Chemical Communications

Electronic Supplementary Information (ESI)

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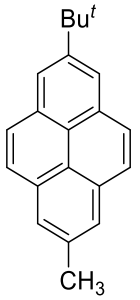
1. Experimental Section

1.1 General

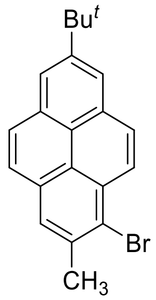
All reagents and starting materials were purchased from commercial sources and used without further purification. Anhydrous dichloromethane (DCM) was distilled from CaH_2. Anhydrous THF and toluene were distilled from sodium-benzophenone immediately prior to use. 1,5-Dibromo-2,6-dimethylnaphthalene (*J. Am. Chem. Soc.* **1942**, *64,* 2875), 2-methyl-1-naphthylboronic acid (*Synlett*, **2003**, *5*, 705), 4-*tert*-butyl-2,6-dimethylbromobenzene (*J. Org. Chem.* **2003**, *68*, 6071) and 2-bromo-7-(*tert*-butyl)pyrene (*Chem. Eur. J.* **2013**, *19*, 16295) were prepared according to the literatures. ^1H and ^{13}C NMR spectra were recorded using 300 MHz, 400 MHz and 500 MHz Bruker spectrometer in $CDCl_3$, CD_2Cl_2, CD_3CN, DMSO or THF-d_8 with tetramethylsilane (TMS) as the internal standard. The chemical shift was recorded in ppm and the following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. HR ESI and APCI mass spectra were recorded on a MicrOTOF-QII instrument. UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Cyclic voltammetry measurements were performed in dry dichloromethane on a CHI 620C electrochemical analyzer with a three-electrode cell, using 0.1 M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, gold disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mV s^{-1} . The potential was externally calibrated against the ferrocene/ferrocenium couple. The single crystal was measured at low temperature (T = 100K) on a four circles goniometer Kappa geometry Bruker AXS D8 Venture equipped with a Photon 100 CMOS active pixel sensor detector using a Copper monochromatized (λ = 1.54178 Å) X-ray radiation. Continuous wave X-band ESR spectra were obtained with a Bruker ELEXSYS E500 spectrometer using a variable temperature Bruker liquid nitrogen cryostat.

1.2 Synthetic procedures and characterization data



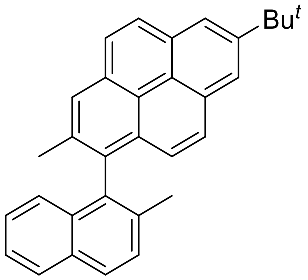
1

A solution of 2-bromo-7-(*tert*-butyl) pyrene (1mmol, 337 mg) in 100 mL of freshly distilled THF was cooled to -78 ºC, and *n*-butyllithium solution (1.1 mmol, 0.55 mL, 2M) was carefully added under nitrogen atmosphere. After stirring for 1h, pure iodomethane (1.5 mmol, 0.1 mL) was added. The mixture was stirred at -78 ºC and was allowed to warm to room temperature through overnight. The mixture was quenched with $Na_2S_2O_3$ solution, and was extracted with ether. The extract was dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the crude product was purified by column chromatography (silica gel, hexanes/DCM =9/1) to afford white compound **1** in 95% yield (258 mg). ^1H NMR (500 MHz, Chloroform-*d*): δ 8.20 (s, 2H), 8.03 (d, *J* = 8.9 Hz, 2H), 7.98 (d, *J* = 9.0 Hz, 2H), 7.97 (s, 2H), 2.80 (s, 3H), 1.59 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 131.17 , 130.83 , 127.73 , 127.09 , 125.62 , 122.26 , 77.16 , 32.12 , 22.22 . HRMS analysis (APCI): calcd for $C_{21}H_{21}$ $(M+H)^+$: 273.1645; found: 273.1638 (error: -2.7 ppm).



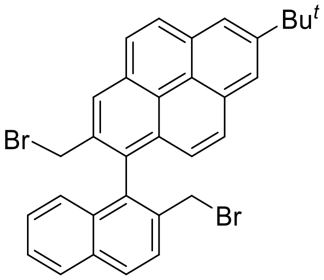
2

A solution of bromine (0.15 mL, 3 mmol) in anhydrous DCM (16 mL) was add dropwise to a degassed solution of compound **1** (1.62 g, 6 mmol) in anhydrous DCM (50 mL) at -78 ℃ under nitrogen atmosphere. The resulting mixture was allowed to slowly warmed up to room temperature and stirred overnight. Br_2 was neutralized with $Na_2S_2O_3$ solution. The organic layer was washed with saturated NaCl solution, dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by column chromatography (silica gel, hexane) to give the compound **2** as white solid in 90% yield (1.9 g). ^{1}H NMR (500 MHz, Methylene Chloride-d_2): δ 8.47 (d, J = 9.3 Hz, 1H), 8.28 – 8.25 (m, 2H), 8.15 (d, J = 9.3 Hz, 1H), 8.06 (d, J = 8.9 Hz, 1H), 8.04 (s, 1H), 7.95 (d, J = 8.9 Hz, 1H), 2.85 (s, 3H), 1.57 (s, 9H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2): δ 130.76 , 130.21 , 129.55 , 128.32 , 126.96 , 126.88 , 126.32 , 123.47 , 123.11 , 53.84 , 32.03 , 24.86 . HRMS analysis (APCI): calcd for $C_{21}H_{20}Br$ $(M+H)^+$: 351.0735; found: 351.0743 (error: 2.3 ppm).



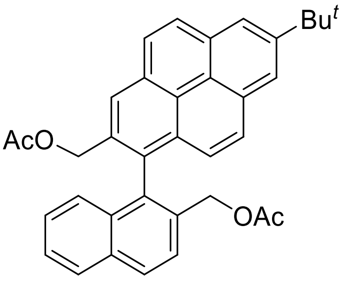
3

An oven-dried two-neck round bottom flask was charged with compound **2** (4.8 mmol, 1.68 g), 2-methyl-1-naphthylboronic acid (14.4 mmol, 2.68 g), Pd-PEPPSI-IPent (8 mmol%, 300 mg), *t*BuOK (14.4 mmol, 1.61g), 4 Å molecular sieve and purged with argon for 5 min. Dioxane (11.5 mL) and *t*BuOH (26.9 mL) were added subsequently under argon, then the mixture was purged with argon under -78 ℃ for 3 times. The resultant mixture was heated at 90 ℃ for 24h. After cooling to room temperature, water was added and the reaction mixture was extracted with dichloromethane. The organic layer was dried over sodium sulfate and then the solvent was removed under vacuum. The crude mixture was subjected to silica gel column chromatography (hexane/DCM=9/1) to afford the title product **3** as white solid in 90% yield (1.78 g). ^{1}H NMR (400 MHz, Methylene Chloride-d_2): δ 8.25 (d, J = 1.8 Hz, 1H), 8.20 (s, 1H), 8.15 (d, J = 1.8 Hz, 1H), 8.10 (s, 2H), 7.94 (dd, J = 8.3, 3.7 Hz, 2H), 7.80 (d, J = 9.2 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.23 (d, J = 9.2 Hz, 1H), 7.16 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 6.93 (d, J = 9.0 Hz, 1H), 2.27 (s, 3H), 2.03 (s, 3H), 1.56 (s, 9H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2): δ 131.31 , 131.00 , 129.21 , 128.38 , 128.09 , 127.96 , 127.91 , 127.33 , 126.71 , 126.52 , 125.91 , 125.39 , 125.35 , 122.77 , 122.58 , 53.84 , 35.51 , 32.06 , 20.74 , 20.30 . HRMS analysis (APCI): calcd for $C_{32}H_{29}$ $(M+H)^+$: 413.2260; found: 413.2264 (error: 1.0 ppm).



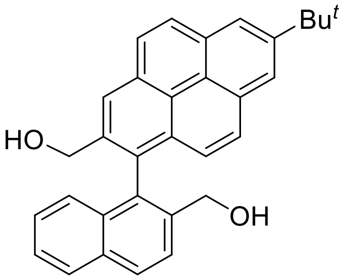
4

Compound **3** (1.76 g, 4.4 mmol), *N*-bromosuccinimide (8.8 mmol, 1.566 g) and benzoyl peroxide (0.88 mmol, 213 mg) were dissolved in 40 mL of CCl_4 and heated at 95 ℃ under nitrogen atmosphere. After 12 hours, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The reside was subjected to silica gel column chromatography using hexane/dichloromethane (9/1) as eluent to afford compound **4** as light yellow solid in 70% yield (1.0 g). ^{1}H NMR (500 MHz, Methylene Chloride-*d*$_2$): δ 8.47 (s, 1H), 8.31 (d, *J* = 1.8 Hz, 1H), 8.21 (d, *J* = 1.8 Hz, 1H), 8.17 (d, *J* = 2.7 Hz, 2H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.27 (d, *J* = 9.2 Hz, 1H), 7.22 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 6.97 (d, *J* = 9.1 Hz, 1H), 4.56 (d, *J* = 10.4 Hz, 1H), 4.48 (d, *J* = 10.4 Hz, 1H), 4.34 (d, *J* = 10.3 Hz, 1H), 4.24 (d, *J* = 10.3 Hz, 1H), 1.56 (s, 9H). ^{13}C NMR (126 MHz, Methylene Chloride-*d*$_2$): δ 150.46 , 135.17 , 135.01 , 133.80 , 131.26 , 130.59 , 129.81 , 128.96 , 128.49 , 128.23 , 127.31 , 127.27 , 127.22 , 127.16 , 127.11 , 123.51 , 123.31 , 122.91 , 53.84 , 33.37 , 33.25 , 32.00 . HRMS analysis (APCI): calcd for $C_{32}H_{27}Br_2$ $(M+H)^+$: 569.0461; found: 569.0474 (error: 2.3 ppm).



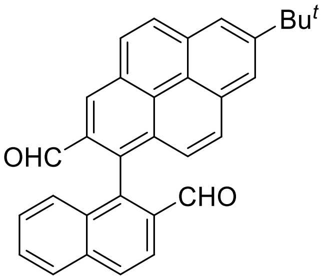
5

The compound **4** (1.14 g, 2 mmol), KOAc (1.96 g, 20 mmol) and *n*-butylammonium bromide (1.288 g, 4 mmol) were dissolved in 30 mL DMF under nitrogen atmosphere. The mixture was heated at 100 °C overnight. After cooling to room temperature, 30 mL ammonium chloride solution was added into the reaction mixture. The mixture was extracted with ethyl acetate (2*30 mL). The combined organic extract was dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexane/EA = 8/2) to afford the target compound **5** (880 mg) in 84% yield. ^{1}H NMR (500 MHz, Methylene Chloride-*d*$_2$): δ 8.38 (s, 1H), 8.31 (d, *J* = 1.8 Hz, 1H), 8.20 (d, *J* = 1.7 Hz, 1H), 8.18 (s, 2H), 8.09 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 9.3 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.26 (s, 1H), 7.22 – 7.18 (m, 1H), 6.97 (d, *J* = 8.6 Hz, 1H), 5.07 – 4.98 (m, 2H), 4.80 (s, 2H), 1.83 (s, 3H), 1.82 (s, 3H), 1.57 (s, 9H). ^{13}C NMR (126 MHz, Methylene Chloride-*d*$_2$): δ 150.18 , 131.50 , 129.11 , 128.68 , 128.67 , 128.50 , 127.53 , 126.97 , 126.71 , 126.63 , 125.37 , 125.35 , 123.35 , 123.12 , 65.31 , 64.93 , 53.84 , 32.03 , 20.83 , 20.77 . HRMS analysis (APCI): calcd for $C_{36}H_{32}O_4$ $(M)^+$: 528.2305; found: 528.2295 (error: -1.8 ppm).



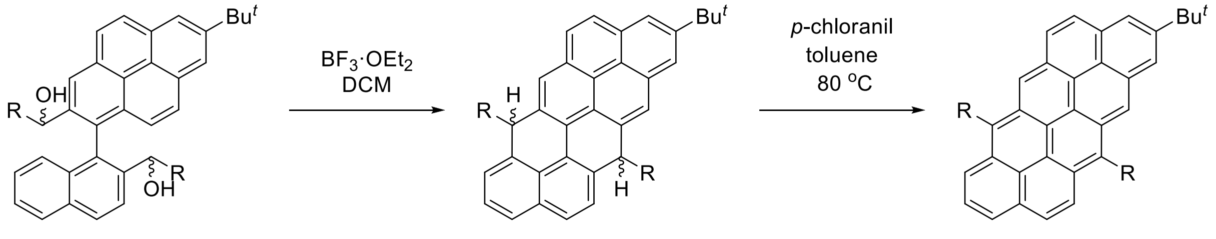
6

The compound **5** (880 mg, 1.67 mmol), KOH (1.87 g, 33.4 mmol) were dissolved in 50 mL methanol under nitrogen atmosphere. The mixture was refluxed overnight. After cooling down to room temperature, the solvent was removed under vacuum and the residue was added with 100 mL water, which was then filtered to give pure white compound **6** (660 mg) in 90% yield. ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.59 (s, 1H), 8.39 (s, 1H), 8.29 (d, *J* = 9.0 Hz, 1H), 8.25 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.94 (dd, *J* = 8.9, 4.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 9.2 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 4.41 (d, *J* = 14.2 Hz, 1H), 4.26 (d, *J* = 14.2 Hz, 1H), 4.11 (d, *J* = 3.4 Hz, 2H), 1.53 (s, 9H). ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 148.85 , 138.65 , 138.51 , 130.11 , 130.07 , 128.14 , 128.01 , 127.93 , 127.66 , 127.37 , 126.43 , 125.55 , 125.34 , 124.86 , 124.17 , 122.91 , 122.45 , 122.17 , 61.09 , 60.85 , 39.52 , 35.00 , 31.64 . HRMS analysis (APCI): calcd for $C_{32}H_{28}O_2$ $(M)^+$: 444.2073; found: 444.2084 (error: 2.4 ppm).



