30 PM



Date:
28 Sep 2009
Document's Title:
13C cmf72 dbcyclooctanone

Spectrum Title:
CM-E172, CDCl3, 13C, 23June09

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Actual Points Count:
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Acquisition Time (sec):
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Spectral Width (ppm):
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Pulse Program:
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Temperature:
683.16
Number of Scans:
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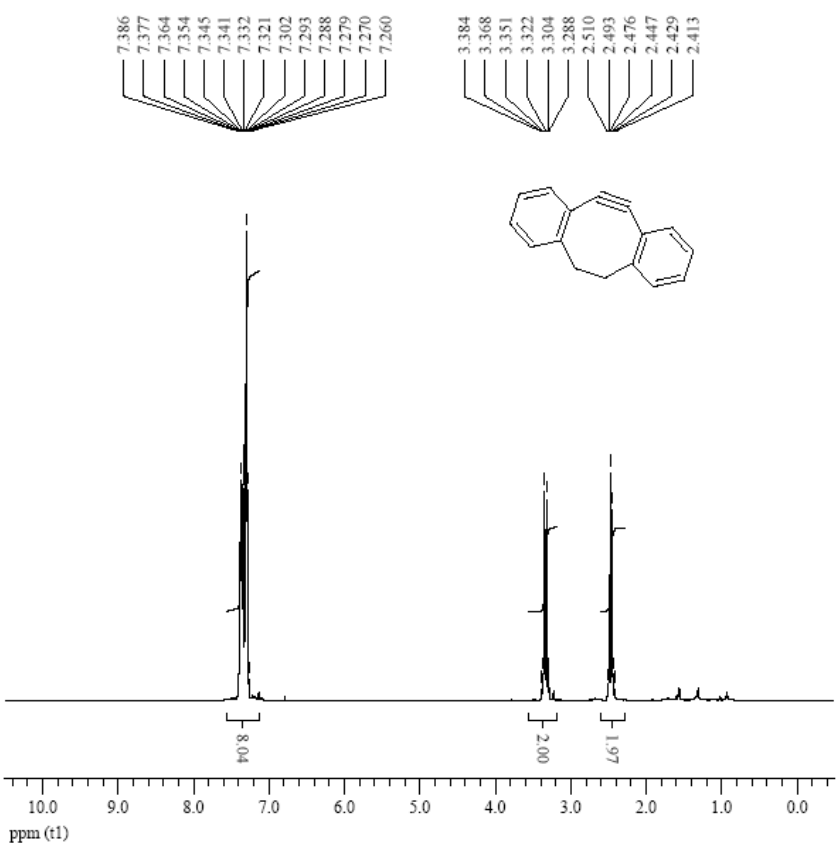
Acq. Date:
Wed Jun 24 09:14:13 AM



Date:
28 Sep 2009
Document's Title:
1H-cmf178 dbcyclooctyne

Spectrum Title:
cm-e178
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Acq. Date:
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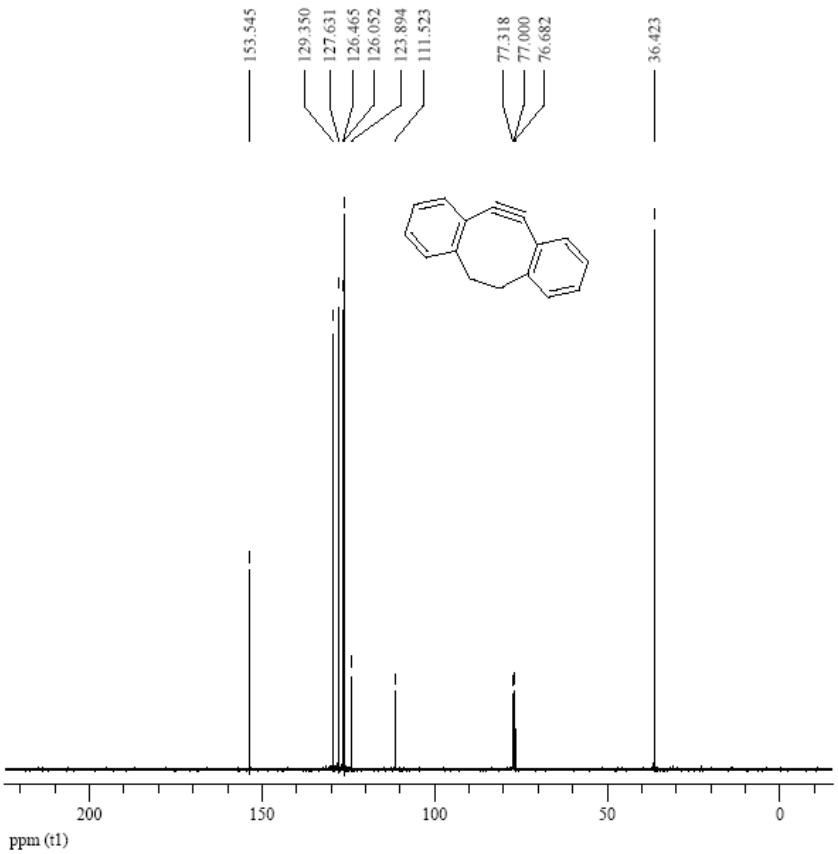

Date:
28 Sep 2009
Document's Title:
13C- cmf178 dbcyclooctyne

Spectrum Title:
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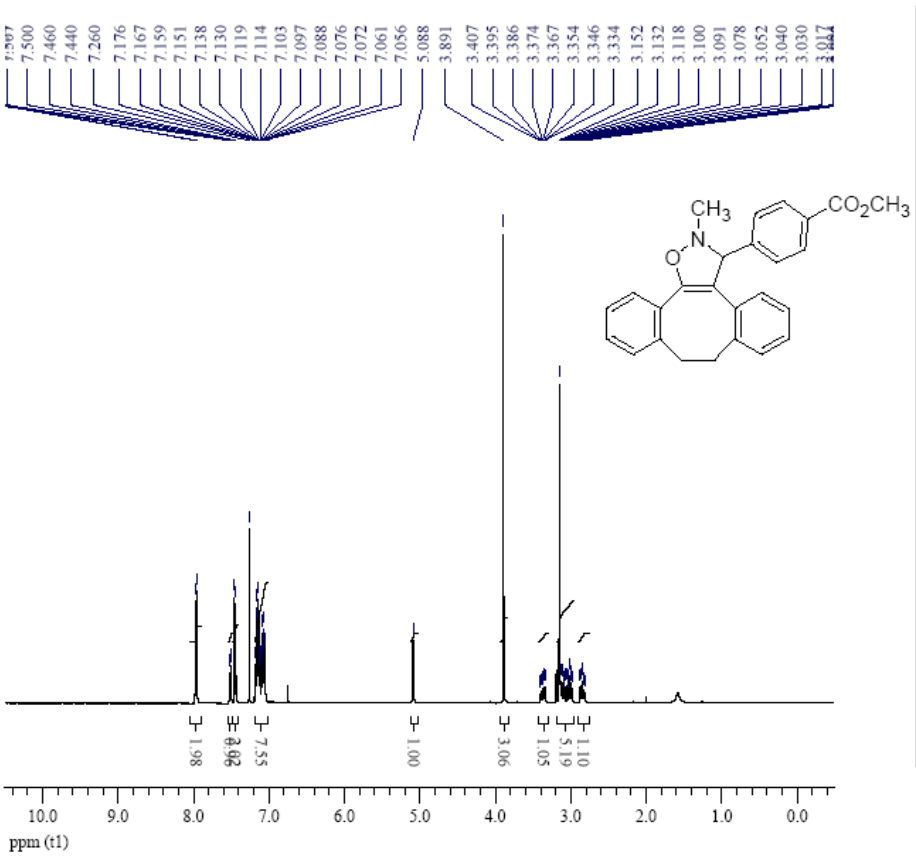

Date:
28 Sep 2009
Document's Title:
1H-CM-F056

Spectrum Title:
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proton RO=0 D1=4 NS=32

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Temperature:
683.16
Number of Scans:
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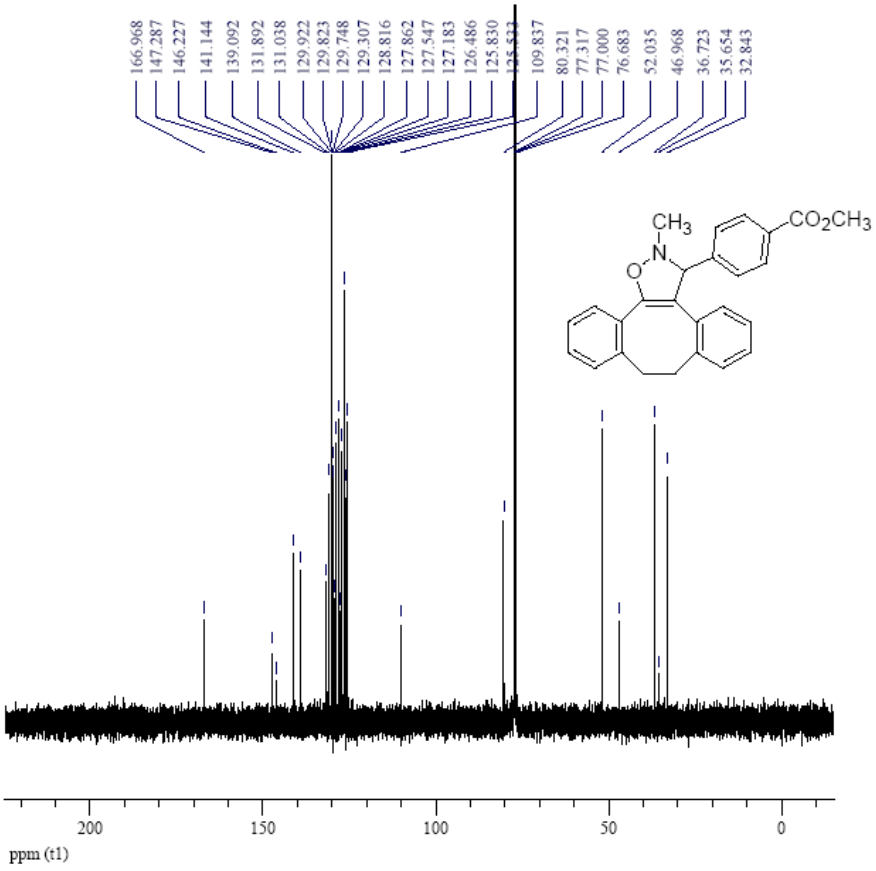
Acq. Date:
Sun Aug 30 09:35:57 AM



