Supplementary Information

Single-Bond Linked and Vinylene-Bridged Azulenyl Bis(squaraine) Dyes: Design, Synthesis and Molecular Self-Assembly Behaviors

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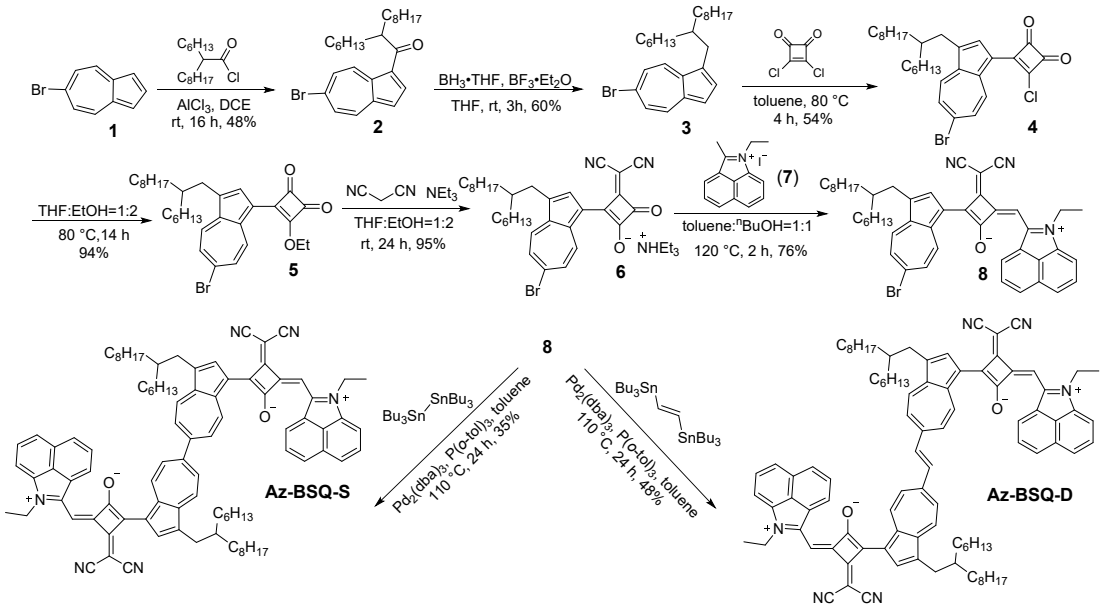
Contents:

1. General Information

All commercially available reagents were obtained and used directly without further purification from TCI, Energy, Sinopharm, J&K, Adamas. NMR spectra were recorded on JEOL 400 MHz spectrometer. ^{1}H NMR chemical shifts were displayed relative to the residual deuterated solvent peaks ($CDCl_3$: δ=7.26 ppm; CD_2Cl_2: δ=5.32 ppm). ^{13}C NMR chemical shifts were given relative to the residual deuterated solvent peaks ($CDCl_3$: δ=77.16 ppm; CD_2Cl_2: δ=53.84 ppm). High resolution mass spectra were carried out on Thermo Fisher Scientific LTQ FTICR-MS and Thermo Scientific Q Exactive HF Orbitrap-FTMS. UV-Vis/NIR absorption spectra were recorded on UH4150. Fluorescence spectra were obtained through Edinburgh FLS980. Cyclic voltammetry curves were measured through Autolab PGSTAT302N with platinum button as working electrode, platinum wire as counter electrode and saturated calomel electrode as reference electrode. Transmission electron microscope images were captured by JEOL JEM2100. Dynamic light scattering experiments were carried out on Malvern Nano Zetasizer. Atomic force microscope images were captured by JPK Nanowizard.

2. Experimental Section



Scheme S1. Synthesis routes of **Az-BSQ-S** and **Az-BSQ-D**

Compound **1** was prepared according to the routes reported by MacDonald *et. al.*[1]

and compound **7** was synthesized following the procedures reported by Wang *et. al.*.[2]

1-(6-bromoazulen-1-yl)-2-hexyldecan-1-one (2): Compound **1** (3 g, 14.5 mmol) was dissolved in 1,2-dichloroethane (20 mL), and was then added a solution of 2-hexyldecanoyl chloride (4 g, 14.5 mmol) in 1,2-dichloroethane (15 mL). After cooling to 0 ℃, $AlCl_3$ (2.1g, 15.95 mmol) was added to the solution mentioned above. The resulting reaction mixture was stirred at room temperature for 16 h. Afterwards, the mixture was filtered through celite and quenched with water, followed by the extraction using dichloromethane for three times. The combined organic phase was then washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed through rotary evaporator and the residue was purified by column chromatography on silica gel (PE:DCM=5:1, V:V) to give **2** (3.1 g, 48%) as purple oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.63 (d, *J* = 10.8 Hz, 1H), 8.32 (d, *J* = 4.2 Hz, 1H), 8.17 (d, *J* = 10.5 Hz, 1H), 7.89 (dd, *J* = 10.8, 2.0 Hz, 1H), 7.76 (dd, *J* = 10.5, 2.0 Hz, 1H), 7.29 (d, *J* = 4.2 Hz, 1H), 3.48 – 3.39 (m, 1H), 1.87 – 1.76 (m, 2H), 1.56 – 1.47 (m, 3H), 1.34 – 1.12 (m, 20H), 0.87 – 0.77 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.9, 143.4, 140.2, 138.8, 137.9, 137.1, 136.5, 132.4, 130.6, 127.4, 119.4, 49.2, 33.3, 32.0, 31.8, 30.1, 29.7, 29.6, 29.4, 28.0, 22.8, 22.7, 14.2, 14.2. HRMS[ESI] (*m/z*): $[M+H]^+$ cacld. for $C_{26}H_{38}BrO$: 445.2101; Found: 445.2091.

6-bromo-1-(2-hexyldecyl)azulene (3): Compound **2** (1.87 g, 4.21 mmol) was first dissolved in THF (40 mL) and then cooled to 0 ℃. BH_3·THF (1 M in THF, 42.1 mmol, 42 mL) and BF_3·Et_2O (8.9 mL, 33.7 mmol) were added slowly in succession. The reaction was stirred at room temperature for 3 h and then quenched with MeOH. The resulting mixture was extracted and washed with saturated NaCl solution. After that, it was concentrated and purified with column chromatography (PE) on the silica gel (treated with NEt_3) to afford **3** (1.08 g, 60%) as blue oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 10.6 Hz, 1H), 7.90 (d, *J* = 10.2 Hz, 1H), 7.76 (d, *J* = 3.8 Hz, 1H), 7.38 (d, *J* = 10.5 Hz, 2H), 7.34 (d, *J* = 3.8 Hz, 1H), 2.95 (d, *J* = 7.0 Hz, 2H), 1.79 – 1.71 (m, 1H), 1.35 – 1.17 (m, 24H), 0.93 – 0.84 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.3, 138.5, 134.5, 134.1, 133.3, 131.7, 125.3, 124.6, 119.0, 40.3,

33.9, 33.8, 32.2, 32.1, 30.2, 29.9, 29.8, 29.5, 26.8, 22.8, 14.3. HRMS[ESI] (*m/z*): $[M+H]^+$ cacld. for $C_{26}H_{40}Br$: 431.2308; Found: 431.2297.

3-(6-bromo-3-(2-hexyldecyl)azulen-1-yl)-4-chlorocyclobut-3-ene-1,2-dione (4): To a 250 mL round-bottom flask were added **3** (1.9 g, 4.42 mmol) and THF (20 mL), then a solution of squaryl chloride (795 mg, 5.3 mmol) in THF (20 mL) was added dropwise. The reaction mixture was heated at 80 ℃ for 4 h and then extracted with ethyl acetate. The combined organic phase was washed with saturated NaCl solution and dried over Na_2SO_4. The residue was then concentrated through rotary evaporator and purified through column chromatography (PE:DCM=1:2, V:V) to afford **4** (1.3 g, 54%) as brown solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.50 (d, *J* = 10.6 Hz, 1H), 8.49 (s, 1H), 8.13 (d, *J* = 10.7 Hz, 1H), 8.00 (dd, *J* = 10.6, 2.0 Hz, 1H), 7.86 (dd, *J* = 10.7, 2.0 Hz, 1H), 2.94 (d, *J* = 7.1 Hz, 2H), 1.81 – 1.72 (m, 1H), 1.33 – 1.23 (m, 24H), 0.89 – 0.84 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.0, 189.6, 184.1, 173.9, 142.7, 141.9, 138.8, 138.4, 138.1, 137.3, 134.2, 133.2, 132.2, 117.8, 39.6, 33.8, 33.8, 32.0, 30.1, 29.8, 29.7, 29.4, 26.8, 22.8, 14.2. HRMS[DART] (*m/z*): $[M+H]^+$ cacld. for $C_{30}H_{39}BrClO_2$: 545.1816; Found: 545.1815.

3-(6-bromo-3-(2-hexyldecyl)azulen-1-yl)-4-ethoxycyclobut-3-ene-1,2-dione (5): Compound **4** (1.3 g, 2.4 mmol) was dissolved in a mixed solvent of THF (15 mL) and EtOH (30 mL). The solution was stirred at 80 ℃ for 14 h and then extracted with ethyl acetate for three times. The combined organic phase was washed with saturated NaCl solution and dried with Na_2SO_4. The organic solvent was then removed under reduced pressure and column chromatography (PE:DCM=1:2, V:V) was carried out to give **5** as brownish green solid (1.26 g, 94%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.40 (d, *J* = 10.5 Hz, 1H), 8.23 (s, 1H), 8.02 (d, *J* = 10.6 Hz, 1H), 7.80 (dd, *J* = 10.5, 1.9 Hz, 1H), 7.66 (dd, *J* = 10.7, 1.9 Hz, 1H), 5.03 (q, *J* = 7.1 Hz, 2H), 2.91 (d, *J* = 7.1 Hz, 2H), 1.78 – 1.69 (m, 1H), 1.62 (t, *J* = 7.1 Hz, 3H), 1.34 – 1.21 (m, 24H), 0.89 – 0.82 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.7, 191.3, 189.9, 171.0, 140.8, 139.8, 138.1, 137.6, 137.5, 135.7, 133.5, 130.9, 129.9, 118.6, 71.2, 39.8, 33.8, 32.0, 30.1, 29.8, 29.7, 29.4, 26.8, 26.8, 22.8, 16.1, 14.2. HRMS[DART] (*m/z*): $[M+H]^+$ cacld. for $C_{32}H_{44}BrO_3$: 555.2468; Found: 555.2463.

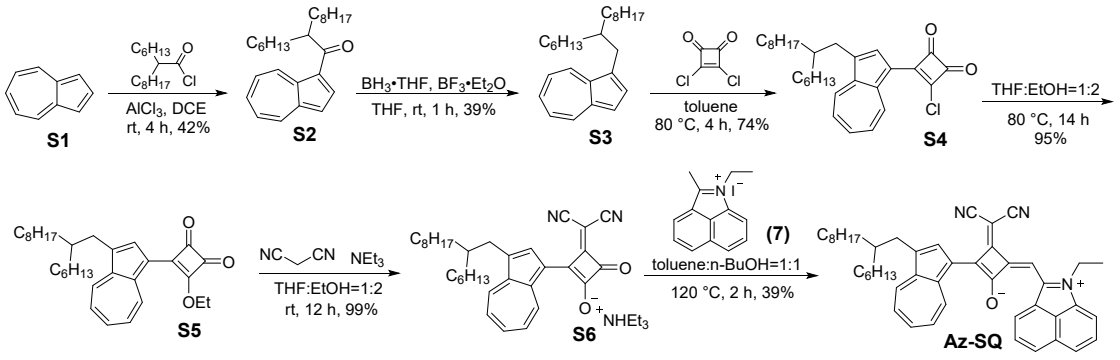
Triethylammonium 2-(6-bromo-3-(2-hexyldecyl)azulen-1-yl)-3-(dicyanomethylene)-4-oxocyclobut-1-en-1-olate (6): Compound **5** (380 mg, 0.69 mmol) was dissolved in the mixed solvent of THF (5 mL) and EtOH (10 mL). Malononitrile (68 mg, 1.03 mmol) and NEt_3 (114 μL, 0.82 mmol) was then added. The solution was stirred at room temperature for 12 h. Then the mixture was concentrated and purified through column chromatography (DCM:MeOH=10:1, V:V) to give **6** as brown oil (490 mg, 95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.93 (d, J = 10.4 Hz, 1H), 8.79 – 9.00 (br, 1H), 8.09 (d, J = 10.3 Hz, 1H), 8.08 (s, 1H), 7.57 (d, J = 10.5 Hz, 1H), 7.53 (d, J = 10.6 Hz, 1H), 3.09 (q, J = 7.1 Hz, 6H), 2.88 (d, J = 6.8 Hz, 2H), 1.82 – 1.71 (m, 1H), 1.14 – 1.28 (m, 33H), 0.82 (q, J = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 193.8, 186.9, 178.1, 163.4, 138.0, 137.9, 137.0, 136.7, 135.7, 133.9, 133.2, 127.0, 126.8, 120.4, 118.5, 117.3, 45.7, 33.1, 32.9, 31.3, 31.2, 29.2, 29.0, 28.8, 28.6, 25.9, 25.8, 22.1, 13.9, 13.9, 8.6. HRMS[DART] (*m/z*): $[M+H]^+$ cacld. for $C_{39}H_{55}BrO_2N_3$: 676.3472; Found: 676.3473.

2-(6-bromo-3-(2-hexyldecyl)azulen-1-yl)-3-(dicyanomethylene)-4-((1-ethylbenzo[cd]indol-1-ium-2-yl)methylene)cyclobut-1-en-1-olate (8): To a 100 mL round-bottom flask were added **6** (210 mg, 0.31 mmol), **7** (108 mg, 0.33 mmol), n-butanol (4 mL) and toluene (4 mL). The reaction mixtures were heated at 120 ℃ for 2 h and then concentrated through rotary evaporator. The residue was subjected to column chromatography (DCM) to afford **8** as red metallic solid (178 mg, 76%). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 9.51 (d, J = 10.6 Hz, 1H), 8.87 (d, J = 7.4 Hz, 1H), 8.43 (s, 1H), 8.28 (d, J = 8.1 Hz, 1H), 8.02 – 7.89 (m, 3H), 7.74 (t, J = 7.3 Hz, 1H), 7.71 (dd, J = 10.3, 1.9 Hz, 1H), 7.60 (dd, J = 10.6, 1.9 Hz, 1H), 7.55 (d, J = 7.3 Hz, 1H), 7.18 (s, 1H), 4.44 (q, J = 7.3 Hz, 2H), 2.92 (d, J = 7.1 Hz, 2H), 1.86 – 1.78 (m, 1H), 1.61 (t, J = 7.3 Hz, 3H), 1.38 – 1.24 (m, 24H), 0.87 (t, J = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 175.2, 171.3, 166.9, 157.3, 156.8, 142.7, 141.7, 141.3, 139.8, 139.1, 138.3, 137.9, 136.2, 134.0, 133.5, 131.0, 130.8, 130.3, 129.6, 129.5, 129.2, 126.6, 124.9, 122.9, 119.1, 118.7, 112.9, 95.2, 45.3, 40.8, 39.9, 34.1, 34.1, 32.6, 32.3, 32.3, 30.4, 30.1, 30.0, 29.7, 27.0, 23.1, 14.6, 14.3. HRMS[ESI] (*m/z*): [M] cacld. for $C_{47}H_{50}ON_3Br$: 751.3132; Found: 751.3124.

2,2'-(3,3'-bis(2-hexyldecyl)-[6,6'-biazulene]-1,1'-diyl)bis(3-(dicyanomethylene)-4-((1-ethylbenzo[cd]indol-1-ium-2-yl)methylene)cyclobut-1-en-1-olate) (Az-BSQ-S): To a 25 mL sealed tube were added compound **8** (300 mg, 0.4 mmol), $Pd_2(dba)_3$ (18.3 mg, 0.02 mmol) and P(*o*-tol)$_3$ (24.3 mg, 0.08 mmol). The tube was evacuated and backfilled with nitrogen for three times, then hexabutylditin (81 μL, 0.16 mmol) was added through microsyringe and degassed dry toluene (8 mL) was added under nitrogen atmosphere. The reactants were heated at 110 ℃ for 24 h and then quenched with KF solution. The resulting mixture was stirred at room temperature for another 8 h and then filtered through celite. The filtrate was extracted with DCM for three times, the organic phase was concentrated under reduced pressure and purified by column chromatography on silica gel (DCM:EA=20:1, V:V) to give **Az-BSQ-S** (75 mg, 35%) as brownish black solid. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 9.73 (d, J = 10.2 Hz, 2H), 8.95 (d, J = 7.3 Hz, 2H), 8.34 (s, 2H), 8.14 (d, J = 10.2 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H), 7.84 (t, J = 7.5 Hz, 2H), 7.72 – 7.61 (m, 6H), 7.51 (d, J = 10.4 Hz, 2H), 7.45 (d, J = 7.0 Hz, 2H), 6.81 (s, 2H), 4.25 (q, J = 7.0 Hz, 4H), 2.88 (d, J = 6.9 Hz, 4H), 1.87 – 1.77 (m, 2H), 1.50 (t, J = 7.2 Hz, 6H), 1.41 – 1.20 (m, 48H), 0.87 (q, J = 6.8, 6.1 Hz, 12H). ^{13}C NMR (125 MHz, Methylene Chloride-d_2) δ 174.8, 169.7, 166.4, 158.5, 155.3, 155.2, 144.3, 143.0, 141.3, 140.2, 139.8, 138.4, 135.4, 134.5, 133.0, 130.2, 130.1, 129.7, 129.5, 129.3, 129.2, 125.6, 124.9, 122.5, 119.2, 119.0, 112.1, 94.5, 44.9, 40.4, 39.6, 34.1, 32.6, 32.4, 30.6, 30.2, 30.1, 29.8, 27.0, 27.0, 23.2, 23.1, 14.5, 14.3, 14.3. HRMS[MALDI] (*m/z*): [M] cacld. for $C_{94}H_{100}O_2N_6$: 1344.7902; Found: 1344.7899.

2,2'-(((E)-ethene-1,2-diyl)bis(3-(2-hexyldecyl)azulene-6,1-diyl))bis(3-(dicyanomethylene)-4-((1-ethylbenzo[cd]indol-1-ium-2-yl)methylene)cyclobut-1-en-1-olate) (Az-BSQ-D): To a 25 mL sealed tube were added compound **8** (200 mg, 0.27 mmol), $Pd_2(dba)_3$ (12.2 mg, 0.013 mmol) and P(*o*-tol)$_3$ (16.2 mg, 0.053 mmol). The tube was evacuated and backfilled with nitrogen for three times, then (*E*)-1,2-bis(tributylstannyl)ethene (56 μL, 0.11 mmol) was added through microsyringe and degassed dry toluene (5 mL) was added through syringe. The reactants were heated at 110 ℃ for 24 h and KF solution was added after cooling to room temperature. The

mixture was stirred at room temperature for 8 h and then filtered through celite. The filtrate was extracted with DCM for three times, the organic solvents were then removed through rotary evaporator. The residue was purified through column chromatography on silica gel (DCM:EA=20:1, V:V) to afford **Az-BSQ-D** (68 mg, 48%) as brownish black solid. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 9.36 (d, J = 9.9 Hz, 2H), 9.06 (d, J = 7.4 Hz, 2H), 8.19 (s, 2H), 8.09 (d, J = 7.9 Hz, 2H), 8.01 (t, J = 7.5 Hz, 2H), 7.85 (d, J = 10.1 Hz, 2H), 7.67 – 7.53 (m, 4H), 7.56 (d, J = 10.4 Hz, 2H), 7.39 (d, J = 6.5 Hz, 2H), 7.33 (s, 2H), 7.26 (d, J = 10.3 Hz, 2H), 6.68 (s, 2H), 4.07 (q, J = 6.6 Hz, 4H), 2.80 (d, J = 6.2 Hz, 4H), 1.826 –1.79 (m, 2H), 1.25 – 1.45 (m. 54H), 0.92 – 0.86 (m, 12H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 174.5, 168.9, 166.7, 158.5, 154.7, 147.5, 144.5, 143.1, 140.5, 139.8, 139.6, 138.3, 136.9, 134.8, 134.0, 133.0, 130.2, 129.6, 129.4, 129.2, 128.3, 128.2, 125.2, 125.1, 122.4, 119.5, 119.1, 111.7, 94.3, 45.0, 40.1, 39.2, 34.2, 32.6, 32.4, 32.4, 30.6, 30.3, 30.2, 29.9, 27.0, 23.2, 23.2, 14.5, 14.4, 14.4. HRMS[MALDI] (*m/z*): [M] cacld. for $C_{96}H_{102}O_2N_6$: 1370.8059; Found: 1370.8071.



Scheme S2. Synthesis routes of **Az-SQ**

Compound **S1** was synthesized according to the methods reported by Nozoe *et. al.*.[3]

1-(azulen-1-yl)-2-hexyldecan-1-one (S2): To a 100 mL round-bottom flask were added compound **S1** (2 g, 15.6 mmol) and dichloroethane (15 mL), then a solution of 2-hexyldecanoyl chloride (4.3 g, 15.6 mmol) in dichloroethane (15 mL) and $AlCl_3$ (2.3 g, 17.16 mmol) were added in batches at 0 ℃. The reactants were stirred at room temperature for 4 h and then quenched with water at 0 ℃. The resulting mixture was extracted with DCM for three times, then the combined organic phases were dried and

concentrated under reduced pressure. The residue was subjected to the column chromatography (PE:DCM=5:1, V:V) to give compound **S2** (2 g, 42%) as purple oil. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 9.92 (d, J = 9.9 Hz, 1H), 8.50 (d, J = 9.7 Hz, 1H), 8.35 (d, J = 4.1 Hz, 1H), 7.84 (t, J = 9.8 Hz, 1H), 7.61 (t, J = 9.9 Hz, 1H), 7.48 (t, J = 9.7 Hz, 1H), 7.31 (d, J = 4.0 Hz, 1H), 3.52 – 3.43 (m, 1H), 1.87 – 1.75 (m, 2H), 1.58 – 1.48 (m, 2H), 1.34 – 1.19 (m, 20H), 0.88 – 0.81 (m, 6H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 202.5, 145.5, 140.6, 140.2, 140.0, 139.9, 138.9, 129.5, 127.6, 126.3, 118.0, 49.2, 33.7, 32.3, 32.2, 30.4, 30.1, 29.9, 29.7, 28.2, 23.1, 23.0, 14.3, 14.2. HRMS[ESI] (*m/z*): $[M+H]^+$ cacld. for $C_{26}H_{39}O$: 367.2995; Found: 367.2999.