7

A solution of oxalyl chloride (3.2 mL, 37.5 mmol) in 100 mL of freshly distilled CH_2Cl_2 was cooled to -78 °C, and DMSO (5.35 mL, 75 mmol) was carefully added under nitrogen atmosphere. After stirring for 15 min, a solution of compound **6** (660 mg, 1.5 mmol) in CH_2Cl_2 (50 mL) was added and the mixture was stirred at -78 °C for 2h. Et_3N (10.4 mL) was added successively and the solution was stirred at -78 °C for 1h. Then the cooling bath was removed, and the reaction mixture was allowed to warm up to room temperature and stirred for 30 min. The solvent was removed under vacuum and the residue was extracted with ethyl acetate (2*30 mL). The extract was washed with saturated aqueous Na_2CO_3 solution, brine and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the crude product was purified by column chromatography (silica gel, hexane/EA =4/1) to afford yellow compound **7** (528 mg) in 80% yield. ^{1}H NMR (500 MHz, Methylene Chloride-*d*$_2$): δ 9.87 (s, 1H), 9.58 (s, 1H), 8.89 (s, 1H), 8.37 (d, *J* = 1.8 Hz, 1H), 8.30 (d, *J* = 9.0 Hz, 1H), 8.25 (d, *J* = 8.9 Hz, 2H), 8.20 (d, *J* = 3.9 Hz, 2H), 8.16 (s, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 9.3 Hz, 1H), 7.65 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H), 7.37 (d, *J* = 9.2 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 1.57 (s, 9H). ^{13}C NMR (126 MHz, Methylene Chloride-*d*$_2$): δ 192.07 , 191.59 , 141.33 , 134.30 , 134.00 , 132.92 , 132.91 , 131.94 , 131.76 , 130.11 , 129.95 , 129.76 , 129.66 , 128.92 , 128.18 , 128.07 , 127.85 , 127.65 , 125.12 , 124.26 , 124.21 , 123.89 , 122.69 , 53.84 . HRMS analysis (APCI): calcd for $C_{32}H_{25}O_2$ $(M+H)^+$: 441.1845; found: 441.1849 (error: 1.0 ppm).

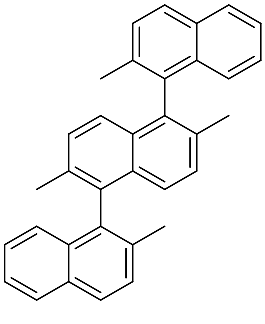


7-a

8

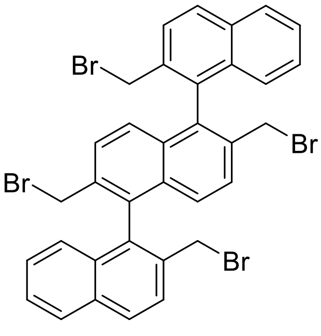
TT-Ar

n-BuLi in hexane (2M, 3 mL, 6 mmol) was added to a solution of 4-*tert*-butyl-2,6-dimethylbromobenzene (1.446 g, 6 mmol) in anhydrous THF (50 mL) at -78 °C and the mixture was stirred at -78 °C for one and half hours. Then the reaction mixture was added with compound **7** (450 mg, 1 mmol) and allowed to warm up to room temperature overnight. The resulting mixture was quenched with water and extracted with ether (3*50 mL). The combined organic extract was dried over Na_2SO_4 and evaporated in vacuum. The crude product was washed by hexane to afford compound **7-a** as a yellow solid (900 mg, quantitative yield), which was used for the next step directly. Boron trifluoride diethyl etherate (0.5 mL) was added to a solution of compound **7-a** (327 mg, 0.3 mmol) in DCM (50 mL) and the yellow solution turned purple immediately. After 30 min, water was added to quench the reaction. The organic layer was separated and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was washed with methanol to afford compound **8** (270 mg) in 90% yield, which was used directly to the next step. Compound **8** (270 mg, 0.27 mmol) was dissolved in 50 mL toluene under nitrogen, *p*-chloranil (246 mg, 1 mmol) was added and the mixture was stirred for 1h at 80 °C. The color of the solution turned to red-orange. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexane/toluene = 4/1) to give the compound **TT-Ar** as red solid in 50% yield (135 mg). ^{1}H NMR (500 MHz, THF-d_8): δ 8.74 (s, 1H), 8.44 (s, 1H), 8.41 (s, 1H), 8.28 (s, 1H), 8.17 (d, J = 6.8 Hz, 1H), 8.05 (d, J = 7.5 Hz, 1H), 8.00 – 7.96 (m, 4H), 7.61 (d, J = 9.4 Hz, 1H), 7.51 (d, J = 4.7 Hz, 4H), 1.99 (s, 6H), 1.87 (s, 7H), 1.59 (s, 9H), 1.56 (d, J = 3.4 Hz, 18H). HRMS analysis (APCI): calcd for $C_{56}H_{55}$ $(M+H)^+$: 727.4313; found: 727.4298 (error: -2.1 ppm).



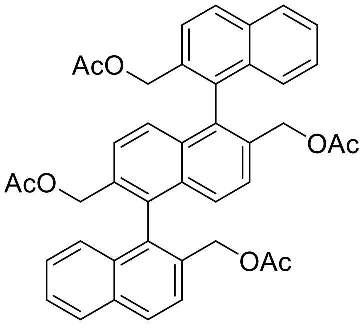
10

An oven-dried two-neck round bottom flask was charged with 1,5-dibromo-2,6-dimethylnaphthalene (126 mg, 0.4 mmol), 1,2-methyl-1-naphthylboronic acid (372 mg, 2 mmol), Pd-PEPPSI-IPent (8 mmol%, 26 mg), *t*BuOK (269 mg, 2.4 mmol), 4 Å molecular sieve and purged with argon for 5 min. Dioxane (1.0 mL) and tBuOH (2.2 mL) were added subsequently under argon, then the mixture was purged under -78 ℃ for three times. The resultant mixture was heated at 90 ℃ for 24h. After cooling to room temperature, water was added and the reaction mixture was extracted with dichloromethane. The organic layer was dried over sodium sulfate and the solvent as removed under vacuum. The crude mixture was subjected to silica gel column chromatography (hexane /DCM=9/1) to afford the compound **10** (104 mg) as white solid in 60% yield. ^{1}H NMR (500 MHz, Methylene Chloride-d_2): δ 7.92 (t, J = 7.5 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.43 (t, J = 7.0 Hz, 1H), 7.28 (t, J = 8.1 Hz, 1H), 7.23 (d, J = 8.6 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 7.08 (d, J = 8.4 Hz, 0H), 7.04 (d, J = 8.6 Hz, 1H), 2.12 (s, 1H), 2.08 (s, 2H), 1.95 (s, 3H). ^{13}C NMR (75 MHz, Methylene Chloride-d_2): δ 133.68 , 133.31 , 132.78 , 131.91 , 129.23 , 128.38 , 127.77 , 126.48 , 126.46 , 126.09 , 125.97 , 125.39 , 125.33 , 125.31 , 53.84 , 20.21 , 19.88 . HRMS analysis (APCI): calcd for $C_{34}H_{29}$ $(M+H)^+$: 437.2259; found: 437.2264 (error: 1.1 ppm).



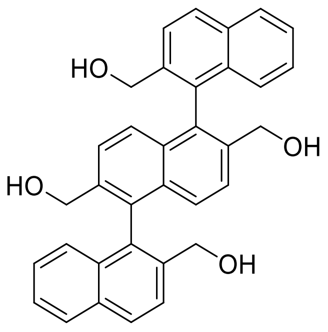
11

Compound **10** (1.0 g, 2.3 mmol), *N*-bromosuccinimide (1.637 g, 9.2 mmol) and benzoyl peroxide (222 mg, 0.92 mmol) were dissolved in 80 mL of CCl_4 and heated at 95 ℃ under nitrogen atmosphere. After 12 hours, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was subjected to silica gel column chromatography using hexane/dichloromethane (4/1) as eluent to afford compound **11** (692 mg) in 40% yield. ^{1}H NMR (500 MHz, Methylene Chloride-*d*$_2$): δ 8.10 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.36 (t, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 8.7 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 4.39 – 4.33 (m, 2H), 4.25 – 4.18 (m, 2H). ^{13}C NMR (126 MHz, Methylene Chloride-*d*$_2$): δ 133.85 , 129.99 , 129.01 , 128.55 , 128.47 , 128.22 , 127.48 , 127.33 , 127.14 , 53.84 , 33.19 , 32.55 . HRMS analysis (APCI): calcd for $C_{34}H_{24}Br_4$ $(M)^+$: 747.8586; found: 747.8606 (error: 2.7 ppm).



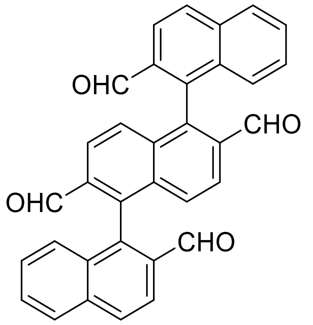
11-a

The compound **11** (2.4 g, 3.2 mmol), KOAc (12.56 g, 128 mmol) and *n*-butylammonium bromide (4.0 g, 12.8 mmol) were dissolved in 40 mL DMF under nitrogen atmosphere. The mixture was heated at 100 °C overnight. After cooling to room temperature, 30 mL ammonium chloride solution was added into the reaction mixture. The mixture was extracted with ethyl acetate (2*30 mL). The combined organic extract was dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexane/EA = 7/3) to afford the target compound **11-a** (1.8 g) in 84% yield. ^{1}H NMR (300 MHz, Methylene Chloride-*d*$_2$): δ 8.07 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.52 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.34 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 1H), 4.93 (d, *J* = 12.6 Hz, 1H), 4.83 (d, *J* = 12.6 Hz, 1H), 4.74 (s, 2H), 1.90 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (75 MHz, Methylene Chloride-*d*$_2$): δ 170.64 , 170.57 , 135.11 , 133.81 , 133.63 , 133.27 , 133.20 , 133.09 , 129.23 , 128.51 , 127.29 , 127.25 , 127.16 , 126.86 , 126.79 , 126.68 , 64.92 , 64.64 , 53.84 , 20.91 , 20.69 . HRMS analysis (APCI): calcd for $C_{42}H_{36}O_8$ $(M)^+$: 668.2417; found: 668.2405 (error: -1.8 ppm).



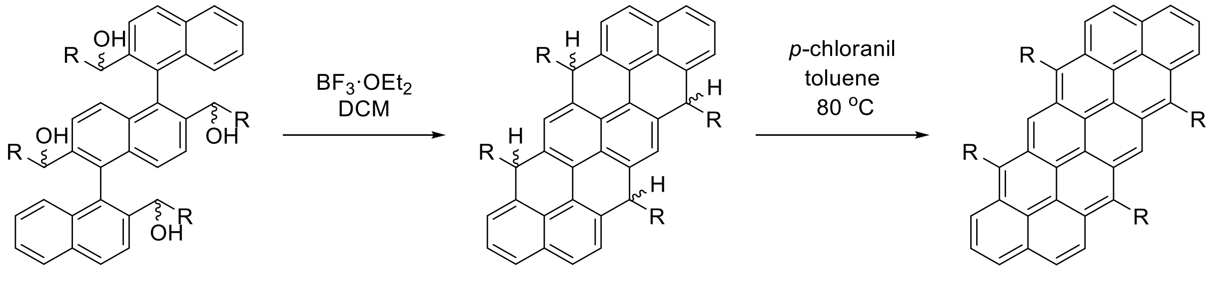
11-b

The compound **11-a** (2.14 g, 3.2 mmol), KOH (7.168 g, 128 mmol) were dissolved in 100 mL methanol under nitrogen atmosphere. The mixture was refluxed overnight. After cooling down to room temperature, the solvent was removed under vacuum and the residue was added with 100 mL water, which was then filtered to give pure white compound **11-b** (1.4 g) in 87.5% yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.12 (d, J = 8.5 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.36 (dd, J = 8.3, 1.2 Hz, 1H), 7.06 (d, J = 8.7 Hz, 1H), 7.02 (d, J = 8.5 Hz, 1H), 5.19 (t, J = 5.0 Hz, 1H), 5.02 (t, J = 5.0 Hz, 1H), 4.15 (qd, J = 13.7, 4.5 Hz, 2H), 4.09 – 3.97 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 138.31 , 137.81 , 132.33 , 131.88 , 131.70 , 131.05 , 128.10 , 127.81 , 126.45 , 125.81 , 125.53 , 125.29 , 125.10 , 124.93 , 60.75 , 60.60 , 39.52 . HRMS analysis (APCI): calcd for $C_{34}H_{28}O_4$ $(M)^+$: 500.1981; found: 500.1982 (error: 0.2 ppm).



12

A solution of oxalyl chloride (6.0 mL, 70 mmol) in 200 mL of freshly distilled CH_2Cl_2 was cooled to -78 °C, and DMSO (9.8 mL, 138 mmol) was carefully added under nitrogen atmosphere. After stirring for 15 min, a solution of compound **11-b** (700 mg, 1.4 mmol) in CH_2Cl_2 (200 mL) was added and the mixture was stirred at -78 °C for 2h. Et_3N (19 mL) was added successively and the solution was stirred at -78 °C for 1h. Then the cooling bath was removed, and the reaction mixture was allowed to warm up to room temperature and stirred for 30 min. The solvent was removed under vacuum and the residue was extracted with ethyl acetate (2*30 mL). The extract was washed with saturated aqueous Na_2CO_3 solution, brine and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the crude product was purified by column chromatography (silica gel, hexane/EA =7/3) to afford light yellow compound **12** (485 mg) in 70% yield. ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 9.73 (s, 1H), 9.61 (s, 1H), 8.24 (s, 2H), 8.11 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.72 (ddd, J = 8.1, 6.8, 1.1 Hz, 1H), 7.56 (d, J = 9.0 Hz, 1H), 7.48 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.33 (d, J = 8.5 Hz, 1H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 190.96 , 190.83 , 136.46 , 135.70 , 133.88 , 133.82 , 130.69 , 130.00 , 129.19 , 129.05 , 128.57 , 127.52 , 124.59 , 123.21 , 53.84 . HRMS analysis (APCI): calcd for $C_{34}H_{21}O_4$ $(M+H)^+$: 493.1436; found: 493.1434 (error: -0.3 ppm).