Date:
28 Sep 2009
Document's Title:
13C-cmf056

Spectrum Title:
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Spectral Width (ppm):
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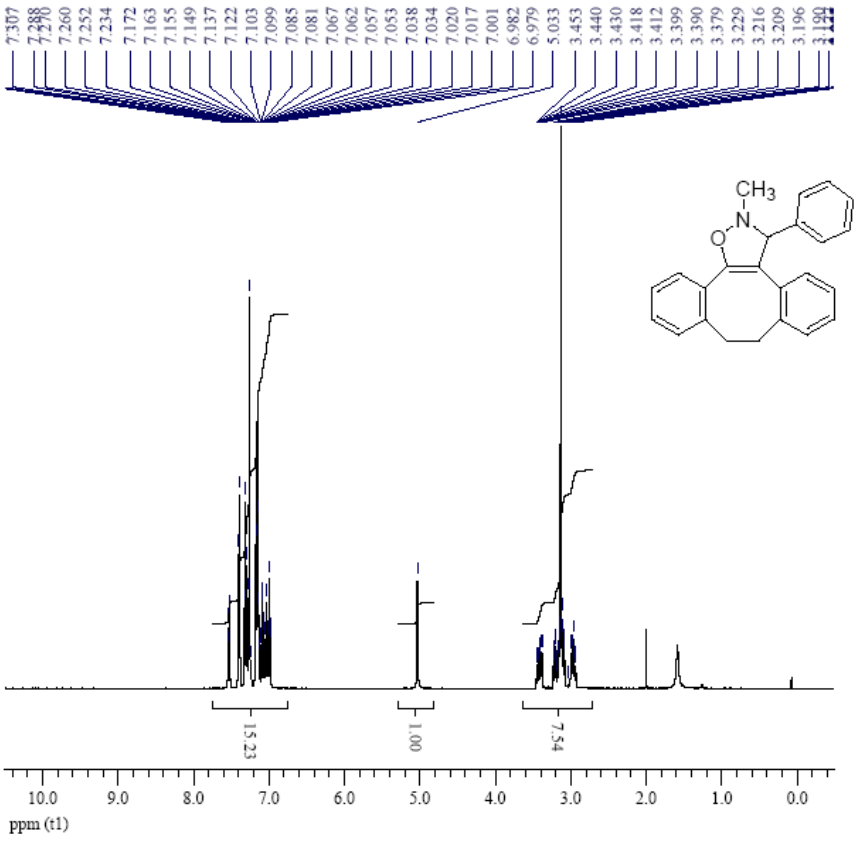
Sun Aug 30 03:31:40 PM



Date:
28 Sep 2009
Document's Title:
1H-NMR CM F034

Spectrum Title:
cm-f034
proton RO=0 D1=4 NS=32

Frequency (MHz):
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Original Points Count:
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Actual Points Count:
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Acquisition Time (sec):
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Spectral Width (ppm):
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Pulse Program:
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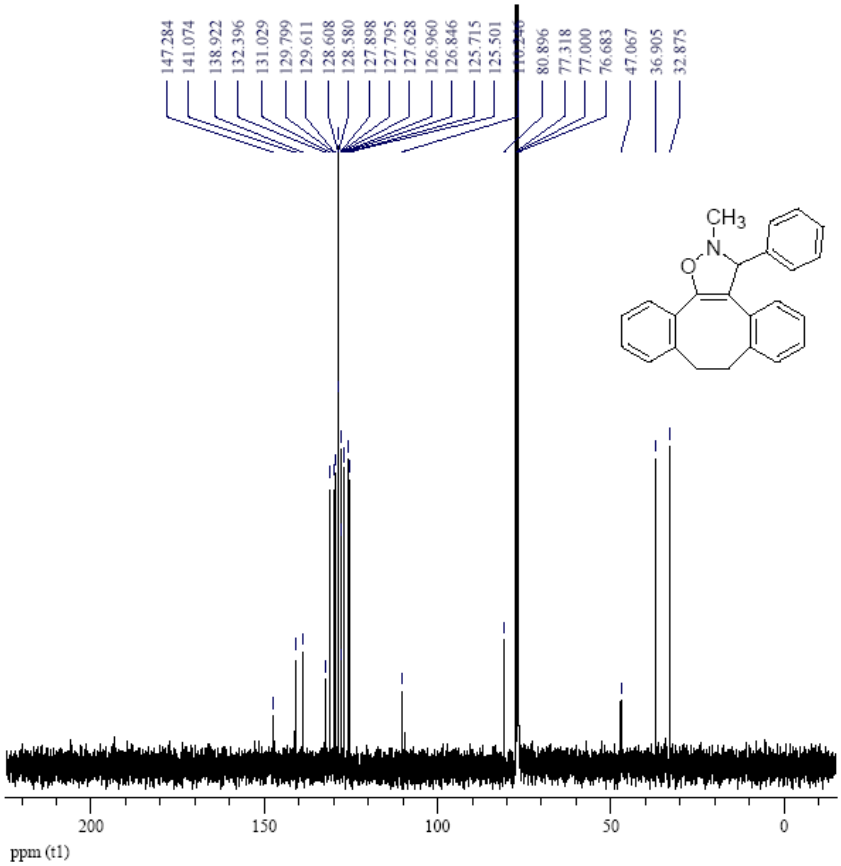
Temperature:
683.16
Number of Scans:
32
Acq. Date:
Fri Aug 28 07:21:42 AM



Date:
28 Sep 2009
Document's Title:
13C NMR CM F034

Spectrum Title:
cm-f034
13C CPD SW=240

Frequency (MHz):
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Spectral Width (ppm):
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Temperature:
683.16
Number of Scans:
3636
Acq. Date:
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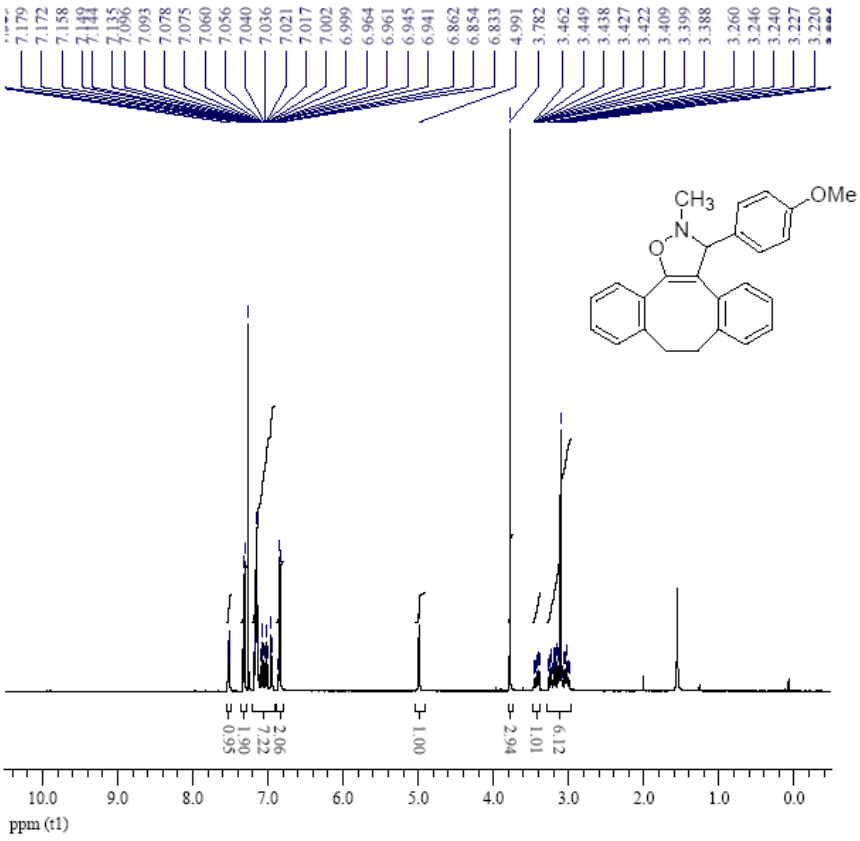

Date:
28 Sep 2009
Document's Title:
1H-NMR CM F057

Spectrum Title:
cm-f057
proton RO=0 D1=4 NS=32

Frequency (MHz):
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Original Points Count:
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Actual Points Count:
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Acquisition Time (sec):
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Spectral Width (ppm):
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Pulse Program:
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Temperature:
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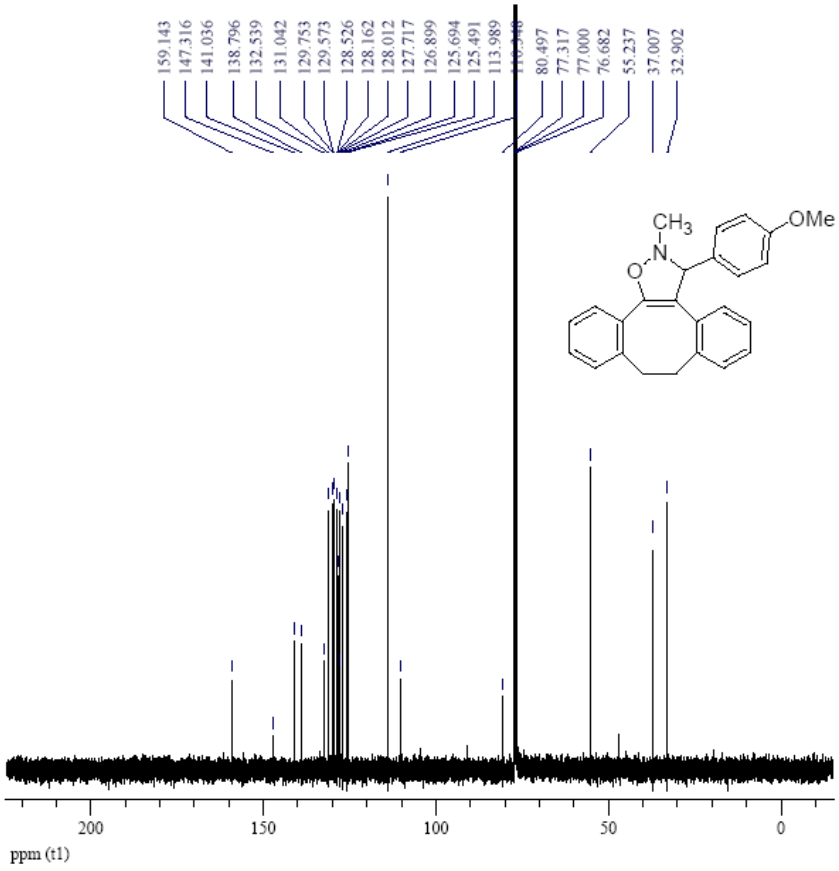
Acq. Date:
Sat Aug 29 07:57:31 AM



