Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is © The Royal Society of Chemistry 2012

Supporting information

Cascade Synthesis of bis-*N*-sulfonylcyclobutenes via Cu(I)/Lewis Acid-Catalyzed (3+2)/(2+2) Cycloadditions: Observation of Aggregation-Induced Emission Enhancement from Restricted C=N Photoisomerization

Kayambu Namitharan and Kasi Pitchumani*

School of Chemistry, Madurai Kamaraj University, Madurai-625021, India.

E-mail:pit12399@yahoo.com

Contents

This journal is © The Royal Society of Chemistry 2012

1. Experimental procedures

General Methods.

All reactions were carried out under a nitrogen atmosphere, with dry, freshly distilled solvents in anhydrous conditions. All chemicals (alkynes, sulfonyl chlorides, metal salts and NH_4 Y) were used without further purification as commercially available unless otherwise noted. NMR spectra were registered on Bruker DRX spectrometer operating at 300, 400 and 500 MHz for ^{1}H and 75, 100 and 125 MHz for ^{13}C. All ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ or DMSO(d_6) or $CDCl_3$ DMSO(d_6) mixtures with TMS as the internal standard. Chemical shifts are expressed in ppm and J values are given in Hz (Coupling constants are calculated according to the actual values given in NMR spectrums, here the decimals are reduced). High-resolution mass spectra (HRMS) were recorded in Thermo-Scientific mass spectrometer. Purifications by column chromatography were performed on silica gel 60-120 mesh. The XRD pattern of the catalyst samples was measured with a PW3050/60 (XPERT-PRO Diffractometer system) instrument using a Cu Kα radiation at room temperature. Fluorescence measurements were made on a Fluoromax-4 Spectrofluorometer. Theoretical studies were carried out in Central Leather Institute (CLRI) Chennai. Sulfonyl azides[1] were prepared according to the published method.

The ground state geometry optimization was performed utilizing density functional theory (DFT) employing B3LYP[2] functional, a 6-31G* basis set, which is a reliable method that has been widely used for calculating the structural and optical properties of many systems[3-5]. UV-Vis spectra were simulated utilizing the first 20 excited states and the time-dependent density functional theory (TDDFT) routine with the aforementioned functional and basis set. In addition to that, HOMO and LUMO were produced form the output. All the calculations were performed with Gaussian 03 software package.[6]

Preparation and characterization of Cu(I)Y zeolite

Cu(I)Y zeolite was prepared according to the procedure reported by Li *et al.*[2] A mixture of CuCl and HY (obtained from deammonification of NH_4Y at 450°C for 6h) was ground by pestle and mortar, it was heated in flowing nitrogen atmosphere at a heating rate of 10°C/min. The ion-exchange of Cu(I) in solid CuCl with H^+ in HY zeolite occurred at over 300°C and the maximum ion-exchange rate was reached at 340°C with the consequent release of HCl gas. Cu(I)Y was prepared at two different temperatures *via* heating the mixture of CuCl/HY at 350°C for 15 h under nitrogen atmosphere. After the preparation was

over, the Cu(I)Y was kept under high vacuum. The prepared Cu(I)Y zeolite was characterized by powder XRD, XPS, and EDX which was found to be in good agreement with the literature.[2]

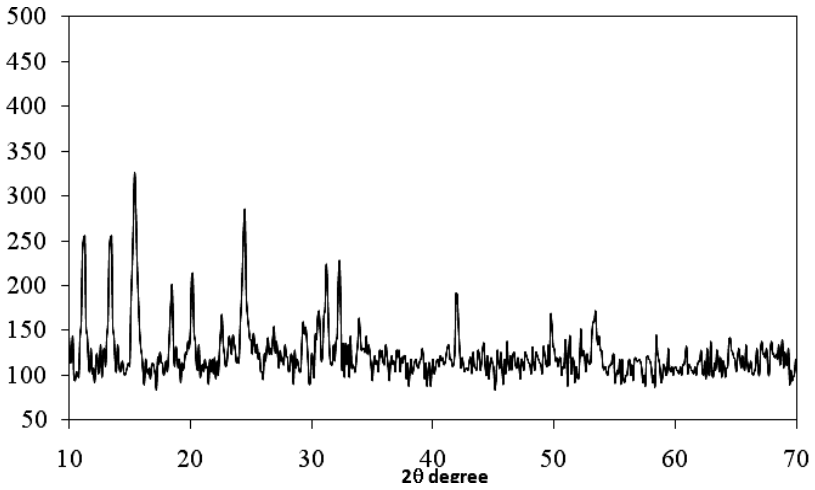


Fig. a. Powder XRD pattern of Cu(I)-Y zeolite

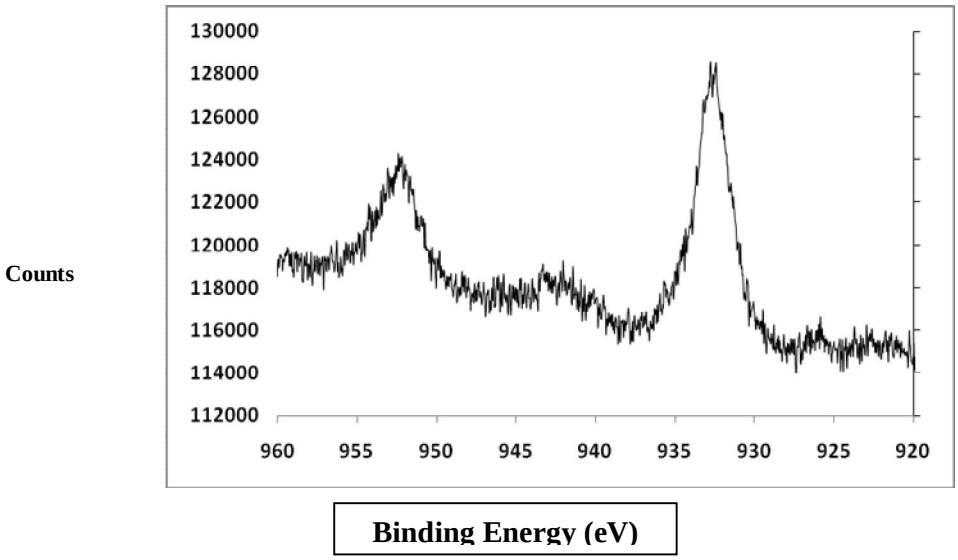


Fig. b. X-Ray photoelectron spectra (XPS) of Cu(I)-Y zeolite

The oxidation states of Cu in the prepared Cu(I)-Y zeolite were examined by X-ray photoelectron spectroscopy (Fig. b). In the Cu 2p core level XPS spectra, the peaks corresponding to the Cu 2p3/2 and 2p1/2 are observed at around 932.7 eV and 953.2 eV, which is match well with the literature values for Cu(I) zeolite (Cu 2p3/2 933.5 and Cu 2p1/2 952.3).[4b]

This journal is © The Royal Society of Chemistry 2012

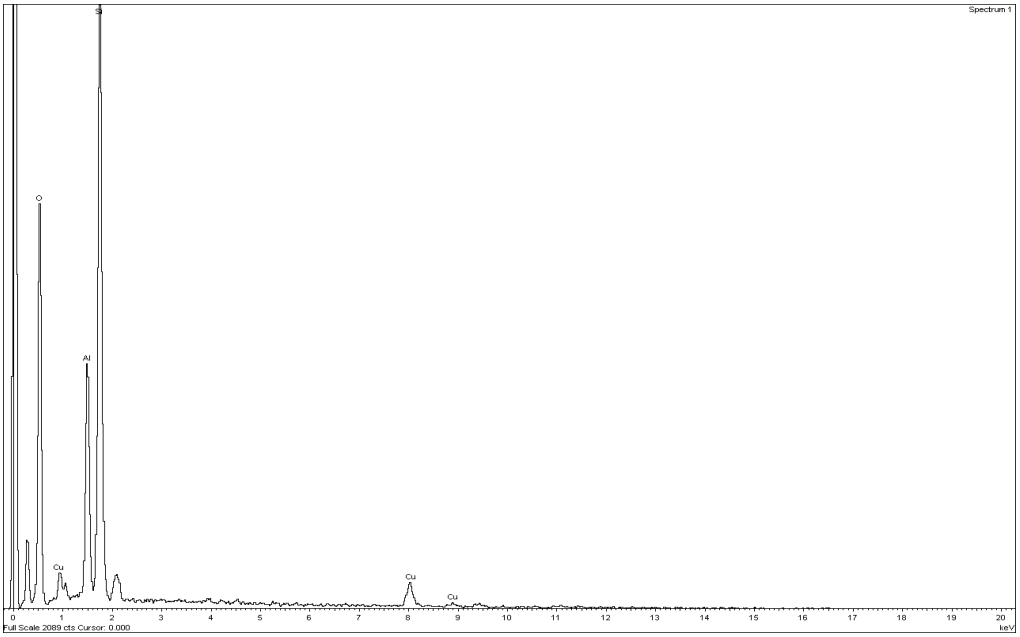


Fig. c. EDX for Cu(I)-Y zeolite

The total copper content in the samples was determined by EDX analysis and it was found to be 7.26 wt% (Figure c).

General procedure for the Cu(I)-zeolite/PhCOCl catalyzed cascade synthesis of bis-*N*-sulfonylcyclobutenes

A solution of alkyne (1 mmol) in one mL of DCM was added slowly to a mixture of Cu(I)-zeolite (20 mg), sulfonyl azide (1 mmol), benzoyl chloride (0.2 mmol) and Et_3N (2 mmol) taken in 2 mL of DCM under N_2 atmosphere. After stirring at room temperature for the 30 minutes, the mixture was diluted with ethyl acetate(5 mL). After removing the catalyst by filtration, followed by solvent evaporation under reduced pressure, the resulting crude product was finally purified by recrystalization and column chromatography on silica gel (60-120 mesh) with ethyl acetate and ethanol as eluting solvent to give the desired product. The recovered catalyst was thoroughly washed with ethyl acetate and used it for next run

ALL THE SYNTHESIZED COMPOUNDS ARE UNKNOWN AND THE CRYSTAL STRUCTURE OF COMPOUND 3A HAS BEEN DEPOSITED AT THE CAMBRIDGE CRYSTALLOGRAPHIC DATA CENTRE AND ALLOCATED THE DEPOSITION NUMBER ***CCDC 822410***

This journal is © The Royal Society of Chemistry 2012

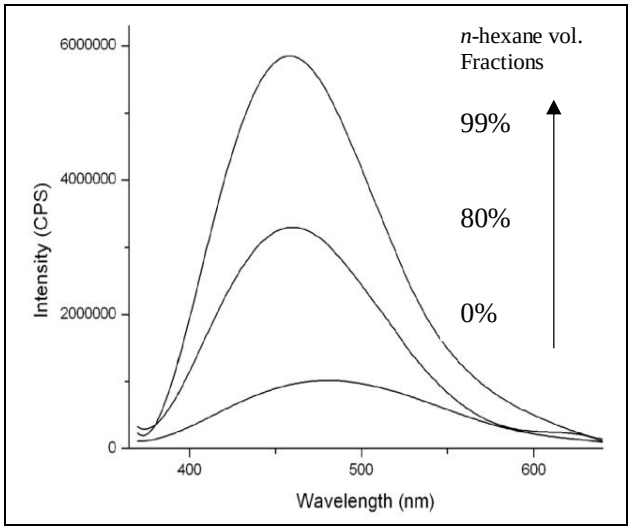


Fig. d. (a) PL spectra of **3e** ($\lambda_{ext.}$ = 350 nm) in different ratios of *n*-hexane/$CHCl_3$ at a concentration of 7 x 10^{-6} m

Fig. e. Emission image of **3a** in pure $CHCl_3$(***solution***) and 99:1 (v/v) *n*-hexane/$CHCl_3$ mixture (***aggregate***) under UV light ($\lambda_{ext.}$ = 350 nm)

This journal is © The Royal Society of Chemistry 2012

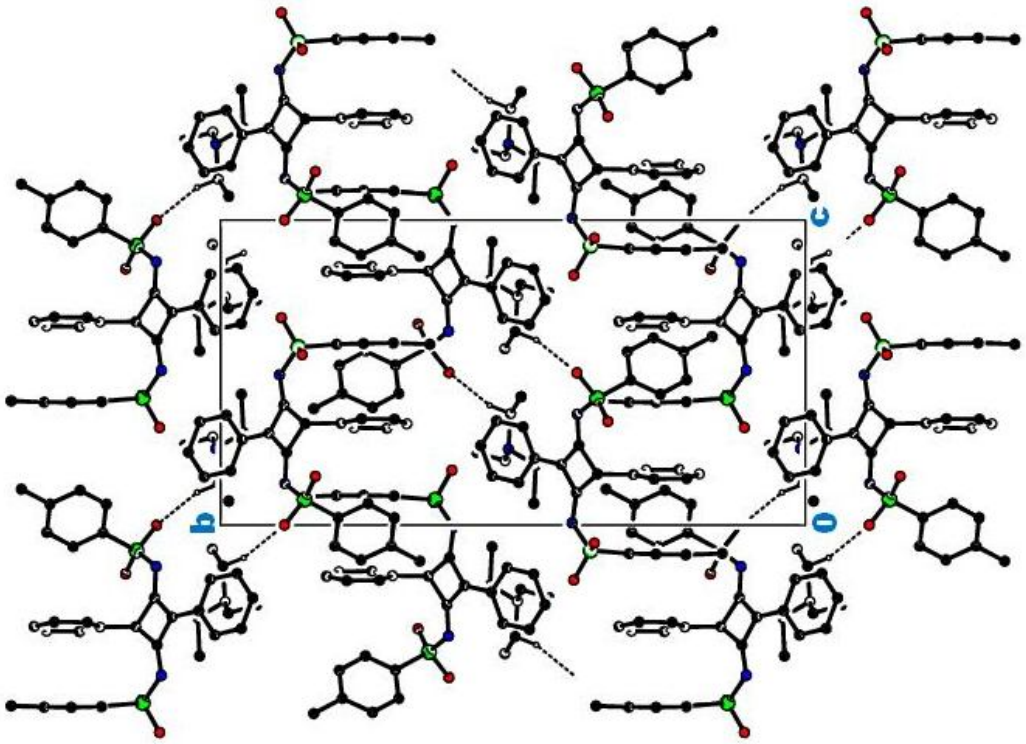


Fig. f. Crystal packing diagram of **3a**

References

1 a) Abramovitch, R. A.; Chellathurai, T.; Holcomb D. W.; McMaster, T. I; Vanderpool, D. P. *J. Org. Chem.* **1977**, *42*, 2920; b) Danheiser, R. L.; Miller, R. F.; Brisbois, R. G.; Park, S. Z. *J. Org. Chem*. **1990**, *55*, 1959.

2. Li, Z.; Xie, K.; Slade, R. C. T. *Appl. Catal. A: Gen*. **2001**, *209*, 107-115.

3. A. D. Becke, *J. Chem. Phys*. **1993**, *98*, 5648-5652.

4. Blouin, N.; Michaud, A.; Gendron, D.; Wakim, S.; Blair, E.;Neagu-Plesu, R.; Belletete, M.; Durocher, G.; Tao, Y.; Leclerc, M. *J.Am. Chem. Soc*. **2008**, 130, 732-742.

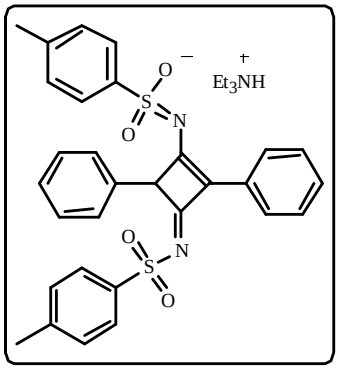
5. Belletête, M.; Blouin, N.; Boudreault, P.-L. T.; Leclerc, M.;Durocher, G. *J. Phys. Chem. A* **2006**, *110*, 13696-13704.