1-(2-hexyldecyl)azulene (S3): A solution of compound **S2** (1.9 g, 5.19 mmol) in THF (30 mL) was added to a 250 mL round-bottom flask, then BH_3·THF (1 M in THF, 51.9 mmol, 52 mL) and BF_3·Et_2O (11 mL, 41.52 mmol) were added in sequence through syringe slowly at 0 ℃. The reaction mixture was stirred at room temperature for 1 h and then quenched with MeOH dropwise at 0 ℃. Then extraction was carried out with PE for three times and the resulting organic phases were dried over Na_2SO_4. The organic solvents were removed through rotary evaporator to give the residue, which was subsequently purified by flash column chromatography (PE), affording **S3** as blue oil (720 mg, 39%). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 8.27 (d, J = 9.9 Hz, 1H), 8.24 (d, J = 9.6 Hz, 1H), 7.77 (d, J = 3.7 Hz, 1H), 7.53 (t, J = 9.8 Hz, 1H), 7.34 (d, J = 3.5 Hz, 1H), 7.08 (t, J = 9.2 Hz, 1H), 7.06 (t, J = 9.4 Hz, 1H), 3.00 (d, J = 7.0 Hz, 2H), 1.83 – 1.74 (m, 1H), 1.40 – 1.23 (m, 24H), 0.89 (q, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 141.1, 138.3, 137.6, 136.6, 136.3, 133.9, 131.2, 122.2, 121.5, 117.1, 40.6, 34.2, 34.2, 32.5, 32.4, 30.5, 30.2, 30.1, 29.8, 27.1, 23.1, 14.3. HRMS[ESI] (*m/z*): $[M+H]^+$ cacld. for $C_{26}H_{41}$: 353.3203; Found: 353.3204.

3-chloro-4-(3-(2-hexyldecyl)azulen-1-yl)cyclobut-3-ene-1,2-dione (S4): To a 50 mL round-bottom flask were added squaryl chloride (330 mg, 2.2 mmol) and toluene (5 mL), a solution of compound **S3** (650 mg, 1.84 mmol) in toluene (5 mL) was subsequently added dropwise. The mixture was stirred at 80 ℃ for 4 h and quenched with H_2O. Then it was extracted with ethyl acetate and washed with saturated NaCl solutions for three times. The organic phase was dried with anhydrous Na_2SO_4 and

concentrated via rotary evaporator. The mixture was purified via column chromatography (PE:DCM=1:1, V:V) on silica gel to afford **S4** as brownish yellow solid (635 mg, 74%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.84 (d, *J* = 9.8 Hz, 1H), 8.49 (s, 1H), 8.46 (d, *J* = 9.9 Hz, 1H), 7.91 (t, *J* = 9.8 Hz, 1H), 7.73 (t, *J* = 9.9 Hz, 1H), 7.61 (t, *J* = 9.7 Hz, 1H), 2.97 (d, *J* = 7.0 Hz, 2H), 1.79 (m, 1H), 1.41 – 1.19 (m, 24H), 0.90 – 0.83 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.2, 189.6, 183.8, 172.1, 144.8, 144.0, 140.8, 140.3, 138.2, 136.2, 135.9, 130.4, 129.3, 116.5, 39.4, 33.8, 33.8, 32.1, 32.0, 30.1, 29.8, 29.7, 29.4, 26.8, 22.8, 14.2. HRMS[ESI] (*m/z*): $[M+H]^+$ cacld. for $C_{30}H_{40}ClO_2$: 467.2711; Found: 467.2715.

3-ethoxy-4-(3-(2-hexyldecyl)azulen-1-yl)cyclobut-3-ene-1,2-dione (S5): To a 50 mL round-bottom flask was added **S4** (550 mg, 1.18 mmol), THF (5 mL) and EtOH (10 mL) were added as solvents. The reaction was heated at 80 ℃ overnight, then was extracted with ethyl acetate for three times. The combined organic layers were dried and concentrated under reduced pressure to give the residue, which was purified through column chromatography (PE:DCM=1:2, V:V) to afford **S5** as brown oil (535 mg, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.72 (d, *J* = 9.7 Hz, 1H), 8.34 (d, *J* = 9.8 Hz, 1H), 8.24 (s, 1H), 7.76 (t, *J* = 9.8 Hz, 1H), 7.52 (t, *J* = 9.8 Hz, 1H), 7.40 (t, *J* = 9.8 Hz, 1H), 5.03 (q, *J* = 7.2 Hz, 2H), 2.94 (d, *J* = 7.0 Hz, 2H), 1.82 – 1.73 (m, 1H), 1.62 (t, *J* = 7.1 Hz, 3H), 1.35 – 1.21 (m, 24H), 0.90 – 0.82 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.9, 190.7, 189.6, 171.4, 142.9, 141.8, 139.9, 139.7, 137.9, 135.5, 134.1, 128.1, 126.9, 117.0, 70.9, 39.6, 33.8, 32.0, 30.2, 29.8, 29.8, 29.5, 26.8, 26.8, 22.8, 16.1, 14.2. HRMS[ESI] (*m/z*): $[M+H]^+$ cacld. for $C_{32}H_{45}O_3$: 477.3363; Found: 477.3366.

Triethylammonium 3-(dicyanomethylene)-2-(3-(2-hexyldecyl)azulen-1-yl)-4-oxocyclobut-1-en-1-olate (S6): Compound **S5** (450 mg, 0.94 mmol) was dissolved in the solvent mixtures of THF (5 mL) and EtOH (10 mL). Then, malononitrile (94 mg, 1.42 mmol) and NEt_3 (157 μL, 1.13 mmol) were then successively added. The reactants were stirred at room temperature overnight and subsequently the organic solvents were removed under reduced pressure. The mixture was subjected to the flash column chromatography (DCM:MeOH=10:1, V:V) to give crude product **S6** as brown oil (525

mg, 99%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.24 (d, J = 9.7 Hz, 1H), 8.84 (bs, 1H), 8.32 (d, J = 9.7 Hz, 1H), 8.08 (s, 1H), 7.71 (t, J = 9.8 Hz, 1H), 7.28 (t, J = 9.8 Hz, 1H), 7.27 (t, J = 9.6 Hz, 1H), 3.09 (q, J = 7.3 Hz, 6H), 2.90 (d, J = 6.7 Hz, 2H), 1.83 – 1.72 (m, 1H), 1.28 – 1.14 (m, 33H), 0.86 – 0.78 (m, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 193.6, 187.1,177.9, 164.6, 139.7, 139.5, 138.9, 138.6, 137.6, 134.8, 131.6, 124.5, 124.4, 118.8, 118.5, 117.7, 45.8, 33.1, 33.0, 31.4, 31.3, 31.3, 29.3, 29.0, 28.9, 28.7, 26.0, 25.9, 22.1, 13.9, 8.6. HRMS[ESI] (*m/z*): $[M\text{-}NHEt_3^+]^-$ cacld. for $C_{33}H_{39}N_2O_2^-$: 495.3017; Found: 495.3015.

3-(dicyanomethylene)-4-((1-ethylbenzo[cd]indol-1-ium-2-yl)methylene)-2-(3-(2-hexyldecyl)azulen-1-yl)cyclobut-1-en-1-olate (Az-SQ): **S6** (370 mg, 0.62 mmol) and **7** (200 mg, 0.62 mmol) were dissolved in toluene (6 mL) and ^{n}butanol (6 mL). The reaction mixtures were heated at 120 ℃ for 2 h. Then the organic solvents were directly removed under reduced pressure after cooling to room temperature. The resulting residue was purified through column chromatography (DCM), affording **Az-SQ** as black solid (163 mg, 39%). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 9.92 (d, J = 9.6 Hz, 1H), 8.82 (d, J = 7.6 Hz, 1H), 8.47 (s, 1H), 8.30 (d, J = 9.6 Hz, 1H), 8.22 (d, J = 8.1 Hz, 1H), 7.95 (t, J = 7.7 Hz, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.77 (t, J = 10.1 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 9.9 Hz, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.42 (t, J = 9.8 Hz, 1H), 7.15 (s, 1H), 4.42 (q, J = 7.4 Hz, 2H), 2.96 (d, J = 7.0 Hz, 2H), 1.90 – 1.80 (m, 1H), 1.60 (t, J = 7.3 Hz, 3H), 1.36 – 1.23 (m, 24H), 0.87 (t, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 175.2, 170.3, 167.0, 159.1, 155.6, 145.6, 144.5, 141.6, 141.2, 140.8, 140.1, 137.5, 135.8, 135.1, 133.1, 130.2, 129.7, 129.4, 129.2, 129.0, 125.5, 125.1, 121.9, 119.3, 119.0. 111.7, 94.5, 45.0, 40.5, 39.7, 34.1, 34.1, 32.6, 32.3, 30.4, 30.1, 30.0, 29.7, 27.0, 23.1, 14.5, 14.3. HRMS[ESI] (*m/z*): $[M+H]^+$ Cacld. for $C_{47}H_{52}N_3O$: 674.4105; Found: 674.4110.

Fabrication of OFET devices

The bottom-gate top-contact OFET devices were fabricated as follows. Firstly, Si/SiO_2 substrates were ultrasonicated in deionized water for 10 min and then heated in the hot mixture (V:V=2:1) of concentrated sulfuric acid (wt%=98%) and hydrogen peroxide

(wt%=30%) for 15 min. Afterwards, the substrates were cleaned through the successive sonication in deionized water, acetone and isopropyl alcohol. Then, the Si/SiO_2 substrates were dried with quick purged nitrogen and modified with octadecyltrichlorosilane under reduced pressure. Finally, the substrates were prepared by ultrasonic cleaning in the sequence of chloroform, hexane, acetone, isopropyl alcohol and drying with N_2. The azulenyl squaraine films were deposited on the substrates through spin-coating from their chloroform solutions (5 mg/mL) at the speed of 3000 rpm. The gold was evaporated as source/drain electrodes onto the compound films by using the shadow mask (channel length: 31 μm; width: 273 μm). Finally, the OFET devices were measured through Keithley 4200-SCS semiconductor analyzer under nitrogen atmosphere.

3. Supplementary Figures and Tables

All calculations were carried out with Gaussian 16 package at B3LYP/6-31G(d,p) level of theory. To reduce the time required, the hexyldecyl chain was replaced with isobutyl chain. Harmonic vibration frequency calculations at the same level were performed to verify all stationary points as local minima (with no imaginary frequency).

The absorption spectra predictions were carried out at TD-DFT/B3LYP/6-31G(d,p) level of theory based on the B3LYP/6-31G(d,p) optimized geometries. Absorption spectra are obtained from calculated excitation energies and oscillator strengths as a sum of Gaussian functions with a parameter σ (width of the band at half-height) of 0.65 eV. TDDFT calculation of the first 50 singly excited states.

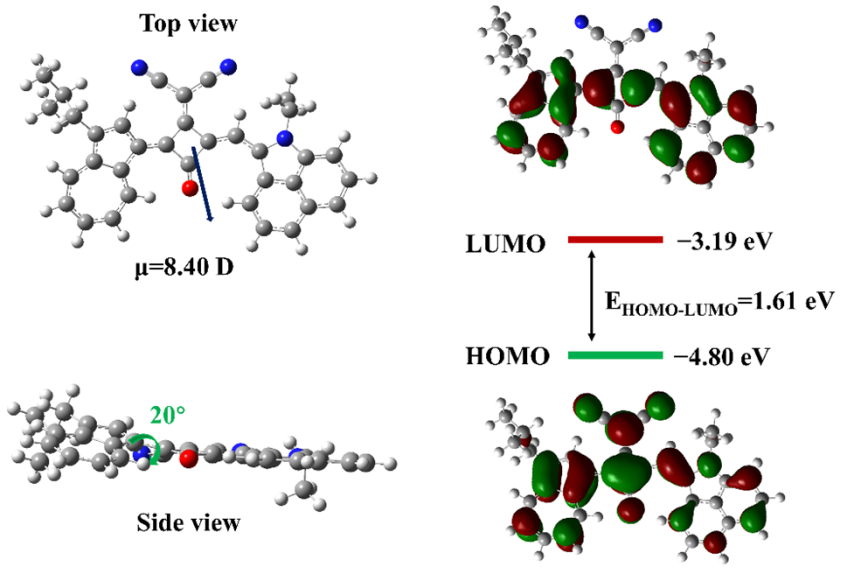


Figure S1. Optimized molecular geometries, frontier molecular orbitals and dipole moment of **Az-SQ**

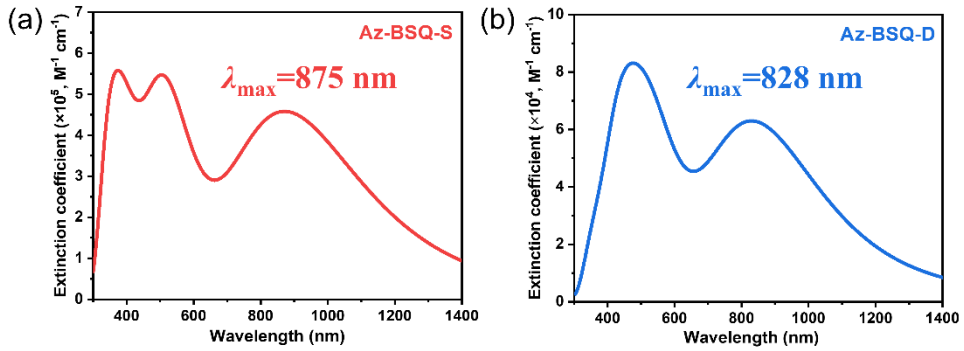


Figure S2. Simulated absorption spectra of **Az-BSQ-S** and **Az-BSQ-D** by TD-DFT calculations

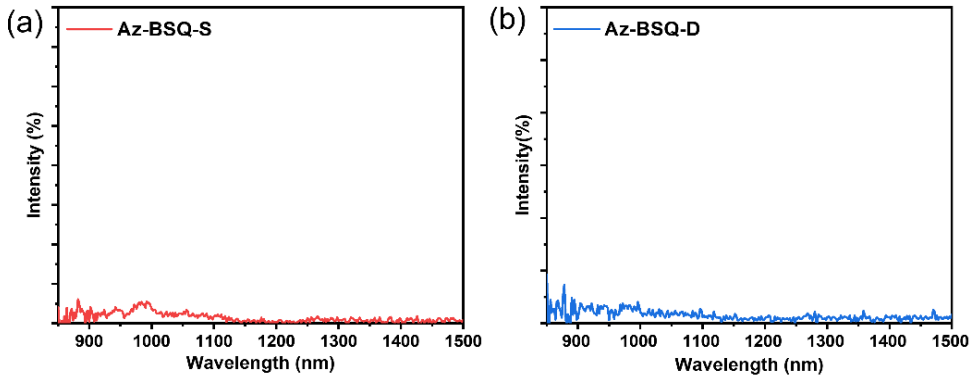


Figure S3. Fluorescence spectra of (a) **Az-BSQ-S** and (b) **Az-BSQ-D** in THF (λ_{ex}=808 nm)

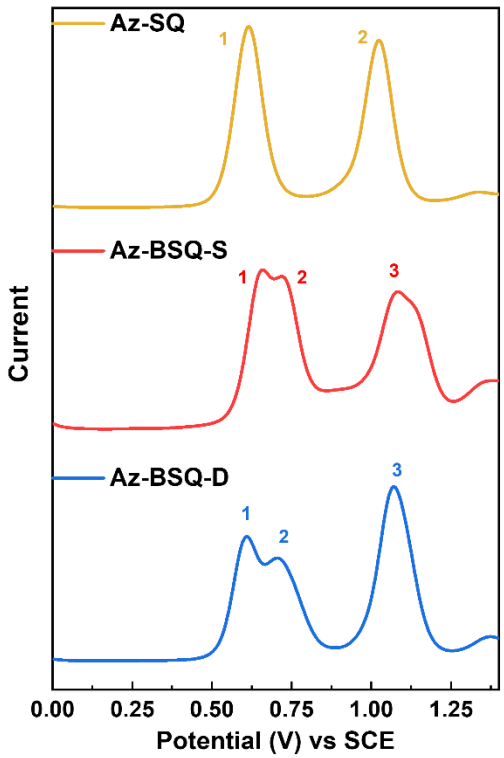


Figure S4. Differential pulse voltammetry curves of **Az-SQ**, **Az-BSQ-S** and **Az-BSQ-D** in DCM in the positive voltage range

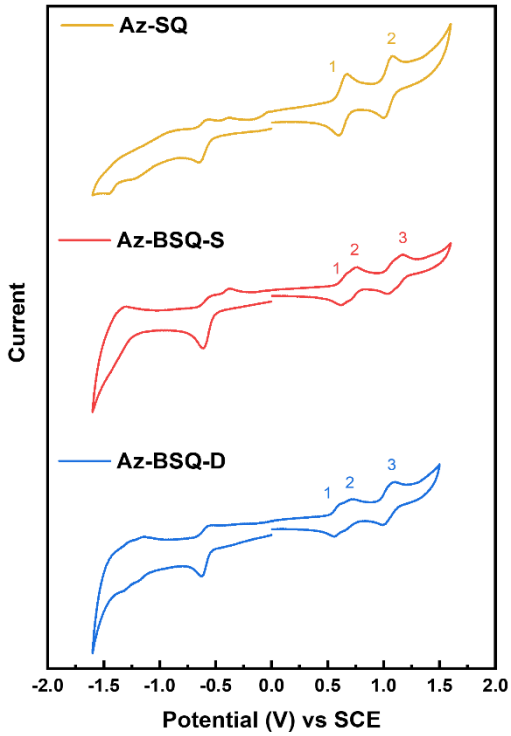


Figure S5. Cyclic voltammetry curves of **Az-SQ**, **Az-BSQ-S** and **Az-BSQ-D** in DCM

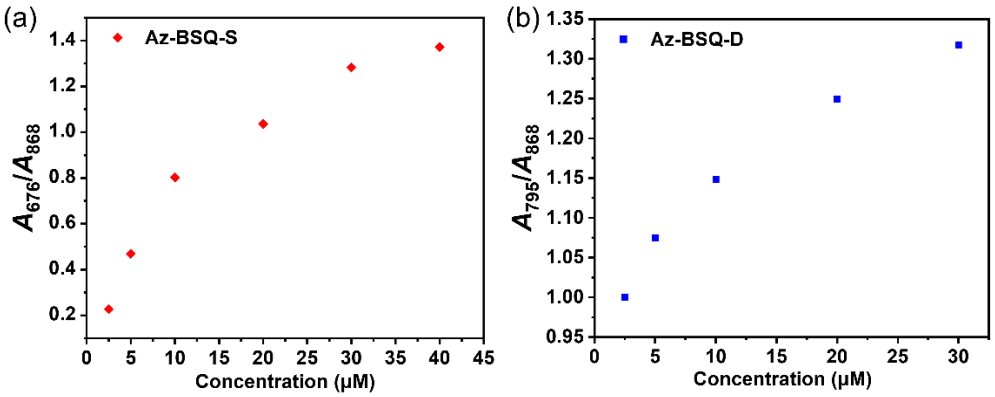


Figure S6. (a) Absorbance ratio (A_{676}/A_{868}) changes versus concentrations of **Az-BSQ-S** in THF/H_2O mixed solvents (f_{water} = 40%) read from Figure 4b. (b) Absorbance ratio (A_{795}/A_{868}) changes versus concentrations of **Az-BSQ-D** in THF/H_2O system (f_{water} = 40%) read from Figure 4d

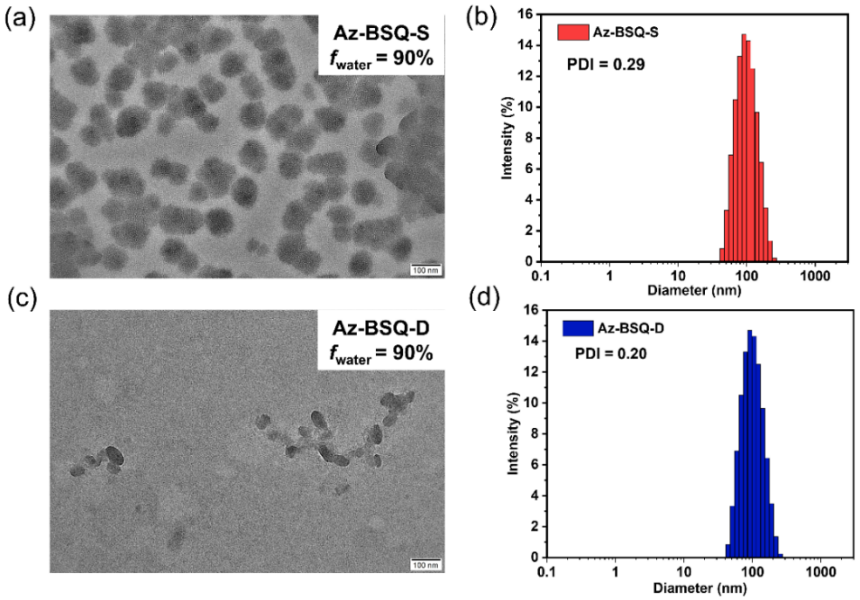


Figure S7. TEM images and DLS distributions of (a, b) **Az-BSQ-S** and (c, d) **Az-BSQ-D** in the THF/H_2O solvent mixtures (f_{water} = 90%, c = 10^{-5} M) (scale bar: 100 nm)

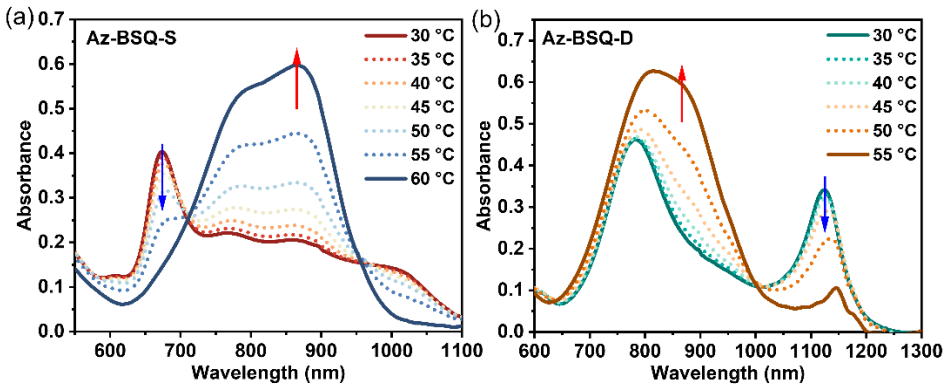


Figure S8. Temperature-dependent absorption spectra of (a) **Az-BSQ-S** and (b) **Az-BSQ-D** (10 μM) in THF/H_2O solvents (f_{water} = 50%).