Date:
28 Sep 2009
Document's Title:
13C NMR CM F057

Spectrum Title:
cmf057
13C CPD SW=240

Frequency (MHz):
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Actual Points Count:
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Acquisition Time (sec):
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Spectral Width (ppm):
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Temperature:
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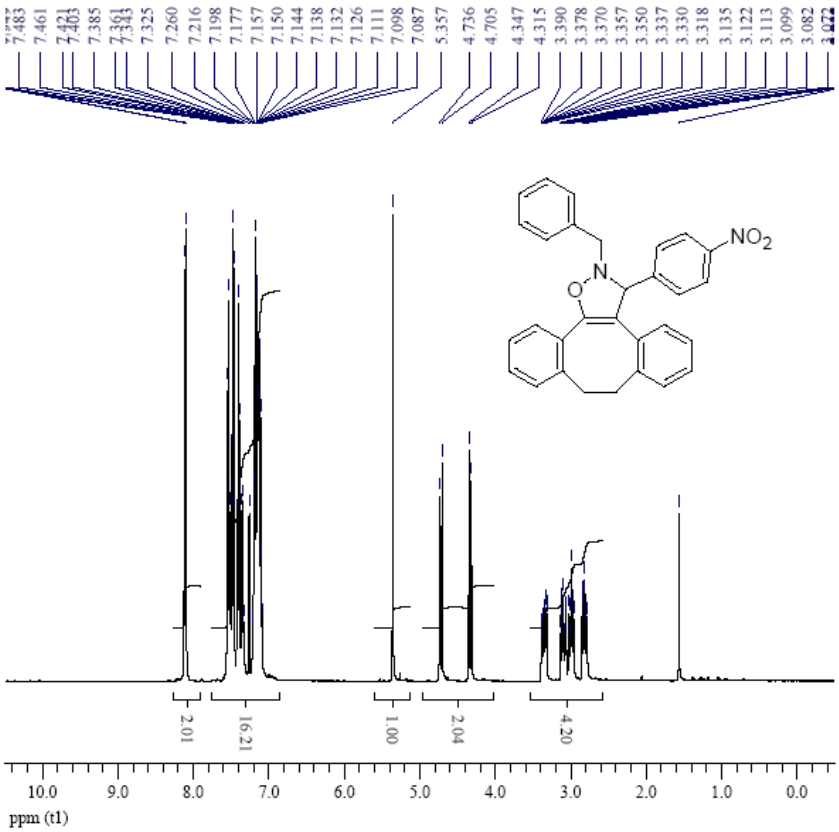

Date:
12 Oct 2009
Document's Title:
1H-CM-F090

Spectrum Title:
cmf090
proton RO=0 D1=4 NS=32

Frequency (MHz):
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Original Points Count:
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Actual Points Count:
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Spectral Width (ppm):
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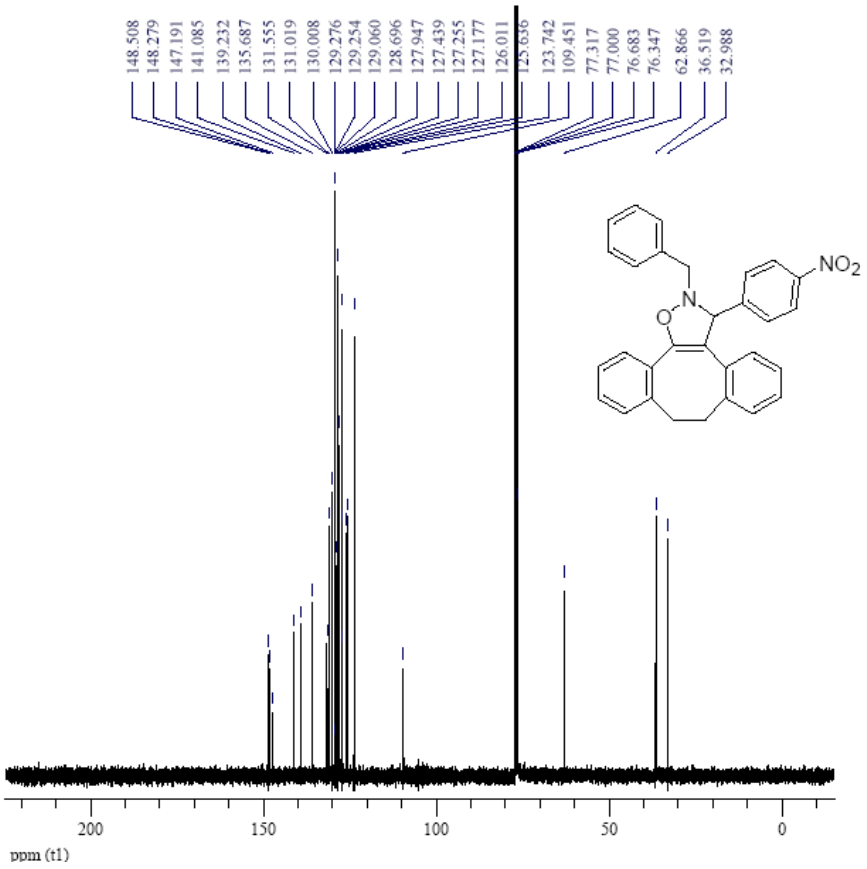

Date:
28 Sep 2009
Document's Title:
13C NMR -CMF079

Spectrum Title:
cmf079
13C CPD SW=240

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Original Points Count:
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Actual Points Count:
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Spectral Width (ppm):
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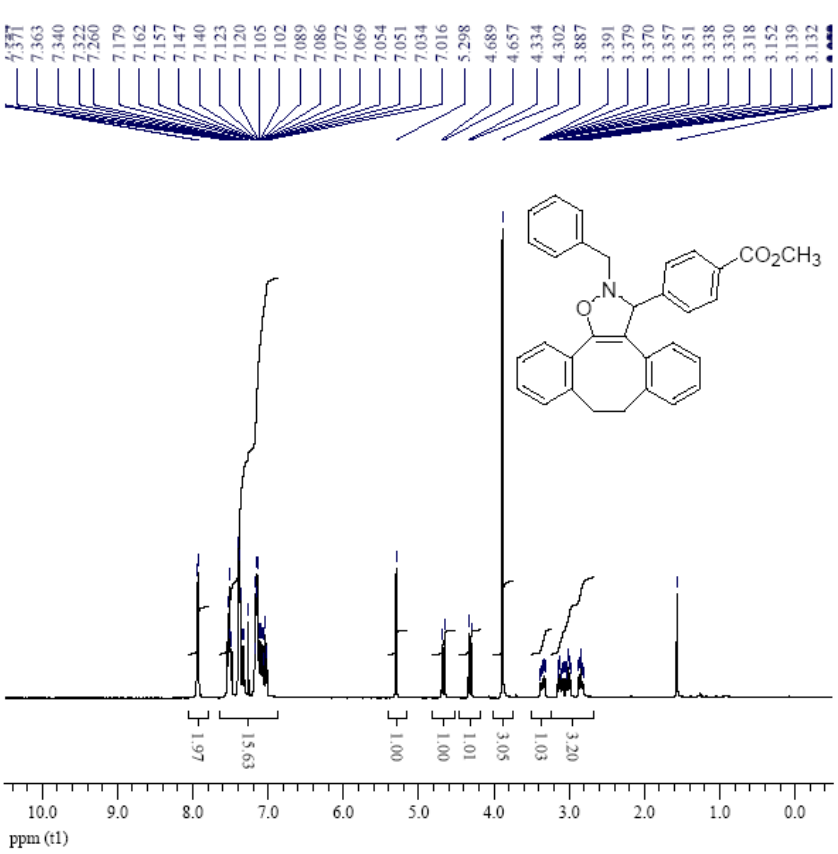
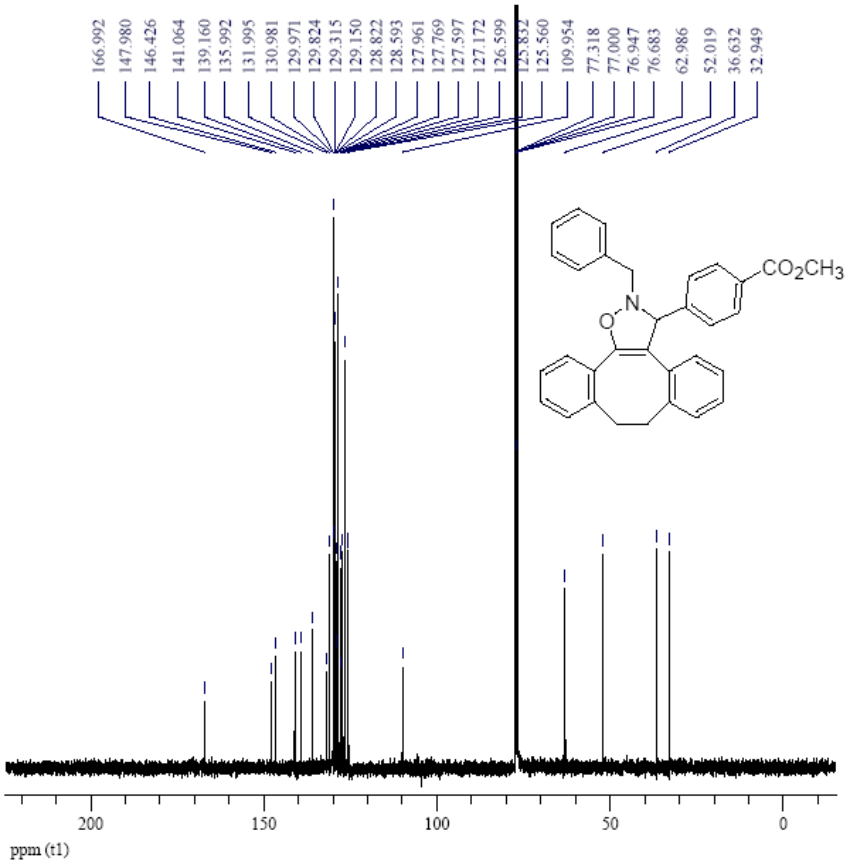