6. Zade, S. S.; Bendikov, M. *Org. Lett.* **2006**, *8*, 5243-5246.

7. Gaussian 03 (Revision E. 01); Gaussian, Inc.: Wallingford, CT, **2004**.

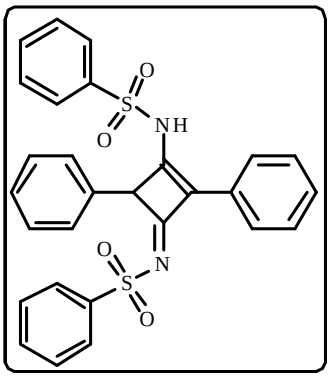
This journal is © The Royal Society of Chemistry 2012

Characterization Data



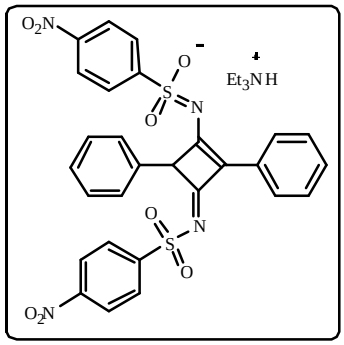
Triethylammonium (*E*)-*N*-2,4-diphenyl-3(tosylimino)cyclobut-1-enyl-4-methylbenzenesulfonimidate (table 2, entry 1)

Compound **3a** was prepared according the general procedure and purified by recrystalization in ethanol as a white solid: mp 195-196 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ 1.19-1.24 (t, 9H, 7.2 Hz), 2.25 (s, 6H), 2.98-3.00 (d, 6H, 7.2Hz), 5.44 (s, 1 H), 6.87-7.25 (m, 17H), 8.02-8.04 (d, 2H, 7.5 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS) δ = 8.8, 21.2, 46.8, 63.2, 125, 126.0, 126.3, 126.5, 127.6, 127.8, 128.6, 129.5, 132.1, 138.8, 140.0, 141.2, 171.5 ppm. HRMS (ESI): m/z calcd for $C_{36}H_{41}N_3O_4S_2$ $(M+H)^+$: 644.2616; found, 644.2526.



(*E*)-*N*,*N*'-(2,4-Diphenylcyclobut-1-ene-1-yl-3-ylidene) dibenzenesulfonamide (table 2, entry 2)

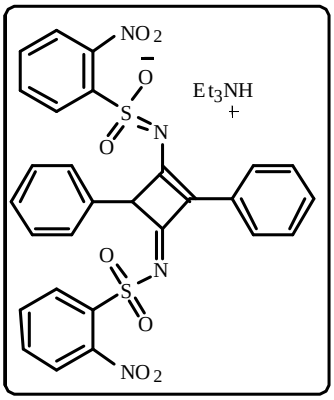
Compound **4a** was prepared according the general procedure and purified by column chromatography on silica gel (60-120 mesh) with ethyl acetate and ethanol as a white solid: mp 168-169 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$-DMSO (d_6), 25°C, TMS): δ 5.36 (s, 1H), 6.84-7.15 (m, 16H) 7.92-7.94 (d, 2H, 7.2 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$-DMSO (d_6), 25°C, TMS) δ = 62.7, 118.6, 120.0, 121.9, 125.7, 126.2, 127.0, 127.2, 127.5, 128.4, 130.3, 131.4, 133.4, 139.8, 170.7. HRMS (ESI): m/z calcd for $C_{28}H_{22}N_2O_4S_2$ $(M-H)^-$: 513.0953; found, 513.1045.



Triethylammonium *(E)*-4-nitro-*N*-(3-(4-nitrophenyl sulfonylimino)-2,4-diphenylcyclobut-1-enyl) benzenesulfonimidate (table 2, entry 3)

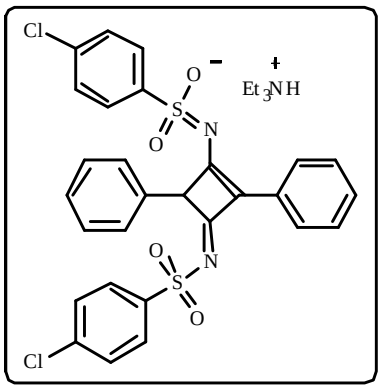
Compound **3b** was prepared according the general procedure and purified by recrystalization in ethanol as a yellow solid: mp 214-215 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ 1.36-1.32 (t, 9H, 7.2 Hz), 3.16-1.08 (q, 6H, 7.2 Hz), 5.48 (s, 1H), 6.99-7.01 (m, 2H), 7.09-7.18 (m, 3H), 7.24-7.34 (m, 9H), 7.86-7.89 (m, 4H), 8.01-8.03 (d, 2H, 7.2 Hz) ppm; ^{13}C NMR (75 MHz, CDCl3, 25°C, TMS) δ = 8.9, 47.2, 62.8, 123.2, 126.4, 126.6, 127.2, 128.0, 129.7, 148.3, 148.9, 172.6 ppm. HRMS (ESI): m/z calcd for $C_{34}H_{35}N_5O_8S_2$ $(M+H)^+$: 706.2005; found, 706.1961.

This journal is © The Royal Society of Chemistry 2012



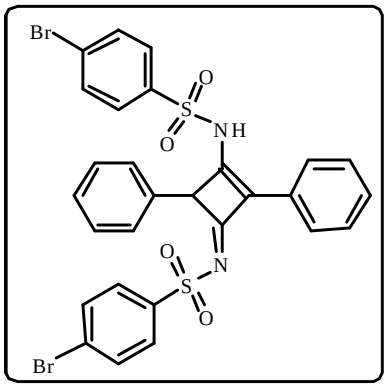
Triethylammonium (*E*)-2-nitro-*N*-(3-(2-nitrophenyl sulfonylimino)-2,4-diphenylcyclobut-1-enyl) benzenesulfonimidate (table 2, entry 4)

Compound **3c** was prepared according the general procedure and purified by recrystalization in ethanol as a yellow solid: mp 203-204 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6, 25°C): δ 1.12-1.15 (t, 9H, 7 Hz), 3.00-3.04 (q, 6H, 7 Hz), 5.08 (s, 1H), 6.89-6.95 (m, 4H), 7.00-7.02 (m, 3H), 7.16-7.18 (m, 1H), 7.28-7.33 (m, 4H), 7.51-7.59 (m, 4H), 7.89-7.90 (d, 2H, 7.5 Hz); ^{13}C NMR (125 MHz, DMSO-d_6, 25°C) δ = 8.9, 46.4, 63.3, 119.8, 123.8, 126.1, 126.5, 127.3, 128.0, 128.3, 128.7, 131.7, 131.9, 133.1, 135.1, 137.6, 147.5, 172.8. HRMS (ESI): m/z calcd for $C_{34}H_{35}N_5O_8S_2$ $(M+H)^+$: 706.2005; found, 706.1908.



Triethylammonium (*E*)-4-chloro-*N*-(3-(4-chlorophenyl sulfonylimino)-2,4-diphenylcyclobut-1-enyl) benzenesulfonimidate (table 2, entry 5)

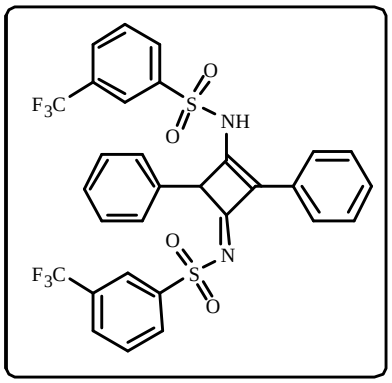
Compound **3d** was prepared according the general procedure and purified by recrystalization in ethanol as a white solid: mp 206-207 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ 1.08-1.12 (m, 9H), 2.91-2.95 (m, 6H), 5.38 (sm, 1H), 6.79-6.82 (m, 4H), 6.98 (m, 4H), 7.12-7.26 (m, 8H), 7.53-7.55 (m, 2H); ^{13}C NMR (75 MHz, DMSO (d_6), 25°C, TMS) δ = 7.9, 45.5, 61.9, 123.7, 124.1, 125.2, 125.3, 126.5, 126.6, 126.7, 128.5, 129.8, 141.7, 170.6. HRMS (ESI): m/z calcd for $C_{34}H_{35}Cl_2N_3O_4S_2$ $(M+H)^+$: 684.1524; found, 684.1428.



(*E*)-*N*,*N*'-(2,4-Diphenylcyclobut-1-ene-1-yl-3-ylidene)bis(4-bromobenzenesulfonamide) (table 2, entry 6)

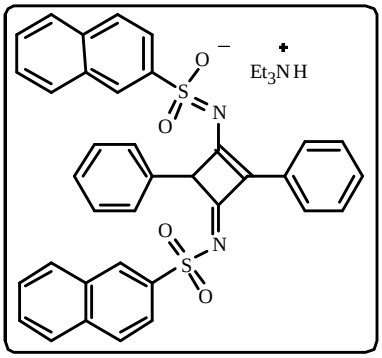
Compound **4b** was prepared according the general procedure and purified by column chromatography on silica gel (60-120 mesh) with ethyl acetate and ethanol as a white solid: mp 172-173 ^{o}C; ^{1}H NMR (500 MHz, DMSO (d_6), 25°C, TMS): δ 5.14 (s, 1 H), 6.87-6.97 (m, 5H), 7.06-7.24 (m, 3H), 7.34-7.37 (m, 2H), 7.44-7.52 (m, 2H), 7.77 (m, 2 H), 7.87-7.96 (m, 2H), 8.02-8.00 (d, 2H, 7.5Hz) ppm; ^{13}C NMR (125 MHz, DMSO (d_6), 25°C, TMS) δ = 63.0, 120.1, 126.2, 127.5, 127.9, 128.5, 128.6, 129.0, 129.7, 130.2, 132.0, 132.7, 134.9, 137.4, 141.4, 172.9 ppm. HRMS (ESI): m/z calcd for $C_{28}H_{20}Br_2N_2O_4S_2$ $(M-H)^-$: 668.9153; found, 668.9244.

This journal is © The Royal Society of Chemistry 2012



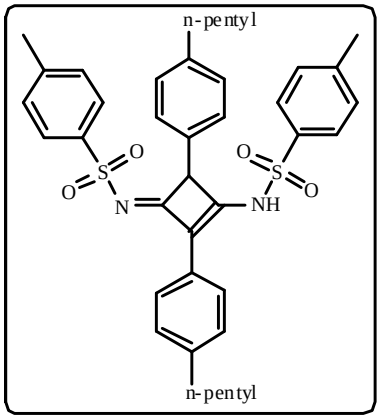
(*E*)-*N*,*N*'-(2,4-Diphenylcyclobut-1-ene-1-yl-3-ylidene)bis(3-(trifluoromethyl)benzenesulfonamide) (table 2, entry 7)

Compound **4c** was prepared according the general procedure and purified by column chromatography on silica gel (60-120 mesh) with ethyl acetate and ethanol as a white solid: mp 148-149 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$-DMSO (d_6), 25°C, TMS): 5.41 (s, 1 H), 6.88-6.91 (m, 2H), 7.01-7.04 (m, 3H), 7.11-7.15 (m, 6H), 7.27-7.32 (m, 3H), 7.44 (m, 4H), 8.04-8.06 (d, 2H, 7.5Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$-DMSO (d_6), 25°C, TMS) δ = 62.4, 121.3, 122.6, 124.9, 125.9, 136.4, 127.3, 128.1, 128.8, 129.0, 129.2, 130.0, 131.4, 137.0, 143.3, 172.3 ppm. HRMS (ESI): m/z calcd for $C_{30}H_{20}F_6N_2O_4S_2$ $(M-H)^-$: 649.0691; found, 649.0711.



Triethylammonium (*E*)-*N*-3-(naphthalen-2-ylsulfonyl imino)-2,4-diphenylcyclobut-1-enylnaphthalene-2-sulfonimidate (table 2, entry 8)

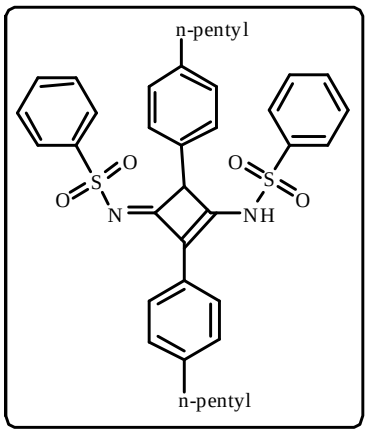
Compound **3e** was prepared according the general procedure and purified by recrystalization in ethanol as a white solid: mp 246-247 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ 1.25-1.29 (t, 9H, 7.2 Hz), 3.02-3.09 (q, 6H, 7.2 Hz), 5.56 (s, 1H), 6.86-6.92 (m, 3H), 7.10-7.12 (m, 1H), 7.19-7.30 (m, 5H), 7.37-7.48 (m, 8H), 7.56-7.60 (m, 4H), 7.69-7.71 (m, 2H), 8.05-8.08 (d, 2H, 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS) δ = 8.8, 46.9, 63.3, 120.9, 122.6, 125.5, 126.3, 126.6, 126.9, 127.47, 127.6, 127.8, 128.0, 129.2, 129.5, 131.9, 134.0, 138.6, 139.7, 171.7. HRMS (ESI): m/z calcd for $C_{42}H_{41}N_3O_4S_2$ $(M+H)^+$: 716.2616; found, 716.2596.



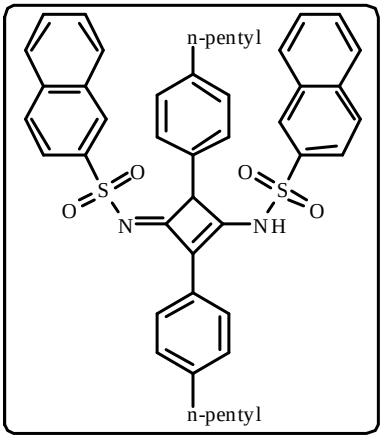
(*E*)-*N*,*N*'-(2,4-Bis(4-(n-pentyl)phenylcyclobut-1-ene-1-yl-3-ylidene)bis(4-(methyl)benzenesulfonamide (table 2, entry 10)

Compound **4d** was prepared according the general procedure and purified by column chromatography on silica gel (60-120 mesh) with ethyl acetate and ethanol as a white solid: mp 146-147 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 0.84-0.94 (m, 6H), 1.26-1.50 (m, 12 H), 2.14 (s, 6H), 2.37-2.46(m, 4H), 2.77-3.02 (m, 8H), 5.39 (s, 1H), 6.60-6.66 (m, 6H), 6.86-7.02(m, 8H), 7.81-7.83 (d, 2H, 6.6Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C,

TMS) δ = 13.9, 21.1, 22.4, 22.6, 31.1, 31.4, 31.8, 35.6, 212.2, 125.9, 126.3, 127.5, 128.0, 128.4, 128.9, 129.2, 134.8, 138.9, 140.3, 141.0, 171.5. HRMS (ESI): m/z calcd for $C_{40}H_{46}N_2O_4S_2$ $(M-H)^-$: 681.2821; found, 681.2855.