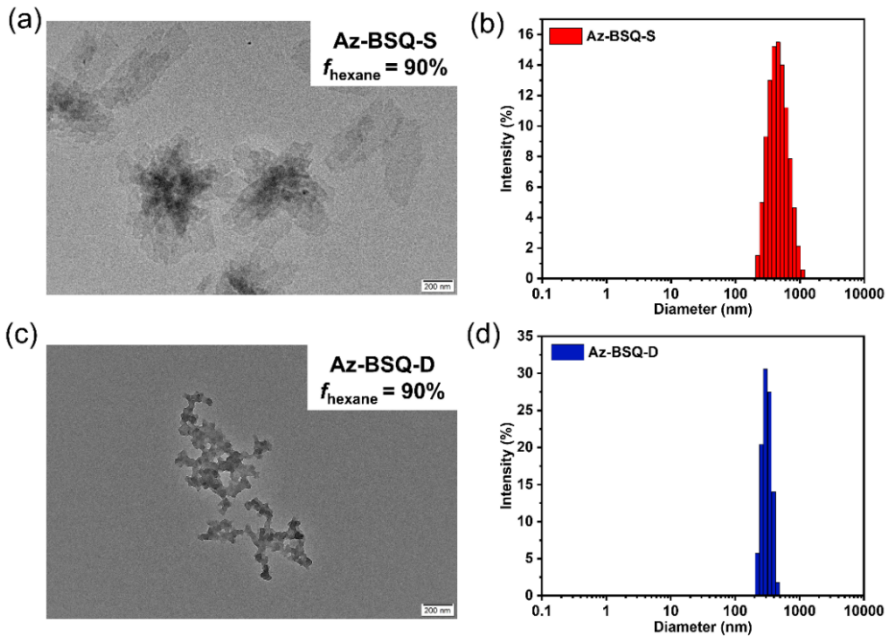


Figure S9. TEM and DLS characterizations of (a, b) **Az-BSQ-S** and (c, d) **Az-BSQ-D** in the THF/hexane system (10 μM, f_{hexane} = 90%) (scale bar: 200 nm)

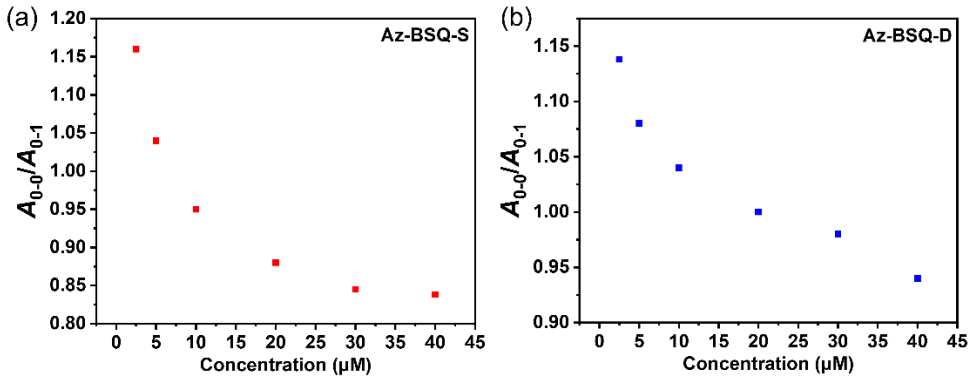


Figure S10. Peak absorbance ratio changes versus concentrations of (a) **Az-BSQ-S** and (b) **Az-BSQ-D** read from figure (5b) and (5d).

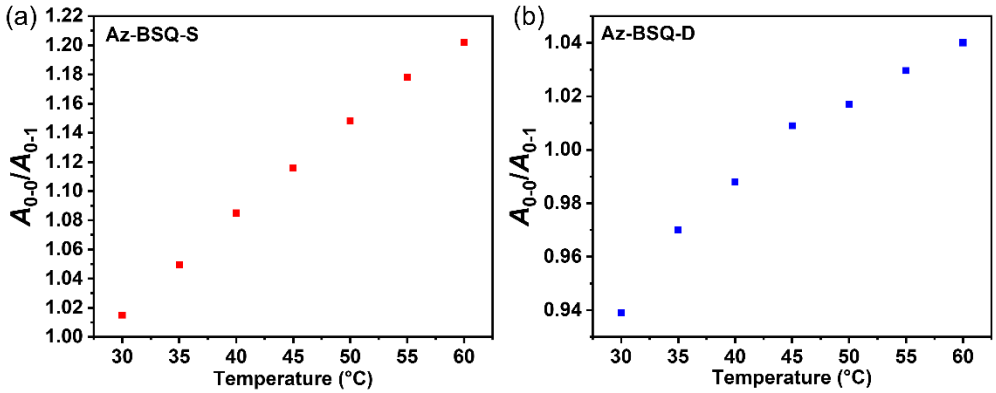


Figure S11. Peak absorbance ratio ($A_{0\text{-}0}/A_{0\text{-}1}$) changing curves of (a) **Az-BSQ-S** and (b) **Az-BSQ-D** as a function of temperatures during heating process in THF/hexane system (10 μM, f_{hexane} = 60%) read from Figure 6a, c.

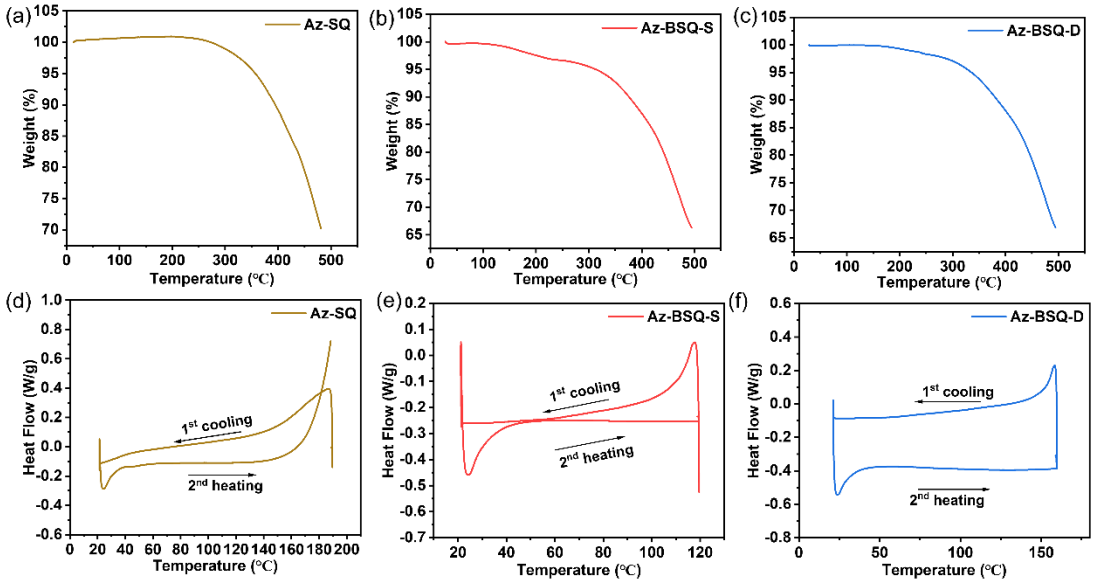


Figure S12. Thermal gravity analysis curves of (a) **Az-SQ**, (b) **Az-BSQ-S** and (c) **Az-BSQ-D**. Differential scanning calorimeter curves of (d) **Az-SQ**, (e) **Az-BSQ-S** and (f) **Az-BSQ-D**

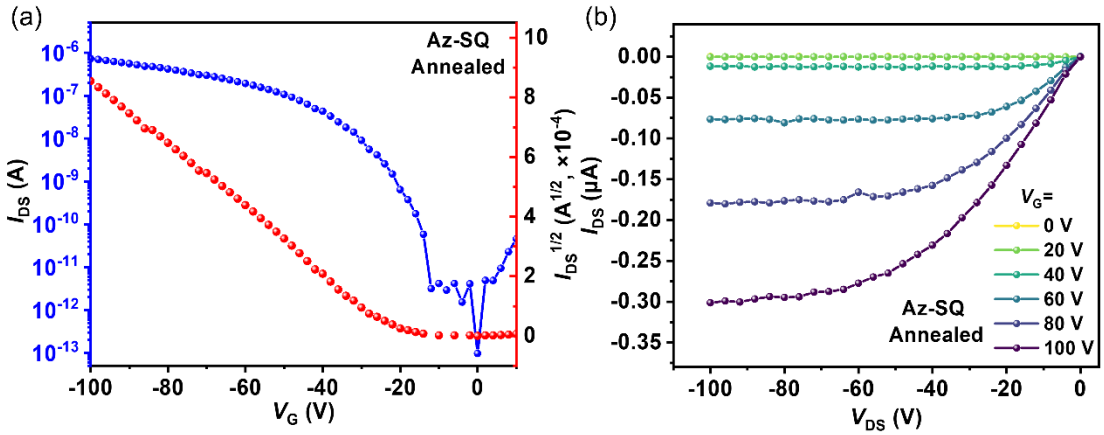


Figure S13. Typical transfer and output curves of OFET devices based on **Az-SQ** films after thermal treatment at 80 °C

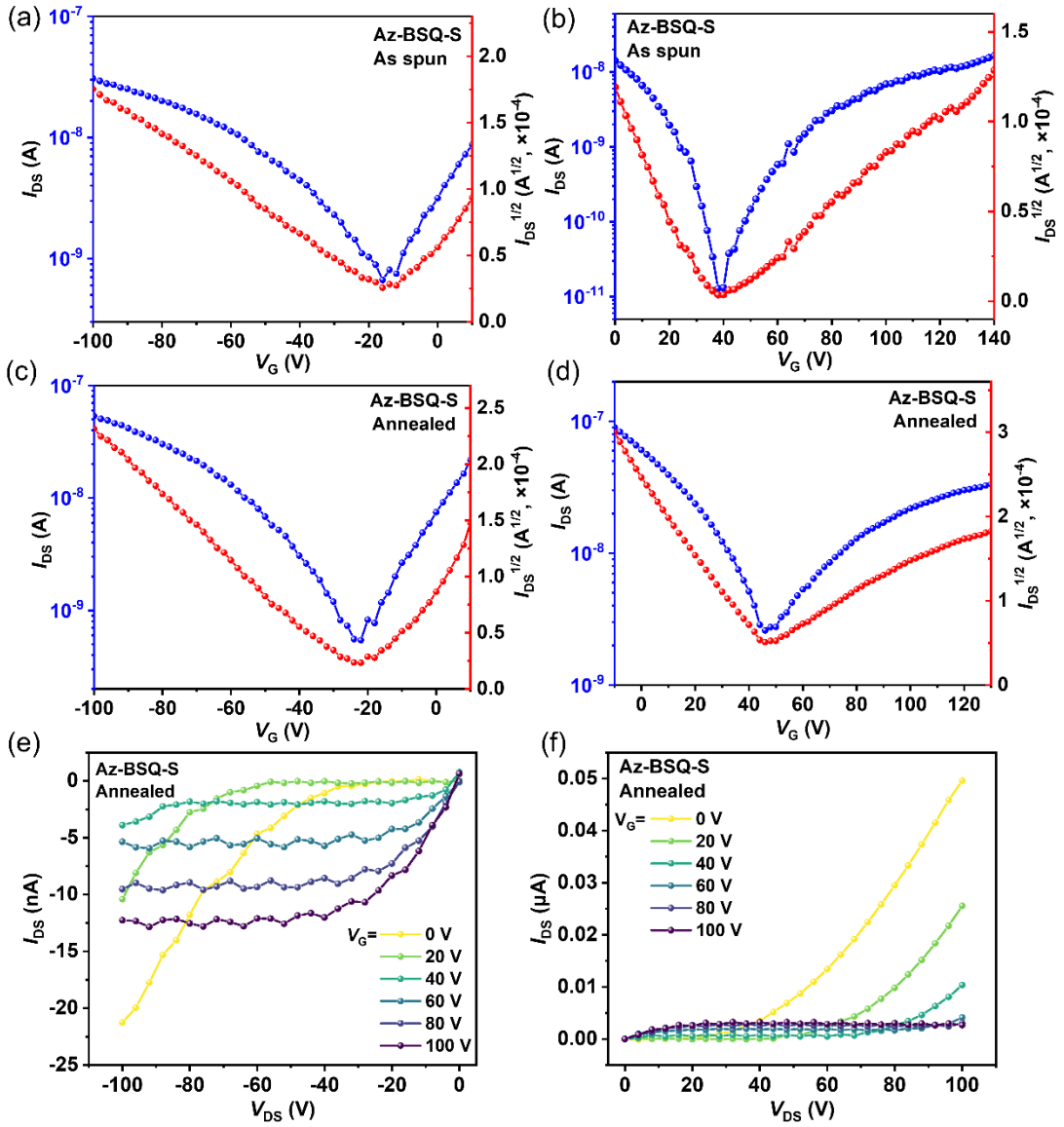


Figure S14. (a-d) Typical transfer curves of OFET devices based on **Az-BSQ-S** before and after thermal annealing at 80 °C. (e, f) Typical output curves of OFET devices based on **Az-BSQ-S** after thermal annealing at 80 °C

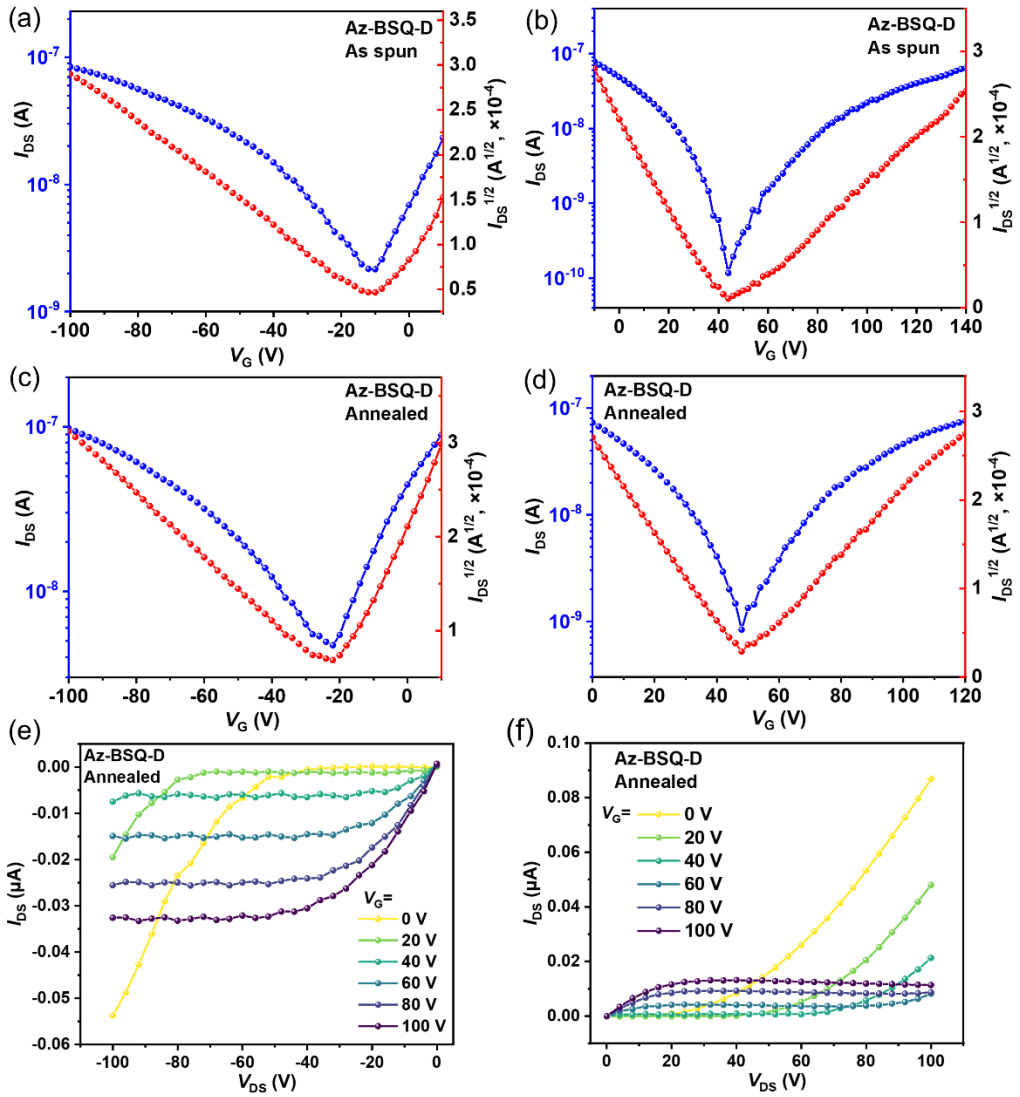


Figure S15. (a-d) Typical transfer curves of OFET devices based on **Az-BSQ-D** before and after thermal annealing at 80 °C. (e, f) Typical output curves of **Az-BSQ-D** based OFET devices after thermal annealing at 80 °C

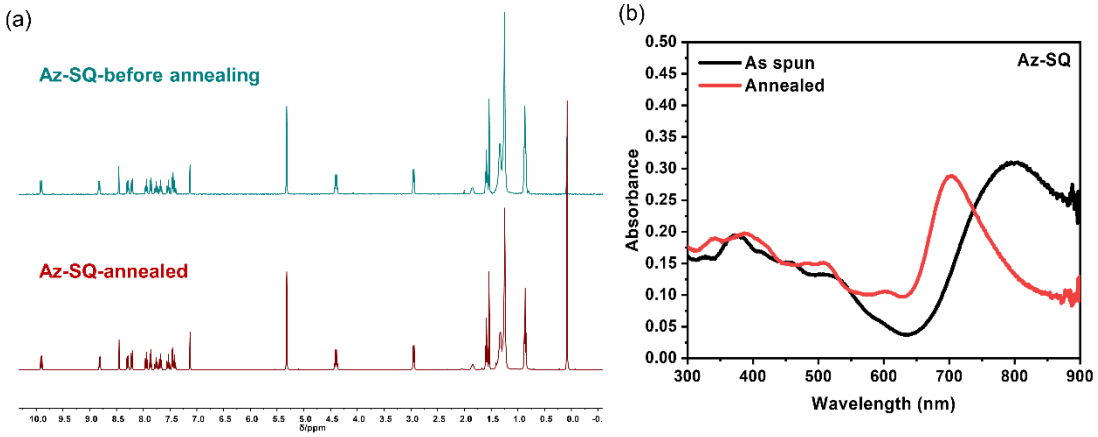


Figure S16. (a) ^{1}H NMR spectra of **Az-SQ** (CD_2Cl_2, 400 MHz) before and after thermal treatment. (b) UV-Vis/NIR absorption spectra of **Az-SQ** film before and after thermal annealing at 80 °C

Table S1. Thin film OFET device performance based on **Az-SQ**, **Az-BSQ-S** and **Az-BSQ-D**

Comp.	T_a/°C[a]	Polarity	$\mu_{e,ave}(\mu_{e,max})$[b] / cm^2 V^{-1} s^{-1}	$V_{T,ave}$[b]/ V	I_{on}/I_{off}[b]	$\mu_{h,ave}(\mu_{h,max})$[b] / cm^2 V^{-1} s^{-1}	$V_{T,ave}$[b]/ V	I_{on}/I_{off}[b]
Az-SQ	80	p	–	–	–	3.0×10^{-3} (4.2×10^{-3})	−19.0	10^5-10^6
Az-BSQ-S	As spun	Ambipolar	2.5×10^{-4} (4.9×10^{-4})	26.8	10^2-10^3	1.0×10^{-4} (1.4×10^{-4})	−5.1	10-10^2
	80		9.0×10^{-5} (1.1×10^{-4})	32.9	10-10^2	2.0×10^{-4} (2.3×10^{-4})	−12.7	10^2-10^3
Az-BSQ-D	As spun	Ambipolar	1.3×10^{-4} (1.7×10^{-4})	39.5	10^2-10^3	1.3×10^{-4} (2.1×10^{-4})	−3.8	10-10^2
	80		3.5×10^{-4} (4.2×10^{-4})	36.6	10^2-10^3	2.6×10^{-4} (3.2×10^{-4})	−9.4	10-10^2

[a]Annealing temperature. [b]The devices are measured under nitrogen atmosphere and the data were calculated from at least 12 devices.