Date:
12 Oct 2009
Document's Title:
1H CM F088

Spectrum Title:
cmf088
proton RO=0 D1=4 NS=32

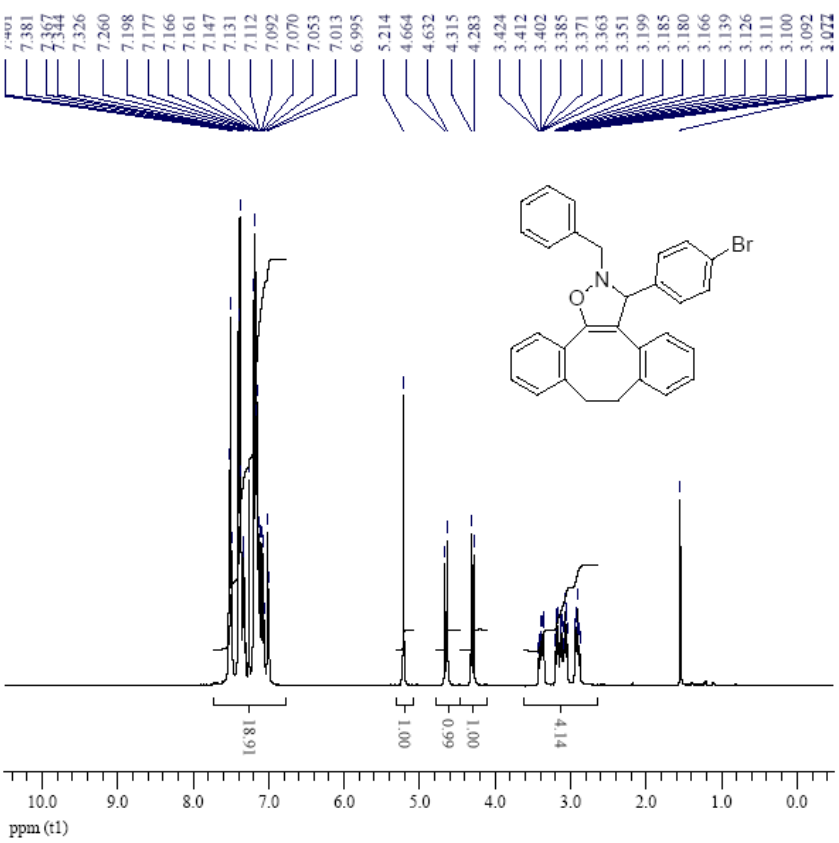
Frequency (MHz):
(f1) 400.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.9923
Spectral Width (ppm):
(f1) 20.552
Pulse Program:
ZG30
Temperature:
683.16
Number of Scans:
32
Acq. Date:
Mon Oct 05 09:59:58 PM



Date:
12 Oct 2009
Document's Title:
13C CM F088

Spectrum Title:
cmf088 p-COOMe
13C CPD SW=240

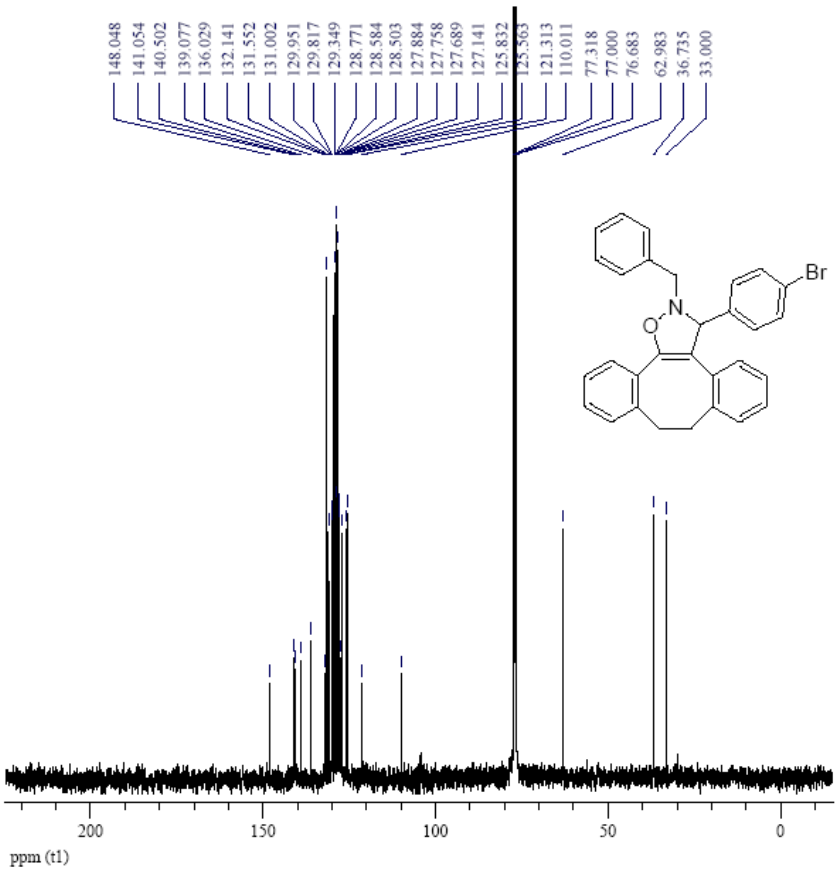
Frequency (MHz):
(f1) 100.623
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 0.6783
Spectral Width (ppm):
(f1) 240.050
Pulse Program:
ZGDC30
Temperature:
683.16
Number of Scans:
10000
Acq. Date:
Tue Oct 06 01:07:15 AM



Date:
12 Oct 2009
Document's Title:
1H CM F089

Spectrum Title:
proton RO=0 D1=4 NS=32

Frequency (MHz):
(f1) 400.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.9923
Spectral Width (ppm):
(f1) 20.552
Pulse Program:
ZG30
Temperature:
683.16
Number of Scans:
32
Acq. Date:
Tue Oct 06 09:32:40 AM



Date:
28 Sep 2009
Document's Title:
13C-CMF078

Spectrum Title:
cmf078
13C CPD SW=240

Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.3566
Spectral Width (ppm):
(f1) 240.075
Pulse Program:
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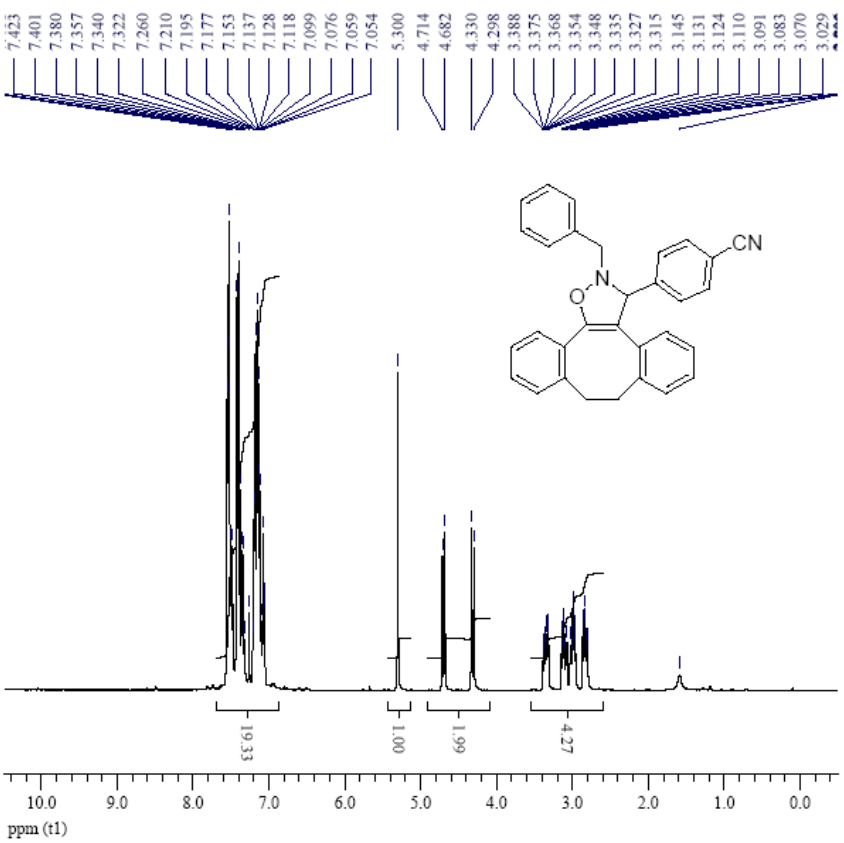
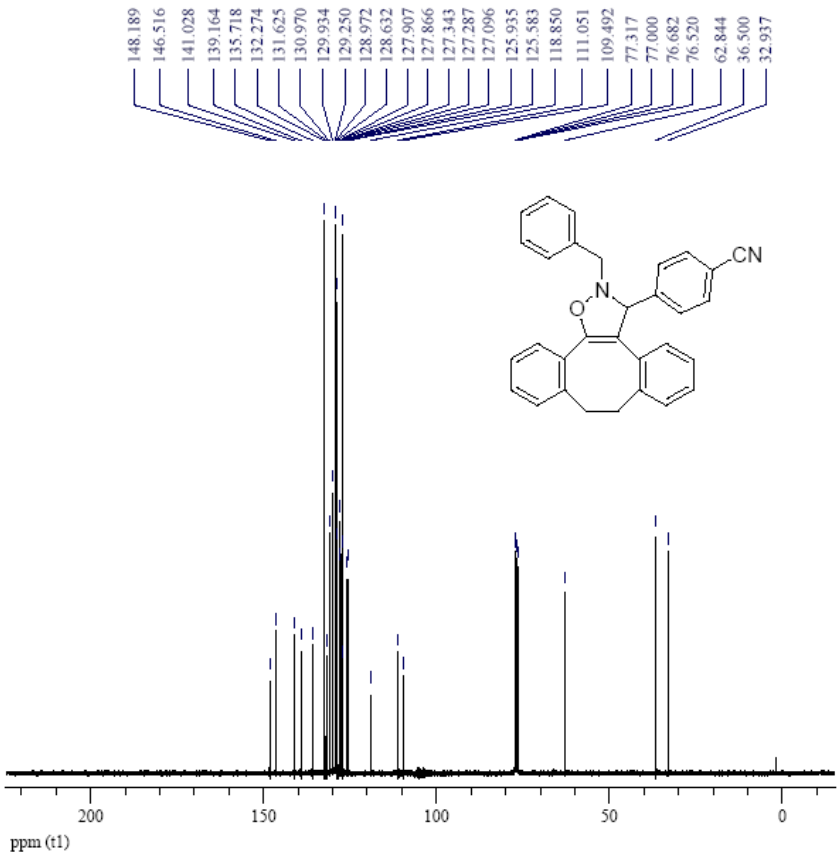