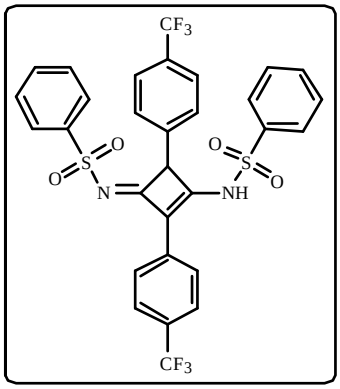


(*E*)-*N*,*N*'-(2,4-Bis(4-(n-pentyl)phenylcyclobut-1-ene-1-yl-3-ylidene)dibenzenesulfonamide (table 2, entry 11) Compound **4e** was prepared according the general procedure and purified by column chromatography on silica gel (60-120 mesh) with ethyl acetate and ethanol as a white solid: mp 127-128 ^oC; ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ 0.84-0.95 (m, 6H), 1.28-1.51 (m, 12 H), 2.24 (m, 2H), 2.5 (m, 6H), 5.36 (s, 1H), 6.44 (m, 2H), 6.76-6.78 (m, 5H), 6.91-7.04 (m, 8H), 7.78-7.81 (d, 2H, 7.2 Hz);^{13}C NMR (75 MHz, $CDCl_3$-DMSO (d_6), 25°C, TMS) δ = 21.6, 55.3, 55.4, 64.7, 65.0, 77.6, 113.4, 113.9, 114.0, 115.2, 118.9, 119.8, 126.5, 126.7, 128.1, 128.2, 128.6, 128.6, 128.7, 129.0, 129.1, 129.3, 129.8, 130.2, 130.8, 134.8, 134.9, 135.8, 141.0, 144.9, 145.0, 160.3, 167.0, 167.7. HRMS (ESI): m/z calcd for $C_{38}H_{42}N_2O_4S_2$ $(M-H)^-$: 653.2508; found, 653.2538.

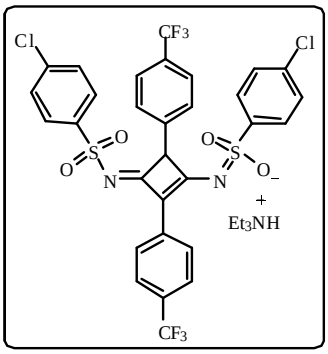


(*E*)-*N*,*N*'-(2,4-Bis(4-(n-pentyl)phenylcyclobut-1-ene-1-yl-3-ylidene)dinaphthalenesulfonamide (table 2, entry 12) Compound **4f** was prepared according the general procedure and purified by column chromatography on silica gel (60-120 mesh) with ethyl acetate and ethanol as a white solid: mp 161-162 ^oC; ^1H NMR (300 MHz, $CDCl_3$-DMSO (d_6), 25°C, TMS): 0.84-0.94 (m, 6H), 1.29-1.38 (m, 12 H), 1.54-1.56 (m, 2H), 2.32 (m, 2H), 5.43 (s, 1H), 6.68-6.71 (m, 2H), 6.99-7.08 (m, 4), 7.23-7.6 (m, 2H), 7.46-7.52 (m, 4H), 7.61-7.65 (m, 3H), 7.76-7.78 (m, 2H), 7.86-7.89 (d, 2H, 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$-DMSO (d_6), 25°C, TMS) δ = 19.0, 19.1, 27.2, 27.3, 35.3, 35.9, 36.0, 36.6, 40.0. 40.4, 67.3, 124.0, 127.6, 130.8, 131.1, 131.5, 132.0, 132.4, 132.6, 132.8, 133.9, 134.0, 136.6, 135.5, 144.5, 145.5, 145.7, 175.9. HRMS (ESI): m/z calcd for $C_{46}H_{46}N_2O_4S_2$ $(M-H)^-$: 753.2821; found, 753.2841.

This journal is © The Royal Society of Chemistry 2012

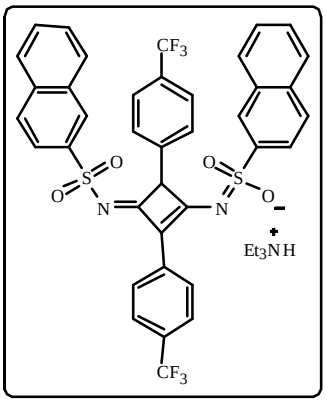


(*E*)-*N*,*N*'-(2,4-Bis(4-(trifluoromethyl)phenyl)cyclobut-1-ene-1-yl-3-ylidene)dibenzenesulfonamide (table 2, entry 13) Compound **4g** was prepared according the general procedure and purified by column chromatography on silica gel (60-120 mesh) with ethyl acetate and ethanol as a white solid: mp 135-136 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$-DMSO (d_6), 25°C, TMS): δ 5.49 (s, 1H), 6.81-6.83 (m, 2H), 7.11-7.19 (m, 10H), 6.73-6.79 (m, 1.05H), 6.98-7.17 (m, 5.41H), 7.25-7.27 (m, 4H), 8.12-8.15 (d, 2H, 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$-DMSO (d_6), 25°C, TMS) δ = 62.6, 119.1, 119.8, 125.2, 127.1, 127.2, 130.1, 142.6, 172.6. HRMS (ESI): m/z calcd for $C_{30}H_{20}F_6N_2O_4S_2$ $(M-H)^-$: 649.0691; found, 649.0723.



Triethylammonium (*E*)-4-chloro-*N*-(3-(4-chlorophenylsulfonylimino)-2,4-bis(4-(trifluoromethyl) phenyl)cyclobut-1-enyl)benzenesulfonimidate (table 2, entry 14)

Compound **3f** was prepared according the general procedure and purified by recrystalization in ethanol as a white solid: mp 191-192 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ 1.18-1.21 (m, 9H), 3.02-3.14 (m, 6H), 5.31 (s, 1H), 6.87-6.89 (m, 4H), 6.96-7.01 (m, 4H), 7.11-7.19 (m, 7H), 7.94-7.95 (m, 2H), 7.26-7.52 (m, 9.16H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS) δ = 8.9, 46.9, 64.1, 122.6, 126.3, 126.6, 127.0, 127.4, 127.6, 127.9, 128.1, 129.3, 129.6, 131.9, 134.1, 139.7, 171.7. HRMS (ESI): m/z calcd for $C_{36}H_{33}Cl_2F_6N_3O_4S_2$ $(M+H)^+$: 819.1272; found, 819.1136.



Triethylammonium (*E*)-*N*-3-(naphthalen-2-ylsulfonyl imino)-2,4-bis(4-(trifluoromethyl)phenyl)cyclobut-1-enylnaphthalene-2-sulfonimidate (table 2, entry 15) Compound **3g** was prepared according the general procedure and purified by recrystalization in ethanol as a white solid: 185-186 mp ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$-DMSO (d_6), 25°C, TMS): δ 1.25-1.30 (t, 9H, 7.2 Hz), 3.05-3.12 (q, 6H, 7.2 Hz), 5.59 (s, 1H), 6.70-6.73 (m, 2H), 7.09-7.12 (m, 2H), 7.21-7.29 (m, 5H), 7.45-7.52 (m, 6H), 7.57-7.75 (m, 10H), 8.13-8.16 (d, 2H, 8.4 Hz); 13C NMR (75 MHz, $CDCl_3$-DMSO (d_6), 25°C) δ = 8.5, 46.4, 63.5, 118.7, 120.0, 121.9, 125.7, 126.2, 127.1, 127.3, 127.5, 128.4, 130.3, 131.4, 133.4, 139.8, 170.7. HRMS (ESI): m/z calcd for $C_{44}H_{39}F_6N_3O_4S_2$ $(M+H)^+$: 851.2364; found, 851.2213.

This journal is © The Royal Society of Chemistry 2012

^{1}H & ^{13}C NMR spectral figures

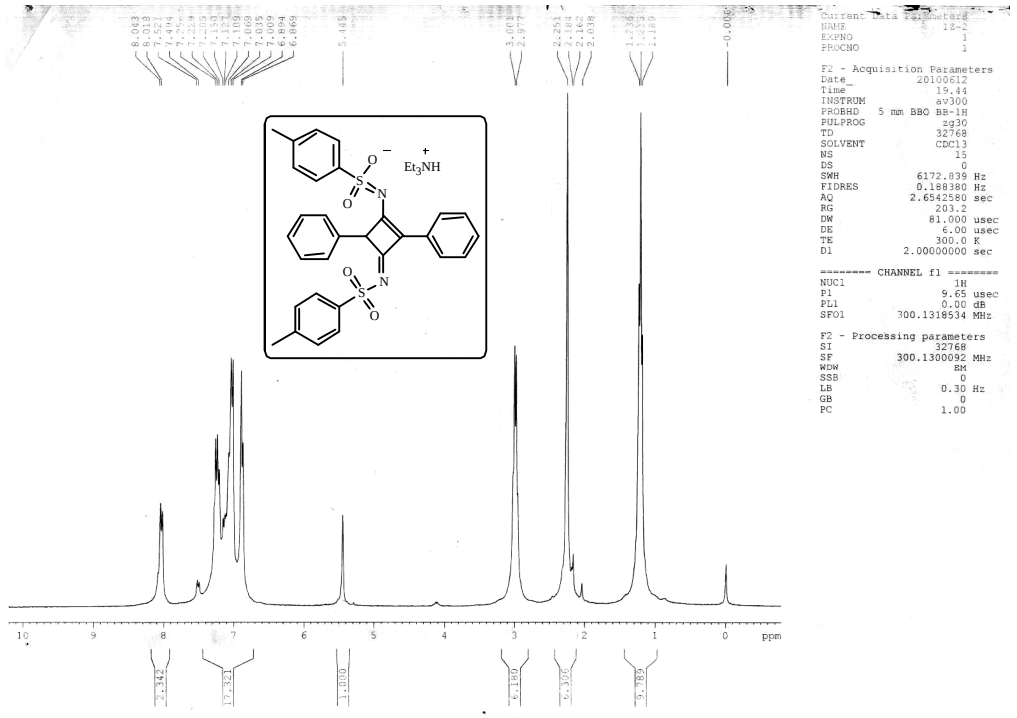


Fig. 1. ^{1}H-NMR spectrum of triethylammonium (*E*)-*N*-2,4-diphenyl-3 (tosylimino) cyclobut-1-enyl-4-methylbenzenesulfonimidate (table 2, entry 1).

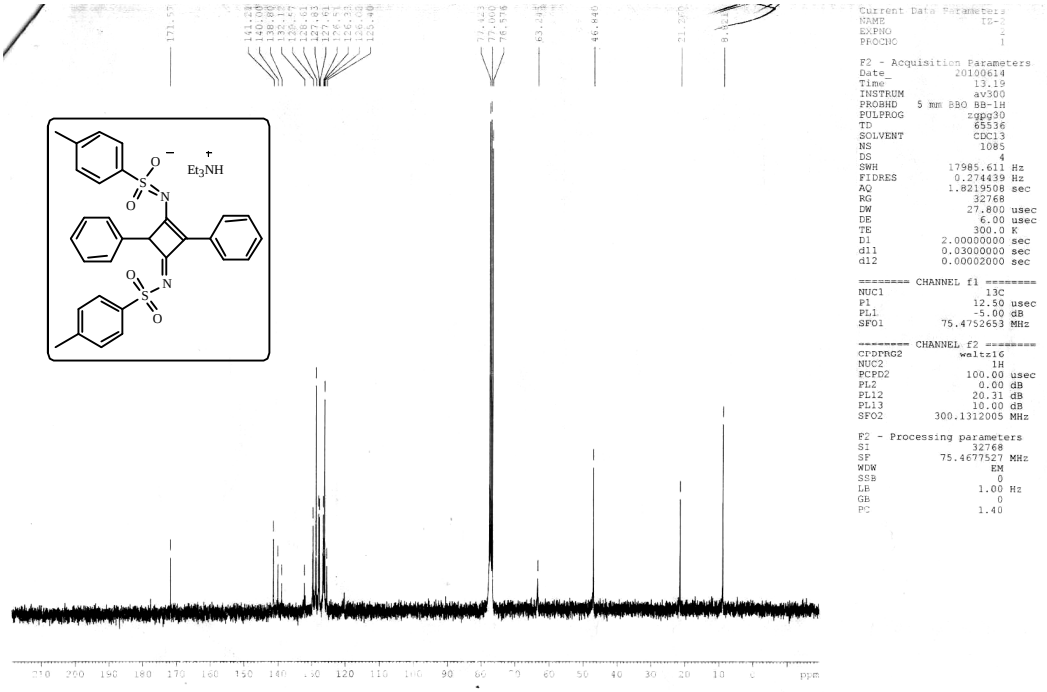


Fig. 2. ^{13}C-NMR spectrum of triethylammonium (*E*)-*N*-2,4-diphenyl-3 (tosylimino) cyclobut-1-enyl-4-methylbenzenesulfonimidate (table 2, entry 1).

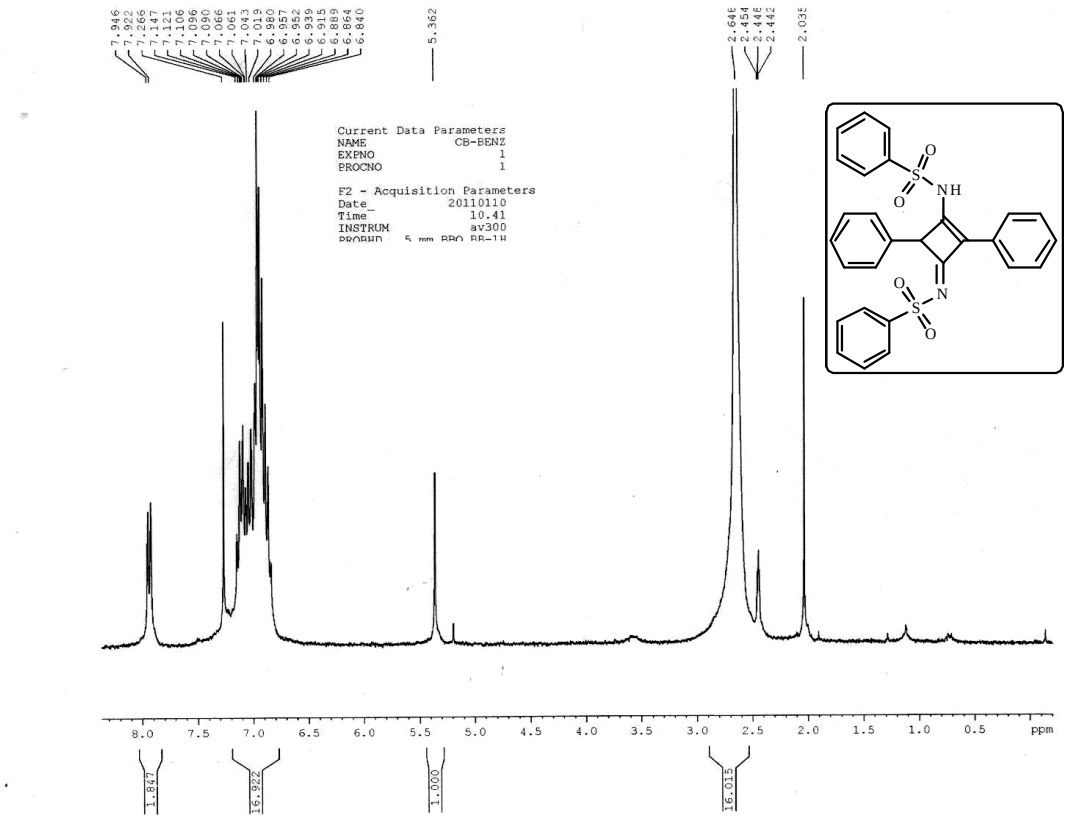


Fig. 3. ^{1}H-NMR spectrum of (*E*)-*N*,*N*'-(2,4-diphenylcyclobut-1-ene-1-yl-3-ylidene) dibenzenesulfonamide (table 2, entry 2).