12-a **13** **PP-Ar**

n-BuLi in hexane (2M, 3.0 mL, 6 mmol) was added to a solution of 4-*tert*-butyl-2,6-dimethylbromobenzene (1.446 g, 6 mmol) in anhydrous THF (20 mL) at -78 °C and the mixture was stirred at -78 °C for one hour. Then the reaction mixture was added with compound **12** (250 mg, 0.5 mmol) and allowed to warm up to room temperature overnight. The resulting mixture was quenched with water and extracted with ether (3*50 mL). The combined organic extract was dried over Na_2SO_4 and evaporated in vacuum. The crude product was washed by hexane to afford compound **12-a** as a yellow solid (542 mg, quantitative yield), which was used for the next step directly. Boron trifluoride diethyl etherate (0.5 mL) was added to a solution of compound **12-a** (342 mg, 0.3 mmol) in DCM (50 mL) and the yellow solution turned green immediately. After 30 min, water was added to quench the reaction. The organic layer was separated and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was washed with methanol to afford compound **13** (270 mg) in 90% yield, which was used directly to the next step. Compound **13** (270 mg, 0.27 mmol) was dissolved in 50 mL toluene under nitrogen, *p*-chloranil (246 mg, 1 mmol) was added and the mixture was stirred for 2h at 80 °C. The color of the solution turned to dark green. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexane/toluene = 4/1) to give the compound **PP-Ar** as green solid in 50% yield (135 mg). ^{1}H NMR (500 MHz, THF-*d*$_8$) δ 8.71 (s, 1H), 8.05 (d, *J* = 6.8 Hz, 1H), 7.88 (dt, *J* = 10.2, 5.6 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 9.3 Hz, 1H), 7.32 (d, *J* = 6.5 Hz, 4H), 1.96 (s, 6H), 1.76 (s, 6H), 1.49 (s, 18H). ^{13}C NMR (126 MHz, THF-*d*$_8$) δ 151.26 , 137.82 , 137.77 , 131.25 , 130.07 , 129.07 , 126.96 , 126.68 , 125.28 , 125.02 , 124.96 , 124.87 , 123.57 , 123.46 , 35.00 , 31.94 , 20.41 . HRMS analysis (APCI): calcd for $C_{82}H_{81}$ $(M+H)^+$: 1065.6335; found: 1065.6333 (error: -0.2 ppm).

1.3 Chemical oxidation of PP-Ar

NO•SbF_6 (5.3 mg, 0.02 mmol) dissolved in dry acetonitrile (50 µl) was added into the 2 mL dry DCM solution of **PP-Ar** (10.6 mg, 0.01 mmol). The oxidized compound was formed in 5 min leading to deep brown color, and the solvent was removed under vacuum to give the dication **PP-Ar^{2+}** without further purification. ^{1}H NMR (500 MHz, Methylene Chloride-*d*$_2$): δ 9.35 (s, 1H), 8.86 (d, *J* = 7.5 Hz, 1H), 8.34 (d, *J* = 9.2 Hz, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 8.08 (t, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 9.1 Hz, 1H), 7.29 (d, *J* = 14.3 Hz, 4H), 1.97 (s, 6H), 1.87 (s, 6H), 1.43 (d, *J* = 6.2 Hz, 18H). Due to its instability under ambient condition, its mass spectrum was not recorded.

2. Fluorescence spectra of TT-AR and PP-AR

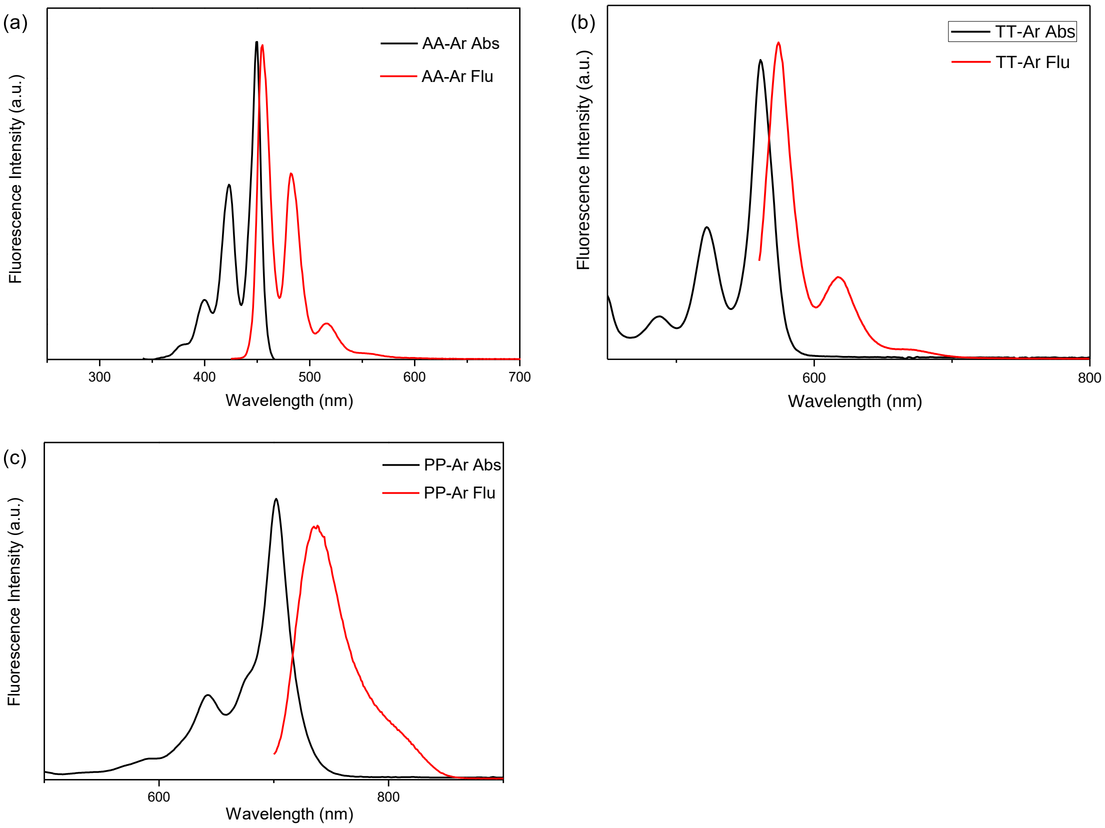


Fig. S1. Normalized absorption (Abs) and fluorescence (Flu) spectra of **AA-Ar**, **TT-Ar** and **PP-Ar** measured in DCM. The excitation wavelength for fluorescence measurements was 400 nm, 580 nm and 702 nm, respectively.

3. Electrochemical data

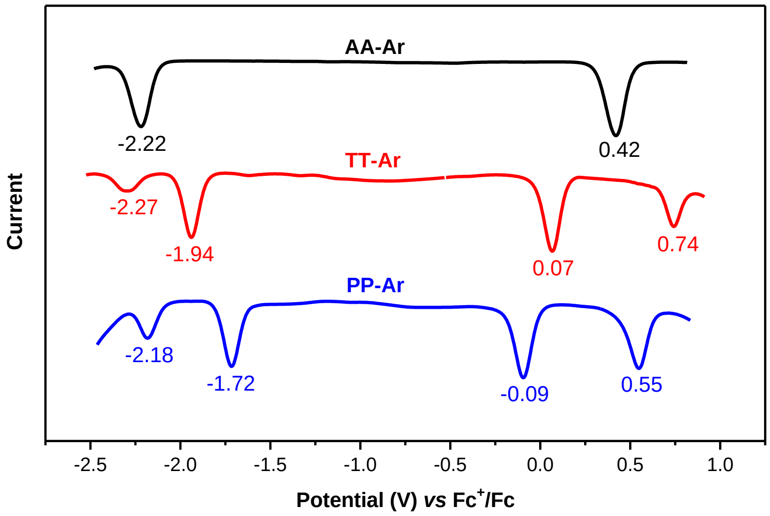


Fig. S2. Differential pulse voltammograms (1×10^{-3} M) of **AA-Ar**, **TT-Ar** and **PP-Ar** in dry dichloromethane with 0.1 M Bu_4NPF_6 as the supporting electrolyte, AgCl/Ag as reference electrode, Au as working electrode (surface area = 12.6 mm^2), Pt wire as counter electrode (potential step = 0.004 V, pulse amplitude = 0.05 V, pulse width = 0.05 s in the oxidation mode). The electrode potential was externally calibrated by Fc^+/Fc couple.

4. ESR spectra of the radical cations and radical anions

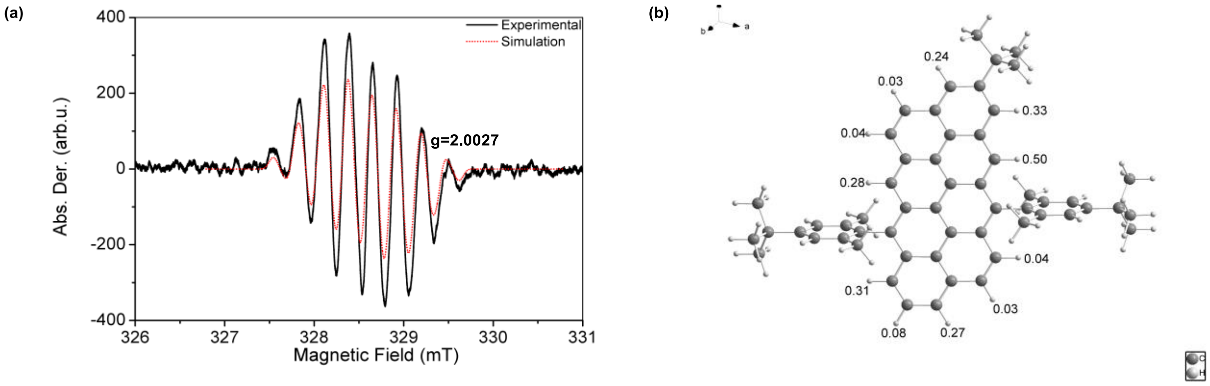


Fig. S3. (a) ESR spectrum of **TT-Ar**$^{\cdot+}$ recorded in DCM (radical cation) at room temperature together with its simulated spectrum and (b) hyperfine coupling constants (in mT) of **TT-Ar**$^{\cdot+}$.

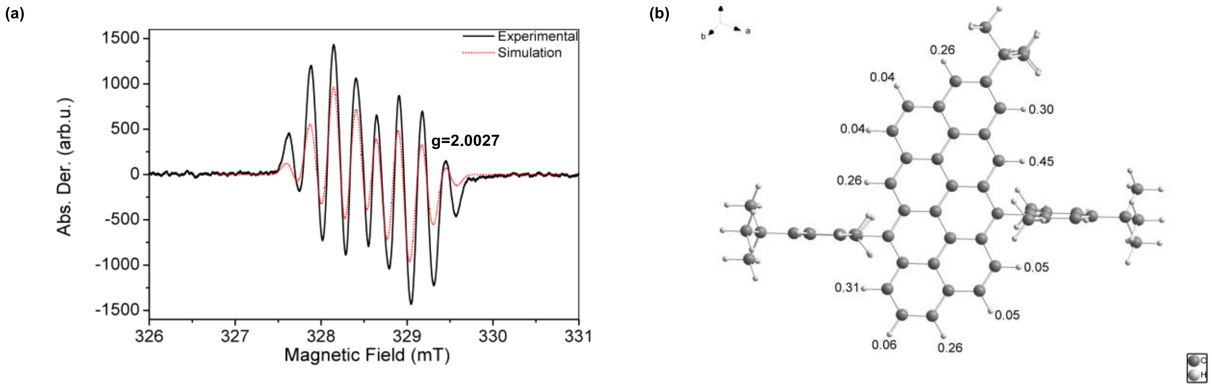


Fig. S4. (a) ESR spectrum of **TT-Ar**$^{\cdot -}$ recorded in THF (radical anion) at room temperature together with its simulated spectrum and (b) hyperfine coupling constants (in mT) of **TT-Ar**$^{\cdot -}$.

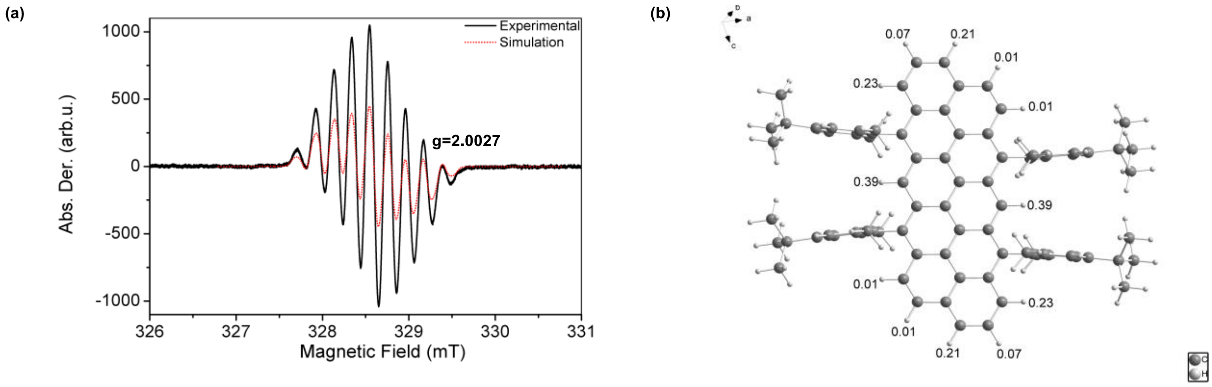


Fig. S5. (a) ESR spectra of **PP-Ar**$^{\cdot +}$ recorded in DCM (radical cation) at room temperature together with its simulated spectrum and (b) hyperfine coupling (in mT) constants of **PP-Ar**$^{\cdot +}$.