4. NMR and HRMS Spectra

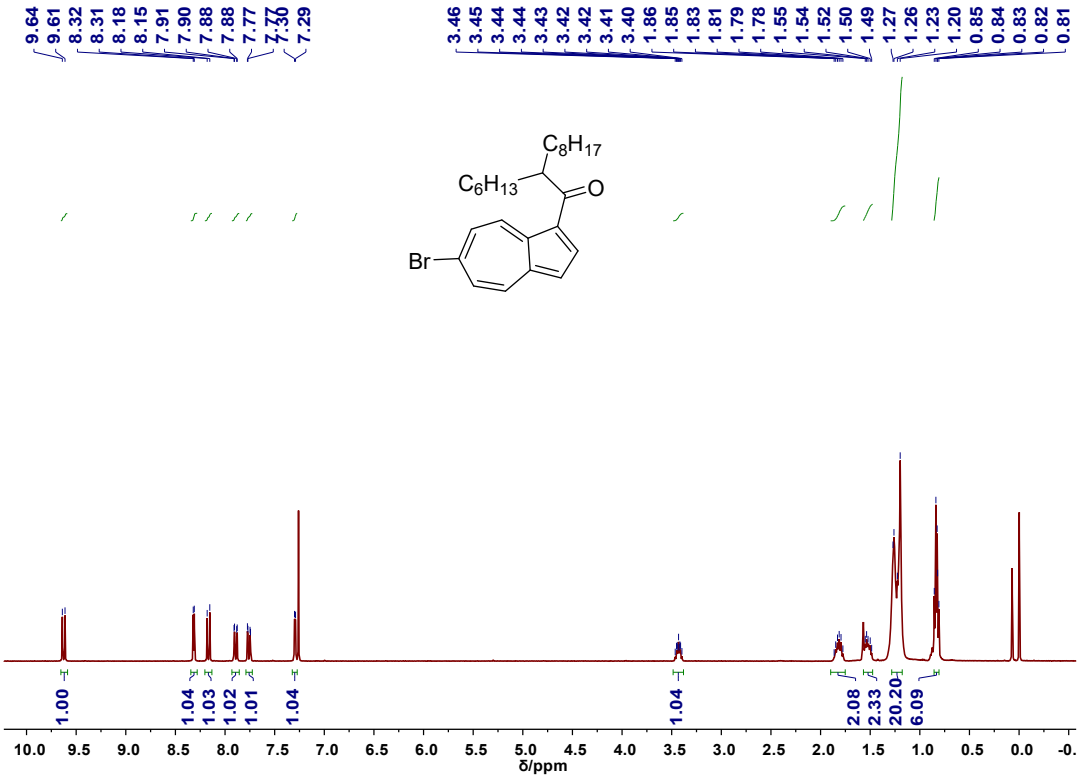


Figure S17. ^{1}H NMR specctrum of **2** ($CDCl_3$, 400 MHz)

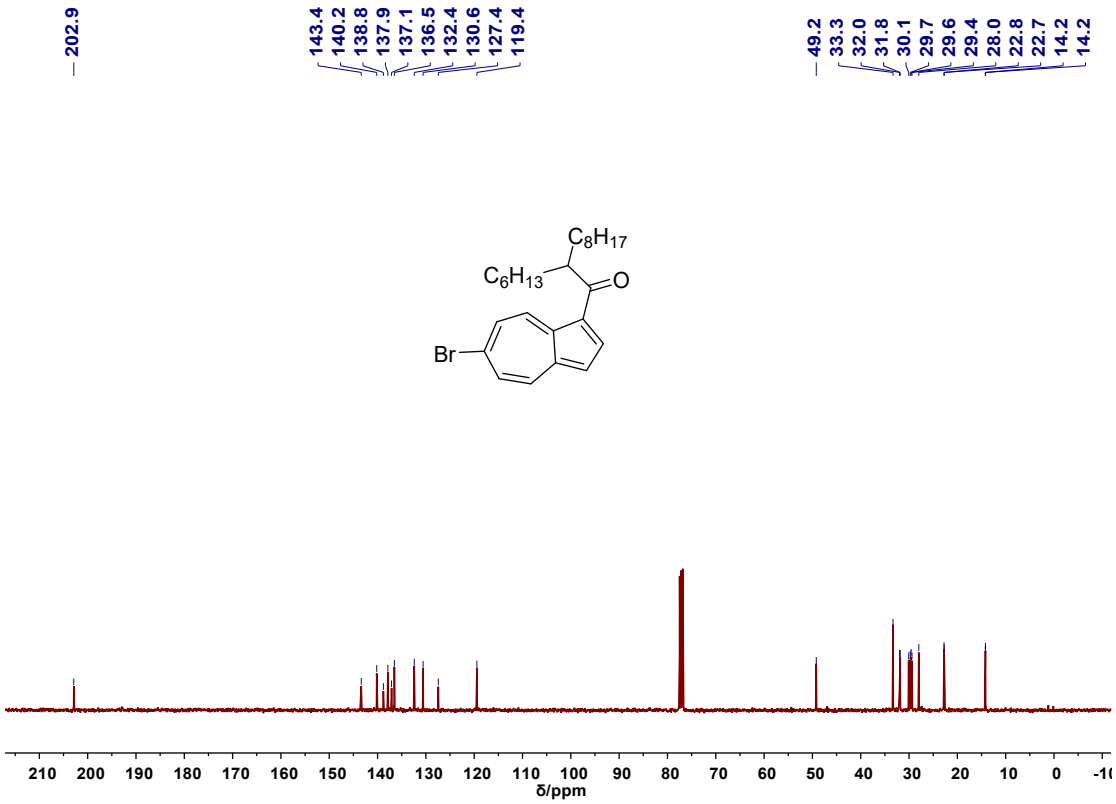


Figure S18. ^{13}C NMR spectrum of **2** ($CDCl_3$, 100 MHz)

High Resolution ESI-MS REPORT

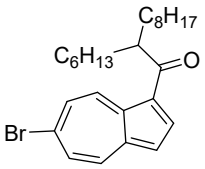
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E231809

Sample Serial Number: yym-10-14

Operator: Songw Date: 2023/07/11

Operation Mode: ESI Positive Ion Mode



Elemental composition search on mass 445.2091

m/z= 440.2091-450.2091

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
445.2091	445.2101	-2.19	7.5	$C_{26}H_{38}OBr$

Figure S19. High resolution ESI-MS report of **2**

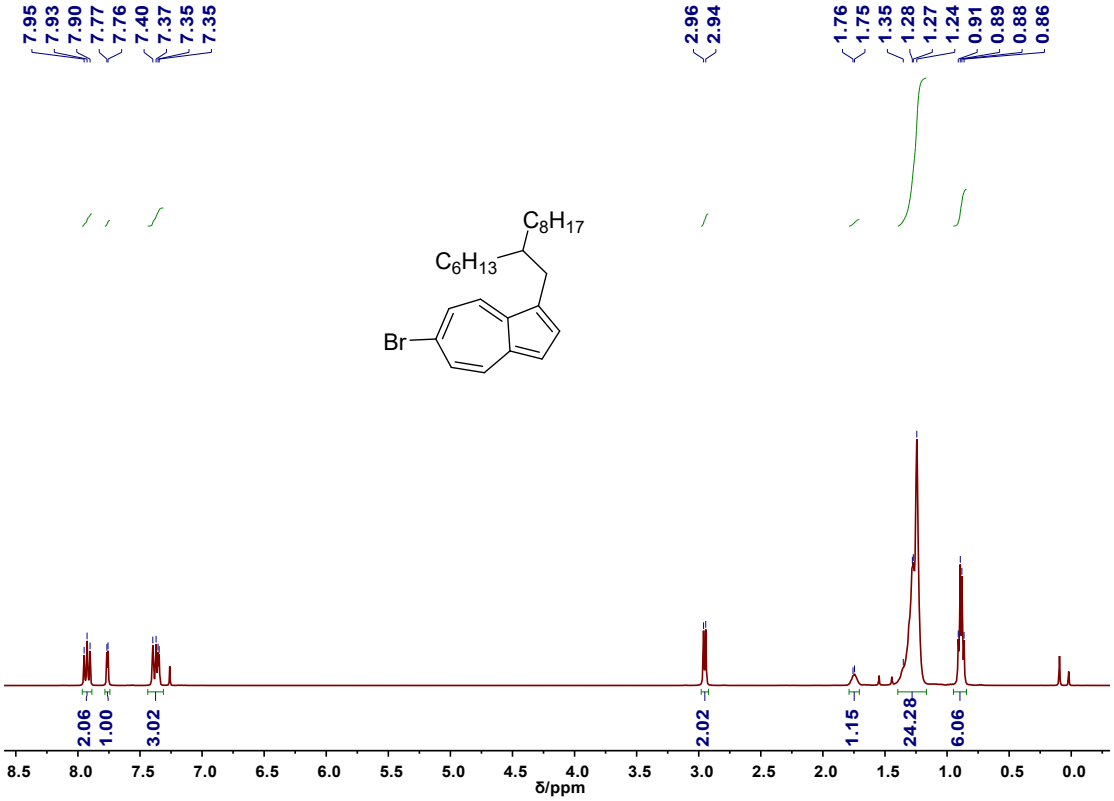


Figure S20. ^{1}H NMR spectrum of **3** ($CDCl_3$, 400 MHz)

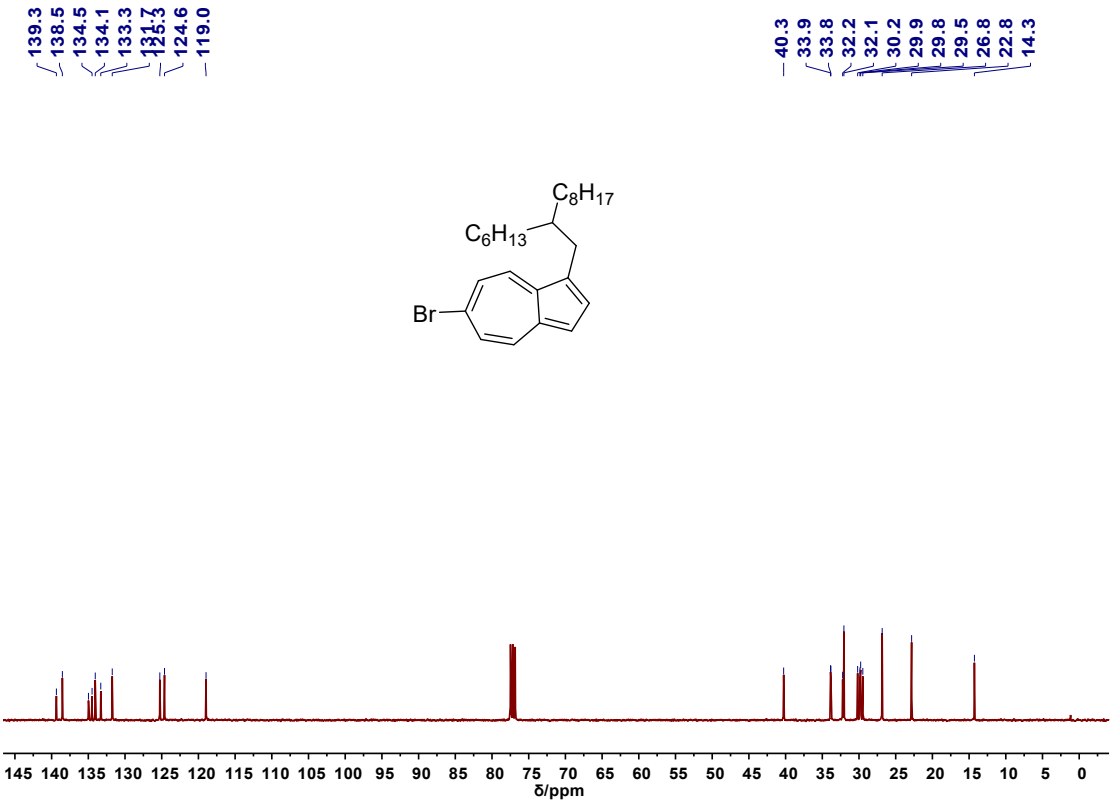


Figure S21. ^{13}C NMR spectrum of **3** ($CDCl_3$, 100 MHz)

High Resolution ESI-MS REPORT

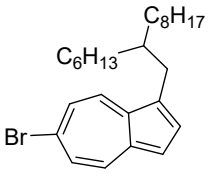
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E231810

Sample Serial Number: yym-10-17

Operator: Songw Date: 2023/07/11

Operation Mode: ESI Positive Ion Mode



Elemental composition search on mass 431.2297

m/z= 426.2297-436.2297

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
431.2297	431.2308	-2.51	6.5	$C_{26}H_{40}Br$

Figure S22. High resolution ESI-MS report of **3**

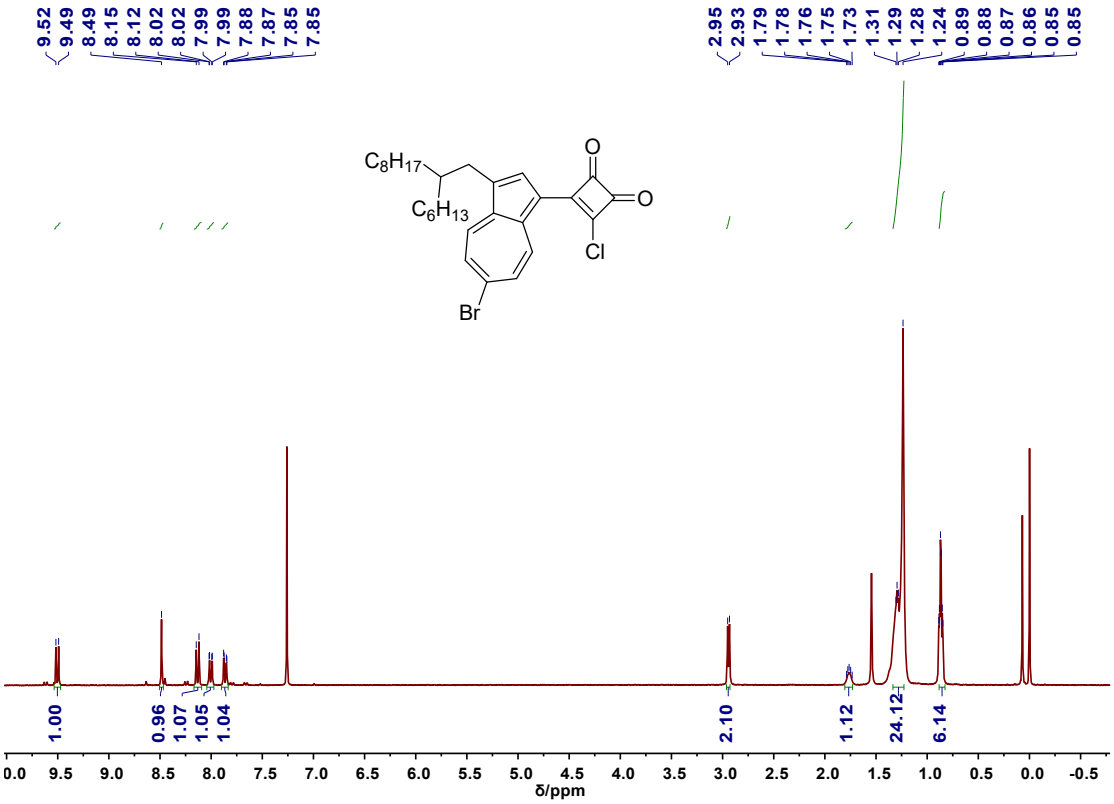


Figure S23. ^{1}H NMR spectrum of **4** ($CDCl_3$, 400 MHz)

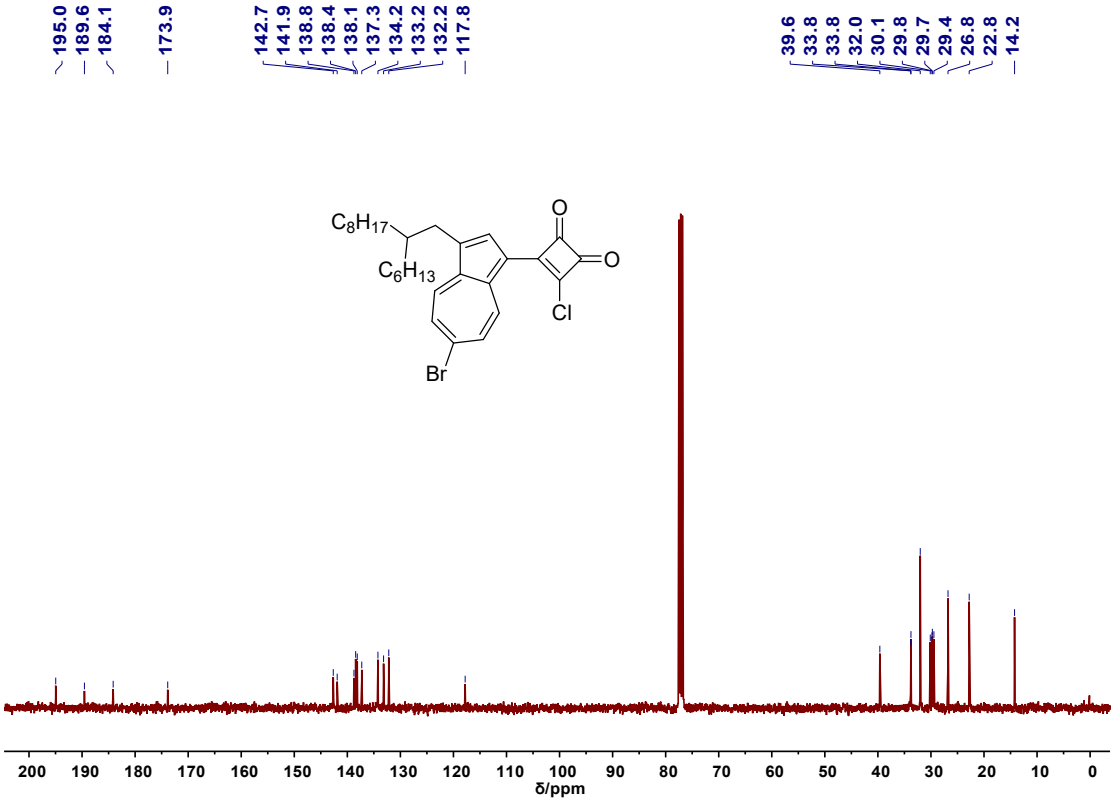


Figure S24. ^{13}C NMR spectrum of **4** ($CDCl_3$, 100 MHz)

High Resolution MS DATA REPORT

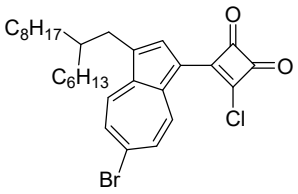
Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D2023500

Sample Serial Number: 2019143-YYM-10-46

Operator : DONG Date: 2023/07/19

Operation Mode: DART POSITIVE



Elemental composition search on mass 545.1815

m/z= 540.1815-550.1815

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
545.1815	545.1816	-0.33	10.5	$C_{30}H_{39}O_2BrCl$
	545.1819	-0.87	22.5	$C_{32}H_{25}O_5N_4$
	545.1824	-1.77	18.0	$C_{29}H_{28}O_4N_5Cl$
	545.1803	2.14	11.0	$C_{28}H_{37}ON_3BrCl$
	545.1798	3.03	15.5	$C_{31}H_{34}O_2N_2Br$
	545.1833	-3.34	22.0	$C_{34}H_{27}O_6N$
	545.1838	-4.23	17.5	$C_{31}H_{30}O_5N_2Cl$
	545.1838	-4.35	19.5	$C_{36}H_{34}Br$

Figure S25. High resolution DART-MS report of **4**

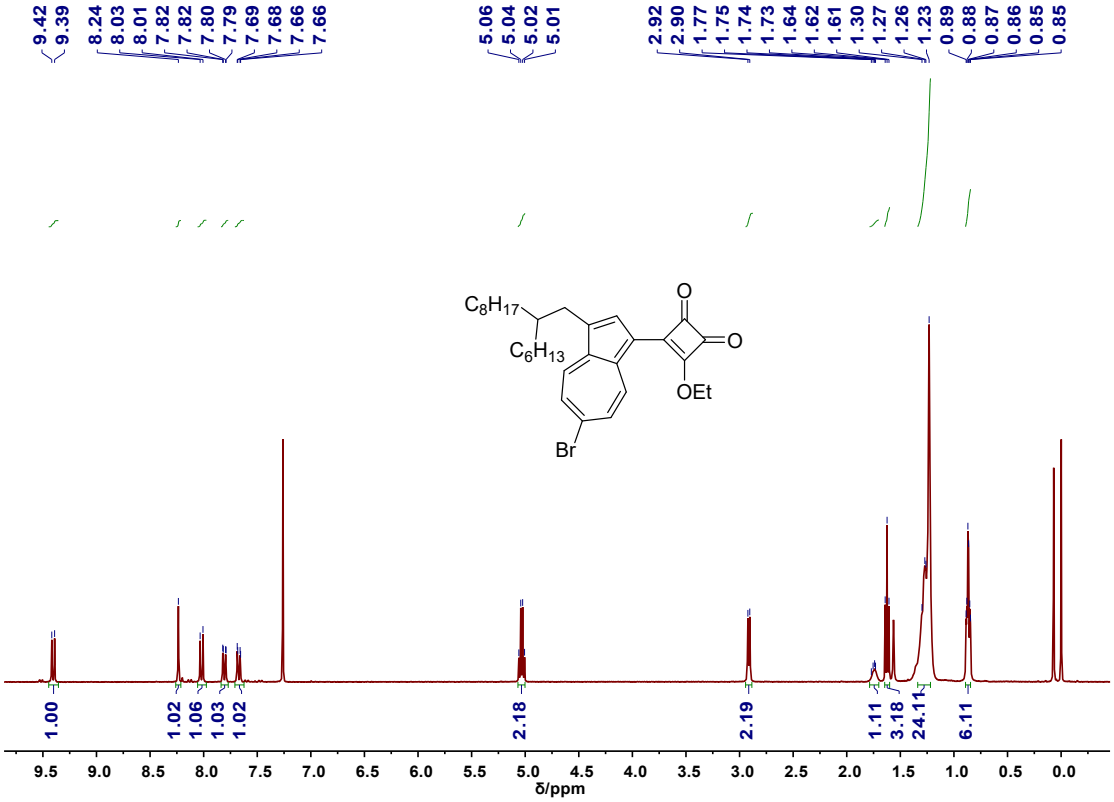


Figure S26. ^{1}H NMR spectrum of **5** ($CDCl_3$, 400 MHz)