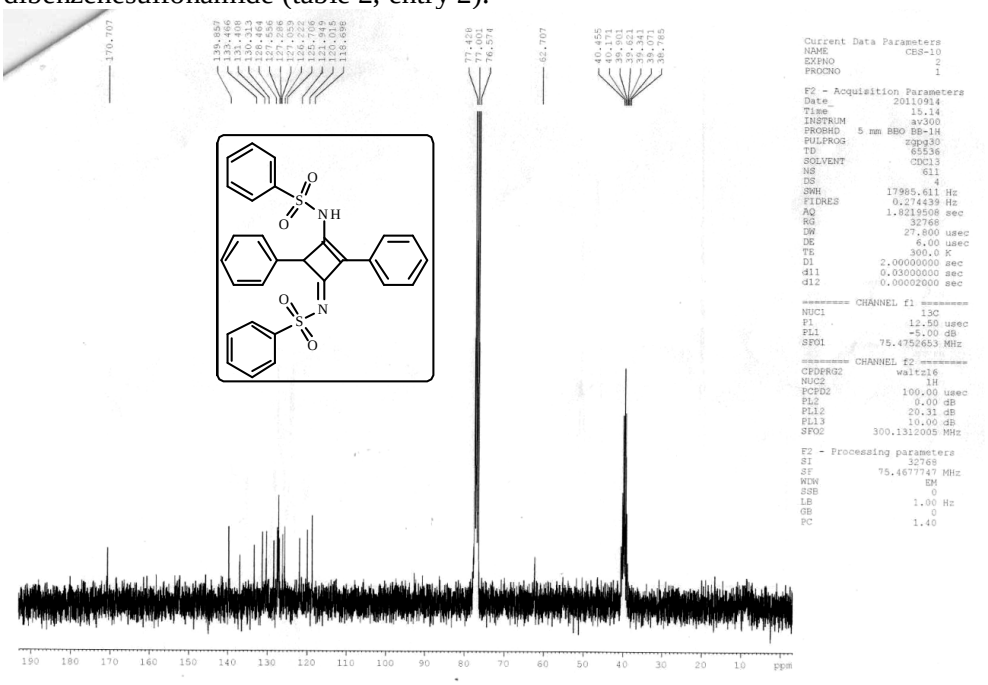


Fig. 4. ^{13}C-NMR spectrum of (*E*)-*N*,*N*'-(2,4-diphenylcyclobut-1-ene-1-yl-3-ylidene) dibenzenesulfonamide (table 2, entry 2).

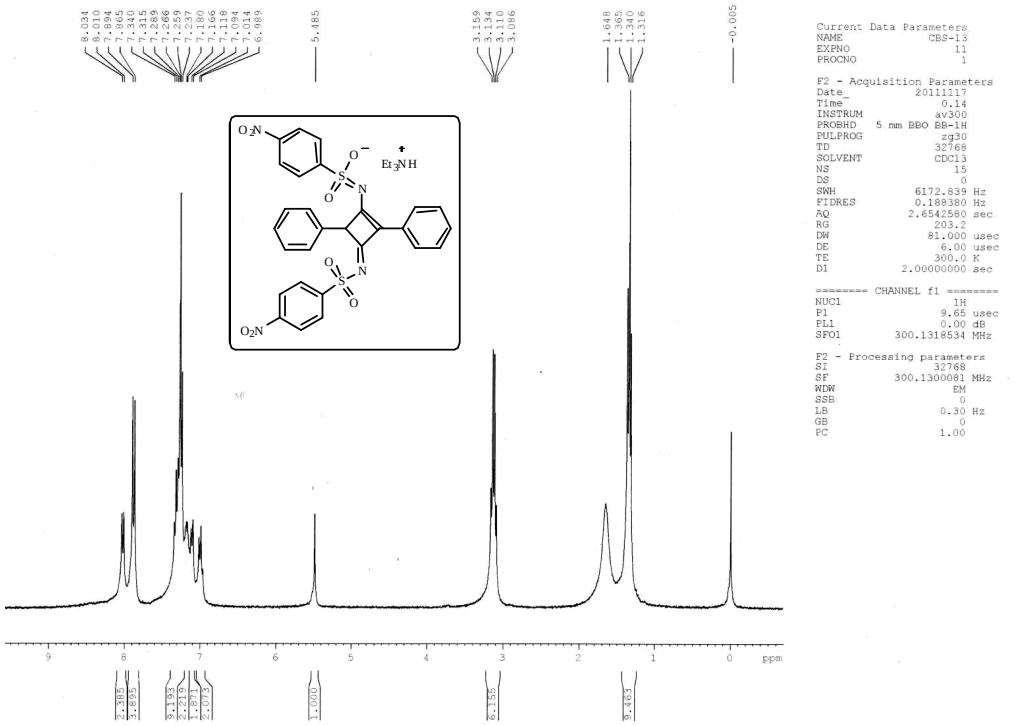


Fig. 5. ^{1}H-NMR spectrum of triethylammonium (*E*)-4-nitro-*N*-(3-(4-nitrophenyl sulfonylimino)-2,4-diphenylcyclobut-1-enyl) benzenesulfonimidate (table 2, entry 3).

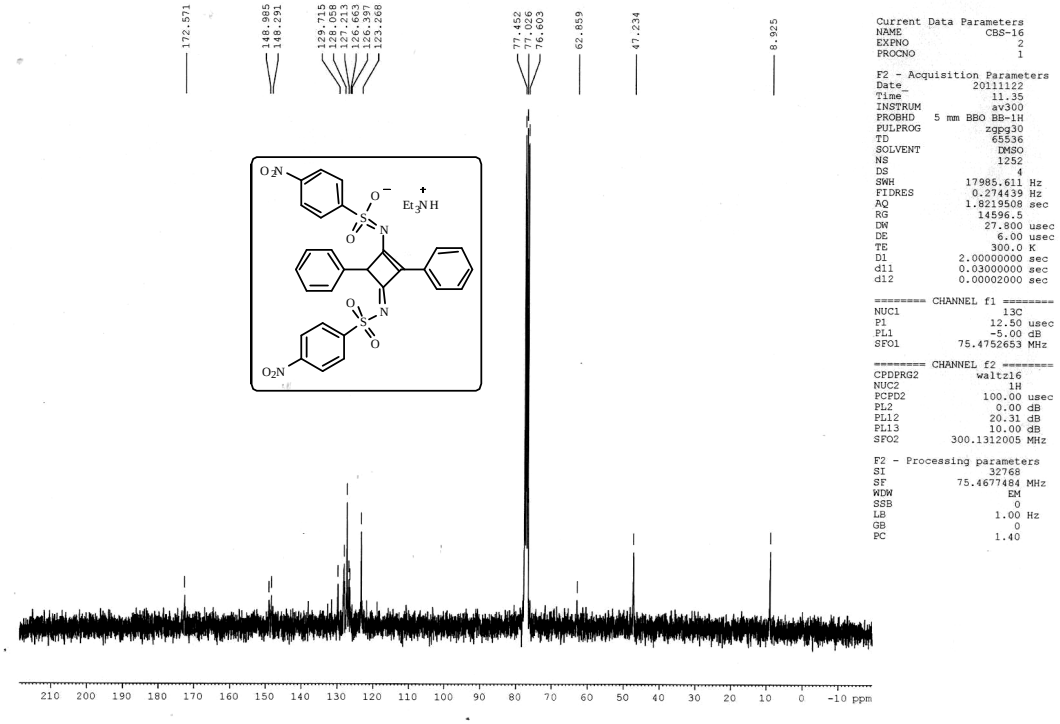


Fig. 6. ^{13}C-NMR spectrum of (triethylammonium (*E*)-4-nitro-*N*-(3-(4-nitrophenyl sulfonylimino)-2,4-diphenylcyclobut-1-enyl) benzenesulfonimidate (table 2, entry 3).

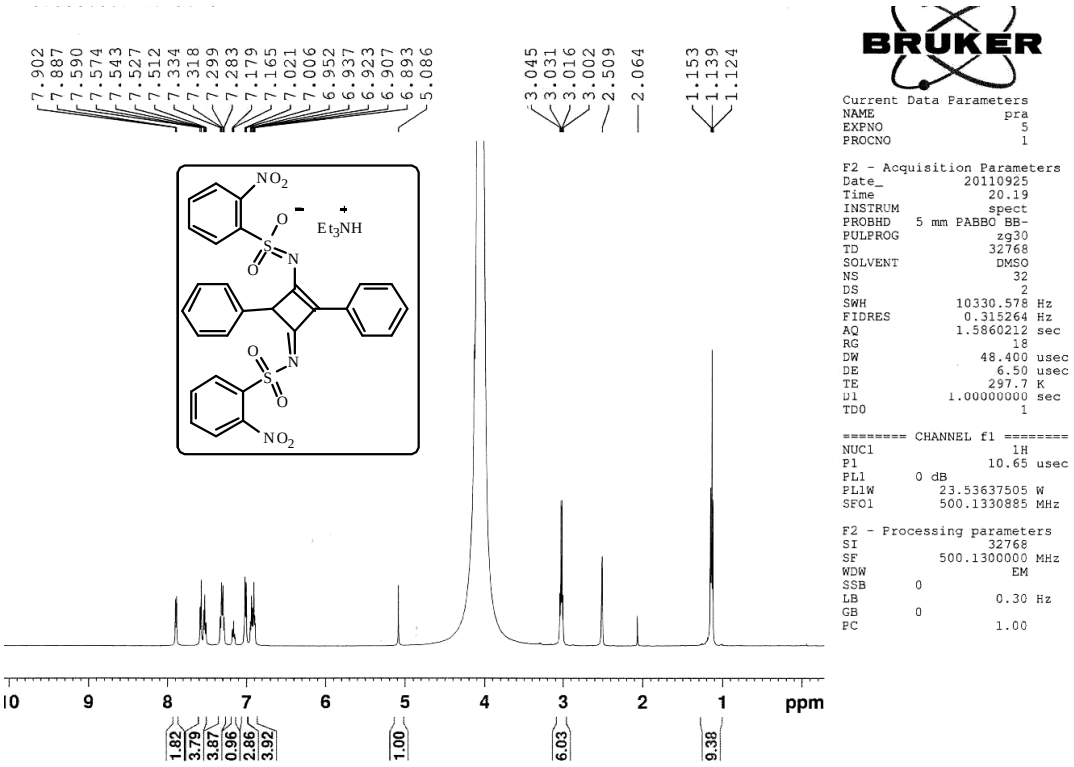


Fig. 7. ^{1}H-NMR spectrum of triethylammonium (*E*)-2-nitro-*N*-(3-(2-nitrophenyl sulfonylimino)-2,4-diphenylcyclobut-1-enyl) benzenesulfonimidate (table 2, entry 4).

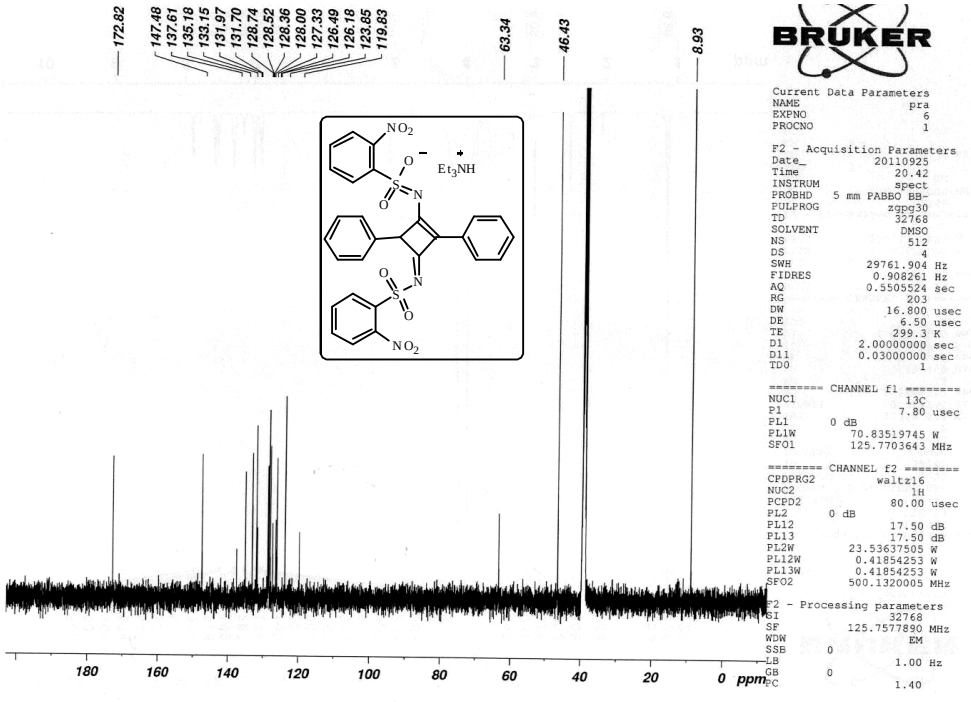


Fig. 8. ^{13}C-NMR spectrum of triethylammonium (*E*)-2-nitro-*N*-(3-(2-nitrophenyl sulfonylimino)-2,4-diphenylcyclobut-1-enyl) benzenesulfonimidate (table 2, entry 4).

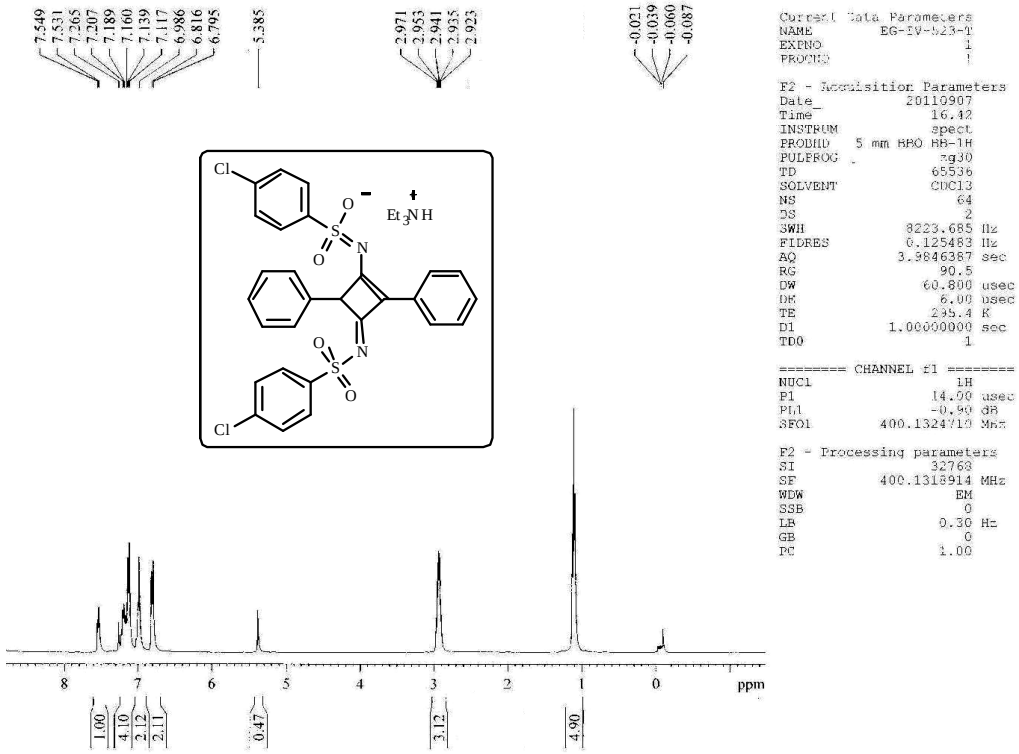


Fig. 9. ^{1}H-NMR spectrum of triethylammonium (*E*)-4-chloro-*N*-(3-(4-chlorophenyl sulfonylimino)-2,4-diphenylcyclobut-1-enyl) benzenesulfonimidate (table 2, entry 5).