Date:
12 Oct 2009
Document's Title:
1H-CM-F077 p-CN

Spectrum Title:
cmf077 p-CN
proton RO=0 D1=4 NS=32

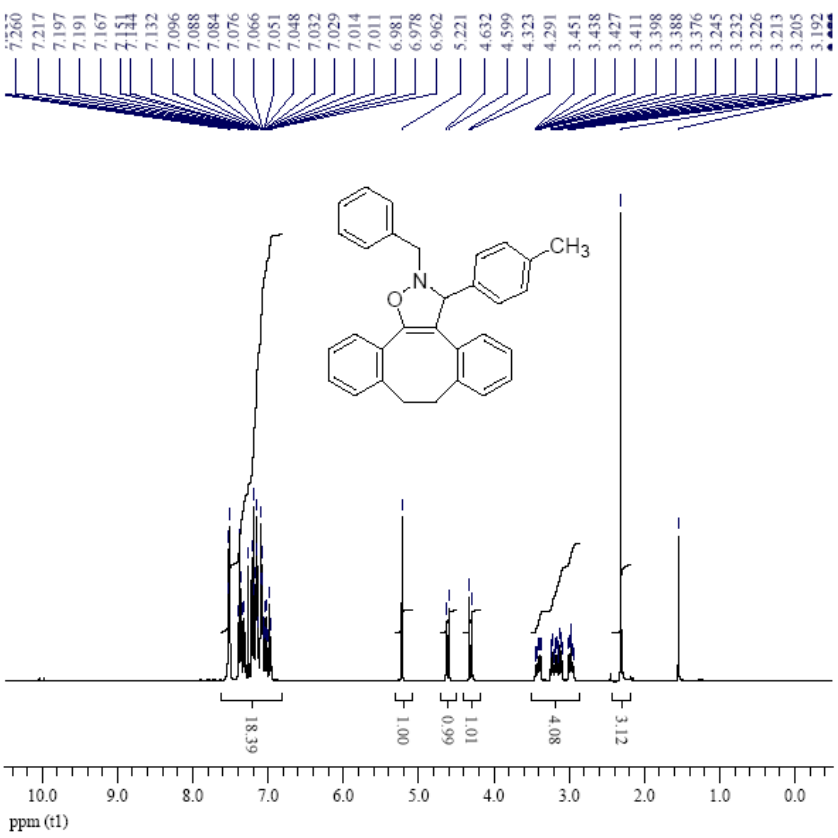
Frequency (MHz):
(f1) 400.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.9923
Spectral Width (ppm):
(f1) 20.552
Pulse Program:
ZG30
Temperature:
683.16
Number of Scans:
32
Acq. Date:
Fri Oct 09 12:35:12 AM



Date:
28 Sep 2009
Document's Title:
13C-CMF077

Spectrum Title:
cmf077
13C CPD SW=240

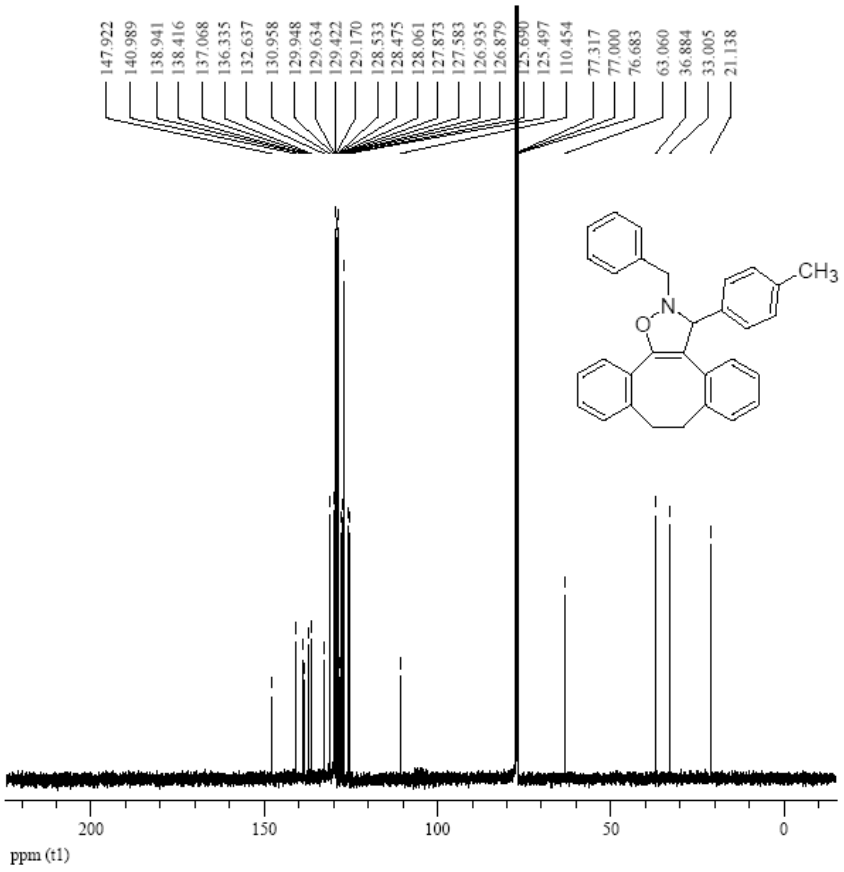
Frequency (MHz):
(f1) 100.623
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 0.6783
Spectral Width (ppm):
(f1) 240.050
Pulse Program:
ZGDC30
Temperature:
683.16
Number of Scans:
14000
Acq. Date:
Sun Sep 20 04:16:22 AM



Date:
12 Oct 2009
Document's Title:
1H CM F080

Spectrum Title:
cmf080
proton RO=0 D1=4 NS=32

Frequency (MHz):
(f1) 400.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.9923
Spectral Width (ppm):
(f1) 20.552
Pulse Program:
ZG30
Temperature:
683.16
Number of Scans:
32
Acq. Date:
Thu Oct 08 12:11:52 AM



Date:
28 Sep 2009
Document's Title:
13C NMR CMF080

Spectrum Title:
cmf080
13C CPD SW=240

Frequency (MHz):
(f1) 100.623
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 0.6783
Spectral Width (ppm):
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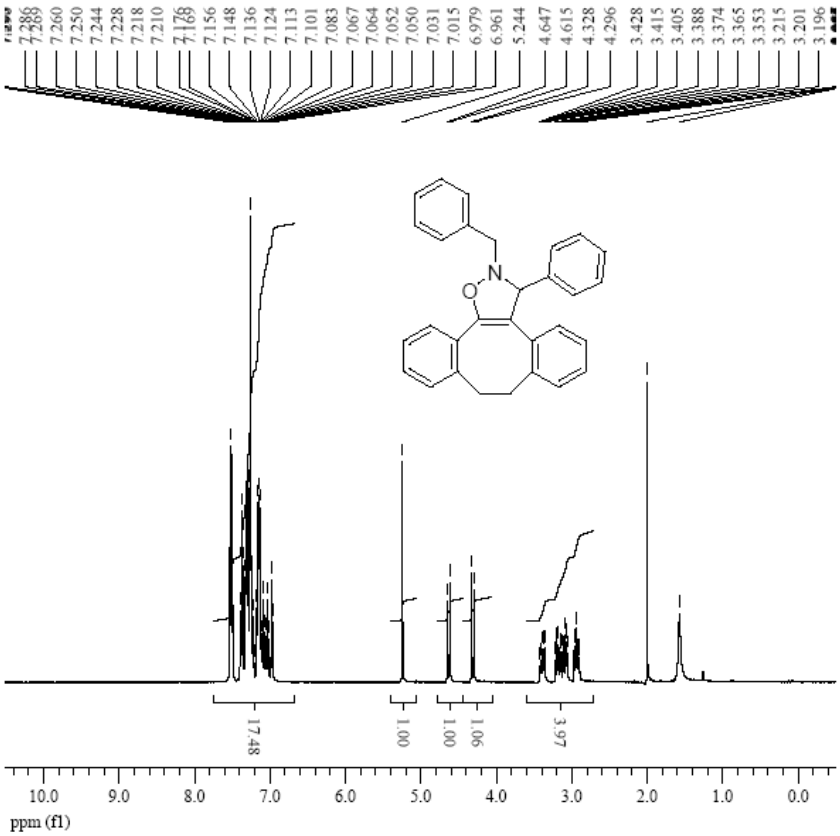
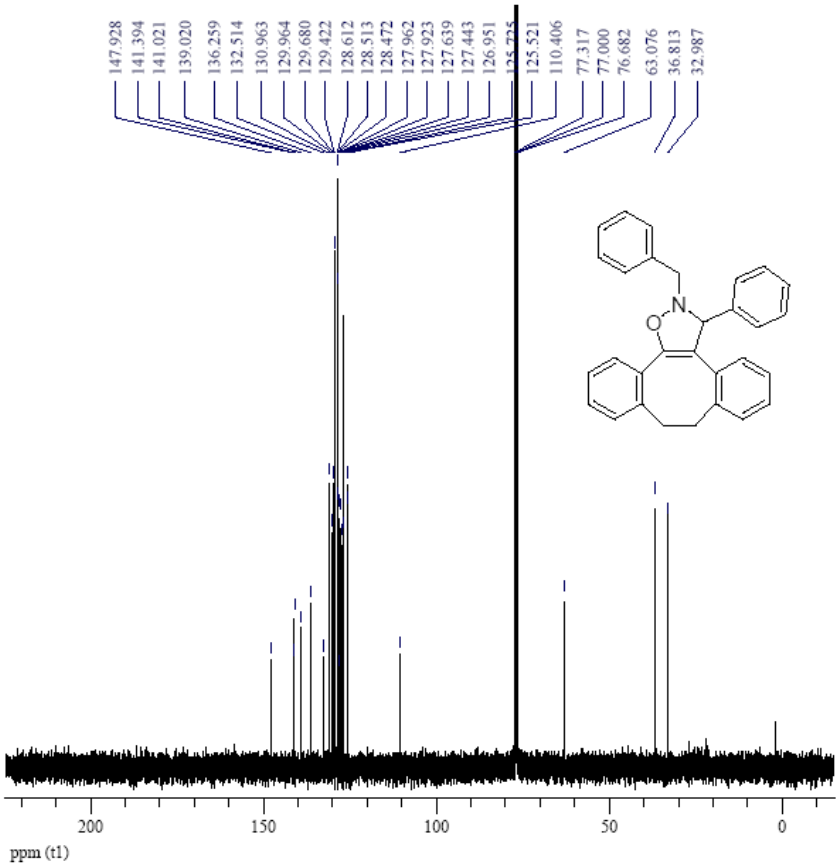
Pulse Program:
ZGDC30
Temperature:
683.16
Number of Scans:
9951
Acq. Date:
Mon Sep 21 07:16:36 PM