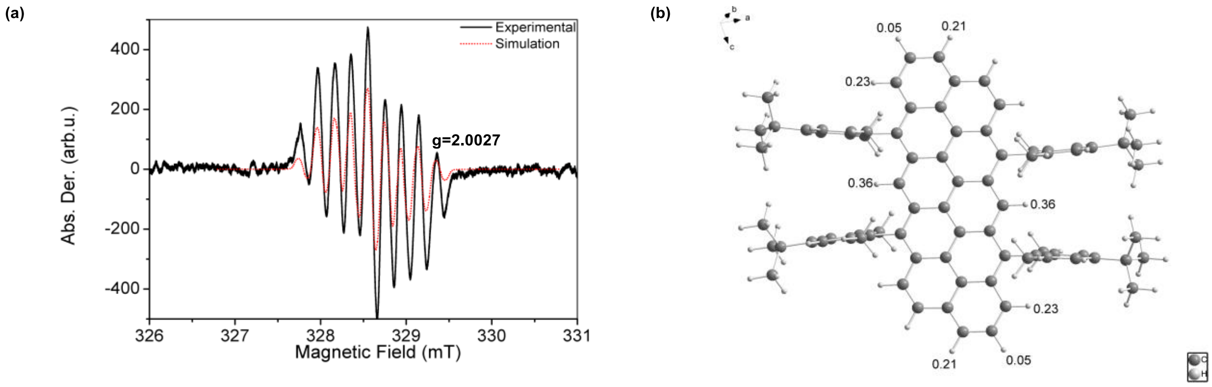


Fig. S6. (a) ESR spectra of **PP-Ar**$^{\cdot -}$ recorded in THF (radical anion) at room temperature together with its simulated spectrum and (b) hyperfine coupling constants (in mT) of **PP-Ar**$^{\cdot -}$.

5. DFT calculations

Theoretical calculations were performed with the Gaussian09 rev. D program suite.[1] All calculations were carried out using the density functional theory (DFT) method with Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional (B3LYP) employing the 6-31G(d,p) basis set for all atoms.[2] NOON (natural orbital occupation number) calculations were done by spin unrestricted UCAM-B3LYP/6-31G(d,p) method and the diradical character (y_0) was calculated according to Yamaguchi's scheme: $y_0 = 1 - (2T/(1 + T^2))$, and $T = (n_{\mathrm{HOMO}} - n_{\mathrm{LUMO}})/2$ (n_{HOMO} is the occupation number n of the HOMO, n_{LUMO} is the occupation number n of the LUMO).[3] Time-dependent DFT (TD-DFT) calculations have been performed at the B3LYP/6-31G(d,p) level of theory. ACID plot was calculated by using the method developed by Herges.[4]

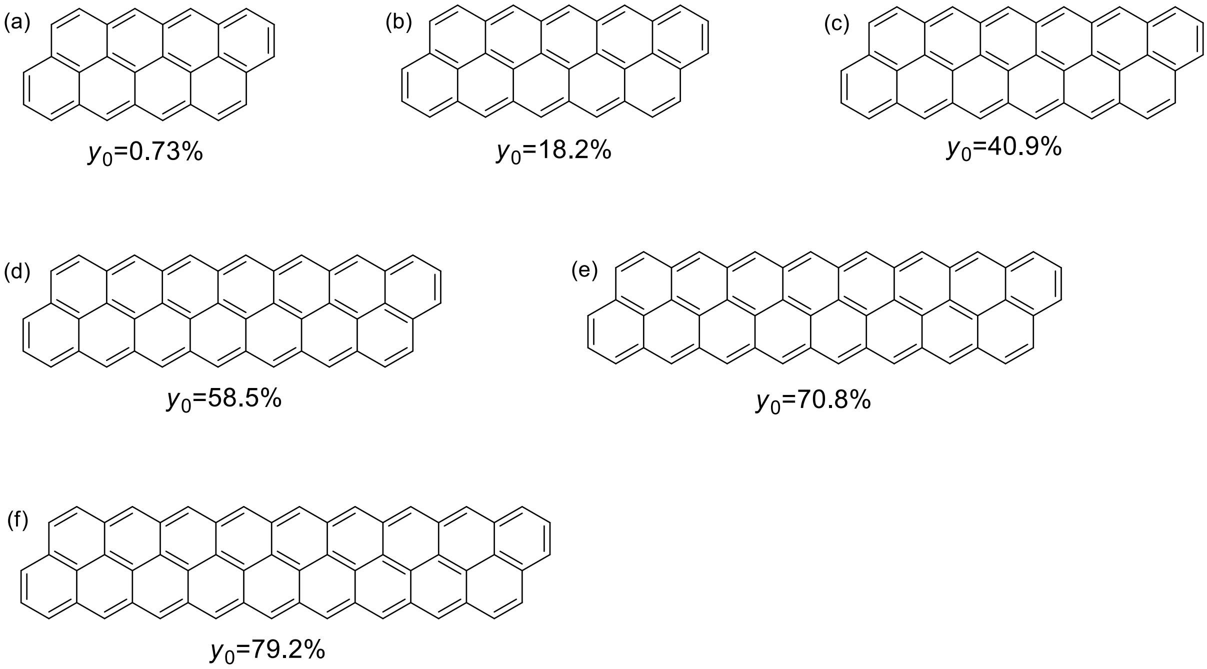


Fig. S7. The calculated (UCAM-B3LYP/6-31G(d,p)) diradical character of a series of [*n*,2]*peri*-acenoacenes: (a) *n*=4, (b) *n*=5, (c) *n*=6, (d) *n*=7, (e) *n*=8, (f) *n*=9.

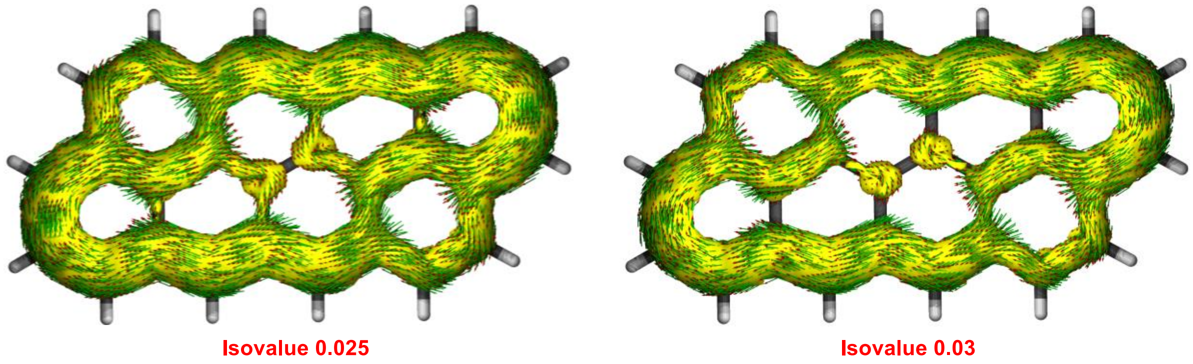


Fig. S8. ACID plots of **TT** with different isovalues.

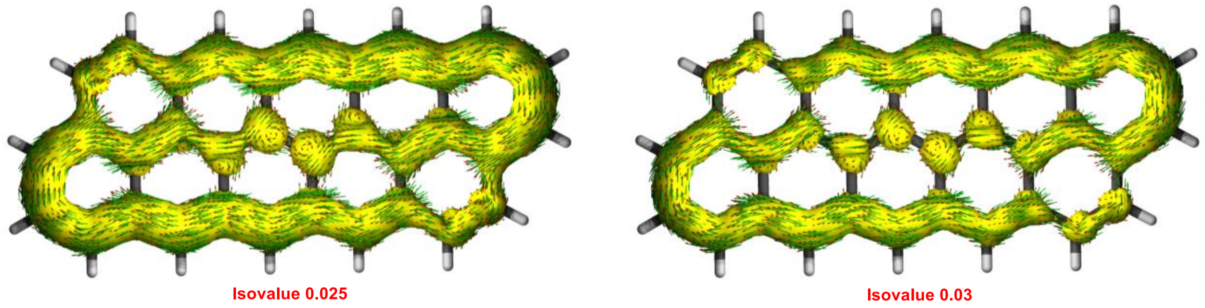


Fig. S9. ACID plots of **PP** with different isovalues.

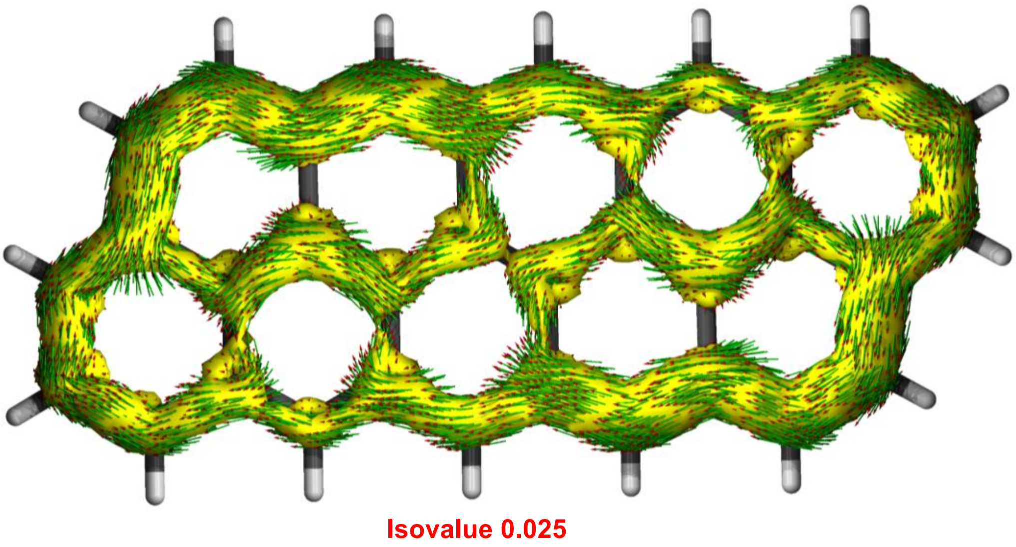


Fig. S10. ACID plots of **PP**$^{2+}$ with isovalue of 0.025.

Table S1. Total Energies (a.u.) of compounds **AA-Ar**, **TT-Ar**, and **PP-Ar** calculated at the B3LYP/6-31G level of DFT (Energy of **AA-Ar** was set as 0).

Compound	Energy (Hartree)
AA-Ar	-1543.29
TT-Ar	-2166.72
PP-Ar	-3173.25

Table S2. The Cartesian coordinates of optimized structure of **TT-Ar**

	X	Y	Z
C	4.60259589	-0.6159037	-0.00966458
C	5.28519597	-0.44315746	-1.22913204
C	6.62920501	-0.04631407	-1.21563671
C	7.32675546	0.18904166	-0.02749505
C	6.62307757	0.00969184	1.17203222
C	5.28407669	-0.38605531	1.20555151
C	4.58778729	-0.67686974	-2.55045307
C	8.80260445	0.62880649	0.00442627
C	8.91410337	2.00446299	0.70381159

C	9.40743685	0.75784817	-1.40619864
C	9.63428418	-0.41204014	0.79099088
C	4.58242049	-0.55992527	2.53353608
C	3.16261379	-1.03659978	-0.00202311
C	2.8255576	-2.41654142	0.00430427
C	3.82356628	-3.43352234	0.01048405
C	3.48215315	-4.77011009	0.01474027
C	2.13339863	-5.16572731	0.01276853
C	1.11550755	-4.21639127	0.00753997
C	1.44435119	-2.81938358	0.0042376
C	0.41470127	-1.8463624	0.00043062
C	0.7543484	-0.47062468	-0.00219023
C	-0.27521521	0.50721018	-0.00351818
C	0.05557319	1.8869341	-0.00516596
C	-0.96276376	2.8674617	-0.00441564
C	-0.63934369	4.25966509	-0.00565062
C	0.75435281	4.63752601	-0.00880137
C	1.73957911	3.70413771	-0.01020098
C	1.44158604	2.29103093	-0.00802998
C	2.43368126	1.3310066	-0.00869725
C	2.14111786	-0.06397974	-0.0042208
C	-0.27574454	-4.59262245	0.00452352
C	-1.26511499	-3.66562699	-0.00065882
C	-0.97804546	-2.24822821	-0.00168501
C	-1.99228531	-1.29484492	-0.00475714
C	-1.66385519	0.10657084	-0.0034836
C	-2.65203647	1.09768822	-0.00245589
C	-2.33805861	2.47161402	-0.00228199
C	-3.33852484	3.47811617	-0.00041797
C	-3.0315307	4.83269662	-0.00090096
C	-1.6662224	5.20207966	-0.00383993
C	-3.43371861	-1.71142825	-0.011831
C	-4.11343422	-1.895109	-1.2312125
C	-5.46064761	-2.28093955	-1.21693598
C	-6.16426263	-2.49355967	-0.02805348
C	-5.463241	-2.30339944	1.17137493
C	-4.1210261	-1.91858867	1.2040482
C	-3.40883127	-1.68790991	-2.5531283
C	-7.64467139	-2.91758301	0.00484845
C	-7.77509432	-4.27672231	0.73260292
C	-8.24312837	-3.07052306	-1.4061001
C	-8.46893057	-1.85111696	0.76446001

C	-3.42155835	-1.73505238	2.53189801
C	-4.16519179	5.87852121	0.00219289
C	-5.04423882	5.68797977	-1.25649328
C	-5.03428976	5.69025672	1.26809927
C	-3.63223422	7.32406782	-0.00130199
H	7.12640853	0.0775768	-2.17119348
H	7.12524212	0.1818291	2.12014894
H	3.72155517	-0.0170159	-2.66825786
H	4.21585882	-1.70382405	-2.6320641
H	5.26667608	-0.49580036	-3.38796257
H	9.95987922	2.33050158	0.74069162
H	8.53933231	1.96986457	1.7307917
H	8.34026165	2.76512084	0.16440144
H	10.45411166	1.07034082	-1.33122172
H	8.88246026	1.50653039	-2.00831216
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H	9.57569902	-1.39790733	0.31833327
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H	3.73190488	0.12374358	2.62979797
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H	-5.97016608	-2.45774387	2.12002937
H	-2.9933336	-0.6777836	-2.63225523
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H	-7.20645934	-5.05486535	0.21304055
H	-8.8245616	-4.59057957	0.76997006
H	-7.40619639	-4.224612	1.76095557
H	-8.20920234	-2.13096109	-1.96704432