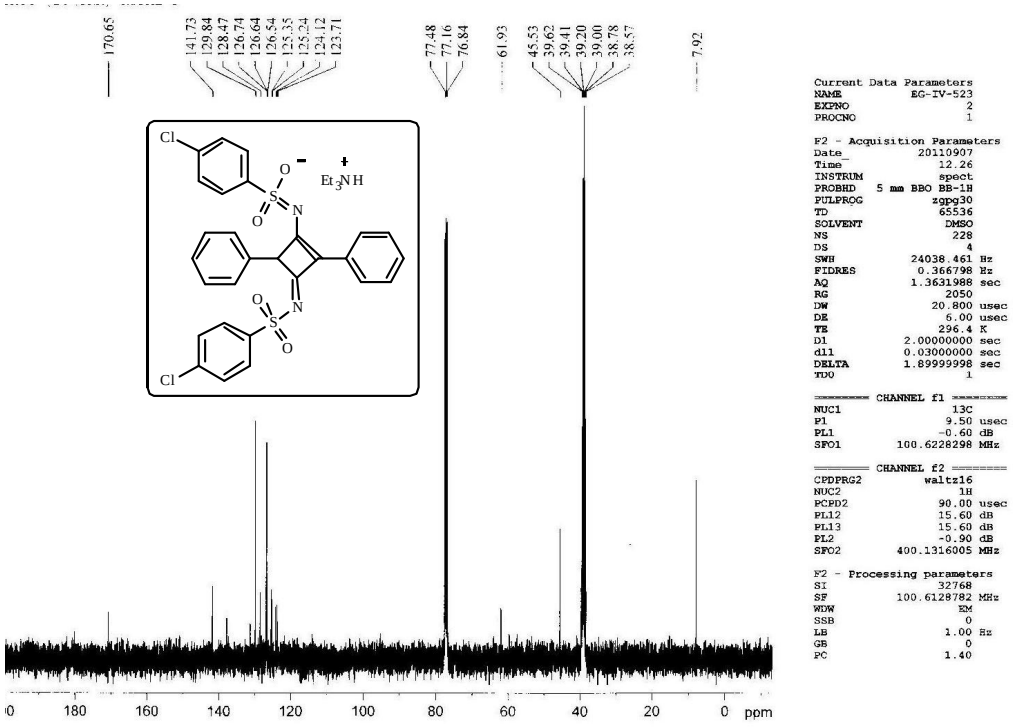


Fig. 10. ^{13}C-NMR spectrum of triethylammonium (*E*)-4-chloro-*N*-(3-(4-chlorophenyl sulfonylimino)-2,4-diphenylcyclobut-1-enyl) benzenesulfonimidate (table 2, entry 5).

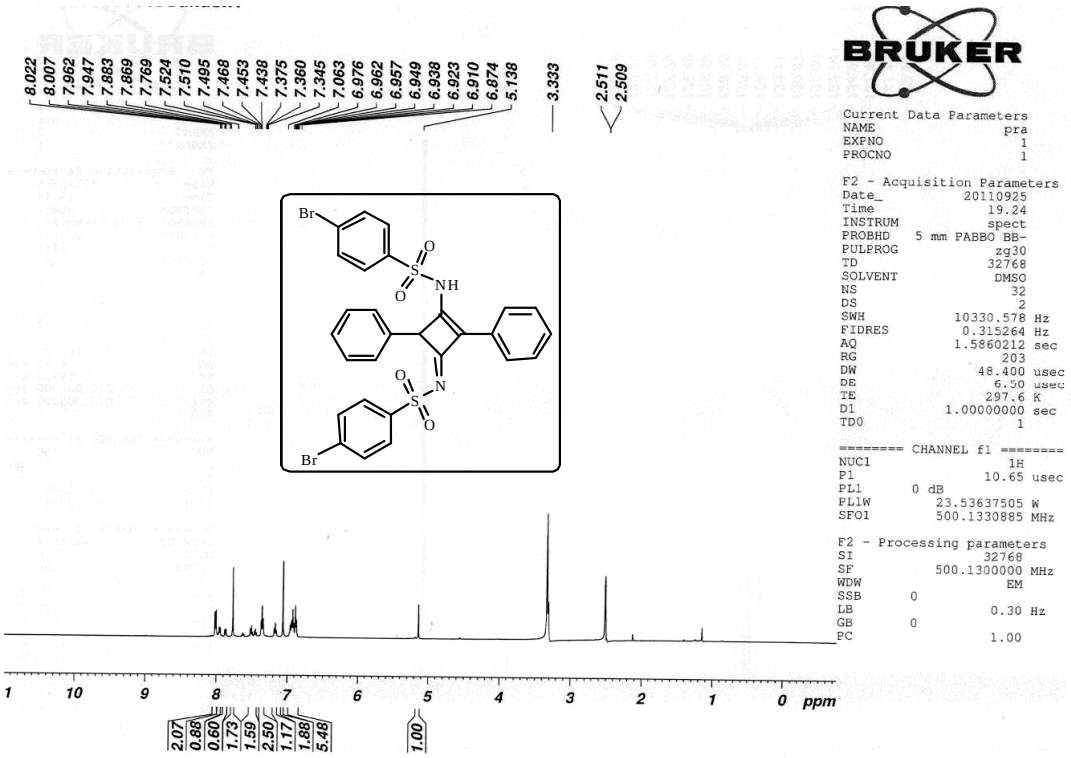


Fig. 11. ^{1}H-NMR spectrum of (*E*)-*N*,*N*'-(2,4-diphenylcyclobut-1-ene-1-yl-3-ylidene)bis(4-bromobenzenesulfonamide) (table 2, entry 6).

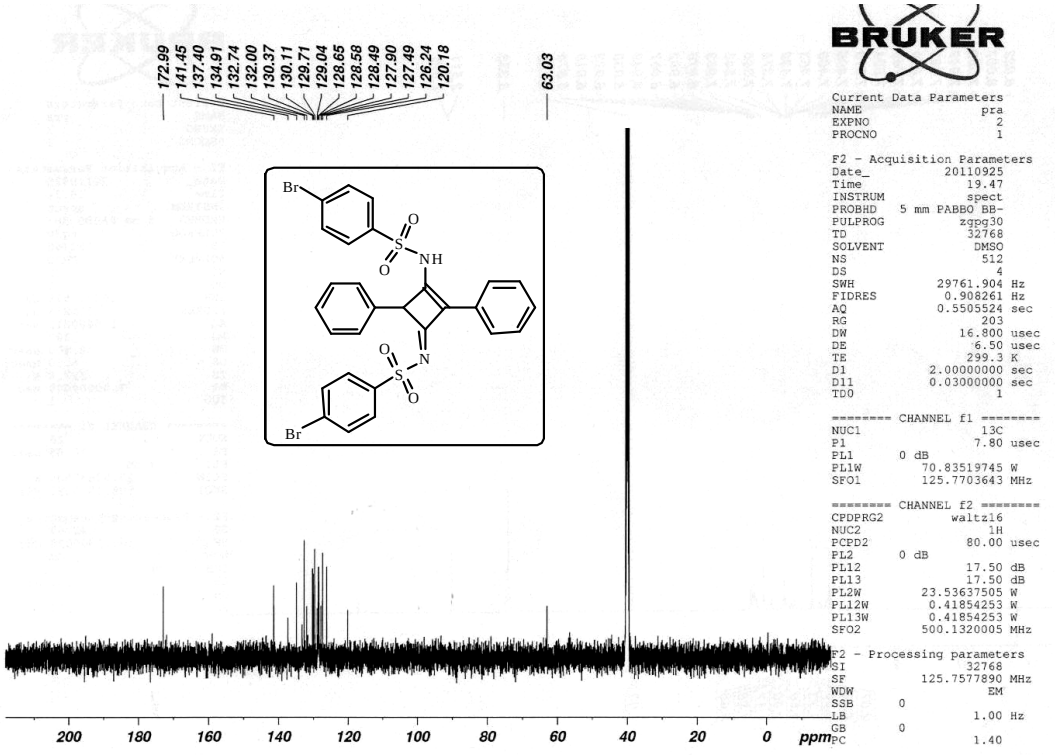


Fig. 12. ^{13}C-NMR spectrum of (*E*)-*N*,*N*'-(2,4-diphenylcyclobut-1-ene-1-yl-3-ylidene)bis(4-bromobenzenesulfonamide) (table 2, entry 6).

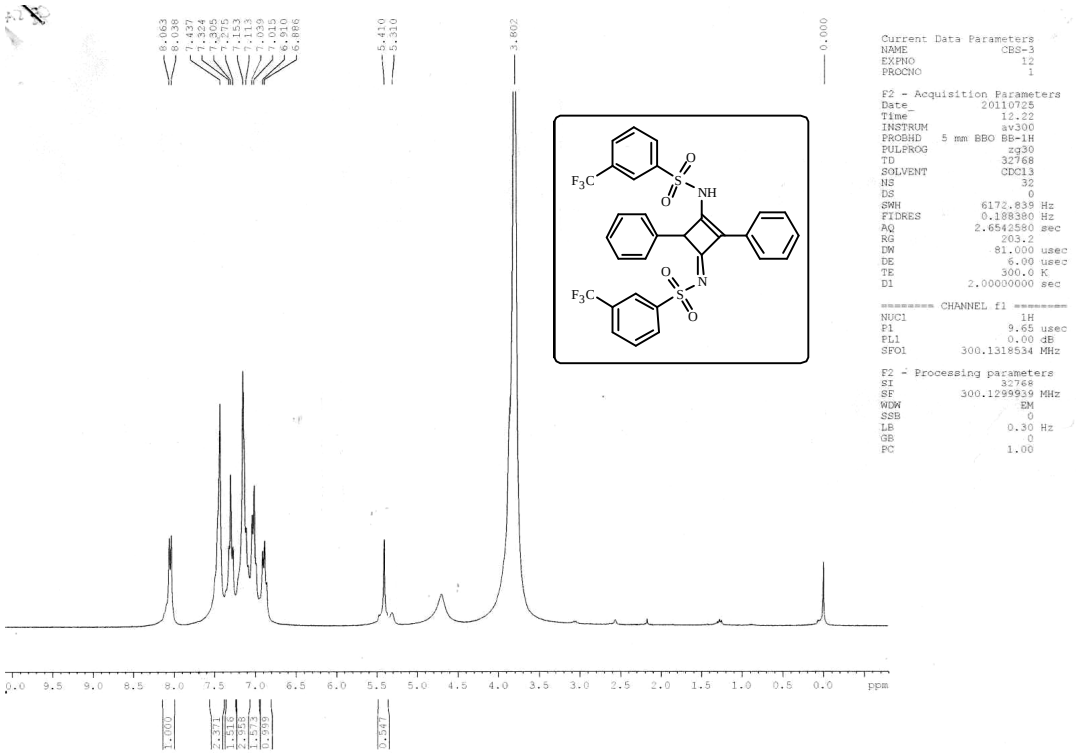


Fig. 13. ^{1}H-NMR spectrum of (*E*)-*N*,*N*'-(2,4-diphenylcyclobut-1-ene-1-yl-3-ylidene)bis(4-(trifluoromethyl)benzenesulfonamide) (table 2, entry 7).

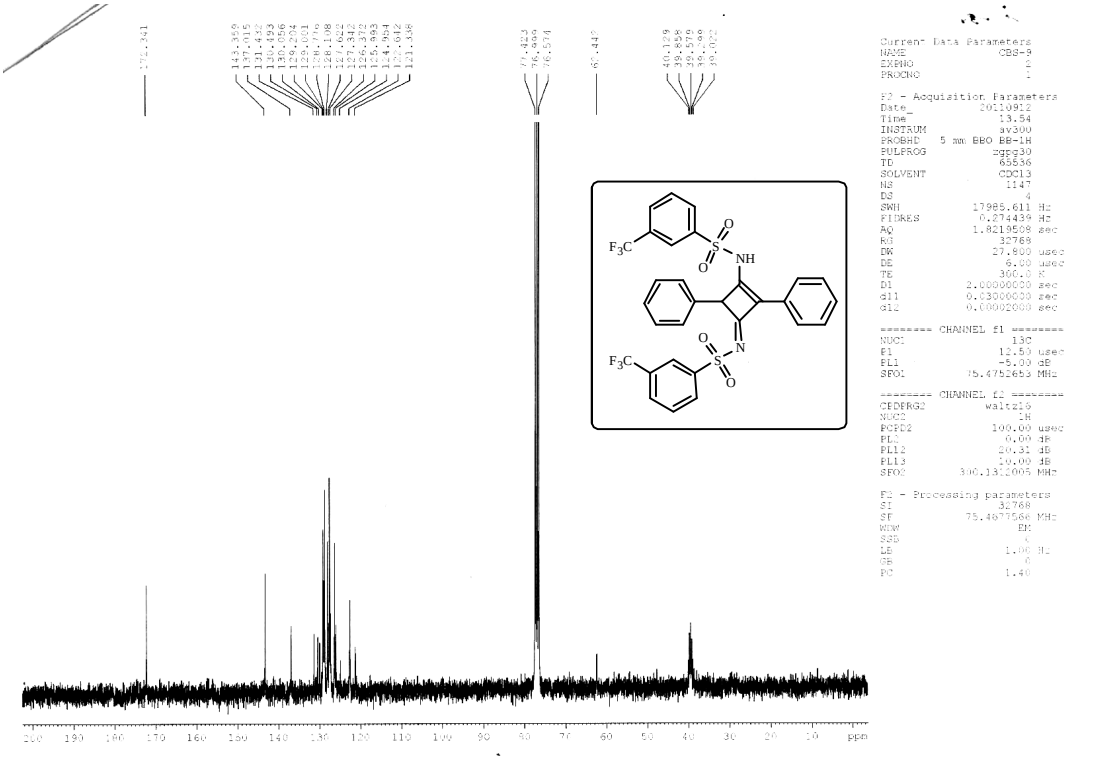


Fig. 14. ^{13}C-NMR spectrum of (*E*)-*N*,*N*'-(2,4-diphenylcyclobut-1-ene-1-yl-3-ylidene)bis(4-(trifluoromethyl)benzenesulfonamide) (table 2, entry 7).

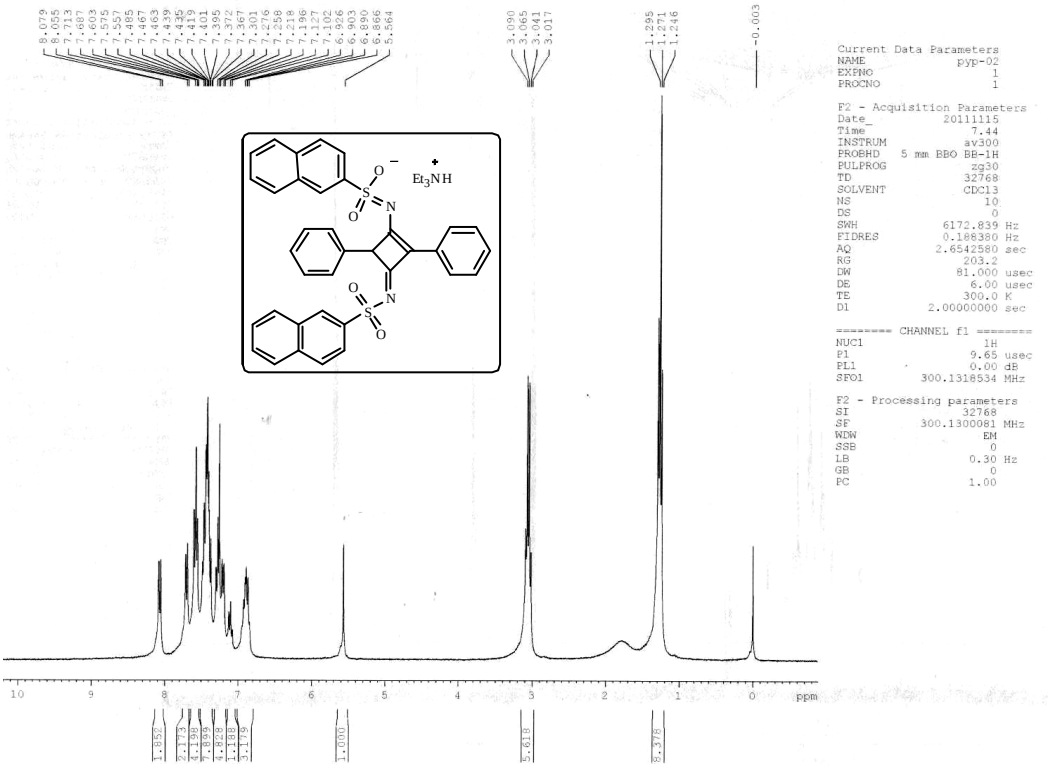


Fig. 15. ^{1}H-NMR spectrum of triethylammonium (*E*)-*N*-3-(naphthalen-2-ylsulfonyl imino)-2,4-diphenylcyclobut-1-enylnaphthalene-2-sulfonimidate (table 2, entry 8).