Date:
28 Sep 2009
Document's Title:
1H NMR CMF039

Spectrum Title:
cm-f039
proton RO=0 D1=4 NS=32

Frequency (MHz):
(f1) 400.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.9923
Spectral Width (ppm):
(f1) 20.552
Pulse Program:
ZG30
Temperature:
683.16
Number of Scans:
32
Acq. Date:
Thu Aug 27 08:40:31 PM



Date:
28 Sep 2009
Document's Title:
13C NMR CM F039

Spectrum Title:
cmf039
13C CPD SW=240

Frequency (MHz):
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Original Points Count:
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Actual Points Count:
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Acquisition Time (sec):
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Spectral Width (ppm):
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Pulse Program:
ZGDC30
Temperature:
683.16
Number of Scans:
10506
Acq. Date:
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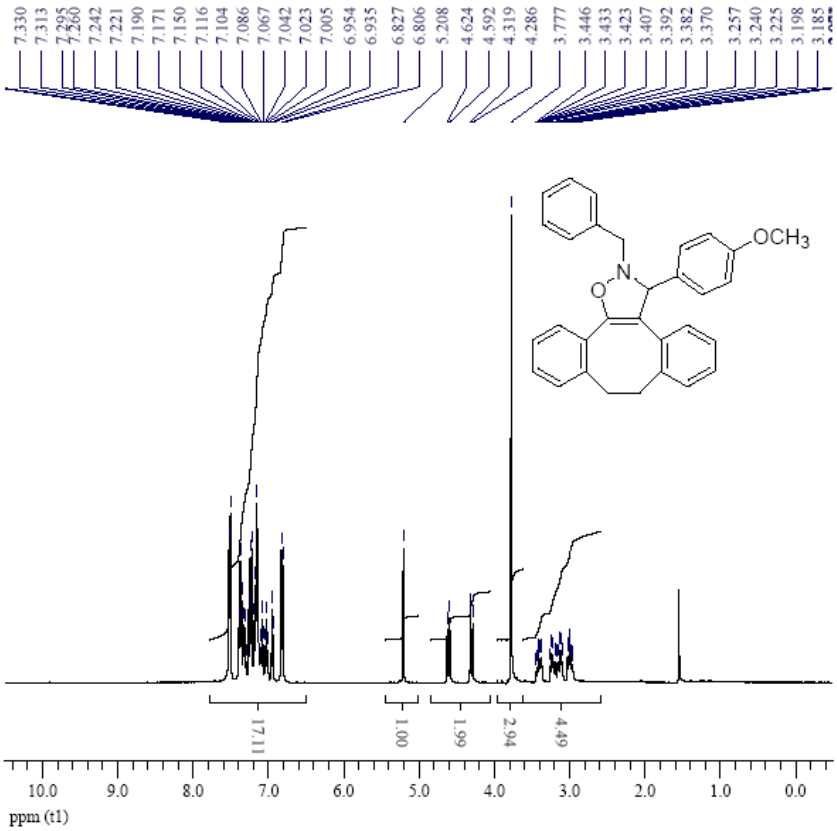
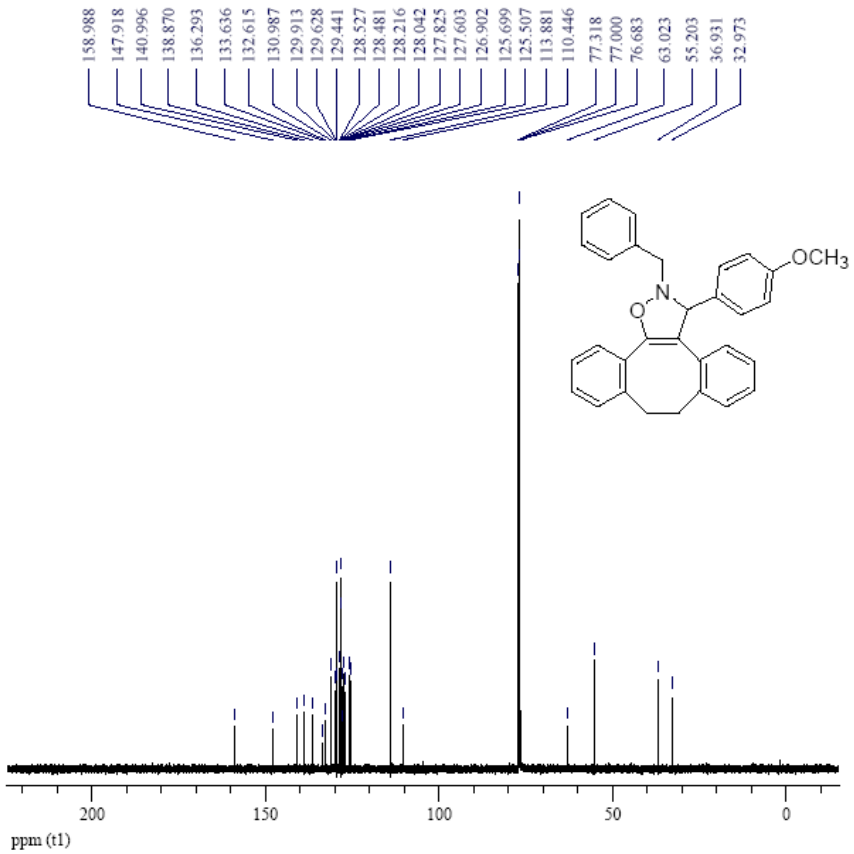


Date:
12 Oct 2009
Document's Title:
CM-F092

Spectrum Title:
cmf092
proton RO=0 D1=4 NS=32

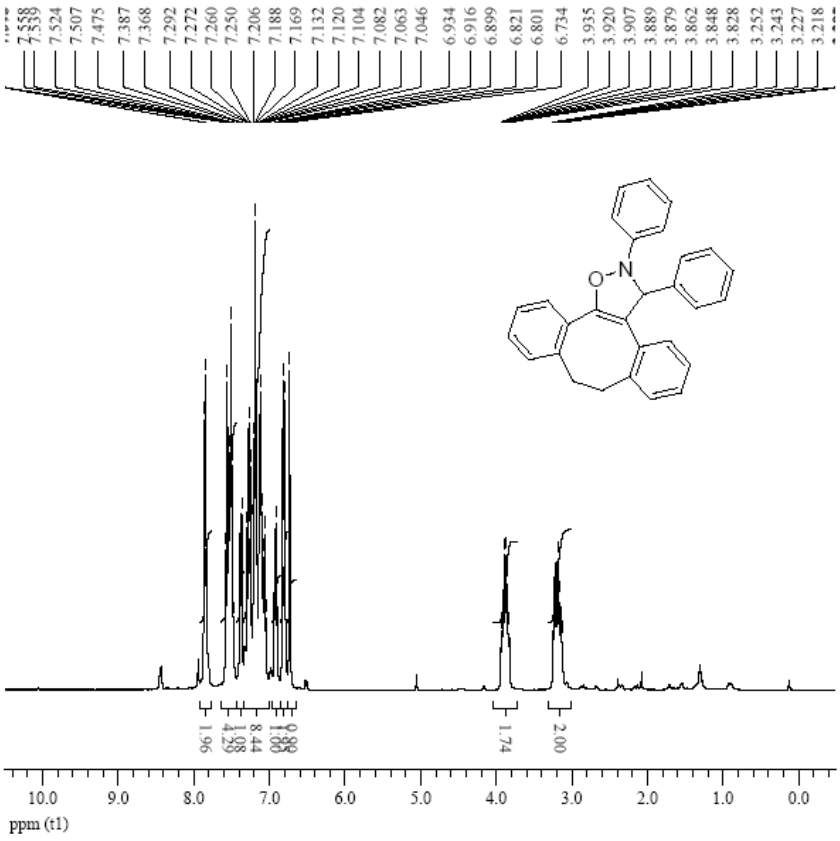
Frequency (MHz):
(f1) 400.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.9923
Spectral Width (ppm):
(f1) 20.552
Pulse Program:
ZG30
Temperature:
683.16
Number of Scans:
32
Acq. Date:
Wed Oct 07 02:51:21 PM