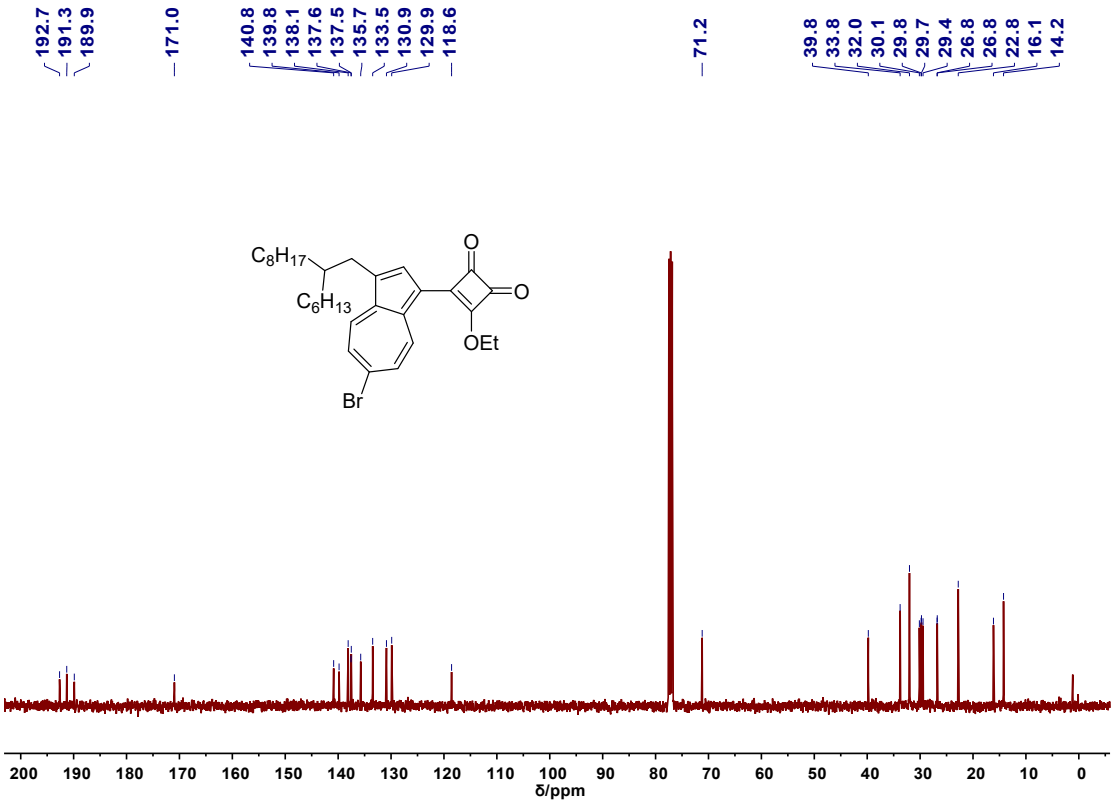


Figure S27. ^{13}C NMR spectrum of **5** ($CDCl_3$, 100 MHz)

High Resolution MS DATA REPORT

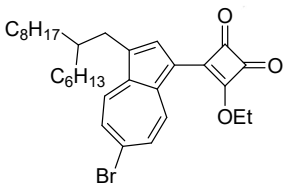
Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D2023498

Sample Serial Number: 2019143-YYM-10-48

Operator : DONG Date: 2023/07/19

Operation Mode: DART POSITIVE



Elemental composition search on mass 555.2463

m/z= 550.2463-560.2463

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
555.2463	555.2468	-0.93	10.5	$C_{32}H_{44}O_3Br$
	555.2455	1.49	11.0	$C_{30}H_{42}O_2N_3Br$
	555.2476	-2.34	18.0	$C_{31}H_{33}O_5N_5$
	555.2490	-4.76	17.5	$C_{33}H_{35}O_6N_2$

Figure S28. High resolution DART-MS report of **5**

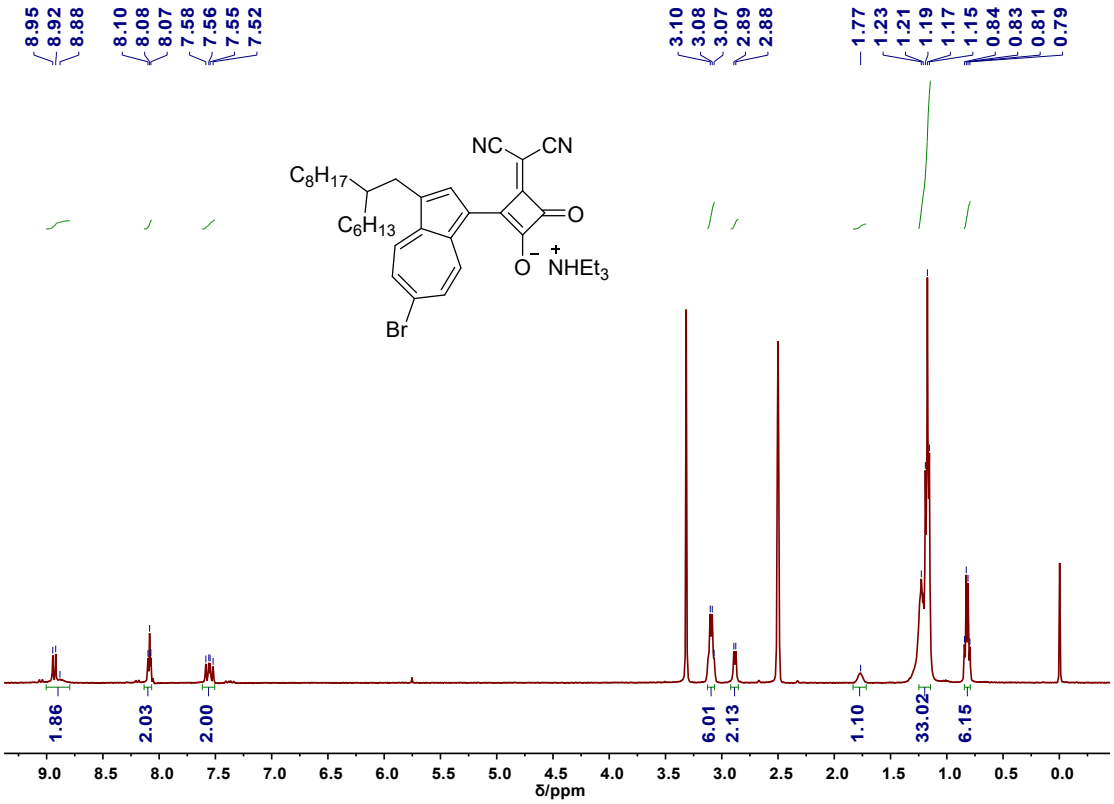


Figure S29. [1]H NMR spectrum of **6** (DMSO-d_6, 400 MHz)

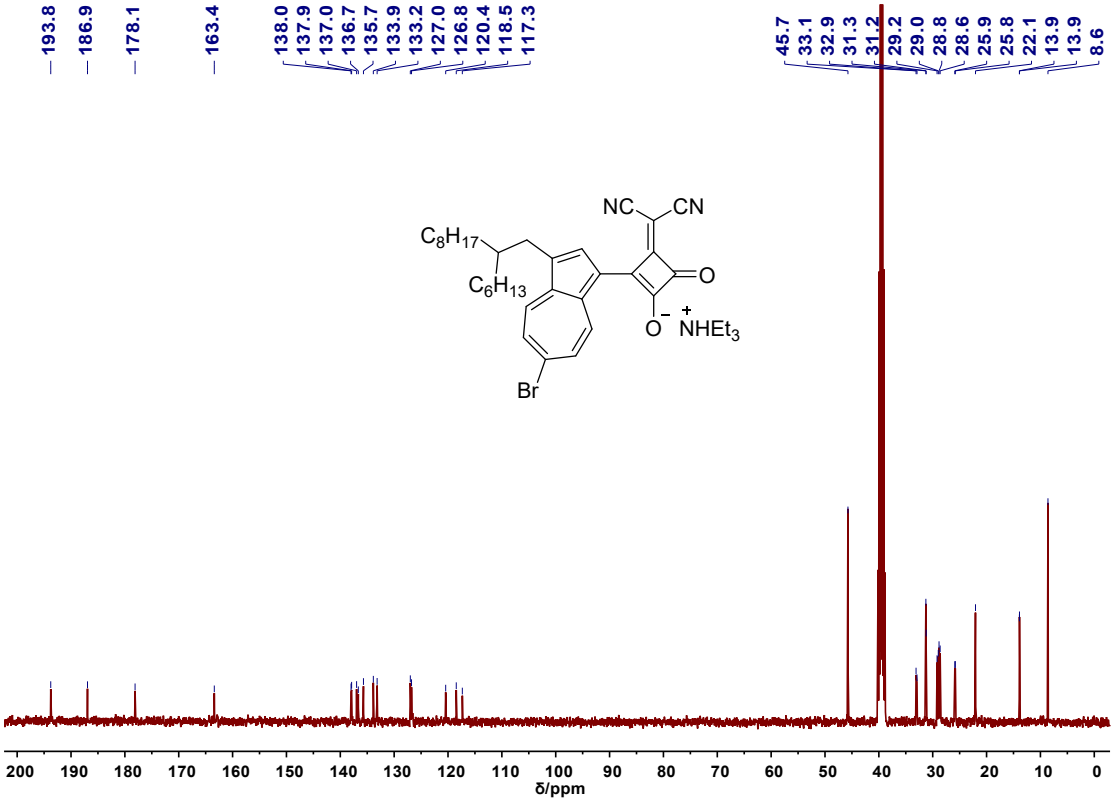


Figure S30. [13]C NMR spectrum of **6** (DMSO-d_6, 100 MHz)

High Resolution MS DATA REPORT

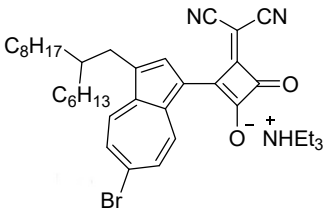
Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D20235656

Sample Serial Number: 2019143-YYM-10-50

Operator : DONG Date: 2023/10/16

Operation Mode: DART POSITIVE



Elemental composition search on mass 676.3473

m/z= 671.3473-681.3473

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
676.3473	676.3473	0.03	6.0	$C_{36}H_{57}O_2BrF_4$
	676.3472	0.09	13.5	$C_{39}H_{55}O_2N_3Br$
	676.3471	0.33	2.5	$C_{31}H_{56}O_2N_3BrF_5$
	676.3469	0.56	17.5	$C_{38}H_{45}O_3N_5F_3$
	676.3480	-1.13	13.5	$C_{35}H_{46}O_4N_5F_4$
	676.3482	-1.43	17.0	$C_{40}H_{47}O_4N_2F_3$
	676.3484	-1.60	9.5	$C_{36}H_{56}O_3N_3BrF$
	676.3484	-1.66	2.0	$C_{33}H_{58}O_3BrF_5$
	676.3461	1.72	10.0	$C_{39}H_{56}OBrF_3$
	676.3459	2.02	6.5	$C_{34}H_{55}ON_3BrF_4$

Figure S31. High resolution DART-MS report of **6**

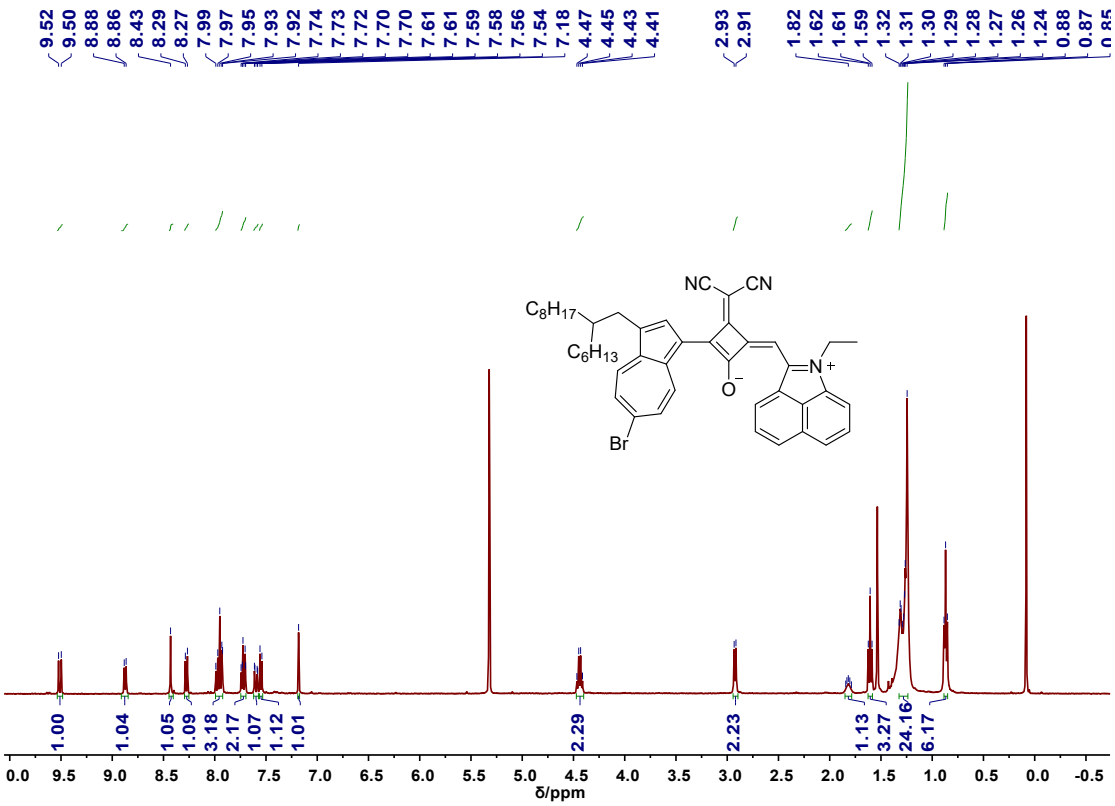


Figure S32. ^{1}H NMR spectrum of **8** (CD_2Cl_2, 400 MHz)

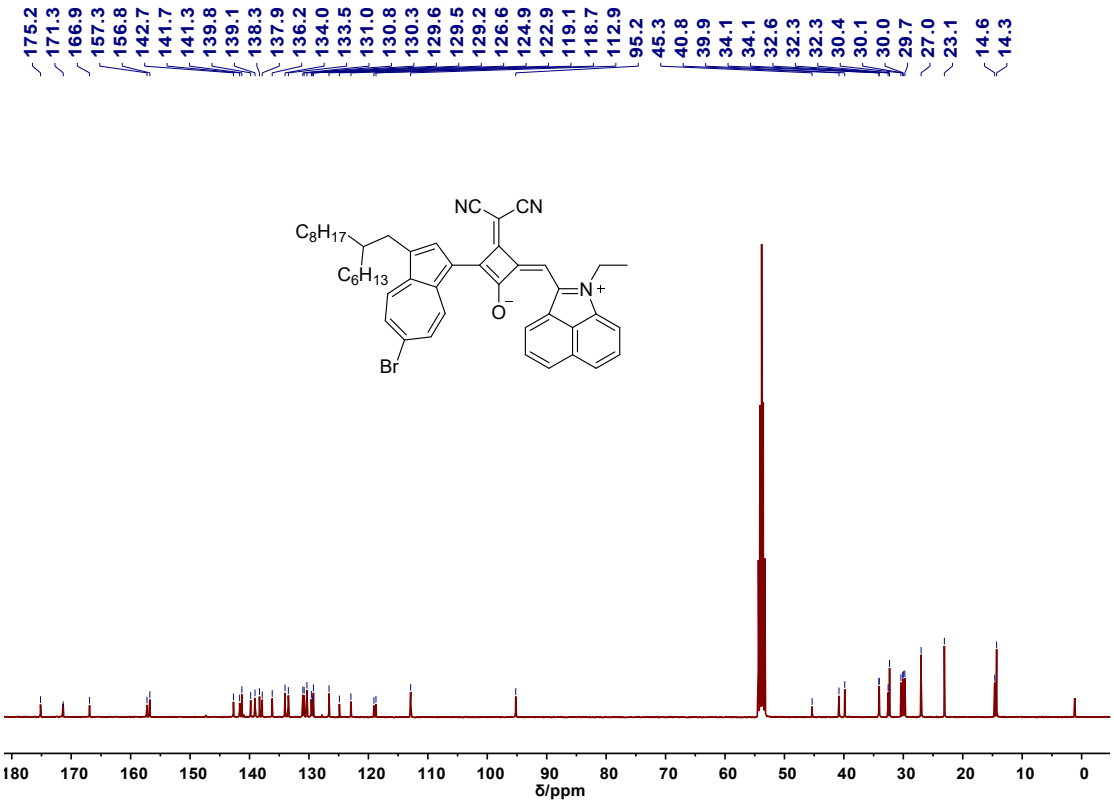


Figure S33. ^{13}C NMR spectrum of **8** (CD_2Cl_2, 100 MHz)

High Resolution ESI-MS REPORT

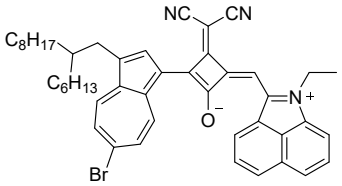
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E231326

Sample Serial Number: YYM-10-52

Operator: Songw Date: 2023/05/04

Operation Mode: ESI Positive Ion Mode



Elemental composition search on mass 751.3124

m/z= 746.3124-756.3124

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
751.3124	751.3132	-0.98	24.0	$C_{47}H_{50}ON_3Br$

Figure S34. High resolution ESI-MS report of **8**

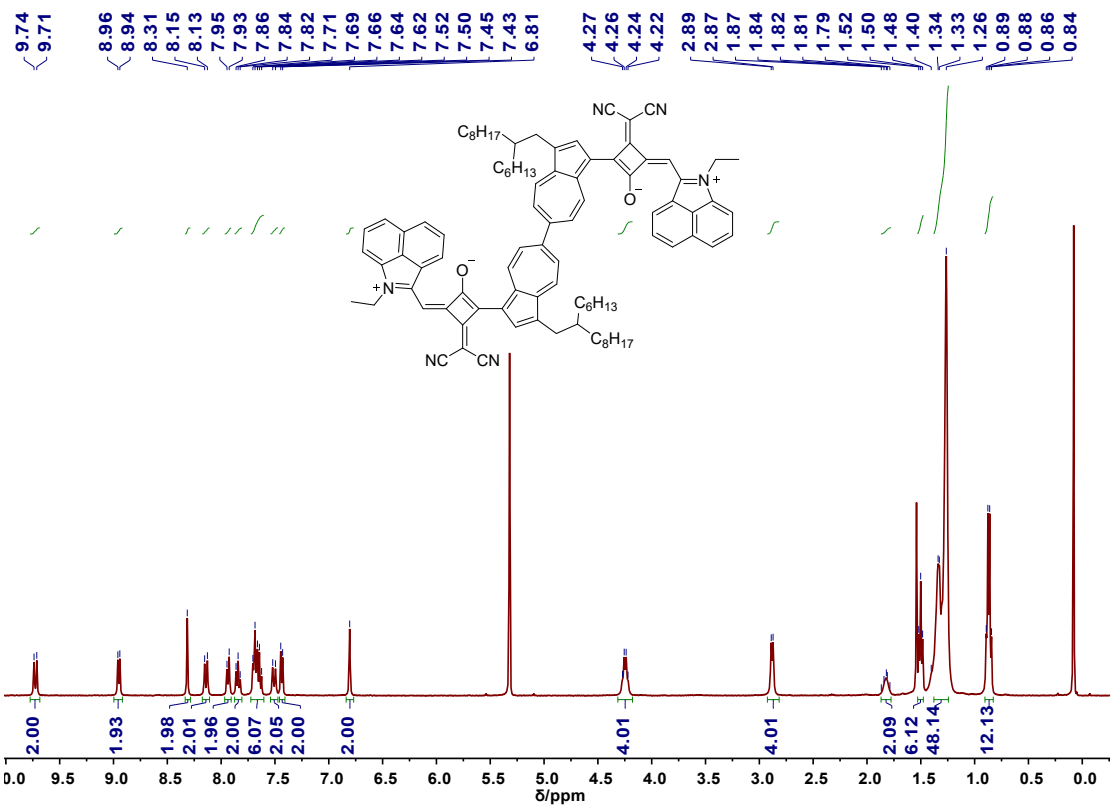


Figure S35. ^{1}H NMR spectrum of **Az-BSQ-S** (CD_2Cl_2, 400 MHz)