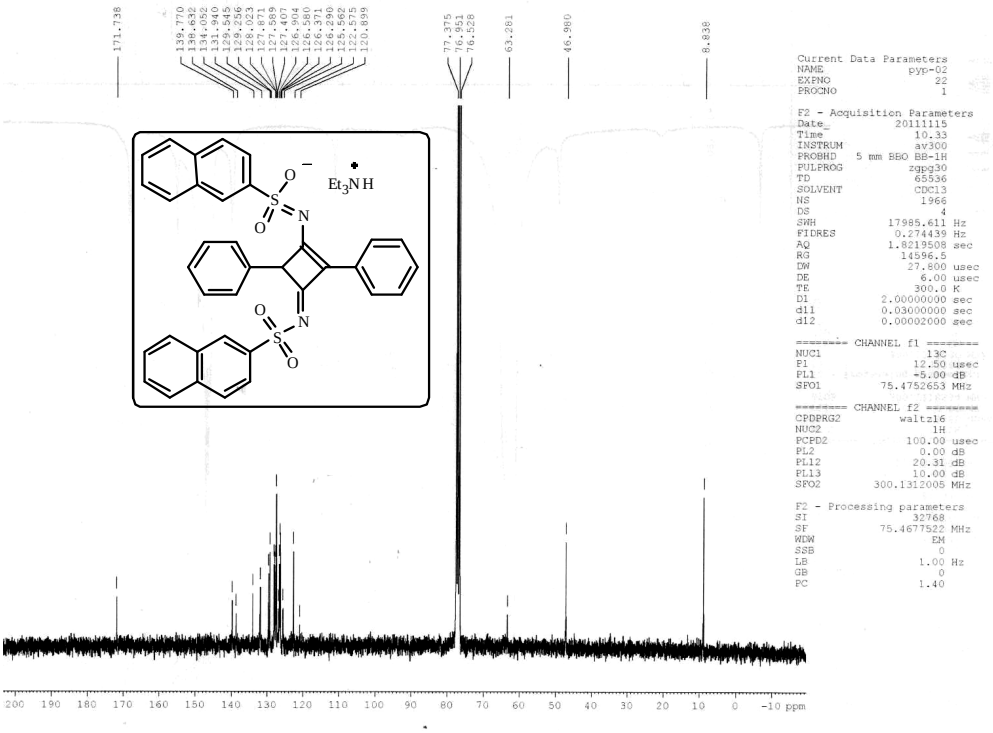


Fig. 16. ^{13}C-NMR spectrum of triethylammonium (*E*)-*N*-3-(naphthalen-2-ylsulfonyl imino)-2,4-diphenylcyclobut-1-enylnaphthalene-2-sulfonimidate (table 2, entry 8).

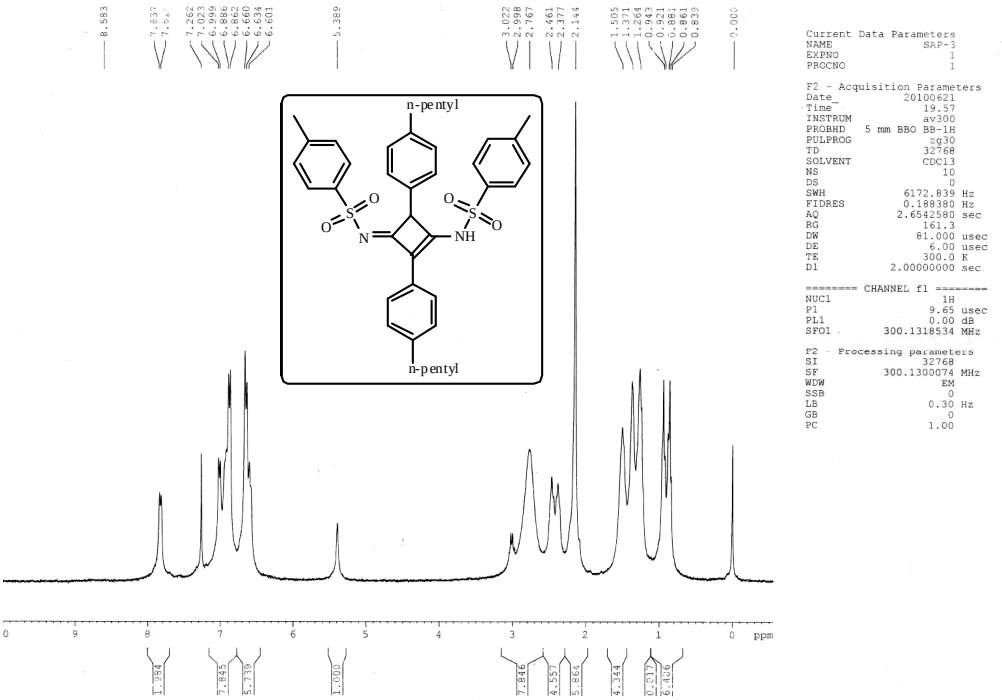


Fig. 17. ^{1}H-NMR spectrum of (*E*)-*N*,*N*'-(2,4-bis(4-(n-pentyl)phenylcyclobut-1-ene-1-yl-3-ylidene)bis(4-(methyl)benzenesulfonamide (table 2, entry10).

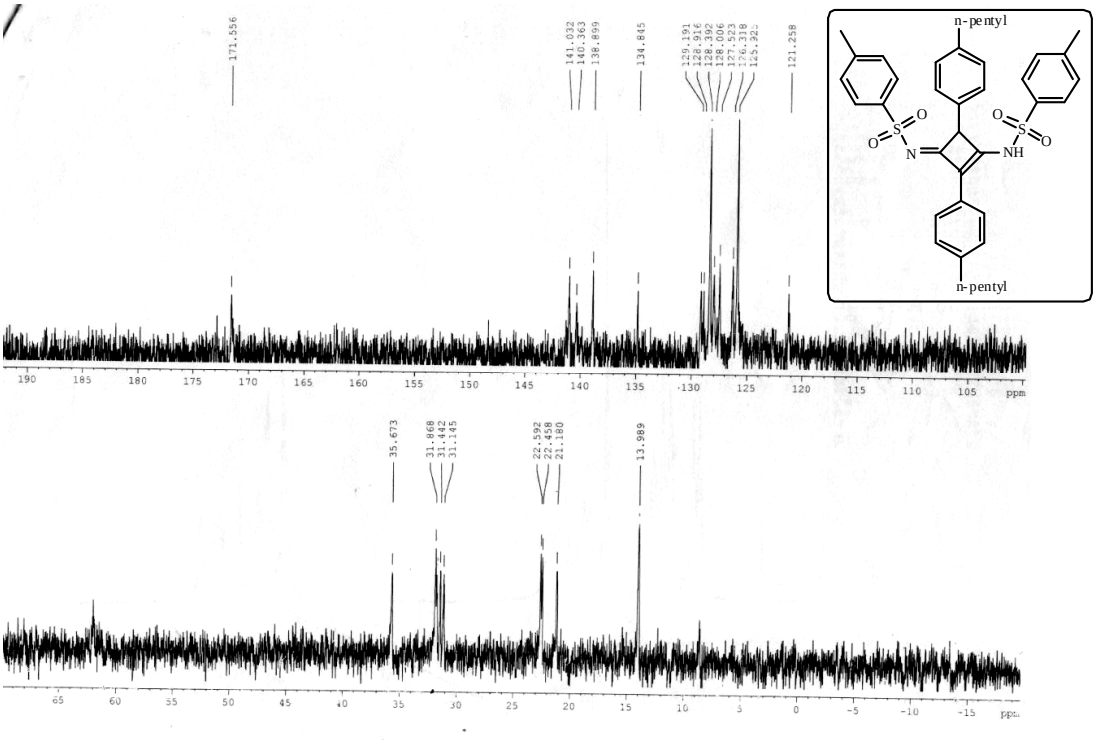


Fig. 18. ^{13}C-NMR spectrum of (*E*)-*N*,*N*'-(2,4-bis(4-(n-pentyl)phenylcyclobut-1-ene-1-yl-3-ylidene)bis(4-(methyl)benzenesulfonamide (table 2, entry 10).

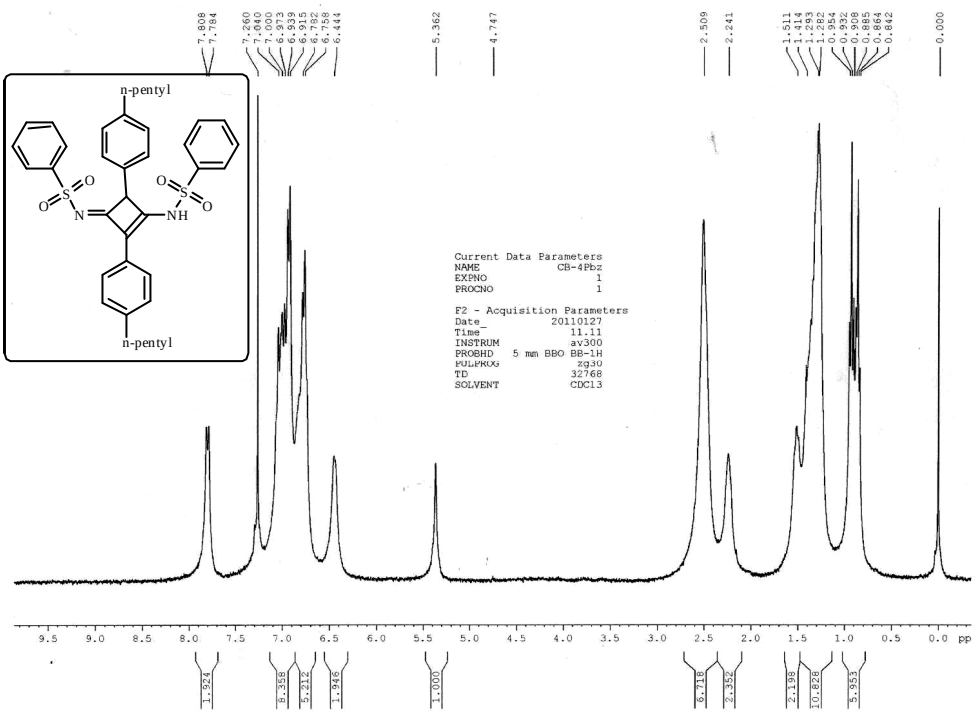


Fig. 19. ^{1}H-NMR spectrum of (*E*)-*N*,*N*'-(2,4-bis(4-(n-pentyl)phenylcyclobut-1-ene-1-yl-3-ylidene)dibenzenesulfonamide (table 2, entry 11).

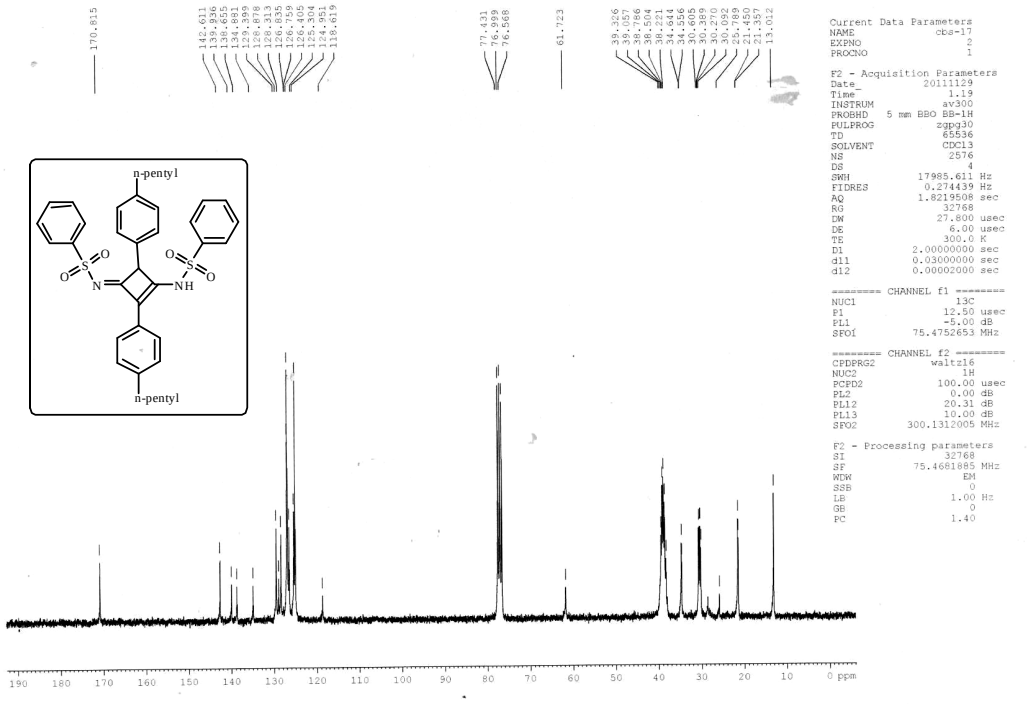


Fig. 20. ^{13}C-NMR spectrum of (*E*)-*N*,*N*'-(2,4-bis(4-(n-pentyl)phenylcyclobut-1-ene-1-yl-3-ylidene)dibenzenesulfonamide (table 2, entry 111).

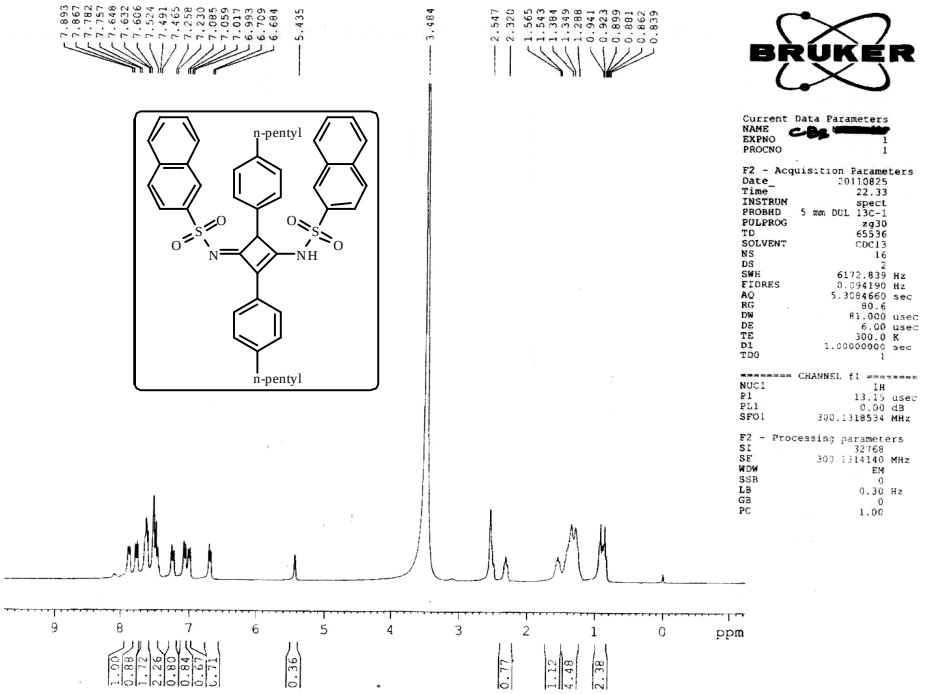


Fig. 21. ^{1}H-NMR spectrum of (*E*)-*N*,*N*'-(2,4-bis(4-(n-pentyl)phenylcyclobut-1-ene-1-yl-3-ylidene)dinaphthalenesulfonamide (table 2, entry 12).