H	-9.29280684	-3.37254177	-1.33044762
H	-7.72125577	-3.83591035	-1.98960329
H	-8.12459658	-1.72886906	1.7955333
H	-9.52611289	-2.13796872	0.79781925
H	-8.39693902	-0.87641325	0.27089193
H	-2.58980239	-2.43863709	2.64732417
H	-4.11380081	-1.89231171	3.36328798
H	-2.99956004	-0.72903367	2.62681221
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H	-5.49478033	4.69190543	-1.29112474
H	-4.45427067	5.81894701	-2.16949422
H	-4.43733631	5.82407718	2.17614823
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H	-4.47268466	8.02538077	0.00074507
H	-3.02979791	7.53495062	-0.89085299
H	-3.02386989	7.53707918	0.88369524

Table S2. The Cartesian coordinates of optimized structure of **PP-Ar**

	X	Y	Z
C	1.0135469	4.18402259	-0.23090256
C	0.50554893	5.52536763	-0.31004555
C	1.38876908	6.59740379	-0.37306009
C	2.77953051	6.38303821	-0.35381712
C	3.29317422	5.1077678	-0.26929908
C	2.43708182	3.96652123	-0.20548089
C	2.9528082	2.65044032	-0.1150106
C	2.06544671	1.54636253	-0.07604608
C	0.63704154	1.76752636	-0.09463353
C	0.12180702	3.08795053	-0.16676245
C	-0.251572	0.66419511	-0.03326245
C	2.53841519	0.21337589	-0.01766736
C	1.68268471	-0.8862713	0.03105857
C	2.19078882	-2.23300467	0.0800065
C	1.31072019	-3.30696673	0.16172095
C	1.7812759	-4.67266796	0.23888451
C	0.92228705	-5.71799407	0.31461547
C	4.43751612	2.45513556	-0.03088717
C	5.08007245	2.5096776	1.22582915
C	6.47168842	2.41502162	1.28459508
C	7.26624975	2.26273359	0.13966981
C	6.60389817	2.18702216	-1.08894676

C	5.20937686	2.28240055	-1.19522697
C	4.2851567	2.68881908	2.49946859
C	4.55564737	2.21894551	-2.55722821
C	8.80028808	2.21763918	0.27037798
C	9.29908516	3.57610967	0.81931949
C	9.21381751	1.09356788	1.24873774
C	9.4970273	1.95940427	-1.07880809
C	3.66789044	-2.48861869	0.01112281
C	4.44550618	-2.54701303	1.18282409
C	5.807674	-2.86468264	1.08981753
C	6.43012245	-3.13318956	-0.13266619
C	5.63647368	-3.04829038	-1.28512999
C	4.27774652	-2.73078303	-1.23953373
C	3.82576748	-2.29637662	2.53915023
C	3.47696154	-2.67395817	-2.52088555
C	7.91171185	-3.53760164	-0.24932938
C	8.64402151	-2.58277391	-1.22083057
C	8.64060896	-3.4937608	1.1068284
C	7.99813719	-4.98241336	-0.7975651
C	-1.01354897	-4.18401563	0.23098714
C	-0.50555301	-5.52536096	0.31014403
C	-1.38877504	-6.59739448	0.37318064
C	-2.7795372	-6.38302753	0.35394262
C	-3.29317952	-5.10775831	0.26940292
C	-2.43708459	-3.9665144	0.2055618
C	-2.95280895	-2.65043807	0.11506381
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C	-7.26624245	-2.26273361	-0.13973043
C	-6.60392273	-2.18704125	1.08890595
C	-5.20940404	-2.28241292	1.19522015

C	-4.28508758	-2.68881677	-2.49945267
C	-4.55571315	-2.21897147	2.55723984
C	-8.80027523	-2.21761133	-0.27048351
C	-9.29908368	-3.57600181	-0.81961175
C	-9.2137385	-1.09340781	-1.24872087
C	-9.49705736	-1.95953707	1.07871099
C	-3.66789399	2.48861226	-0.01109511
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H	-4.36584952	-4.95429444	0.25241852
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H	-3.52970473	-1.90446994	-2.6150181
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H	-6.37817026	2.90730538	-2.01100377
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H	-4.58144265	2.33673754	-3.32799711
H	-3.05524117	3.03966265	-2.77117976

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H	-4.12464122	2.80779002	3.39142983
H	-2.95758111	1.71623002	2.62771664
H	-2.70890239	3.45501664	2.54953589
H	-9.70117134	2.85957268	1.30184929
H	-8.58903068	1.5479383	0.86854182
H	-8.21578826	2.61443992	2.22661949
H	-9.68999739	3.77463202	-0.97120901
H	-8.20423638	4.19278277	-1.82750153
H	-8.61993215	2.4918536	-1.54834761
H	-9.04473633	5.29237459	0.89759474
H	-7.52713536	5.06999224	1.78089984
H	-7.49825514	5.68644791	0.12413179
H	7.52700846	-5.06992073	-1.78102716

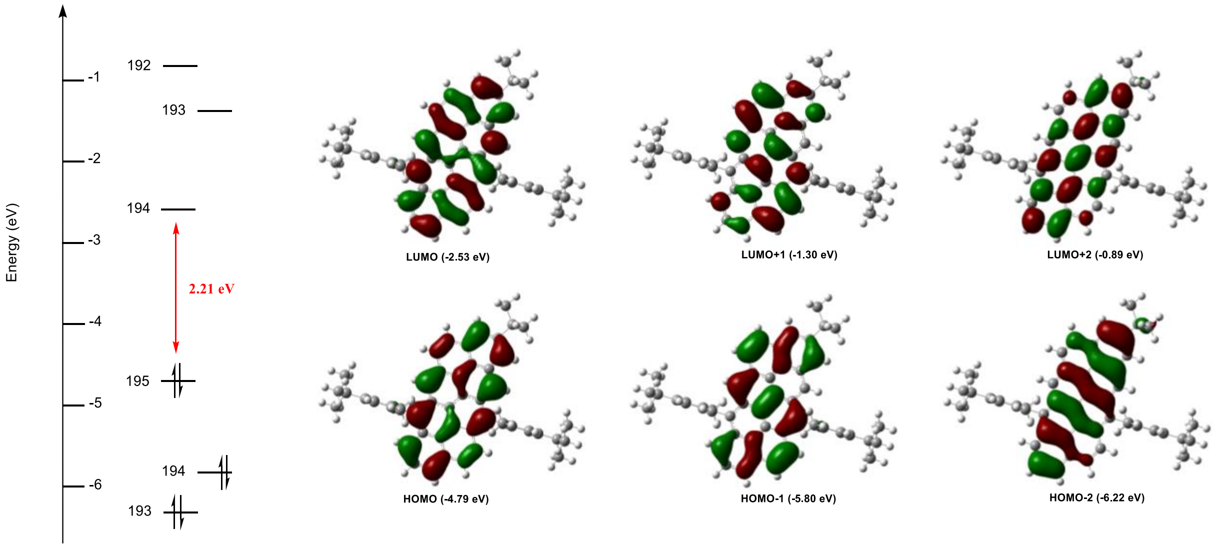


Fig. S11. Frontier molecular orbital profiles and energy diagram of **TT-Ar** obtained by B3LYP/6-31G(d,p) level calculation.

Table S4. Selected TD-DFT (B3LYP/6-31G (d,p)) calculated wavelength, oscillator strength and compositions of major transitions of **TT-Ar**.

Wavelength (nm)	Osc. Strength	Major contributions
620.5	0.5278	HOMO->LUMO (99%)
464.2	0.0008	H-1->LUMO (62%), HOMO->L+1 (38%)
438.7	0.0026	H-1->LUMO (36%), HOMO->L+1 (60%)
417.4	0.0013	H-2->LUMO (52%), HOMO->L+2 (47%)
385.6	0.0001	H-4->LUMO (10%), H-3->LUMO (88%)
368.4	0.0013	H-5->LUMO (97%)
367.3	0.0015	H-6->LUMO (97%)

348.8	1.1336	H-2->LUMO (40%), HOMO->L+2 (45%)
340.7	0.0717	H-7->LUMO (53%), HOMO->L+3 (40%)
327.5	0.0095	H-8->LUMO (62%), HOMO->L+4 (28%)
316.4	0.0648	H-7->LUMO (33%), HOMO->L+3 (44%), HOMO->L+4 (15%)
314.4	0.2146	H-8->LUMO (27%), H-1->L+1 (17%), HOMO->L+4 (38%)
310.2	0.0089	HOMO->L+5 (12%), HOMO->L+6 (83%)
309.3	0.0041	HOMO->L+5 (87%), HOMO->L+6 (10%)
302.2	0.001	H-9->LUMO (35%), H-2->L+1 (18%), H-1->L+2 (34%
299.3	0.5776	H-1->L+1 (68%), HOMO->L+4 (13%)
290.9	0.0275	H-9->LUMO (28%), H-2->L+1 (22%), H-1->L+2 (13%), HOMO->L+7 (17%)
287.9	0.0011	HOMO->L+8 (85%)

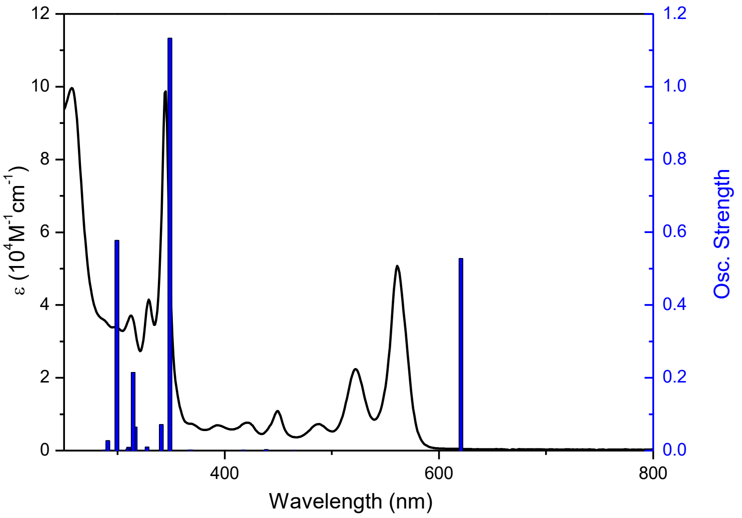


Fig. S12. Calculated (B3LYP/6-31G (d,p)) absorption spectrum of **TT-Ar** along with the experimental spectrum.

Table S5. Selected TD-DFT (UB3LYP/6-31G (d,p)) calculated wavelength, oscillator strength and compositions of major transitions of **TT-Ar**$^{+\cdot}$.

Wavelength (nm)	Osc. Strength	Major contributions
947.2	0.2365	HOMO(A)->LUMO(A) (91%)
820.2	0.1888	HOMO(B)->LUMO(B) (95%)
484.4	0.2405	H-6(B)->LUMO(B) (72%)
459.6	0.0487	H-5(A)->LUMO(A) (10%), H-4(A)->LUMO(A) (45%), H-8(B)->LUMO(B) (16%), H-5(B)->L+1(B) (10%)
406.0	0.1554	H-4(A)->LUMO(A) (10%)
398.9	0.0368	H-7(A)->LUMO(A) (14%), H-1(A)->LUMO(A) (19%), HOMO(B)->L+1(B) (22%)
380.0	0.1455	H-8(B)->LUMO(B) (32%), HOMO(B)->L+2(B) (10%)

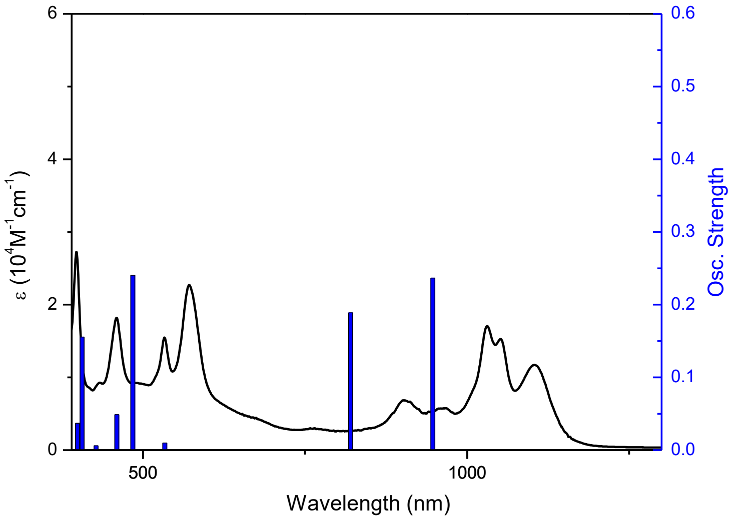


Figure S13. Calculated (UB3LYP/6-31G (d,p)) absorption spectrum of **TT-Ar**$^{+\cdot}$ along with the experimental spectrum.

Table S6. Selected TD-DFT (UB3LYP/6-31G (d,p)) calculated wavelength, oscillator strength and compositions of major transitions of **TT-Ar**$^{-\cdot}$.