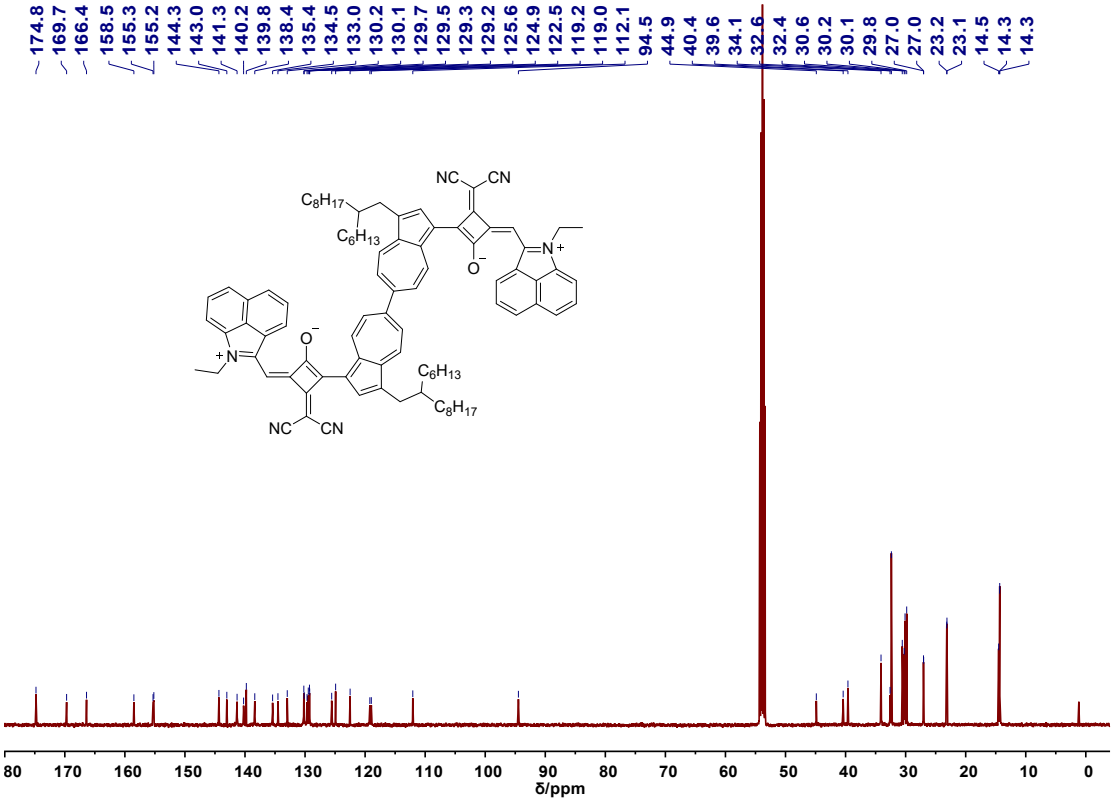


Figure S36. ^{13}C NMR spectrum of **Az-BSQ-S** (CD_2Cl_2, 125 MHz)

High Resolution ESI-MS REPORT

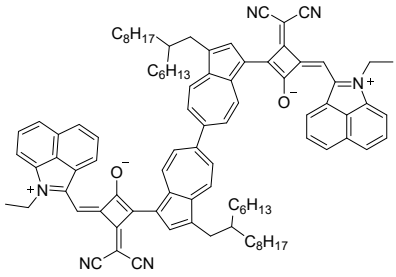
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E-W2024011605

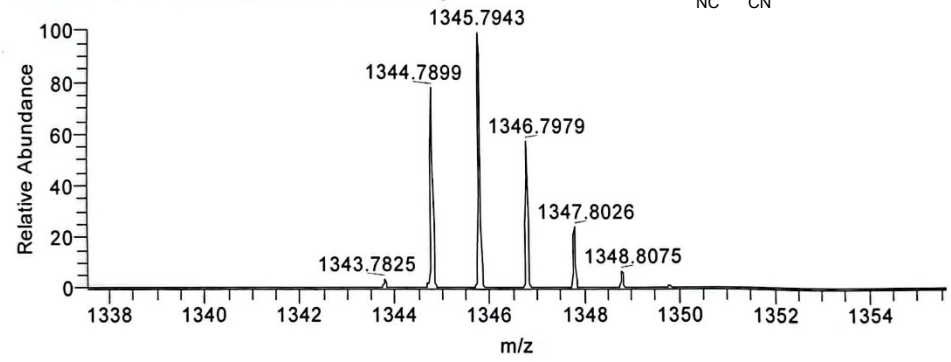
Sample Serial Number: 2019143-yym-11-13

Operator: Wang HY Date: 2024/01/15

Operation Mode: AP-MALDI Positive Ion Mode



2019143-yym-11-13 #214 RT: 1.17 AV: 1 NL: 4.67E4
T: FTMS + p NSI Full ms [300.0000-2000.0000]



Elemental composition search on mass 1344.7899

m/z= 1339.7899-1349.7899

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1344.7899	1344.7902	-0.23	48.0	$C_{94}H_{100}O_2N_6$

Figure S37. High resolution MALDI-MS report of **Az-BSQ-S**

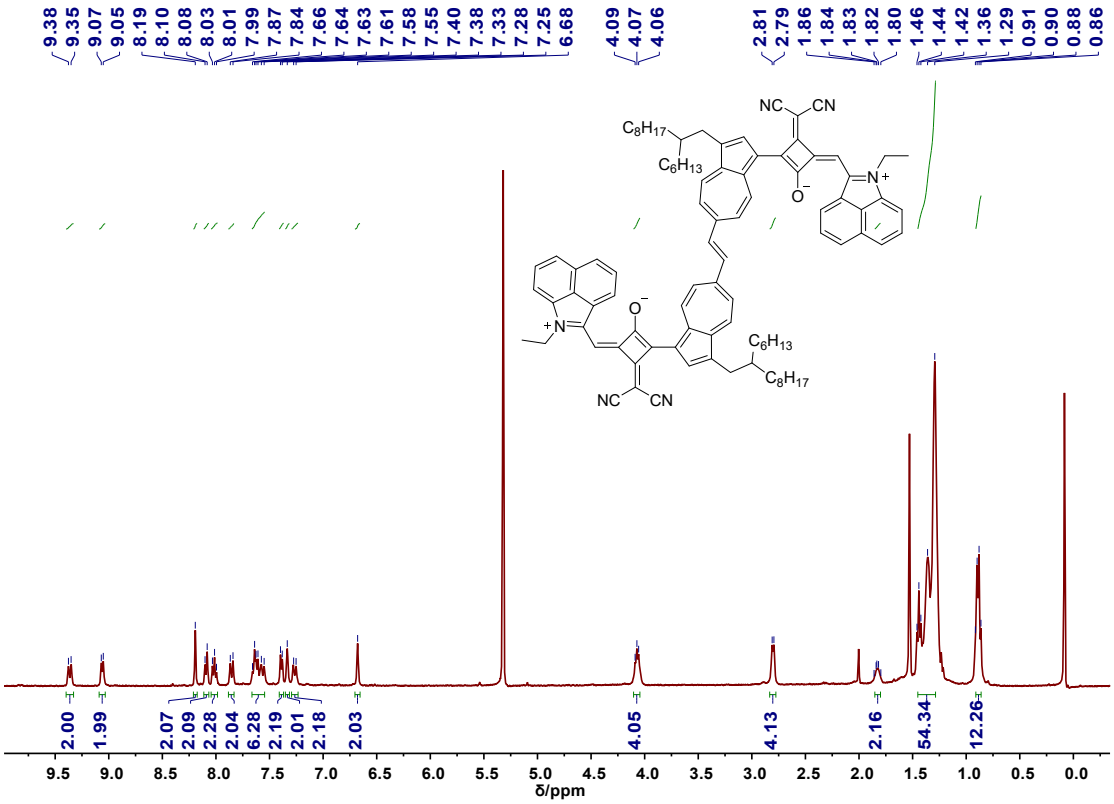


Figure S38. ^{1}H NMR spectrum of **Az-BSQ-D** (CD_2Cl_2, 400 MHz)

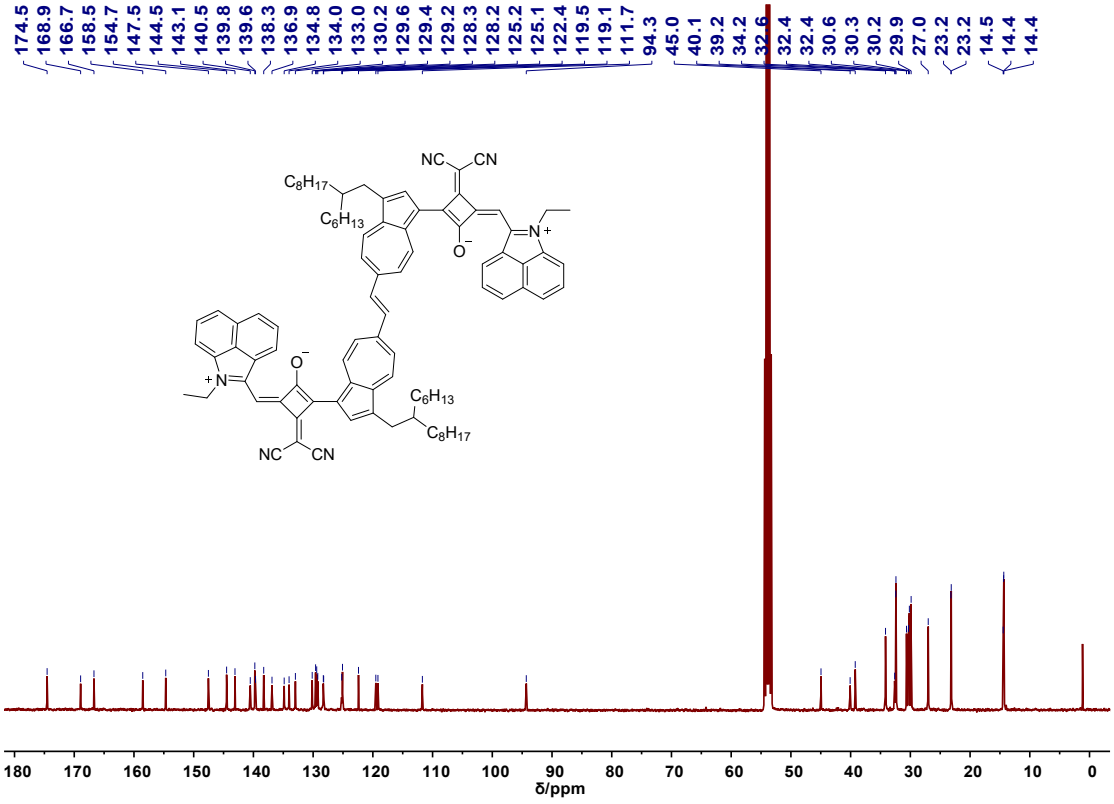


Figure S39. ^{13}C NMR spectrum of **Az-BSQ-D** (CD_2Cl_2, 100 MHz)

High Resolution ESI-MS REPORT

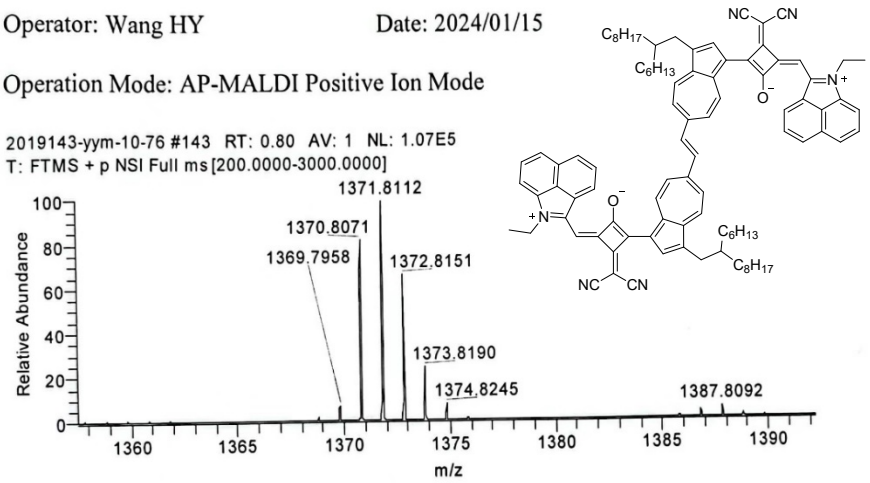
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E-W2024011604

Sample Serial Number: 2019143-yym-10-76

Operator: Wang HY Date: 2024/01/15

Operation Mode: AP-MALDI Positive Ion Mode



Elemental composition search on mass 1370.8071

m/z= 1365.8071-1375.8071

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1370.8071	1370.8059	0.91	49.0	$C_{96}H_{102}O_2N_6$

Figure S40. High resolution MALDI-MS report of **Az-BSQ-D**

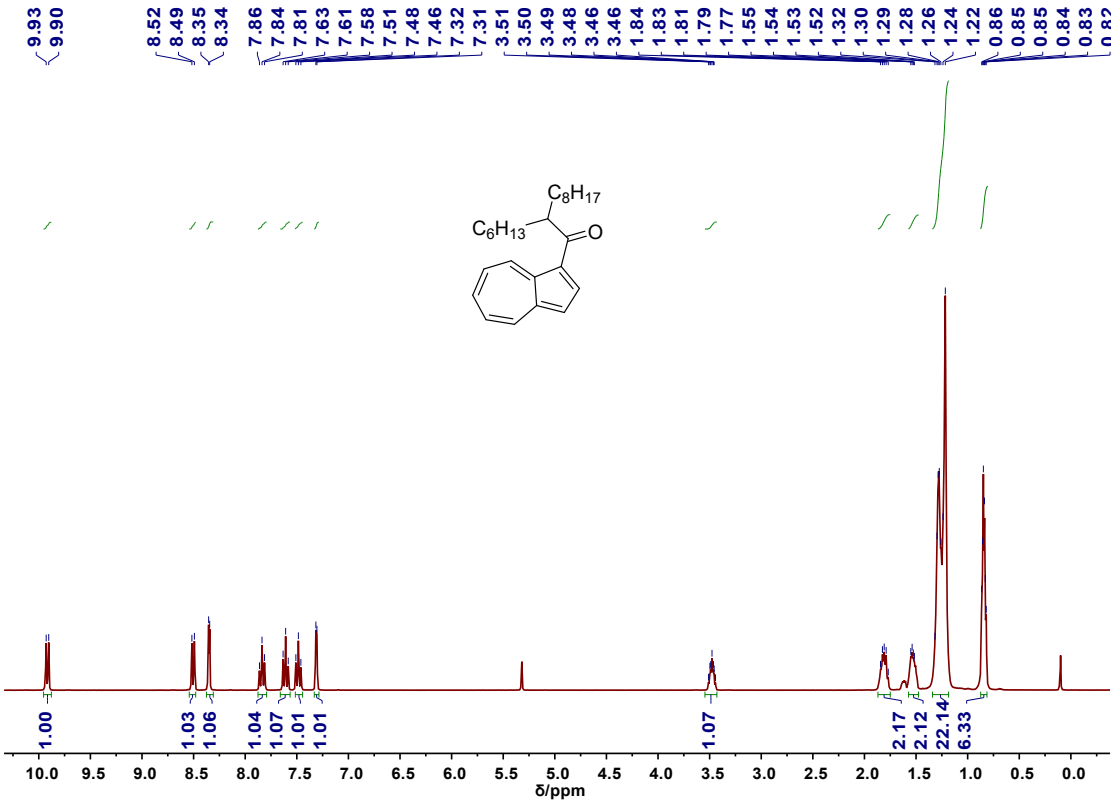


Figure S41. ^{1}H NMR spectrum of **S2** (CD_2Cl_2, 400 MHz)

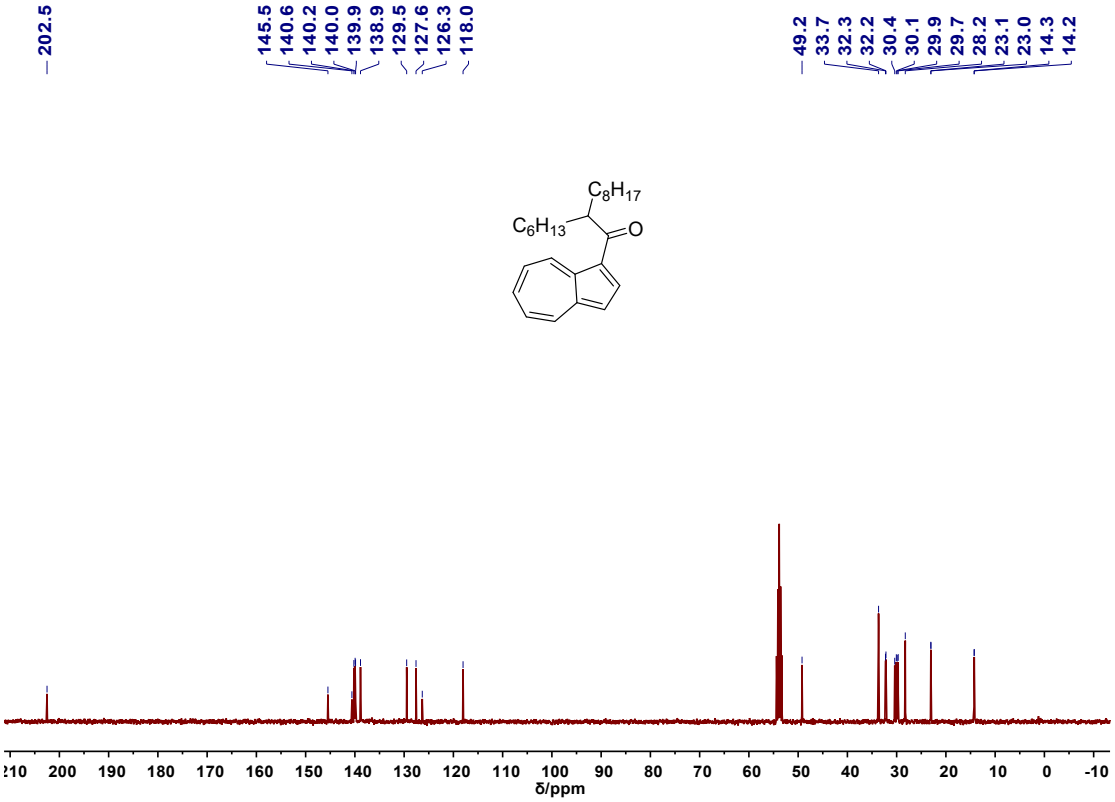


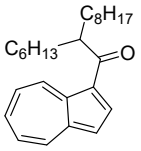
Figure S42. ^{13}C NMR spectrum of **S2** (CD_2Cl_2, 100 MHz)

High Resolution ESI-MS REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E232383

Sample Serial Number: yym-11-62



Operator: Songw Date: 2023/09/13

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 367.2999

m/z= 362.2999-372.2999

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
367.2999	367.2995	0.92	7.5	$C_{26}H_{39}O$

Figure S43. High resolution ESI-MS report of **S2**

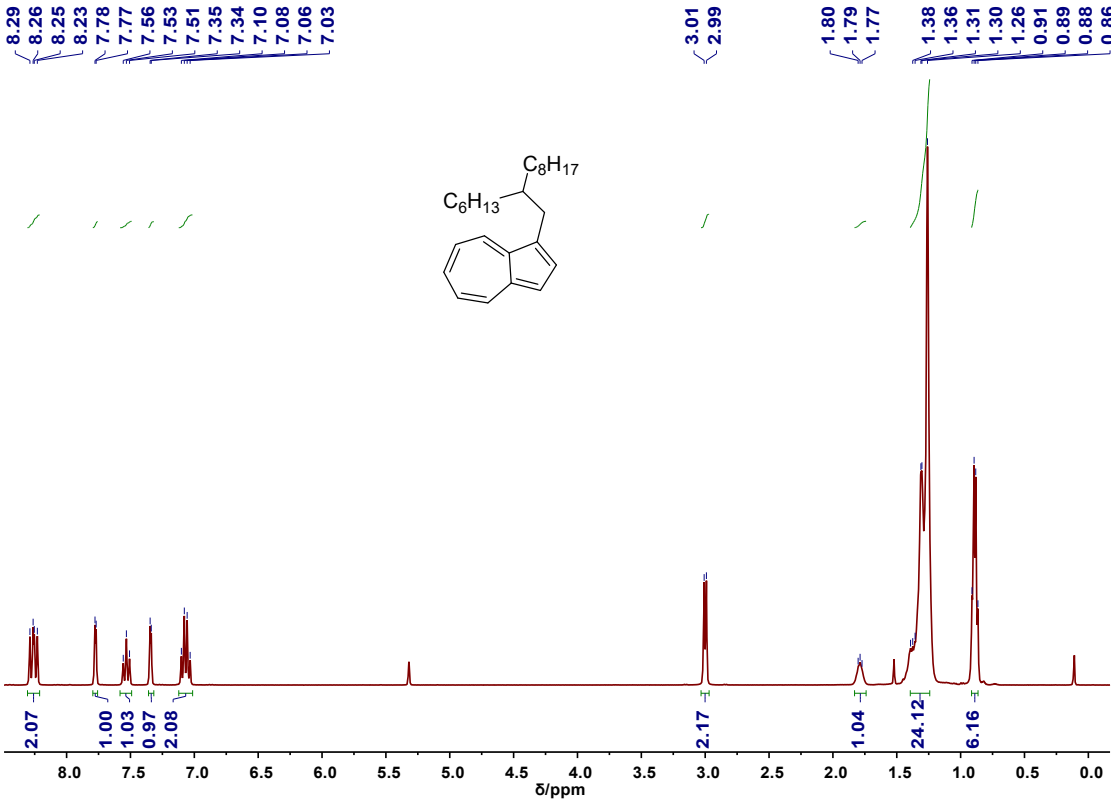


Figure S44. ^{1}H NMR spectrum of **S3** (CD_2Cl_2, 400 MHz)