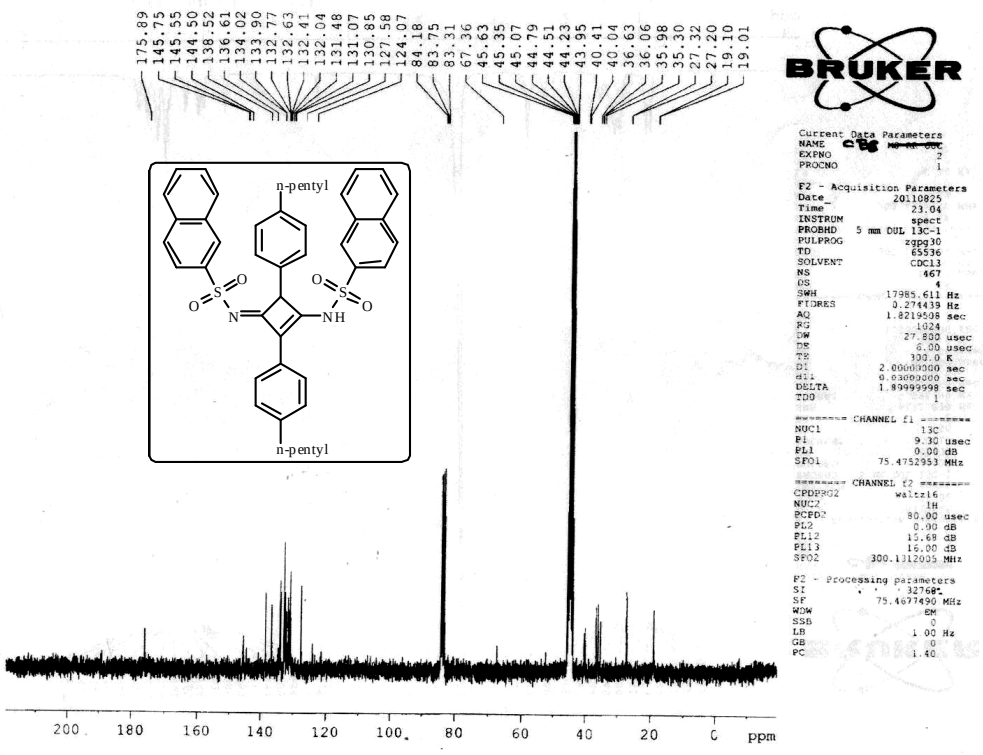


Fig. 22. ^{13}C-NMR spectrum of (*E*)-*N*,*N*'-(2,4-bis(4-(n-pentyl)phenylcyclobut-1-ene-1-yl-3-ylidene)dinaphthalenesulfonamide (table 2, entry 12).

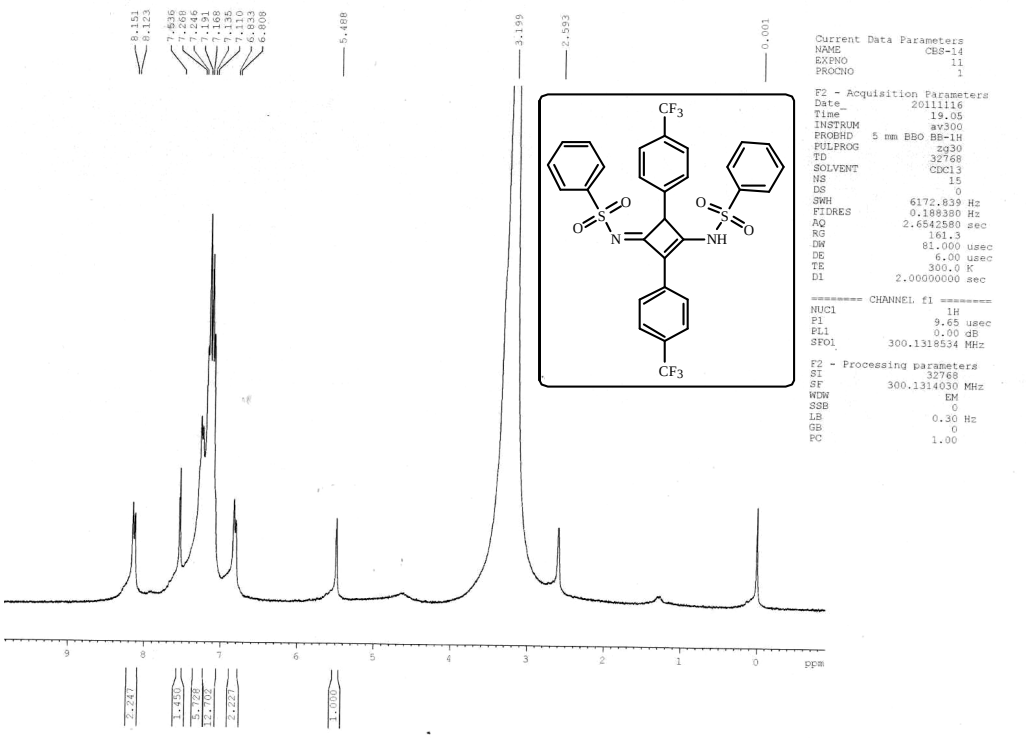


Fig. 23. ^{1}H-NMR spectrum of (*E*)-*N*,*N*'-(2,4-bis(4-(trifluoromethyl)phenyl)cyclobut-1-ene-1-yl-3-ylidene)dibenzenesulfonamide (table 2, entry 13).

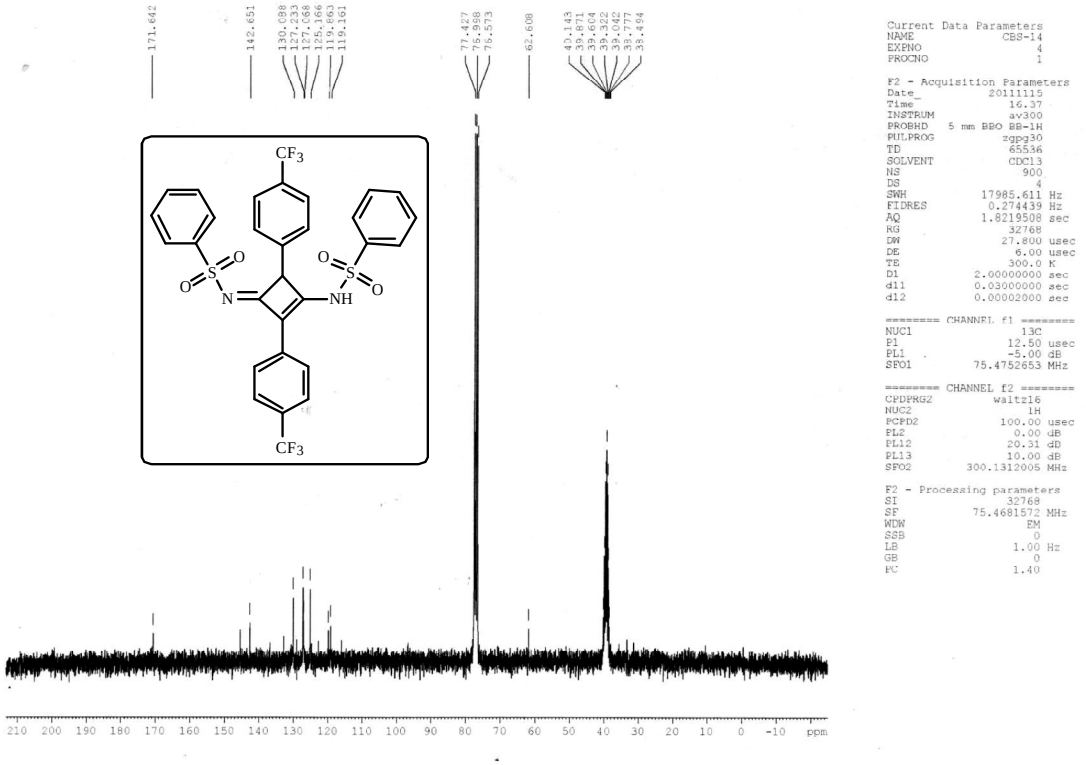


Fig. 24. ^{13}C-NMR spectrum of (*E*)-*N*,*N*'-(2,4-bis(4-(trifluoromethyl)phenyl)cyclobut-1-ene-1-yl-3-ylidene)dibenzenesulfonamide (table 2, entry 13).

This journal is © The Royal Society of Chemistry 2012

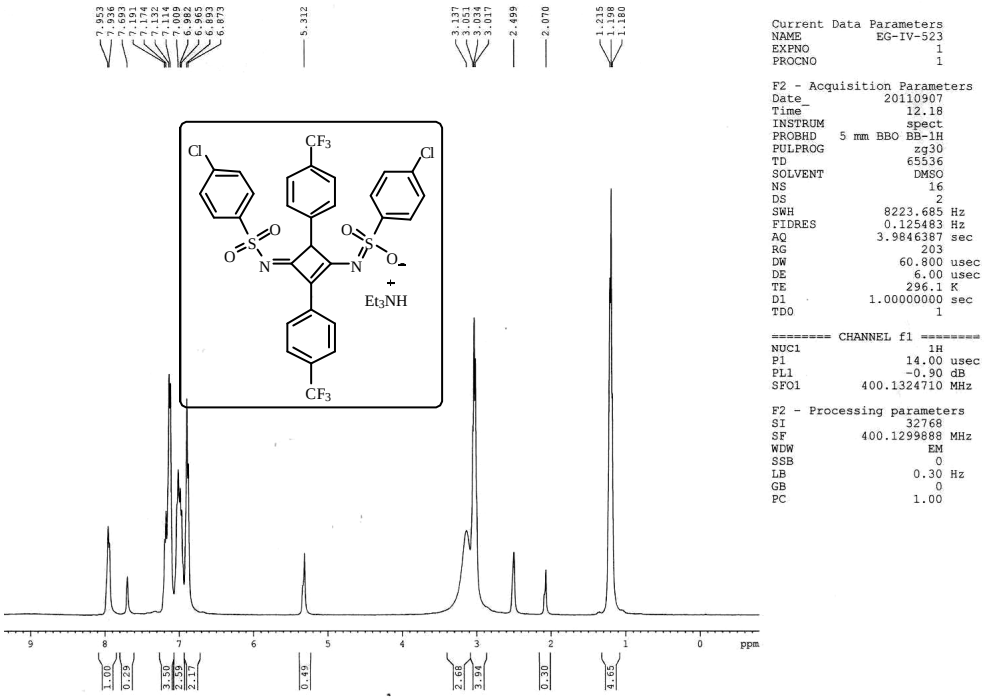


Fig. 25. ^{1}H-NMR spectrum of triethylammonium (*E*)-4-chloro-*N*-(3-(4-chlorophenylsulfonylimino)-2,4-bis(4-(trifluoromethyl)phenyl)cyclobut-1-enyl)benzenesulfonimidate (table 2, entry 14).

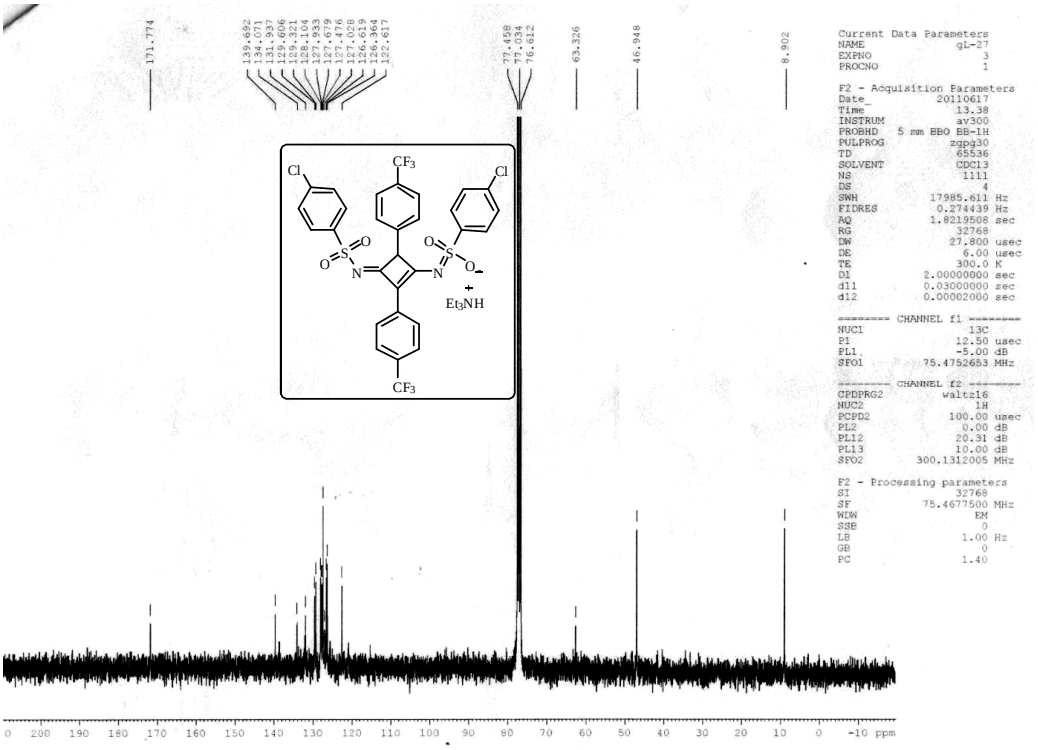


Fig. 26. ^{13}C-NMR spectrum of triethylammonium (*E*)-4-chloro-*N*-(3-(4-chlorophenylsulfonylimino)-2,4-bis(4-(trifluoromethyl)phenyl)cyclobut-1-enyl)benzenesulfonimidate (table 2, entry 14).

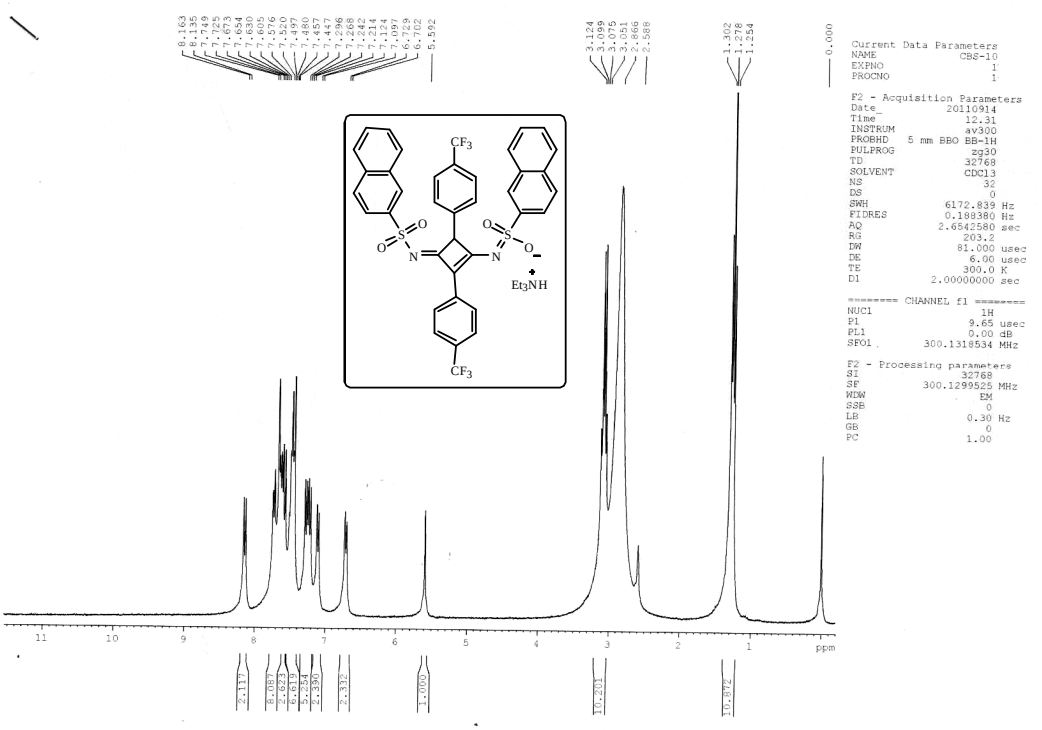


Fig. 27. ^{1}H-NMR spectrum of triethylammonium (*E*)-*N*-3-(naphthalen-2-ylsulfonyl imino)-2,4-bis(4-(trifluoromethyl)phenyl)cyclobut-1-enylnaphthalene-2-sulfonimidate (table 2, entry 15).