Wavelength (nm)	Osc. Strength	Major contributions
1006.6	0.2545	HOMO(B)->LUMO(B) (92%)
786.7	0.1668	HOMO(A)->LUMO(A) (96%)
485.0	0.1966	HOMO(A)->L+2(A) (77%)
445.0	0.1234	HOMO(B)->L+2(B) (61%)
407.1	0.0206	HOMO(A)->L+5(A) (10%), H-1(B)->LUMO(B) (17%), HOMO(B)->L+1(B) (18%), HOMO(B)->L+5(B) (17%)
402.5	0.1311	H-2(B)->LUMO(B) (11%), H-1(B)->L+1(B) (11%), HOMO(B)->L+2(B) (14%)
370.2	0.097	H-1(A)->L+1(A) (14%), HOMO(A)->L+8(A) (12%), HOMO(A)->L+9(A) (16%), H-2(B)->LUMO(B) (15%)
369.5	0.0121	HOMO(A)->L+4(A) (72%)
334.2	0.0156	HOMO(A)->L+6(A) (38%), HOMO(A)->L+7(A) (24%)
333.1	0.0625	HOMO(A)->L+6(A) (10%), HOMO(A)->L+7(A) (12%), H-2(B)->LUMO(B) (18%), HOMO(B)->L+8(B) (11%)
328.0	0.0533	HOMO(A)->L+5(A) (11%), HOMO(A)->L+6(A) (39%), HOMO(A)->L+7(A) (34%)

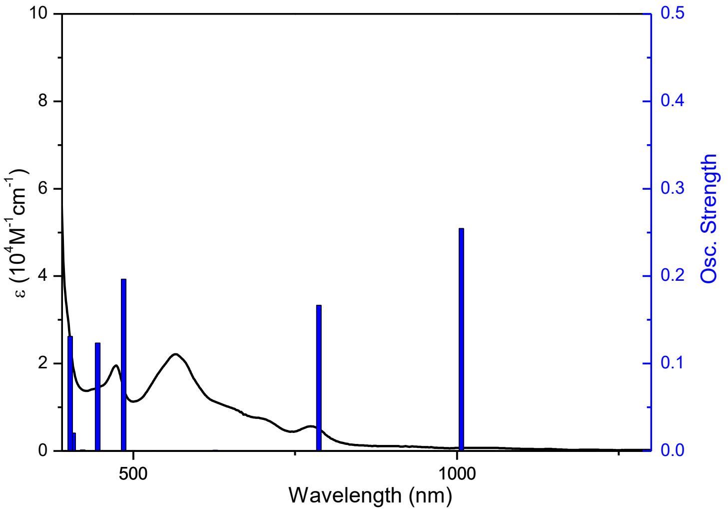


Figure S13. Calculated (UB3LYP/6-31G (d,p)) absorption spectrum of **TT-Ar**$^{\cdot-}$ along with the experimental spectrum.

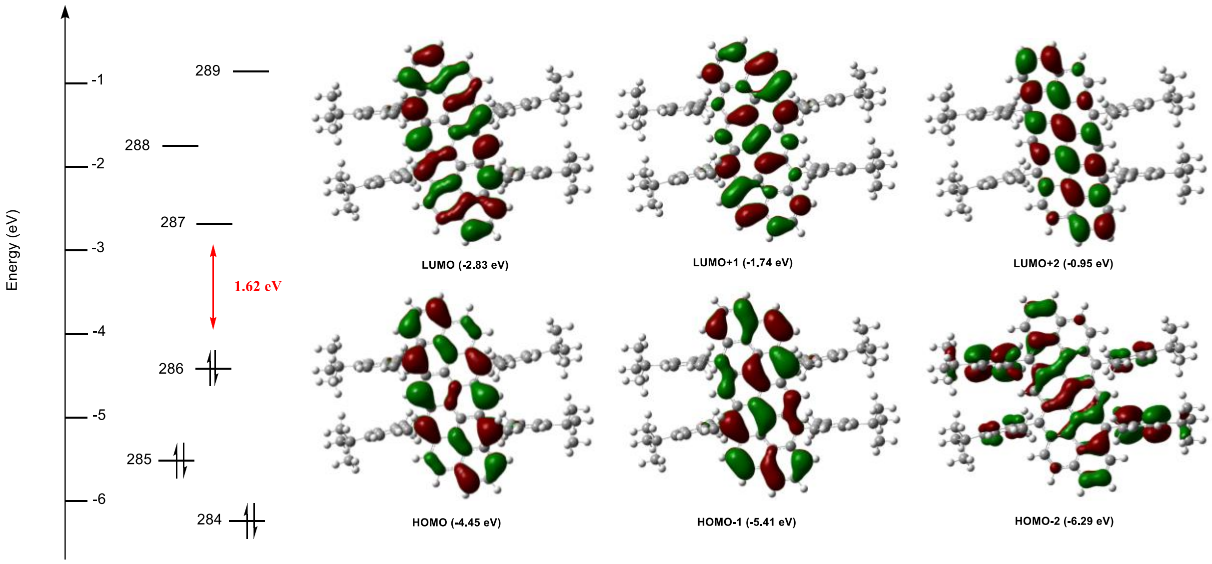


Fig. S14. Frontier molecular orbital profiles and energy diagram of **PP-Ar** obtained by B3LYP/6-31G(d,p) level calculation.

Table S7. Selected TD-DFT (B3LYP/6-31G (d,p)) calculated wavelength, oscillator strength and compositions of major transitions of **PP-Ar**.

Wavelength (nm)	Osc. Strength	Major contributions
815.7	0.4808	HOMO->LUMO (99%)
444.9	0.001	H-4->LUMO (22%), H-2->LUMO (21%), HOMO->L+2 (50%)
421.0	0.001	H-6->LUMO (15%), H-4->LUMO (26%), H-2->LUMO (57%)
414.5	0.0013	H-6->LUMO (74%), H-4->LUMO (21%)
402.3	0.002	H-11->LUMO (14%), H-9->LUMO (15%), H-8->LUMO (66%)
401.0	0.0091	H-11->LUMO (50%), H-8->LUMO (25%)
396.7	0.0006	H-11->LUMO (15%), H-9->LUMO (78%)
388.6	0.3453	H-1->L+1 (49%), HOMO->L+2 (14%), HOMO->L+4 (17%)

373.1	0.6408	H-4->LUMO (14%), HOMO->L+2 (21%), HOMO->L+4 (52%)
358.9	1.6036	H-11->LUMO (11%), H-1->L+1 (48%), HOMO->L+2 (12%), HOMO->L+4 (16%)
324.7	0.0024	HOMO->L+6 (99%)

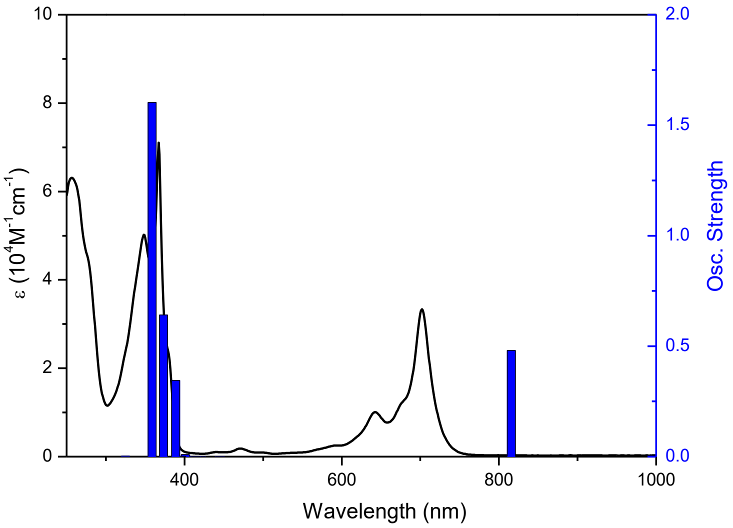


Fig. S15. Calculated (B3LYP/6-31G (d,p)) absorption spectrum of **PP-Ar** along with the experimental spectrum.

Table S8. Selected TD-DFT (UB3LYP/6-31G (d,p)) calculated wavelength, oscillator strength and compositions of major transitions of **PP-Ar**$^{+\cdot}$.

Wavelength (nm)	Osc. Strength	Major contributions
1528.0	0.2899	HOMO(A)->LUMO(A) (95%)
945.3	0.2353	HOMO(B)->LUMO(B) (95%)
538.6	0.0116	H-11(A)->LUMO(A) (13%), H-1(A)->L+1(A) (17%), H-10(B)->LUMO(B) (15%), HOMO(B)->L+2(B) (24%)
476.0	0.0816	H-8(A)->LUMO(A) (44%), H-10(B)->LUMO(B) (17%)
450.9	0.0945	H-6(B)->LUMO(B) (15%), H-4(B)->LUMO(B) (37%)
445.6	0.2045	H-11(A)->LUMO(A) (11%), H-10(B)->LUMO(B) (37%), H-4(B)->LUMO(B) (10%)
419.0	0.0002	H-1(B)->LUMO(B) (82%)
409.3	0.0033	H-8(B)->LUMO(B) (63%), H-4(B)->LUMO(B) (20%)
400.3	0.1834	H-11(A)->LUMO(A) (14%), H-10(B)->LUMO(B) (12%), HOMO(B)->L+2(B) (19%)
389.8	0.003	H-8(B)->LUMO(B) (12%), H-6(B)->LUMO(B) (60%), H-4(B)->LUMO(B) (12%)

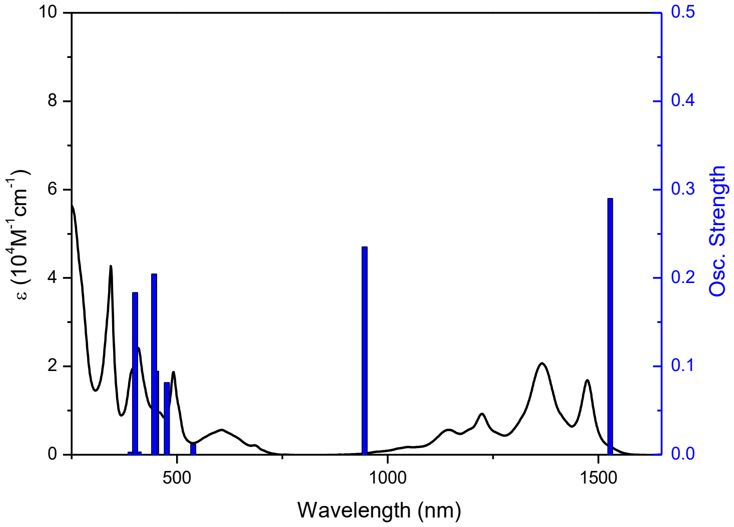


Figure S16. Calculated (UB3LYP/6-31G (d,p)) absorption spectrum of **PP-Ar**$^{+\cdot}$ along with the experimental spectrum.

Table S9. Selected TD-DFT (B3LYP/6-31G (d,p)) calculated wavelength, oscillator strength and compositions of major transitions of **PP-Ar**$^{2+}$.

Wavelength (nm)	Osc. Strength	Major contributions
1097.1	0.2623	HOMO->LUMO (99%)
962.2	0.002	H-1->LUMO (94%)
924.7	0.0053	H-6->LUMO (51%), H-3->LUMO (39%)
909.5	0.0048	H-6->LUMO (31%), H-3->LUMO (56%)
877.1	0.0029	H-8->LUMO (82%), H-6->LUMO (14%)
551.9	0.0011	H-2->L+1 (94%)
537.8	0.0012	H-4->L+1 (93%)
531.7	0.0025	H-5->L+1 (89%)
529.4	0.3869	H-11->LUMO (91%)
517.9	0.0003	H-7->L+1 (91%)

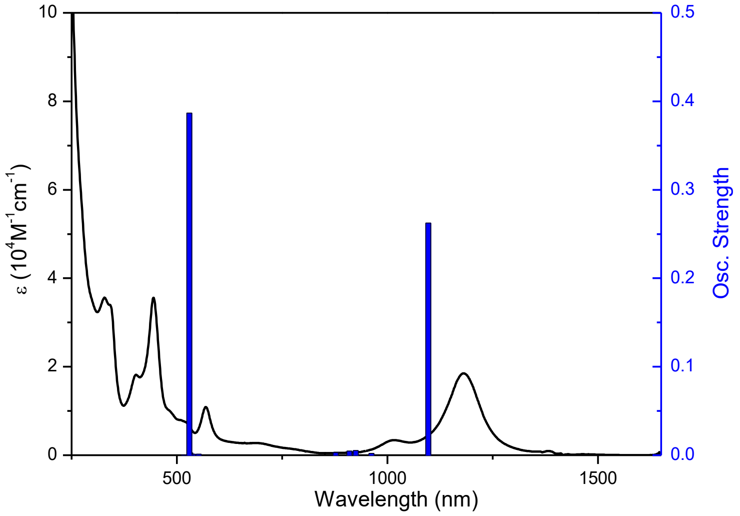


Figure S17. Calculated (B3LYP/6-31G (d,p)) absorption spectrum of **PP-Ar**$^{2+}$ along with the experimental spectrum.

Table S10. Selected TD-DFT (UB3LYP/6-31G (d,p)) calculated wavelength, oscillator strength and compositions of major transitions of **PP-Ar**$^{\cdot-}$.

Wavelength (nm)	Osc. Strength	Major contributions
865.8	0.2467	HOMO(A)->LUMO(A) (95%)
529.5	0.0195	H-2(A)->LUMO(A) (26%), HOMO(A)->L+2(A) (14%), H-1(B)->L+1(B) (20%)
482.1	0.0465	HOMO(A)->L+2(A) (27%), HOMO(B)->L+2(B) (56%)
447.0	0.3413	HOMO(A)->L+2(A) (39%), HOMO(B)->L+2(B) (28%)
391.7	0.1871	H-2(A)->LUMO(A) (13%), H-1(A)->L+1(A) (14%), HOMO(A)->L+2(A) (11%), HOMO(A)->L+13(A) (11%), H-2(B)->LUMO(B) (11%)
374.6	0.1115	H-2(B)->LUMO(B) (14%), HOMO(B)->L+4(B) (26%)
356.9	0.0005	H-6(A)->L+6(A) (14%), H-5(A)->L+7(A) (10%), H-6(B)->L+8(B) (13%), H-5(B)->L+7(B) (14%)
356.3	0.0002	H-8(A)->L+5(A) (13%), H-7(A)->L+4(A) (12%), H-8(B)->L+6(B) (13%), H-7(B)->L+5(B) (14%)
348.0	0.0731	H-1(A)->L+3(A) (10%), HOMO(A)->L+10(A) (11%), HOMO(A)->L+12(A) (28%)
345.5	0.4112	H-3(B)->LUMO(B) (13%), H-2(B)->LUMO(B) (14%), HOMO(B)->L+4(B) (10%)

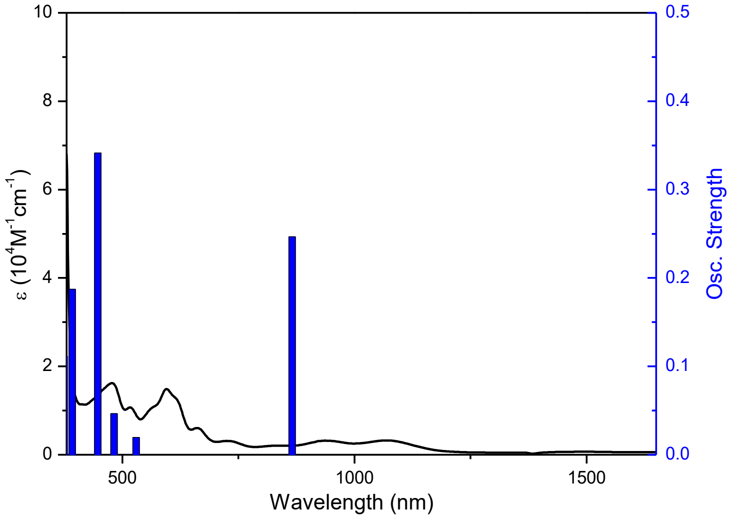


Figure S18. Calculated (UB3LYP/6-31G (d,p)) absorption spectrum of **PP-Ar**$^{\cdot-}$ along with the experimental spectrum.