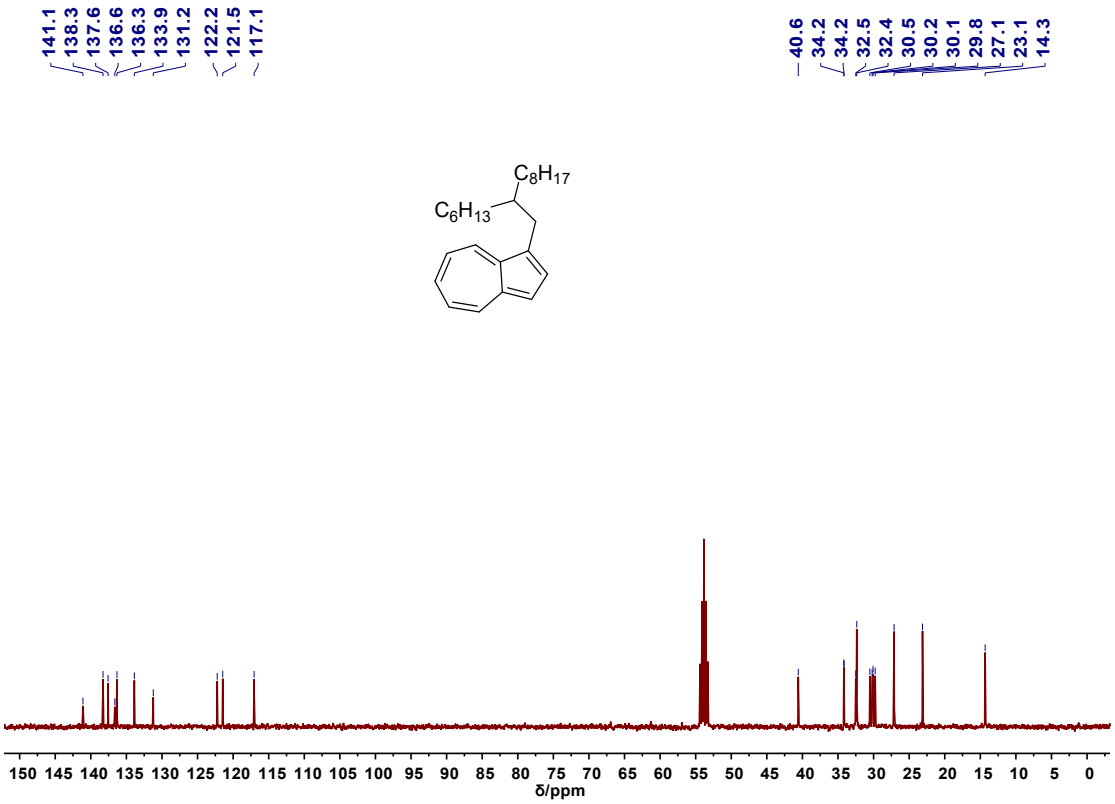


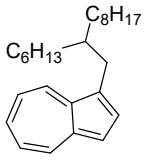
Figure S45. ^{13}C NMR spectrum of **S3** (CD_2Cl_2, 100 MHz)

High Resolution ESI-MS REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E232384

Sample Serial Number: yym-11-63



Operator: Songw Date: 2023/09/13

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 353.3204

m/z= 348.3204-358.3204

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
353.3204	353.3203	0.43	6.5	$C_{26}H_{41}$

Figure S46. High resolution ESI-MS report of **S3**

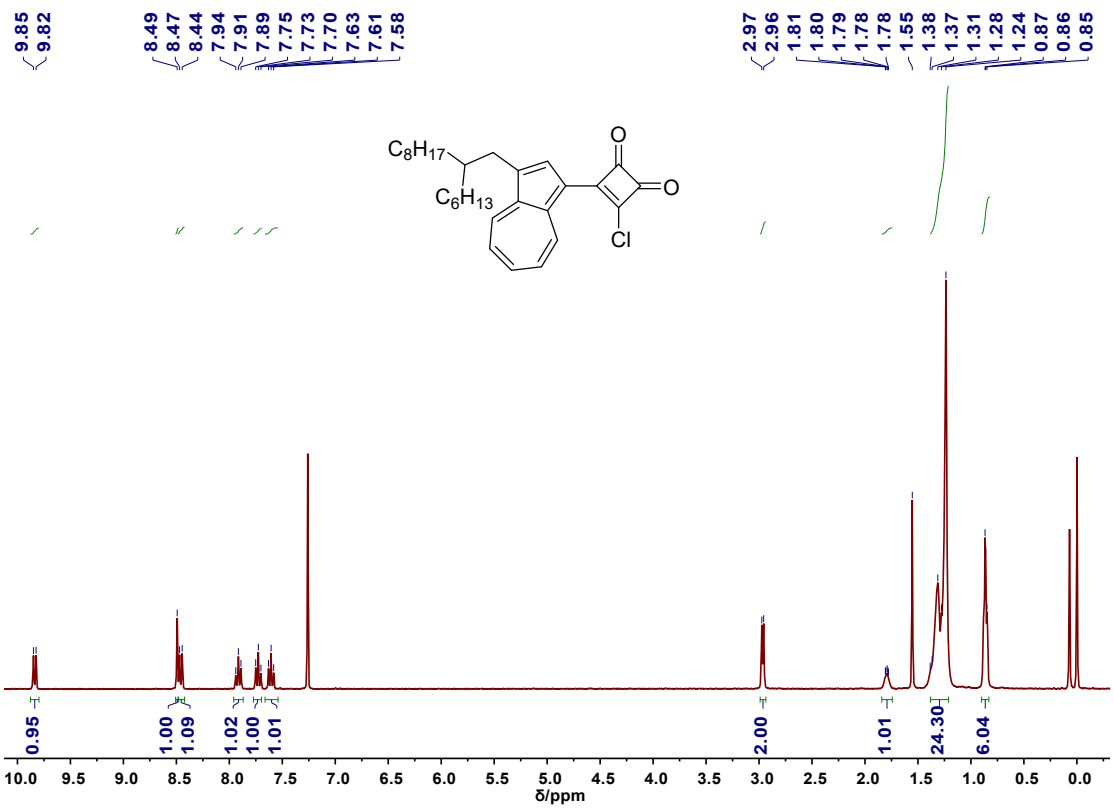


Figure S47. ^{1}H NMR spectrum of **S4** ($CDCl_3$, 400 MHz)

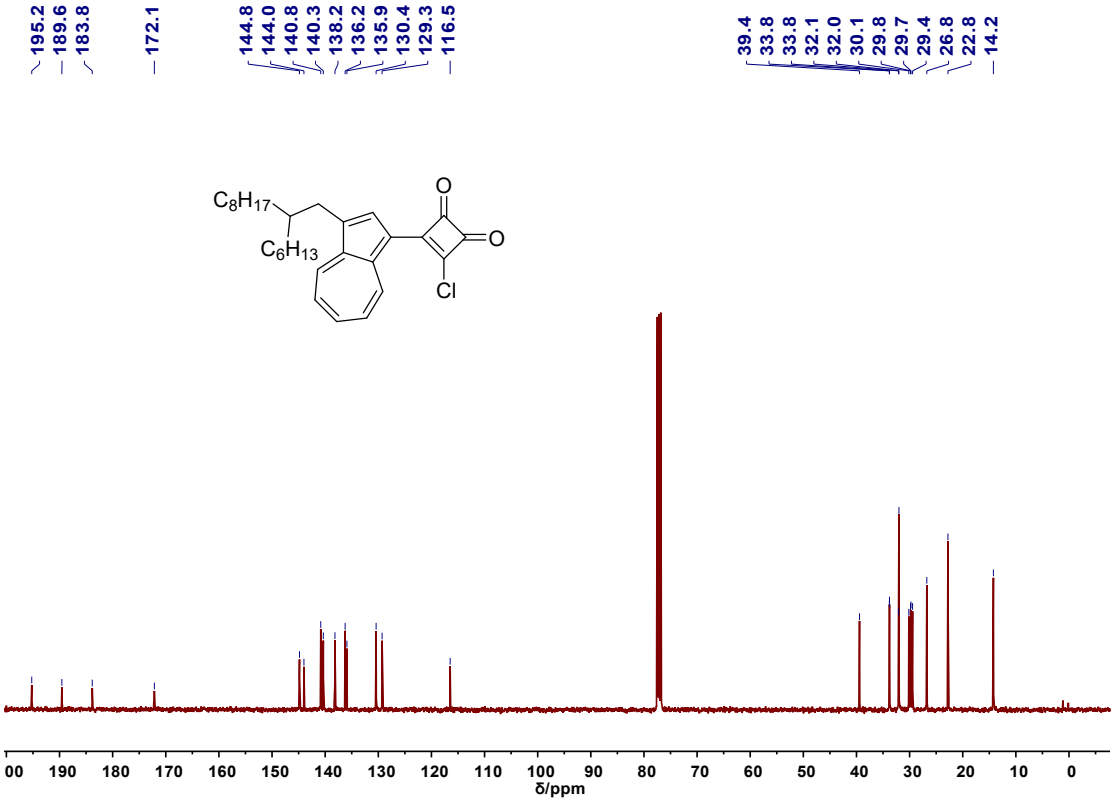


Figure S48. ^{13}C NMR spectrum of **S4** ($CDCl_3$, 100 MHz)

High Resolution ESI-MS REPORT

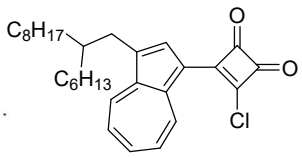
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E232385

Sample Serial Number: yym-11-64

Operator: Songw Date: 2023/09/13

Operation Mode: ESI Positive Ion Mode



Elemental composition search on mass 467.2715

m/z= 462.2715-472.2715

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
467.2715	467.2711	0.67	10.5	$C_{30}H_{40}O_2Cl$
	467.2733	-4.02	19.5	$C_{36}H_{35}$
	467.2693	4.59	15.5	$C_{31}H_{35}O_2N_2$

Figure S49. High resolution ESI-MS report of **S4**

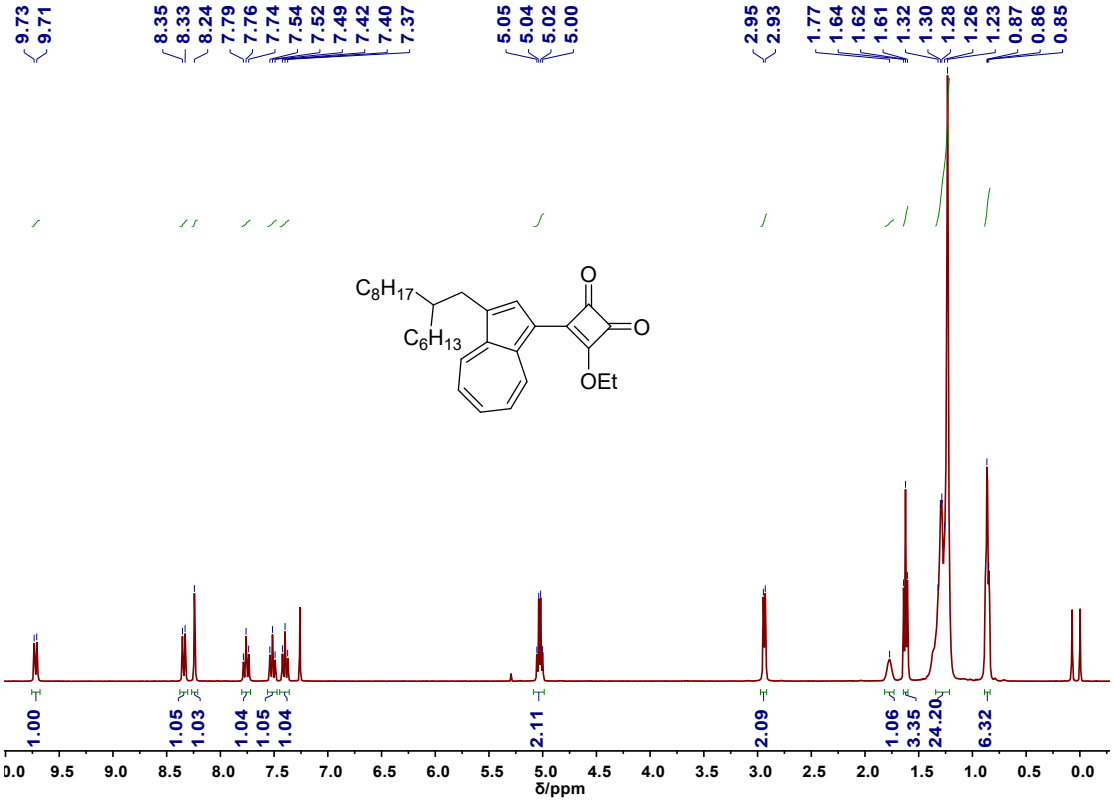


Figure S50. ^{1}H NMR spectrum of **S5** ($CDCl_3$, 400 MHz)

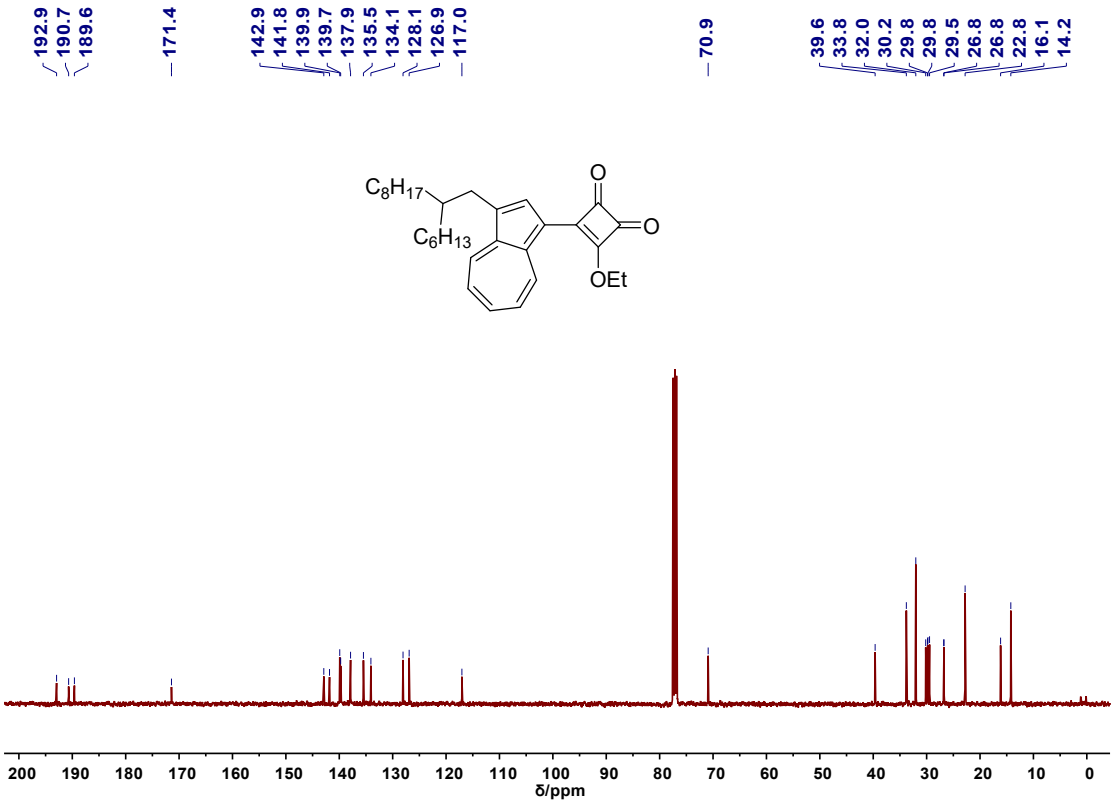


Figure S51. ^{13}C NMR spectrum of **S5** ($CDCl_3$, 100 MHz)

High Resolution ESI-MS REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E232386

Sample Serial Number: yym-11-65

Operator: Songw Date: 2023/09/13

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 477.3366

m/z= 472.3366-482.3366

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
477.3366	477.3363	0.60	10.5	$C_{32}H_{45}O_3$

Figure S52. High resolution ESI-MS report of **S5**

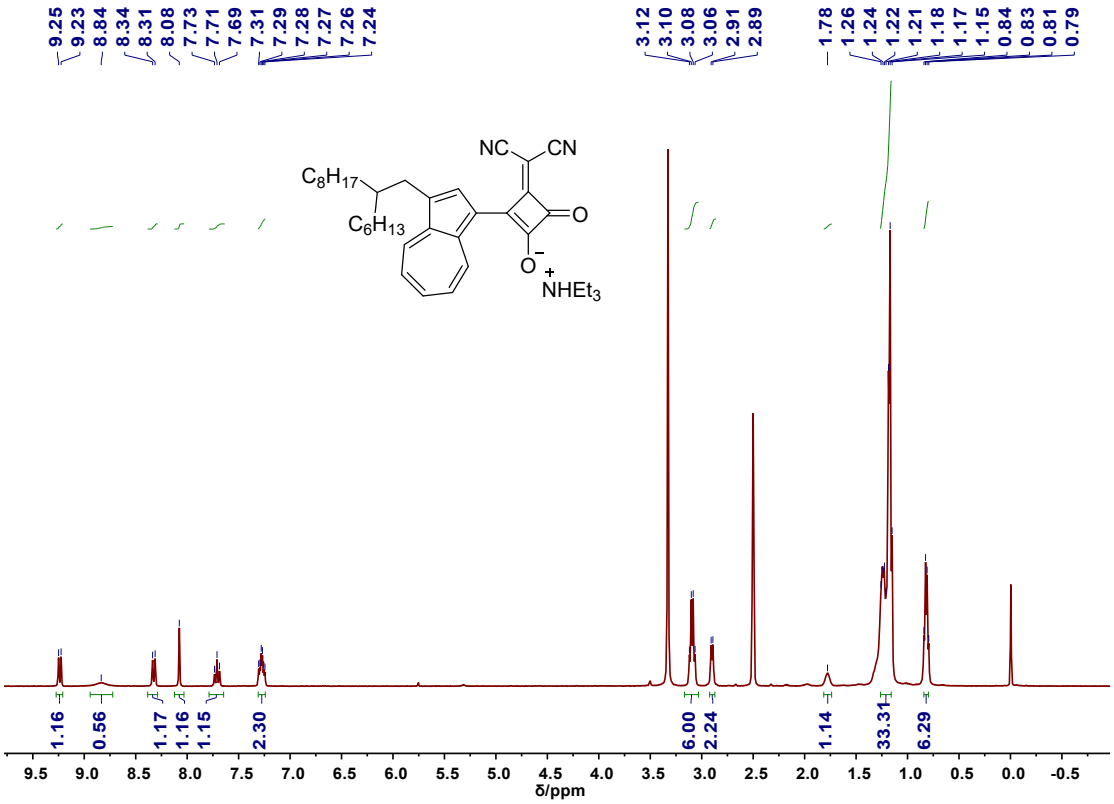


Figure S53. [1]H NMR spectrum of **S6** (DMSO-d_6, 400 MHz)

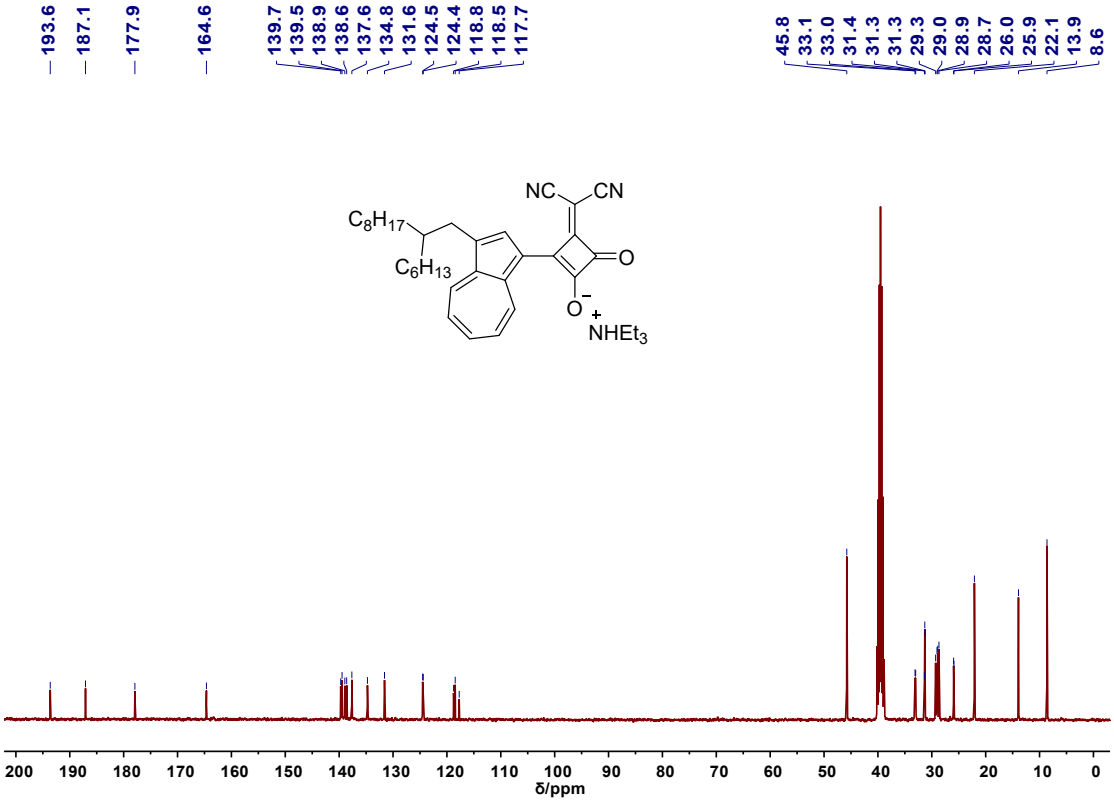


Figure S54. [13]C NMR spectrum of **S6** (DMSO-d_6, 100 MHz)

High Resolution ESI-MS REPORT

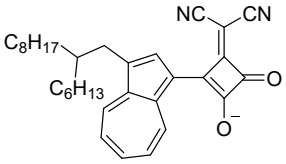
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E232389

Sample Serial Number: yym-11-66

Operator: Songw Date: 2023/09/13

Operation Mode: ESI Negative Ion Mode



Elemental composition search on mass 495.3015

m/z= 490.3015-500.3015

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
495.3015	495.3017	-0.45	15.5	$C_{33}H_{39}O_2N_2$
	495.3004	2.26	16.0	$C_{31}H_{37}ON_5$
	495.2990	4.96	11.0	$C_{30}H_{41}O_5N$