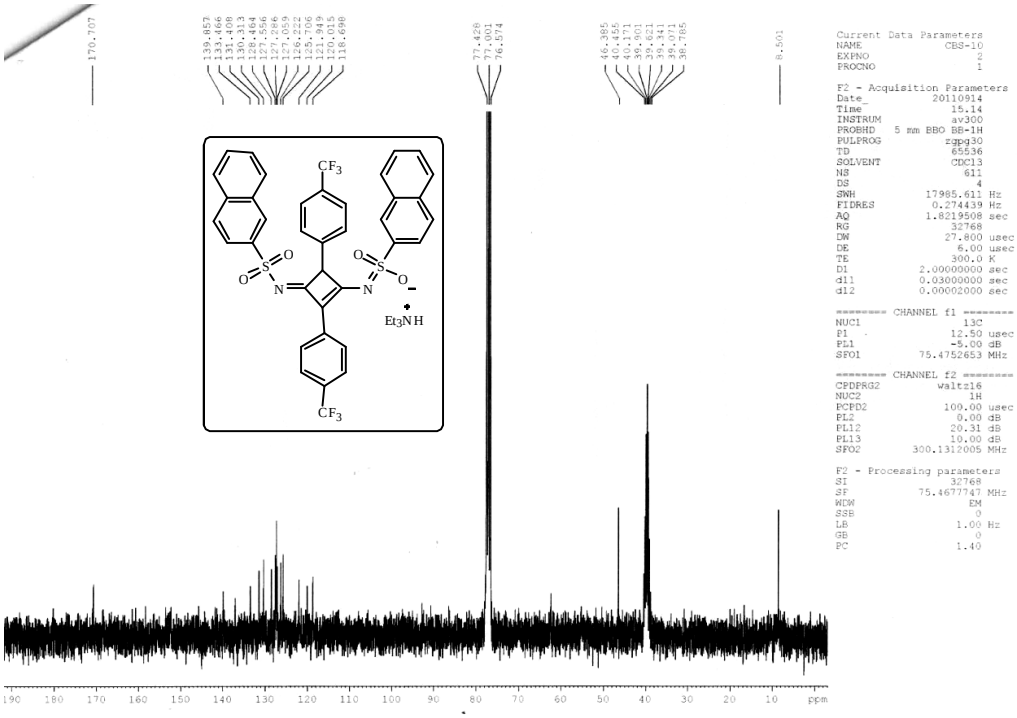


Fig. 28. ^{13}C-NMR spectrum of triethylammonium (*E*)-*N*-3-(naphthalen-2-ylsulfonyl imino)-2,4-bis(4-(trifluoromethyl)phenyl)cyclobut-1-enylnaphthalene-2-sulfonimidate (table 2, entry 15).

This journal is © The Royal Society of Chemistry 2012

Excitation energies and oscillator strengths:

```
 Excited State   1:      Singlet-A      3.6103 eV  343.42 nm  f=0.2926
<S**2>=0.000
     171 ->172         0.70214

 Excited State   2:      Singlet-A      4.0538 eV  305.85 nm  f=0.2073
<S**2>=0.000
     171 ->173         0.69941

 Excited State   3:      Singlet-A      4.1551 eV  298.39 nm  f=0.0679
<S**2>=0.000
     171 ->174         0.69750

 Excited State   4:      Singlet-A      4.3127 eV  287.49 nm  f=0.0847
<S**2>=0.000
     170 ->172         0.59827
     170 ->173        -0.20485
     171 ->175        -0.26335

 Excited State   5:      Singlet-A      4.3367 eV  285.89 nm  f=0.1719
<S**2>=0.000
     170 ->172         0.25229
     171 ->175         0.61901
     171 ->176         0.12707

 Excited State   6:      Singlet-A      4.4784 eV  276.85 nm  f=0.0573
<S**2>=0.000
     171 ->175        -0.14501
     171 ->176         0.48949
     171 ->177        -0.39552
     171 ->178         0.25865

 Excited State   7:      Singlet-A      4.5650 eV  271.60 nm  f=0.0346
<S**2>=0.000
     167 ->172        -0.11381
     167 ->175        -0.14494
     171 ->176         0.28703
     171 ->177         0.13171
     171 ->178        -0.20468
     171 ->179         0.53928

 Excited State   8:      Singlet-A      4.5886 eV  270.20 nm  f=0.0252
<S**2>=0.000
     171 ->176         0.37855
     171 ->177         0.45775
     171 ->178        -0.13446
     171 ->179        -0.32851

 Excited State   9:      Singlet-A      4.6750 eV  265.21 nm  f=0.0155
<S**2>=0.000
     171 ->177         0.31324
     171 ->178         0.58760
     171 ->179         0.15572

 Excited State  10:      Singlet-A      4.7221 eV  262.56 nm  f=0.0011
<S**2>=0.000
     166 ->172         0.27608
     166 ->173        -0.12838
     170 ->172         0.21262
```

```
     170 ->173         0.53727
     170 ->174         0.14146
     171 ->178        -0.10201

 Excited State  11:      Singlet-A      4.9309 eV  251.44 nm  f=0.0057
<S**2>=0.000
     166 ->172        -0.24479
     167 ->172        -0.12361
     168 ->172         0.51839
     169 ->172        -0.16952
     170 ->173         0.21294

 Excited State  12:      Singlet-A      4.9663 eV  249.65 nm  f=0.0725
<S**2>=0.000
     166 ->172         0.19965
     168 ->172         0.20912
     171 ->180         0.60086

 Excited State  13:      Singlet-A      4.9800 eV  248.96 nm  f=0.0290
<S**2>=0.000
     163 ->172        -0.10134
     166 ->172         0.38506
     166 ->173        -0.10343
     168 ->172         0.36607
     169 ->172         0.11794
     170 ->173        -0.22125
     171 ->180        -0.30084

 Excited State  14:      Singlet-A      5.0224 eV  246.86 nm  f=0.0203
<S**2>=0.000
     166 ->172        -0.14225
     170 ->174         0.51403
     170 ->175         0.39914
     171 ->180         0.10621

 Excited State  15:      Singlet-A      5.0904 eV  243.56 nm  f=0.0159
<S**2>=0.000
     166 ->172        -0.22305
     167 ->172         0.39944
     168 ->172         0.11721
     169 ->172         0.47480
     171 ->179         0.10643

 Excited State  16:      Singlet-A      5.1196 eV  242.17 nm  f=0.0613
<S**2>=0.000
     167 ->172         0.43770
     169 ->172        -0.40365
     170 ->174        -0.19945
     170 ->175         0.24415

 Excited State  17:      Singlet-A      5.1199 eV  242.16 nm  f=0.0083
<S**2>=0.000
     167 ->172        -0.30427
     169 ->172         0.13463
     170 ->174        -0.36429
     170 ->175         0.47067

 Excited State  18:      Singlet-A      5.2295 eV  237.08 nm  f=0.0029
<S**2>=0.000
     165 ->172         0.43674
     165 ->173        -0.29869
```

```
     165 ->174        -0.10977
     168 ->173        -0.20143
     169 ->177         0.21879
     169 ->178         0.19490

 Excited State  19:      Singlet-A      5.2396 eV  236.63 nm  f=0.0044
<S**2>=0.000
     163 ->172        -0.11843
     165 ->173         0.11976
     168 ->173        -0.24618
     168 ->175         0.10609
     168 ->176         0.19951
     168 ->177        -0.11254
     170 ->174         0.11087
     170 ->176        -0.20352
     170 ->177        -0.29225
     170 ->178         0.30875
     170 ->180         0.10145

 Excited State  20:      Singlet-A      5.2891 eV  234.42 nm  f=0.0025
<S**2>=0.000
     160 ->174         0.12516
     161 ->172         0.21081
     161 ->174         0.10684
     162 ->172         0.43138
     162 ->173         0.12572
     164 ->173        -0.10607
     164 ->174         0.31209
     164 ->175        -0.11367
     170 ->176         0.16255
```

This journal is © The Royal Society of Chemistry 2012

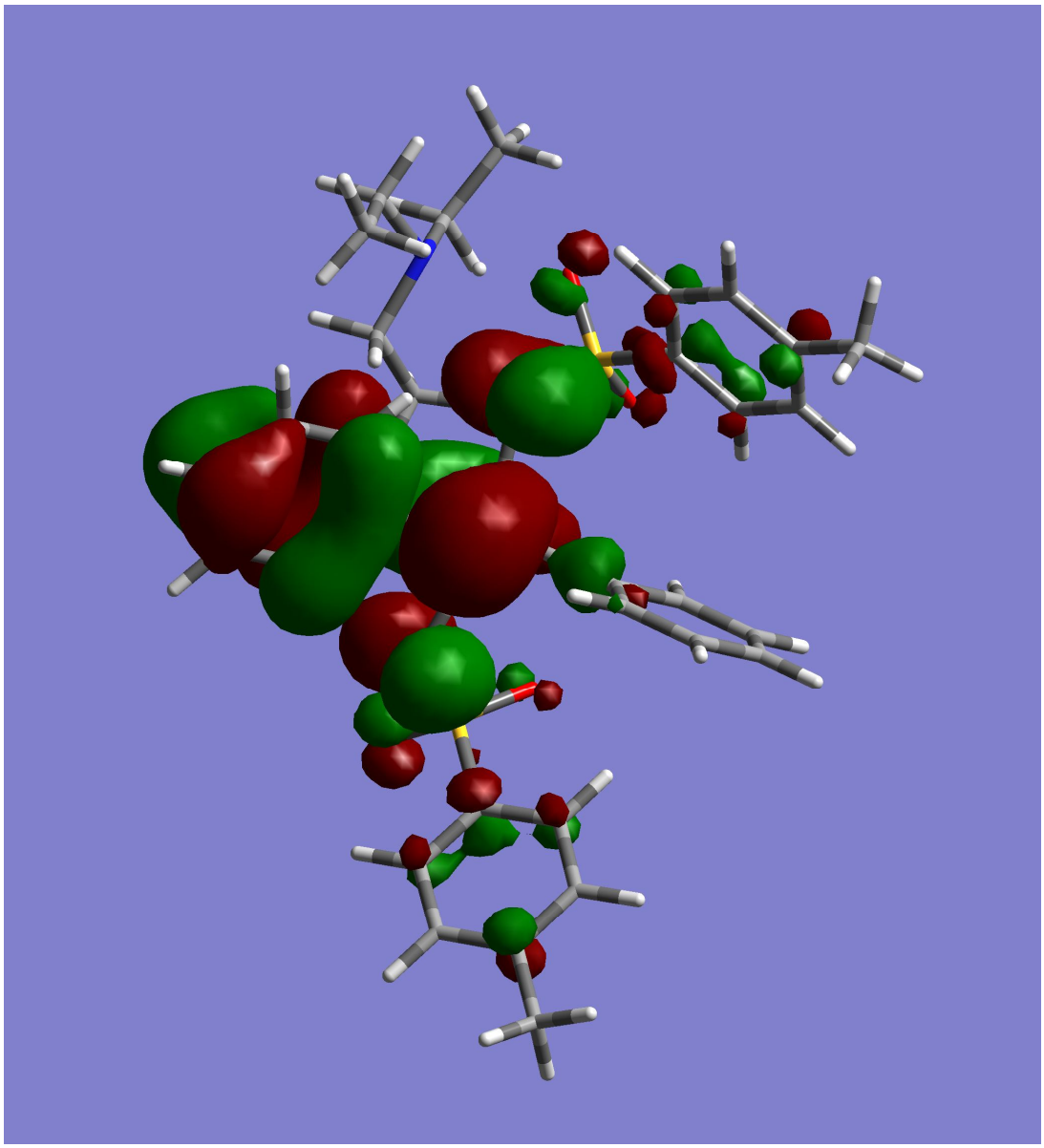


Fig. g. HOMO

This journal is © The Royal Society of Chemistry 2012

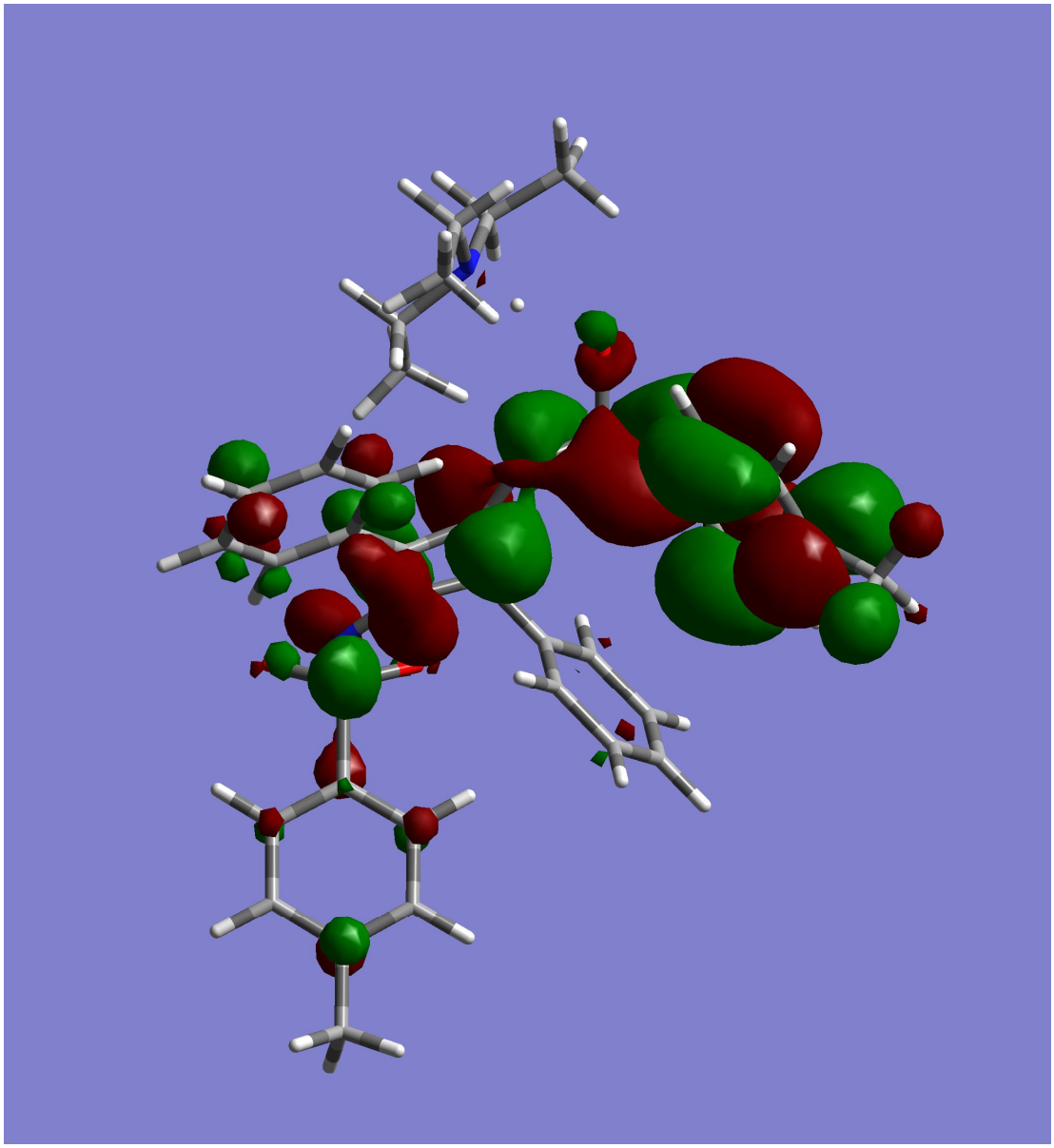


Fig.h. LUMO