6. Appendix Ⅰ: X-ray crystallographic data

Table S11. Sample and crystal data for **TT-Ar**.

Formula weight	896.84	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.2300(4) Å	a= 76.3090(10)°.
	b = 12.6110(4) Å	b= 83.0330(10)°.
	c = 16.0096(5) Å	g = 87.2420(10)°.
Volume	2380.85(13) Å3	
Z	2	
Density (calculated)	1.251 Mg/m3	
Absorption coefficient	2.538 mm-1	
F(000)	948	
Crystal size	0.480 x 0.478 x 0.234 mm3	
Theta range for data collection	2.859 to 66.572°.	

Index ranges	-14<=h<=14, -14<=k<=14, -19<=l<=19
Reflections collected	28278
Independent reflections	8240 [R(int) = 0.0368]
Completeness to theta = 66.572°	98.0 %
Absorption correction	None
Max. and min. transmission	0.7533 and 0.5786
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	8240 / 122 / 660
Goodness-of-fit on F2	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0883, wR2 = 0.2578
R indices (all data)	R1 = 0.0905, wR2 = 0.2602
Extinction coefficient	n/a
Largest diff. peak and hole	0.837 and -1.195 e.Å-3

Table S12. Crystal data and structure refinement for **PP-Ar**.

Formula weight	1249.72	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 13.8073(9) Å	a= 90°.
	b = 15.3067(11) Å	b= 97.551(4)°.
	c = 17.2865(12) Å	g = 90°.
Volume	3621.7(4) Å3	
Z	2	
Density (calculated)	1.146 Mg/m3	
Absorption coefficient	0.480 mm-1	
F(000)	1344	
Crystal size	0.352 x 0.268 x 0.080 mm3	
Theta range for data collection	3.229 to 66.595°.	
Index ranges	-16<=h<=16, -16<=k<=18, -20<=l<=19	
Reflections collected	25252	
Independent reflections	6289 [R(int) = 0.0810]	
Completeness to theta = 66.595°	98.1 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7533 and 0.4002
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	6289 / 30 / 475
Goodness-of-fit on F2	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0925, wR2 = 0.2383
R indices (all data)	R1 = 0.1149, wR2 = 0.2693
Extinction coefficient	n/a
Largest diff. peak and hole	0.603 and -0.537 e.Å-3

7. Appendix Ⅱ: ^{1}H NMR, ^{13}C NMR and Mass spectra of all new compounds

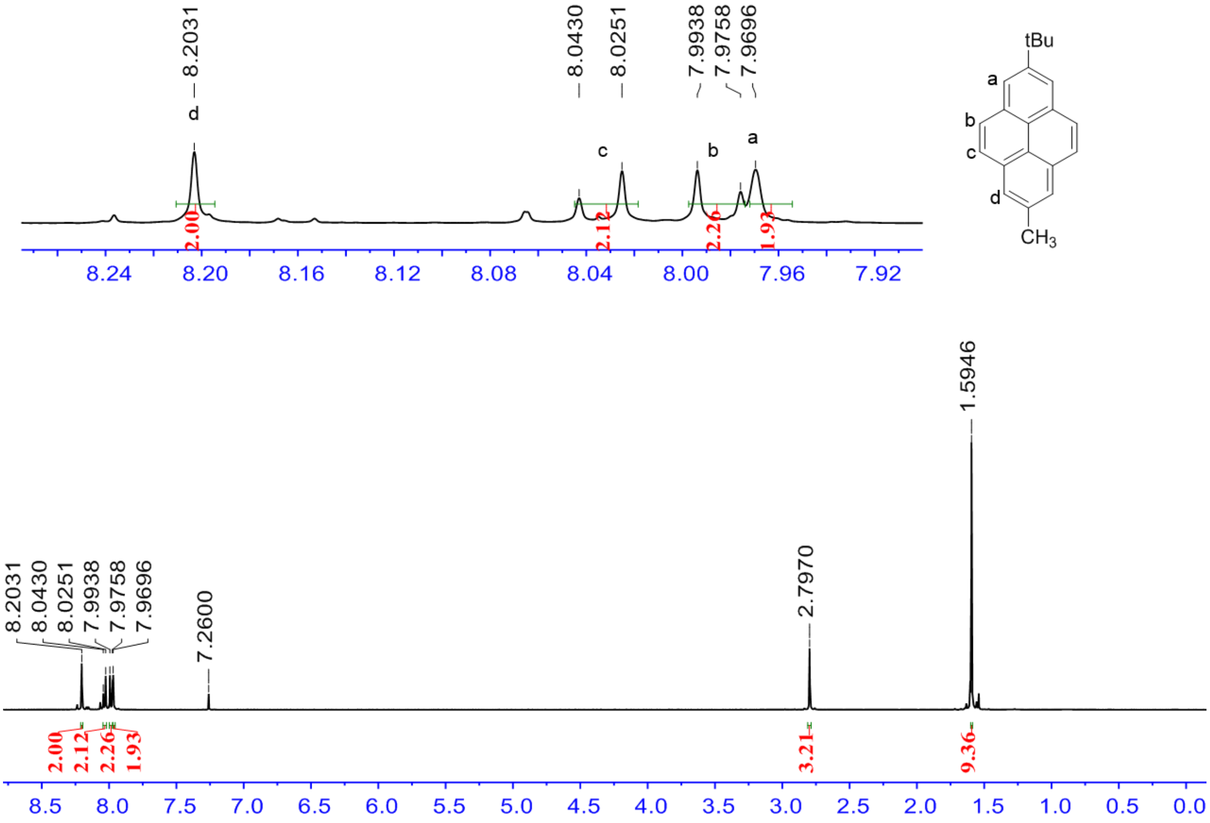


Fig. S19. ^{1}H NMR spectrum of compound **1** (500 MHz, Chloroform-*d*).

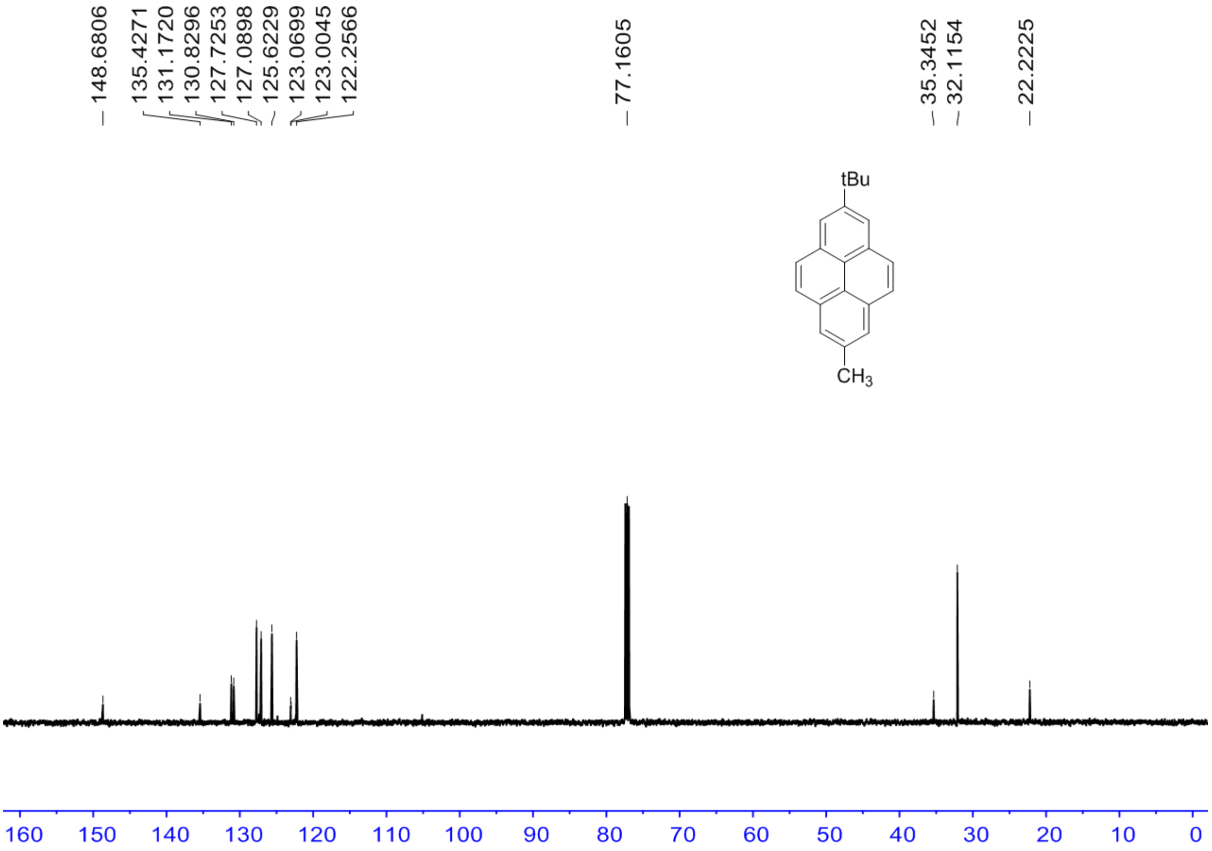
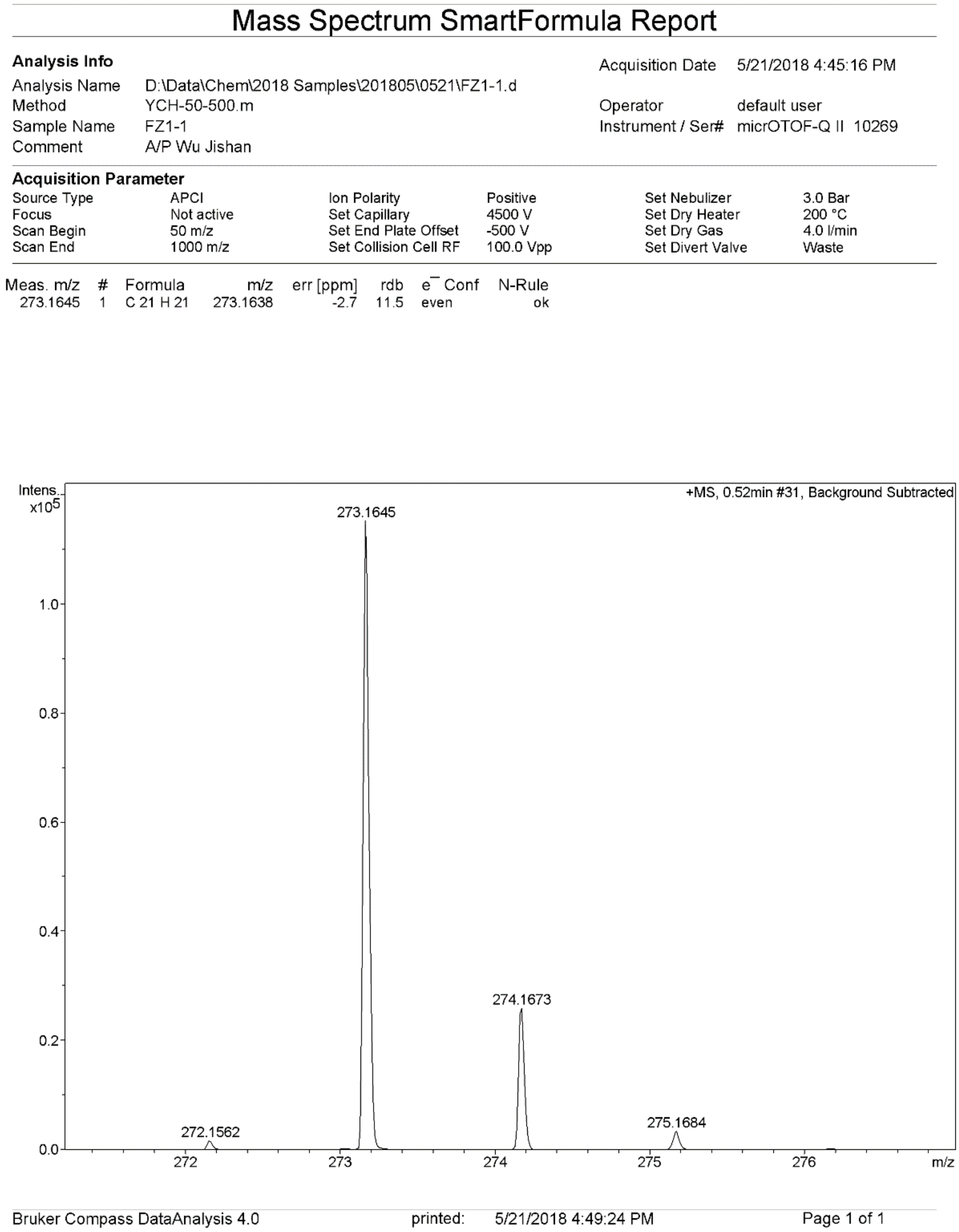


Fig. S20. ^{13}C NMR spectrum of compound **1** (126 MHz, Chloroform-*d*).