Figure S55. High resolution ESI-MS report of **S6**

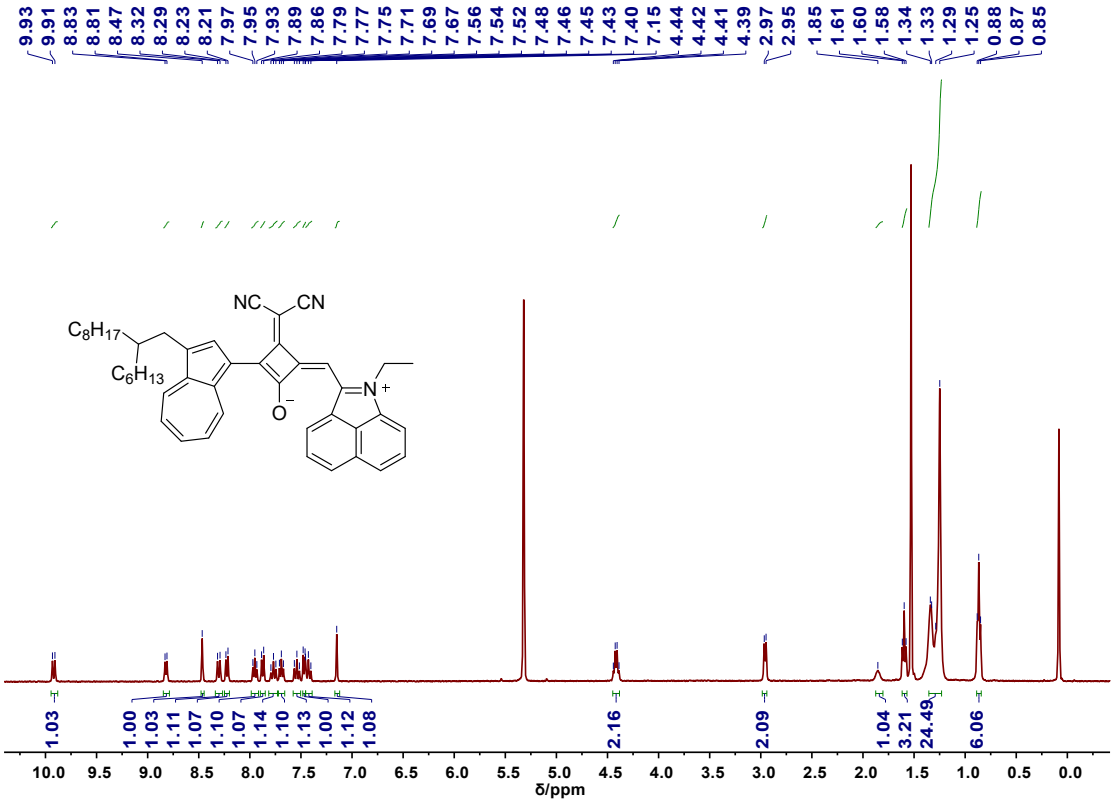


Figure S56. ^{1}H NMR spectrum of **Az-SQ** (CD_2Cl_2, 400 MHz)

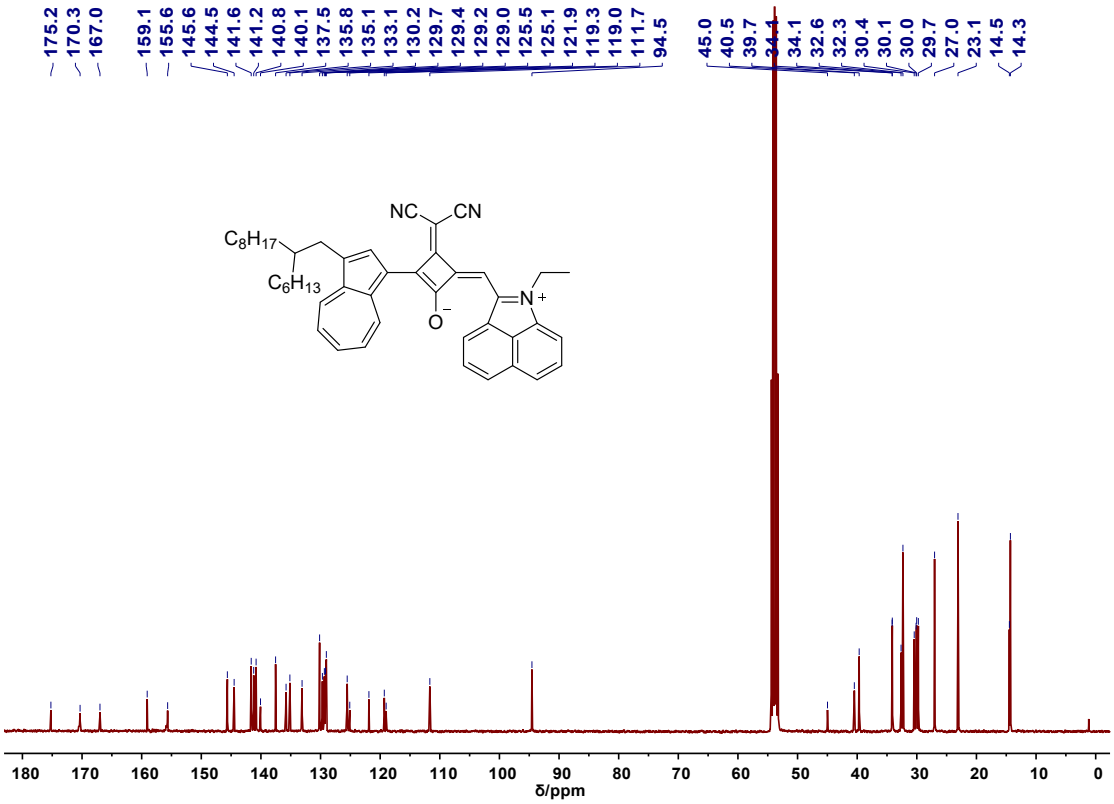


Figure S57. ^{13}C NMR spectrum of **Az-SQ** (CD_2Cl_2, 100 MHz)

High Resolution ESI-MS REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E232387

Sample Serial Number: yym-11-67

Operator: Songw Date: 2023/09/13

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 674.4110

m/z= 669.4110-679.4110

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
674.4110	674.4105	0.77	23.5	$C_{47}H_{52}ON_3$
	674.4078	4.75	19.0	$C_{44}H_{54}O_4N_2$

Figure S58. High resolution ESI-MS report of **Az-SQ**

5. Cartesian Coordinates in DFT calculations

Table S2. Cartesian coordinates of optimized **Az-SQ** based on B3LYP/6-31G(d,p)

Atom	x	y	z
C	-0.419913	-1.278074	0.049513
C	-1.183463	-0.04078	0.018601

C	0.072083	0.734386	0.129738
C	0.842256	-0.534562	0.040759
C	-2.543634	0.293626	-0.162764
O	0.346629	1.925487	0.259078
C	2.138543	-1.032078	-0.037717
C	-3.556571	-0.597229	-0.629327
C	-4.789068	0.033326	-0.717512
C	-4.612533	1.387539	-0.300765
C	-3.184908	1.574583	0.037801
C	-5.630478	2.341846	-0.233891
C	-5.572652	3.679952	0.151673
C	-4.460404	4.417868	0.575808
C	-3.14039	4.001857	0.718576
C	-2.573152	2.737286	0.485557
C	3.408742	-0.445853	-0.093449
N	4.532639	-1.269097	-0.159676
C	3.907716	0.938347	-0.112648
C	5.31179	0.842986	-0.176184
C	5.704286	-0.503697	-0.197018
C	6.20596	1.921296	-0.21596
C	7.589909	1.584092	-0.275541
C	7.974987	0.253134	-0.290299
C	7.048129	-0.825959	-0.250493
C	3.343852	2.209104	-0.087366
C	4.21735	3.323711	-0.126469
C	5.601125	3.206077	-0.189158
C	4.546348	-2.735588	-0.115667
C	-6.056811	-0.647709	-1.159812
C	4.499776	-3.297255	1.307416
H	-4.656777	5.45894	0.826082
H	-2.440821	4.760984	1.061208
H	-6.617265	1.987933	-0.523703
H	-5.85968	-1.169137	-2.106334
H	-6.841277	0.087814	-1.382117
H	-3.388456	-1.630626	-0.894575
H	2.269809	2.354377	-0.024461
H	3.776863	4.316643	-0.104596
H	6.220881	4.098901	-0.216624
H	8.340561	2.368795	-0.307904
H	9.033339	0.011823	-0.333218
H	7.408445	-1.849456	-0.260135
H	3.711306	-3.120296	-0.705672
H	5.460277	-3.051574	-0.626966
H	5.348533	-2.939406	1.899838

H	3.573823	-3.010039	1.813161
H	4.532356	-4.390542	1.269797
H	2.161846	-2.112791	-0.06456
H	-6.515683	4.220732	0.118014
H	-1.502076	2.670012	0.658669
C	-6.611682	-1.682212	-0.144726
H	-5.80197	-2.391048	0.076959
C	-7.774768	-2.464184	-0.770166
H	-8.153995	-3.223727	-0.076984
H	-8.610473	-1.797177	-1.021988
H	-7.46583	-2.975508	-1.689642
C	-7.037575	-1.021198	1.172657
H	-6.207433	-0.481608	1.64096
H	-7.857108	-0.307497	1.009043
H	-7.39171	-1.77238	1.887793
C	-0.693119	-2.644807	0.121482
C	-1.990152	-3.18799	0.332956
C	0.359706	-3.602596	0.061786
N	-3.041775	-3.660023	0.517718
N	1.230814	-4.378528	-0.00076

Table S3. Cartesian coordinates of optimized **Az-BSQ-S** based on B3LYP/6-31G(d,p)

Atom	x	y	z
C	-7.148436	-2.416297	-0.540801
C	-5.840273	-1.977014	-0.080047
C	-6.259447	-0.567618	-0.235308
C	-7.623665	-1.030512	-0.603879
C	-4.681756	-2.611886	0.425565
O	-5.701243	0.521662	-0.119348
C	-8.898925	-0.56612	-0.900993
C	-7.769706	-3.62182	-0.866965
C	-4.594198	-3.978111	0.832772
C	-3.329262	-4.28681	1.31571
C	-2.534939	-3.106133	1.225436
C	-3.383037	-2.029433	0.675569
C	-1.189856	-3.011891	1.587782
C	-0.315173	-1.929701	1.538491
C	-0.546654	-0.606309	1.110116
C	-1.75656	-0.096217	0.620771
C	-2.99802	-0.720299	0.422222
C	-9.488817	0.703745	-0.963892
N	-10.834649	0.806842	-1.309705
C	-9.013914	2.076814	-0.731531
C	-10.120589	2.914737	-0.971152

C	-11.237666	2.147931	-1.333226
C	-10.128587	4.312194	-0.868369
C	-11.367262	4.953603	-1.162493
C	-12.468142	4.193909	-1.524704
C	-12.436216	2.774587	-1.621709
C	-7.815464	2.675257	-0.358525
C	-7.785725	4.08696	-0.24417
C	-8.89117	4.894722	-0.48537
C	-11.729039	-0.294163	-1.686974
C	-2.925237	-5.642134	1.831326
C	-11.617175	-0.682829	-3.163126
C	7.254937	2.355881	-0.043962
C	5.931036	1.862103	0.304253
C	6.348456	0.490852	-0.060004
C	7.724984	0.992929	-0.31073
C	4.760009	2.420122	0.866334
O	5.781441	-0.597486	-0.135264
C	9.006201	0.568195	-0.641163
C	7.892879	3.591315	-0.158337
C	4.662236	3.712877	1.471146
C	3.386009	3.95243	1.957798
C	2.596269	2.797013	1.680616
C	3.456258	1.811165	0.998223
C	1.251918	2.649928	2.02389
C	0.379386	1.584195	1.814202
C	0.614352	0.343879	1.187519
C	1.828895	-0.086599	0.634125
C	3.073951	0.554354	0.548005
C	9.590955	-0.681477	-0.886595
N	10.946314	-0.742153	-1.205391
C	9.102358	-2.069431	-0.887766
C	10.211423	-2.869878	-1.224794
C	11.342827	-2.066522	-1.428771
C	10.209356	-4.266132	-1.343444
C	11.453093	-4.865244	-1.69903
C	12.568198	-4.06873	-1.904761
C	12.546387	-2.651612	-1.777549
C	7.890401	-2.707657	-0.64822
C	7.85014	-4.119373	-0.758943
C	8.958173	-4.889742	-1.092781
C	11.857823	0.395321	-1.377096
C	2.930098	5.214576	2.636744
C	11.794782	1.012829	-2.776153
C	-7.102566	-4.87589	-0.932528

N	-6.581116	-5.917729	-1.005064
C	-9.146456	-3.65701	-1.232414
N	-10.278764	-3.676748	-1.51898
C	7.23802	4.84837	-0.044891
N	6.731225	5.897243	0.031057
C	9.280082	3.668932	-0.474653
N	10.420408	3.722454	-0.722475
H	2.312326	4.965823	3.51132
H	3.811157	5.740237	3.027151
C	2.136241	6.199695	1.735702
H	1.26057	5.662145	1.341184
C	2.968842	6.688915	0.543543
H	3.874918	7.208961	0.877744
H	3.289566	5.861651	-0.09693
H	2.388892	7.386322	-0.072429
C	1.62859	7.379621	2.576783
H	1.03181	8.06851	1.967876
H	1.003747	7.042326	3.413211
H	2.46758	7.949998	2.995604
H	-3.30396	-6.400353	1.133919
H	-1.832223	-5.749478	1.829704
C	-3.455531	-5.982335	3.249137
H	-4.547271	-5.852746	3.227111
C	-2.888928	-5.044124	4.322727
H	-1.797323	-5.144433	4.395371
H	-3.117104	-3.994956	4.106256
H	-3.306579	-5.28116	5.308114
H	-3.774822	-0.070011	0.02844
H	-1.731386	0.947942	0.319797
H	0.686524	-2.131704	1.908028
H	-0.751799	-3.928118	1.977377
H	-5.405193	-4.689311	0.774082
H	-9.584612	-1.369259	-1.132382
H	-11.526097	-1.15659	-1.048099
H	-12.743917	0.037457	-1.44938
H	-11.845673	0.168506	-3.813017
H	-10.612601	-1.044245	-3.399455
H	-12.321063	-1.491807	-3.381608
H	-13.329038	2.232065	-1.914941
H	-13.404481	4.697132	-1.748448
H	-11.44746	6.035455	-1.104355
H	-8.807549	5.973713	-0.381981
H	-6.848825	4.554789	0.045094
H	-6.921066	2.08913	-0.170905

H	0.81336	3.49906	2.544297
H	-0.622616	1.724815	2.21042
H	3.855444	-0.032463	0.072215
H	1.804853	-1.072203	0.176404
H	5.477554	4.416673	1.551802
H	10.80029	1.417677	-2.982792
H	12.509867	1.838573	-2.842919
H	12.038721	0.272096	-3.545023
H	12.862961	0.020077	-1.16419
H	11.639528	1.148445	-0.616654
H	9.702751	1.390864	-0.723267
H	6.993812	-2.149827	-0.396157
H	6.902676	-4.617848	-0.574078
H	8.866094	-5.970697	-1.163272
H	11.52603	-5.943487	-1.809911
H	13.508328	-4.539522	-2.177814
H	13.450411	-2.0784	-1.955392
C	-3.158198	-7.44993	3.586093
H	-3.559994	-7.717225	4.570325
H	-3.600137	-8.128056	2.846896
H	-2.076347	-7.637128	3.607791

Table S4. Cartesian coordinates of optimized **Az-BSQ-D** based on B3LYP/6-31G(d,p)

Atom	x	y	z
C	8.505709	1.642523	0.603762
C	7.053237	1.602965	0.544205
C	7.116521	0.270986	-0.094005
C	8.598945	0.386929	-0.146584
C	6.010678	2.503213	0.859741
O	6.286626	-0.57638	-0.41798
C	9.741245	-0.252893	-0.616107
C	9.480517	2.459599	1.176155
C	6.176033	3.898955	1.12361
C	4.960312	4.51527	1.381621
C	3.945895	3.514629	1.292914
C	4.595335	2.237515	0.94461
C	2.58139	3.729588	1.499074
C	1.512965	2.841284	1.444868
C	1.49237	1.454605	1.169559
C	2.61384	0.673379	0.835054
C	3.967981	1.01085	0.749413
C	9.970291	-1.411296	-1.37309
N	11.28409	-1.827544	-1.600351
C	9.0966	-2.350605	-2.080777

C	9.953214	-3.273089	-2.710554
C	11.29901	-2.968414	-2.428626
C	9.531025	-4.342754	-3.514852
C	10.556194	-5.160964	-4.066973
C	11.879536	-4.867019	-3.792617
C	12.285873	-3.775351	-2.976841
C	7.725083	-2.494307	-2.259427
C	7.267771	-3.565659	-3.062661
C	8.12635	-4.467787	-3.678177
C	12.425397	-1.106487	-0.999101
C	4.802962	5.975202	1.712921
C	0.164597	0.828261	1.235552
C	13.807143	-1.721097	-1.186494
C	-8.463112	-1.417813	0.989844
C	-7.007773	-1.372172	0.94527
C	-7.076057	-0.157607	0.102447
C	-8.555033	-0.287549	0.061513
C	-5.956002	-2.192795	1.409855
O	-6.248469	0.626957	-0.35737
C	-9.689303	0.254398	-0.533169
C	-9.451508	-2.150306	1.64863
C	-6.111308	-3.51349	1.945839
C	-4.890173	-4.071503	2.284023
C	-3.881138	-3.105115	1.980024
C	-4.540227	-1.916546	1.413766
C	-2.515238	-3.284545	2.202077
C	-1.44539	-2.426378	1.965568
C	-1.43011	-1.116613	1.436781
C	-2.559154	-0.408649	0.980755
C	-3.913996	-0.750024	0.981445
C	-9.919136	1.308971	-1.425763
N	-11.230093	1.607332	-1.795678
C	-9.059167	2.262329	-2.145016
C	-9.926417	3.059368	-2.917795
C	-11.256546	2.662878	-2.714758
C	-9.54059	4.103026	-3.769666
C	-10.595864	4.773565	-4.454757
C	-11.90862	4.377777	-4.254565
C	-12.276825	3.314681	-3.383181
C	-7.695608	2.522845	-2.223843
C	-7.268124	3.570942	-3.075649
C	-8.14237	4.344656	-3.830455
C	-12.443831	0.906877	-1.360236
C	-4.655821	-5.419946	2.918473

C	-12.764138	-0.327876	-2.206486
C	-0.102427	-0.491121	1.363608
C	9.194223	3.546048	2.048241
N	8.987638	4.436355	2.774438
C	10.866827	2.192012	0.983216
N	12.001473	1.971083	0.815262
C	-9.202225	-3.132974	2.64555
N	-9.036738	-3.941551	3.471222
C	-10.832192	-1.894106	1.405179
N	-11.961934	-1.68166	1.197725
H	-6.973365	1.951168	-1.649228
H	7.01544	-1.82808	-1.77966
H	5.341366	6.563925	0.957877
H	3.751543	6.283217	1.637945
C	5.344068	6.372512	3.112197
H	6.387178	6.032024	3.169088
C	5.328962	7.899023	3.27004
H	4.30548	8.293329	3.209457
H	5.742028	8.196677	4.240568
H	5.923229	8.388974	2.489571
C	4.561111	5.693802	4.243631
H	4.587523	4.602409	4.155481
H	4.981479	5.958786	5.220404
H	3.508441	6.009418	4.239639
H	-4.46095	-5.26989	3.991776
H	-3.735394	-5.866205	2.512821
C	-5.797869	-6.448525	2.769613
H	-6.729948	-5.977563	3.110133
C	-5.533537	-7.65881	3.677086
H	-5.454885	-7.361372	4.729444
H	-6.34366	-8.392378	3.596957
H	-4.598692	-8.164379	3.399709
C	-5.980274	-6.894998	1.311247
H	-6.820789	-7.59226	1.219349
H	-6.173169	-6.048761	0.643699
H	-5.080087	-7.408617	0.947322
H	12.431524	-0.085544	-1.397056
H	12.224558	-1.018617	0.073123
H	14.129038	-1.718274	-2.231303
H	14.513467	-1.102421	-0.62426
H	13.867597	-2.738853	-0.790512
H	13.341716	-3.614909	-2.817121
H	12.659308	-5.492849	-4.21757
H	10.300085	-6.006133	-4.699628

H	7.723432	-5.272826	-4.287732
H	6.196272	-3.681956	-3.199197
H	-12.342359	0.633887	-0.307513
H	-13.258221	1.635128	-1.416276
H	-12.89898	-0.060141	-3.259818
H	-11.965193	-1.071499	-2.136076
H	-13.685374	-0.792163	-1.840946
H	-10.593033	-0.257761	-0.234197
H	-6.202682	3.774672	-3.137102
H	-7.75499	5.135905	-4.467502
H	-10.371085	5.592072	-5.132825
H	-12.701697	4.89709	-4.785102
H	-13.321765	3.045221	-3.269343
H	0.542408	3.282411	1.661971
H	2.306915	4.752115	1.748471
H	4.623296	0.193214	0.459154
H	2.403863	-0.362506	0.585308
H	7.124198	4.416076	1.111952
H	10.642083	0.272821	-0.335072
H	0.730066	-1.181887	1.477484
H	-0.667032	1.52932	1.228578
H	-0.471686	-2.823002	2.245397
H	-2.353204	0.562212	0.539675
H	-4.573582	0.003397	0.558037
H	-2.239118	-4.243641	2.635336
H	-7.06154	-4.009395	2.063261

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