Date:
28 Sep 2009
Document's Title:
13C-cmf053

Spectrum Title:
cm-f053
13C CPD SW=240

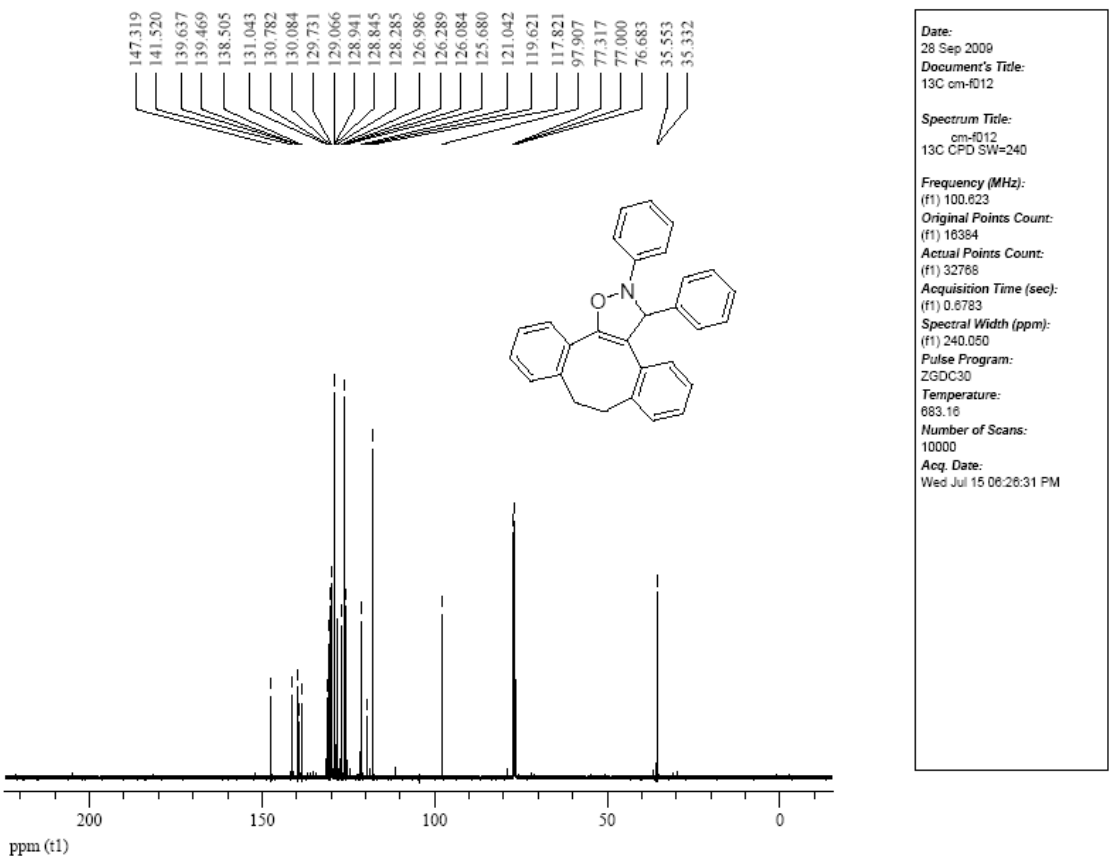
Frequency (MHz):
(f1) 100.623
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 0.6783
Spectral Width (ppm):
(f1) 240.050
Pulse Program:
ZGDC30
Temperature:
683.16
Number of Scans:
10000
Acq. Date:
Wed Aug 26 03:32:07 AM

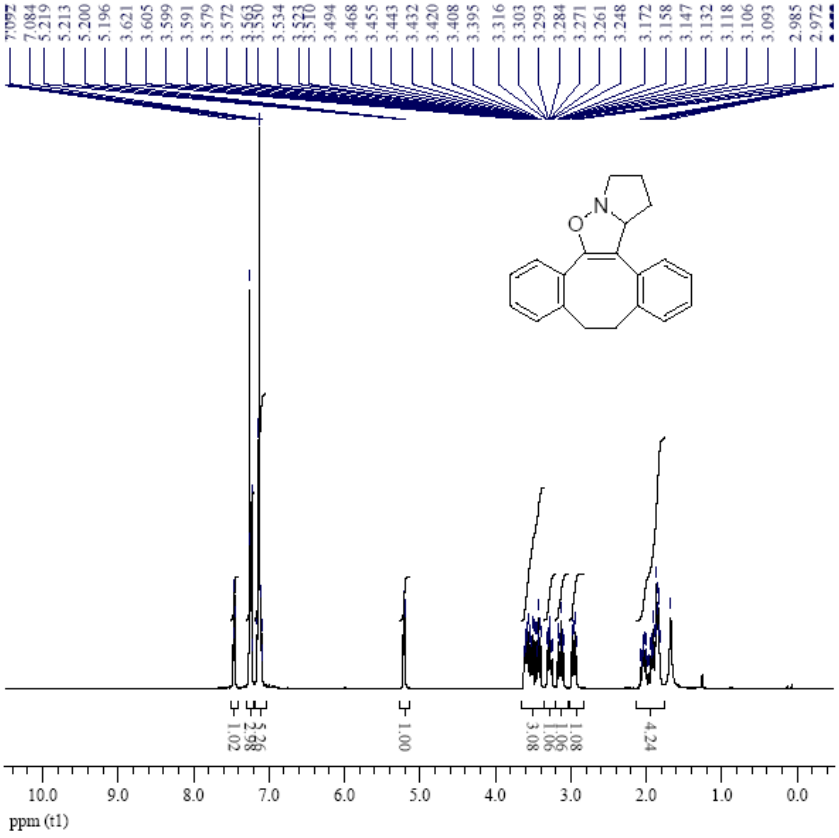


Date:
28 Sep 2009
Document's Title:
1H cmf012

Spectrum Title:
cm-f012
proton RO=0 D1=4 NS=32

Frequency (MHz):
(f1) 400.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.9923
Spectral Width (ppm):
(f1) 20.552
Pulse Program:
ZG30
Temperature:
683.16
Number of Scans:
32
Acq. Date:
Wed Jul 15 03:17:23 PM

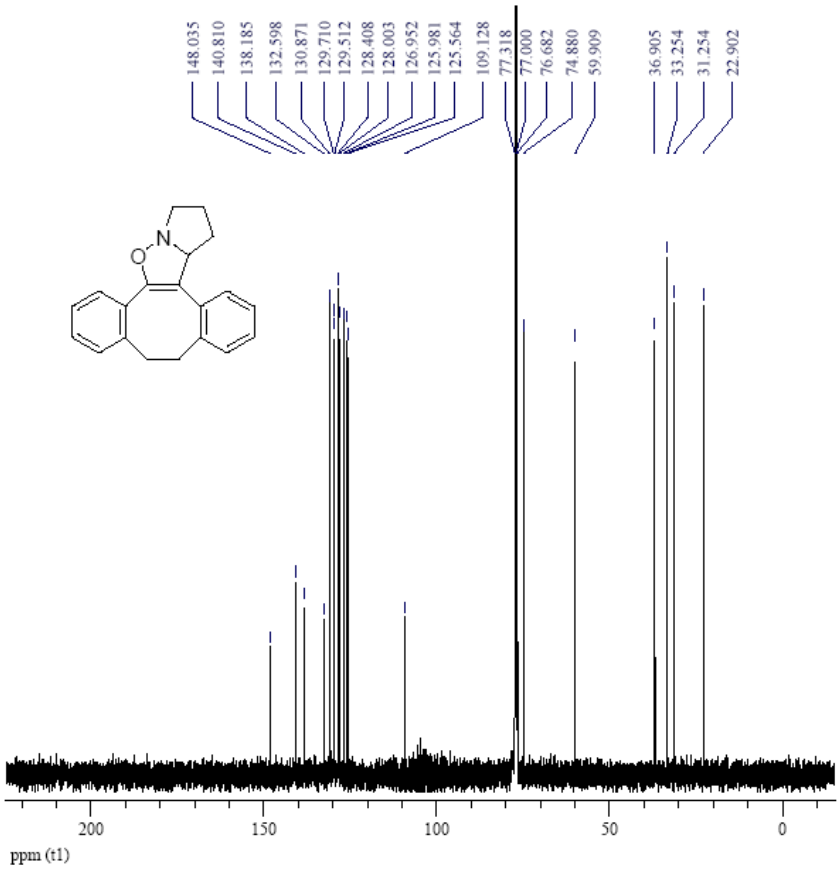

147.319
141.520
139.637
139.469
138.505
131.043
130.782
130.084
129.731
129.066
128.941
128.845
128.285
126.986
126.289
126.084
125.680
121.042
119.621
117.821
97.907
77.317
77.000
76.683
35.553
35.332
O
N
200
150
100
50
0
ppm (t1)
Date:
28 Sep 2009
Document's Title:
13C cm-f012
Spectrum Title:
cm-f012
13C CPD SW=240
Frequency (MHz):
(f1) 100.623
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 0.6783
Spectral Width (ppm):
(f1) 240.050
Pulse Program:
ZGDC30
Temperature:
683.16
Number of Scans:
10000
Acq. Date:
Wed Jul 15 06:26:31 PM



Date:
28 Sep 2009
Document's Title:
1H-CMF067

Spectrum Title:
cmf067
proton RO=0 D1=4 NS=32

Frequency (MHz):
(f1) 400.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.9923
Spectral Width (ppm):
(f1) 20.552
Pulse Program:
ZG30
Temperature:
683.16
Number of Scans:
32
Acq. Date:
Thu Sep 17 06:16:20 PM



Date:
28 Sep 2009
Document's Title:
13C-CMFO67

Spectrum Title:
cmf067
13C CPD SW=240

Frequency (MHz):
(f1) 100.623
Original Points Count:
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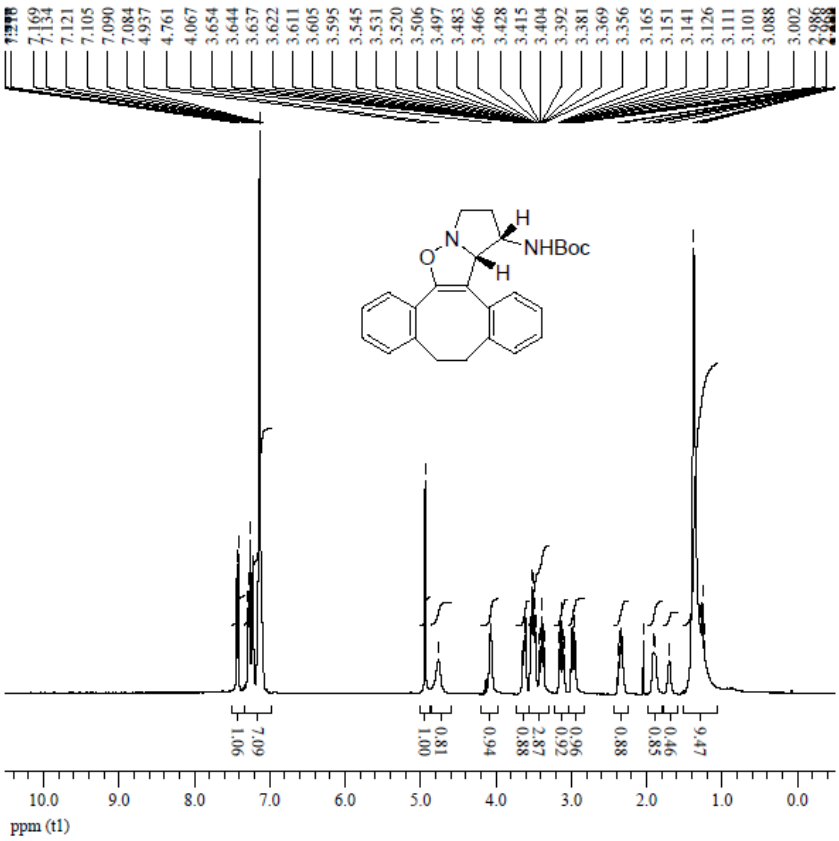
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 0.6783
Spectral Width (ppm):
(f1) 240.050
Pulse Program:
ZGDC30
Temperature:
683.16
Number of Scans:
9010
Acq. Date:
Thu Sep 17 09:05:00 PM



Date:
30 Nov 2009
Document's Title:
1H-CMf082.mrc

Spectrum Title:
cmf082
proton RO=0 D1=4 NS=32

Frequency (MHz):
(f1) 400.132
Original Points Count:
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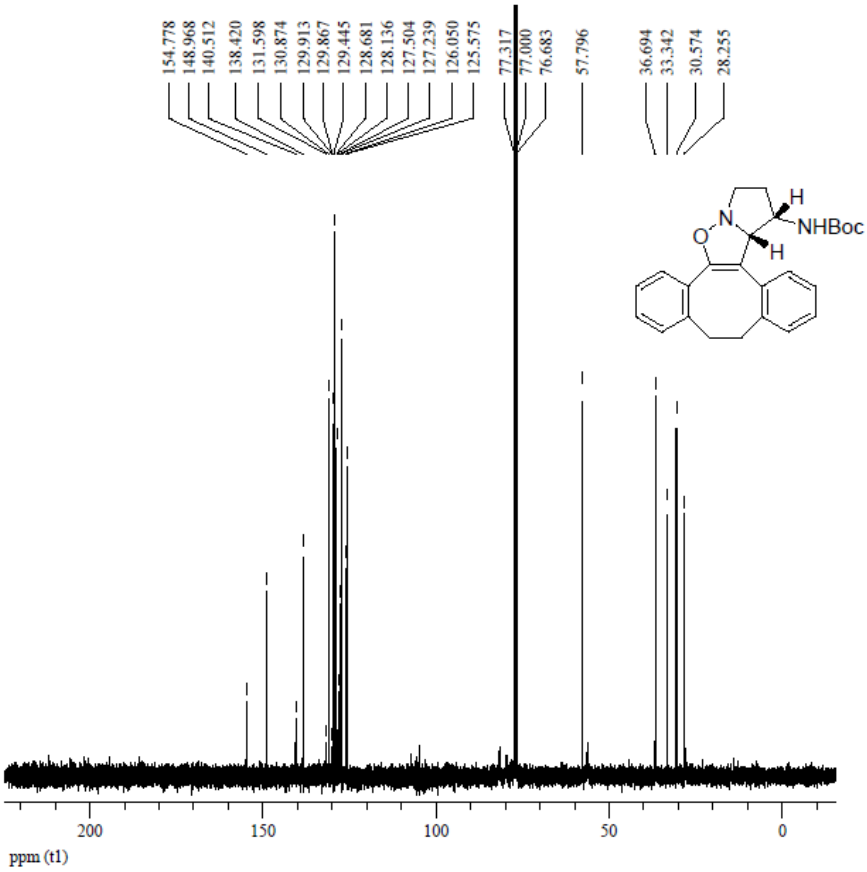
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.9923
Spectral Width (ppm):
(f1) 20.552
Pulse Program:
ZG30
Temperature:
683.16
Number of Scans:
32
Acq. Date:
Tue Sep 22 11:02:51 PM



Date:
30 Nov 2009
Document's Title:
cmf082- 13C NMR.mrc

Spectrum Title:
cmf082
13C CPD SW=240

Frequency (MHz):
(f1) 100.623
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 0.6783
Spectral Width (ppm):
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Pulse Program:
ZGDC30
Temperature:
683.16
Number of Scans:
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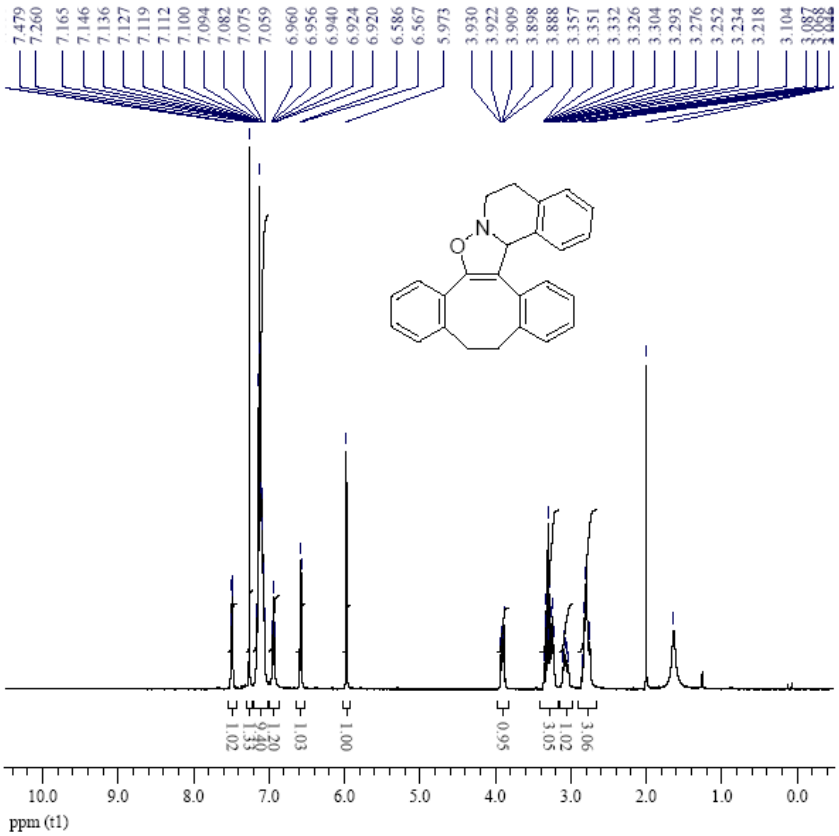
Acq. Date:
Wed Sep 23 12:00:49 AM



Date:
28 Sep 2009
Document's Title:
1H-cmf062

Spectrum Title:
proton RO=0 D1=4 NS=32

Frequency (MHz):
(f1) 400.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.9923
Spectral Width (ppm):
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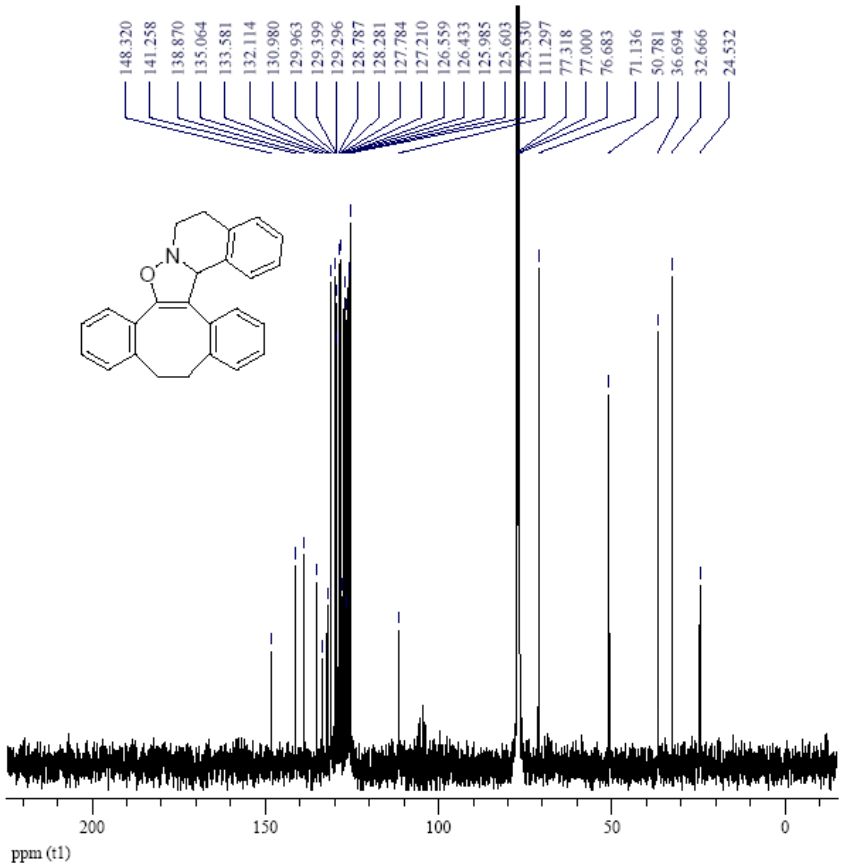
Pulse Program:
ZG30
Temperature:
683.16
Number of Scans:
32
Acq. Date:
Thu Sep 17 09:42:35 PM



Date:
28 Sep 2009
Document's Title:
13C CMF062

Spectrum Title:
cmf062
13C CPD SW=240

Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.3566
Spectral Width (ppm):
(f1) 240.075
Pulse Program:
Unknown

References

(1) A. Chatterjee, D.K. Maiti, P. K. Bhattacharya, *Org. Lett.* 2003, **5**, 3967.

(2) C. Gella, E. Ferrer, R. Alibes, F. Busque, P. de March, M. Figueredo, J. Font, *J. Org. Chem.* 2009, **74**, 6365.

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