Mass Spectrum SmartFormula Report

Analysis Info

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Method YCH-50-500.m
Sample Name FZ1-1
Comment A/P Wu Jishan

Acquisition Date 5/21/2018 4:45:16 PM

Operator default user
Instrument / Ser# micrOTOF-Q II 10269

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
273.1645	1	C 21 H 21	273.1638	-2.7	11.5	even	ok

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Fig. S21. HR APCI mass spectrum of compound [**1**+H]$^+$

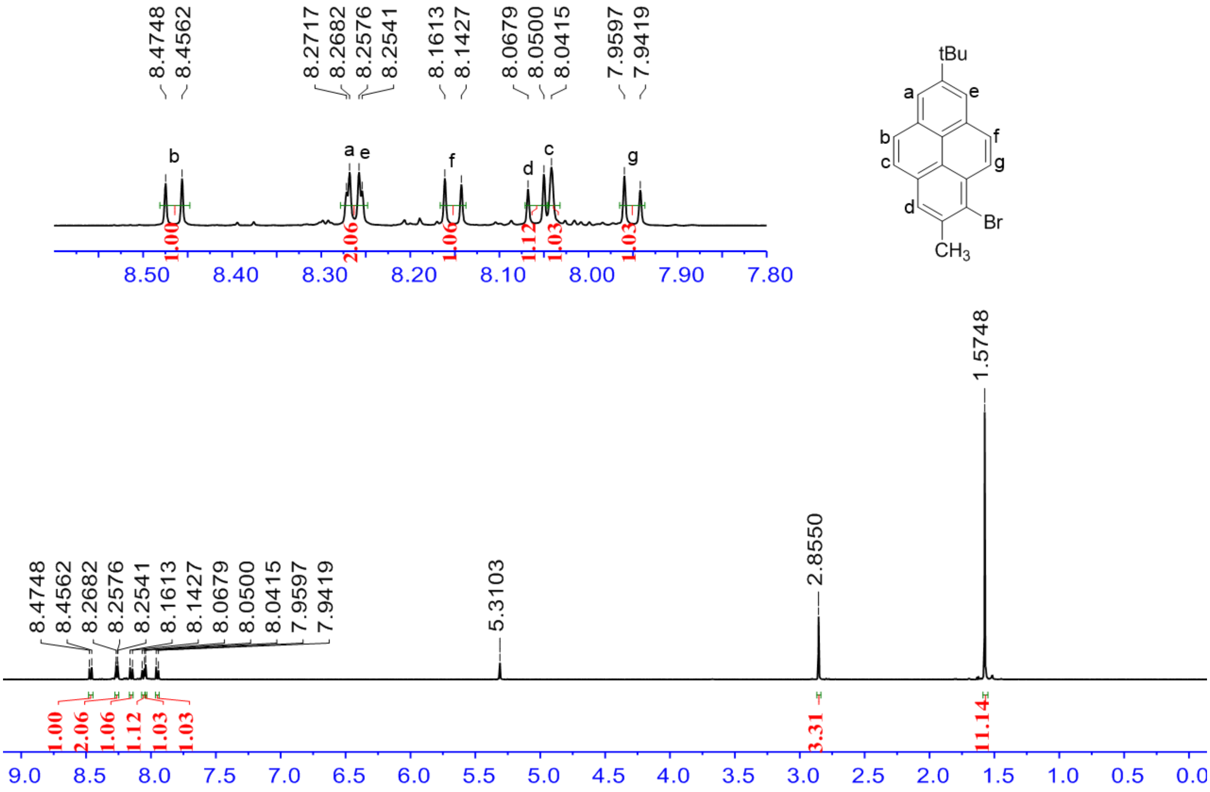


Fig. S22. ^{1}H NMR spectrum of compound **2** (500 MHz, Methylene Chloride-*d*$_2$).

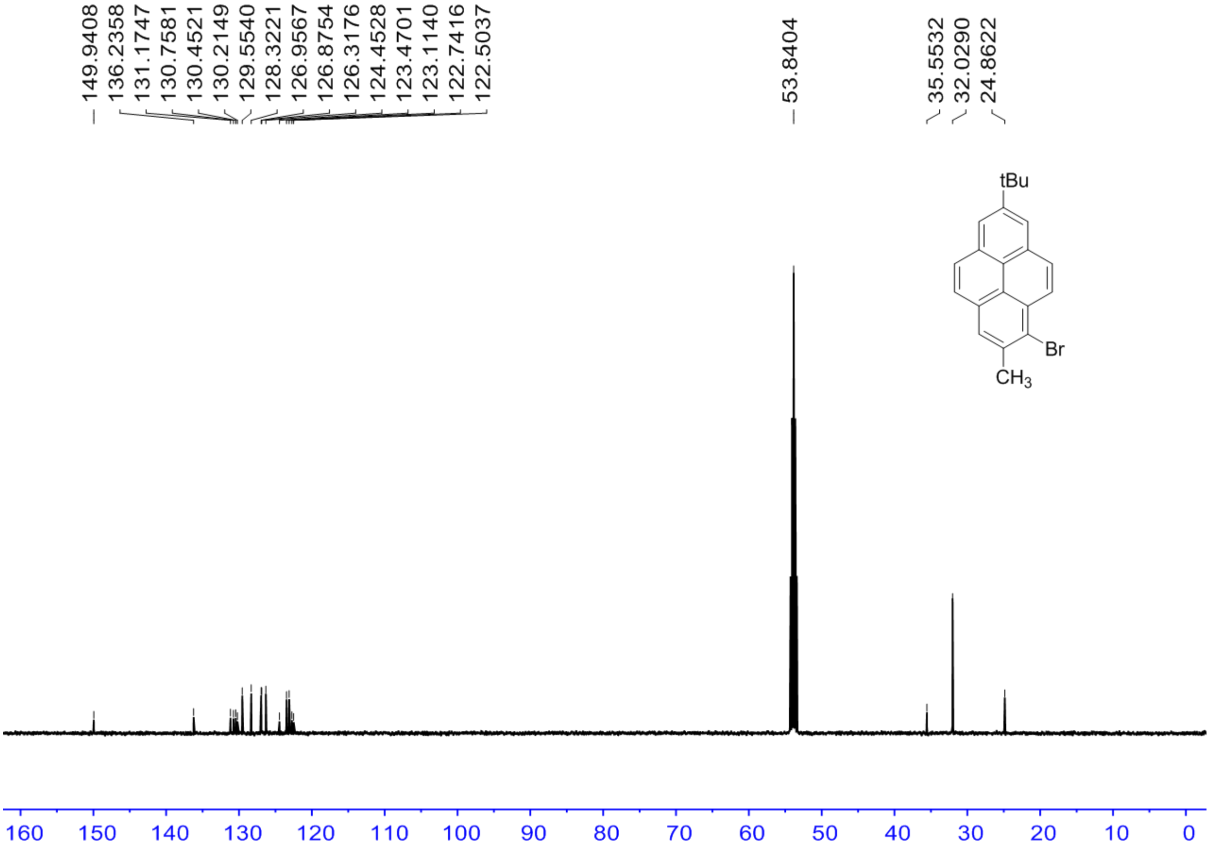
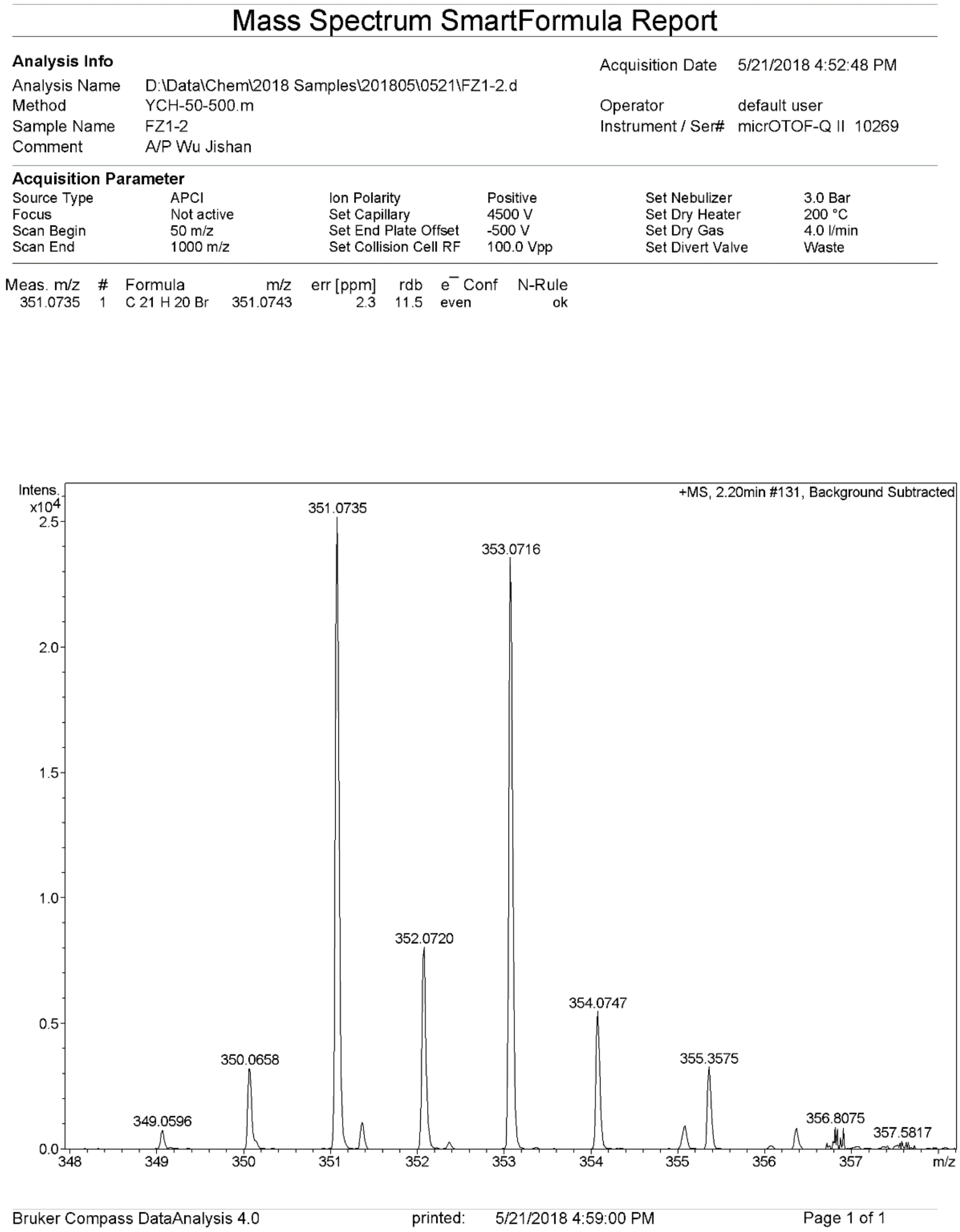


Fig. S23. ^{13}C NMR spectrum of compound **2** (126 MHz, Methylene Chloride-*d*$_2$).



Mass Spectrum SmartFormula Report

Analysis Info

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Comment	A/P Wu Jishan		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
351.0735	1	C 21 H 20 Br	351.0743	2.3	11.5	even	ok

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Fig. S24. HR APCI mass spectrum of compound [**2**+H]$^+$

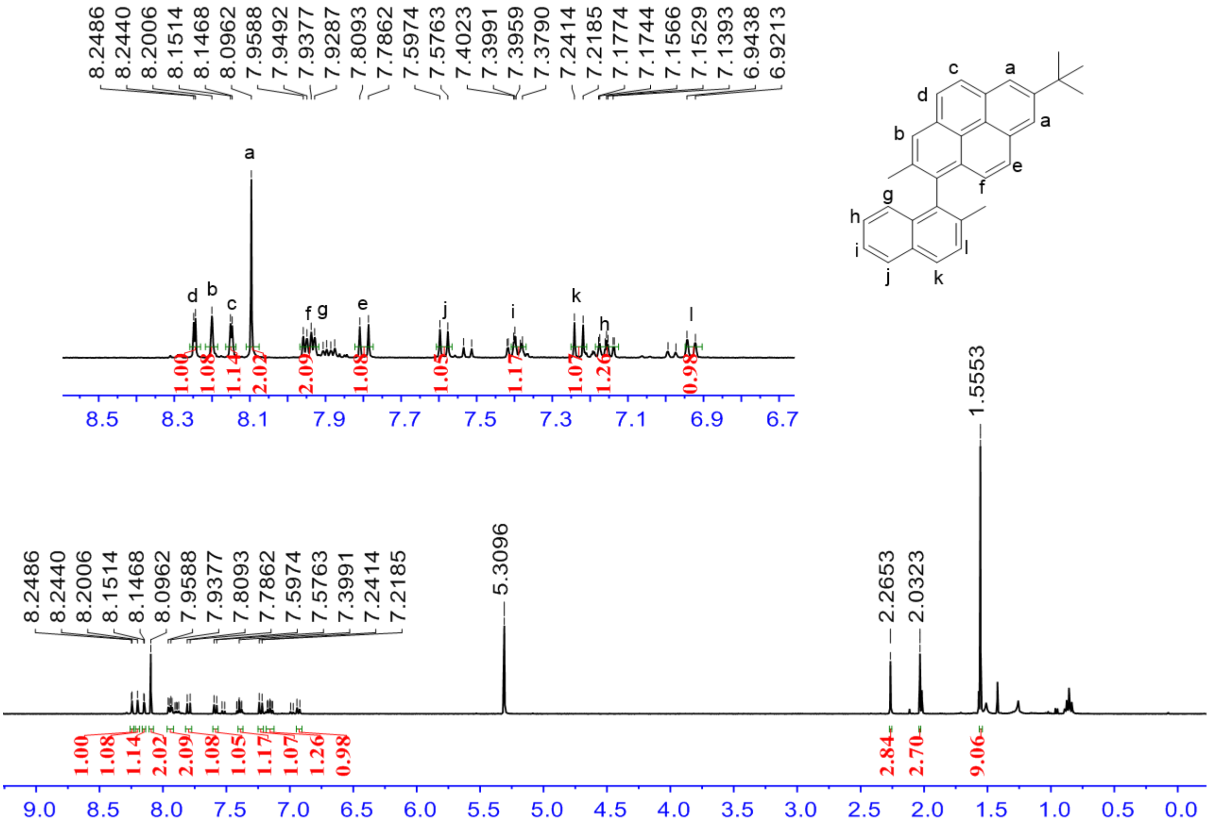


Fig. S25. ^{1}H NMR spectrum of compound **3** (400 MHz, Methylene Chloride-*d*$_2$).

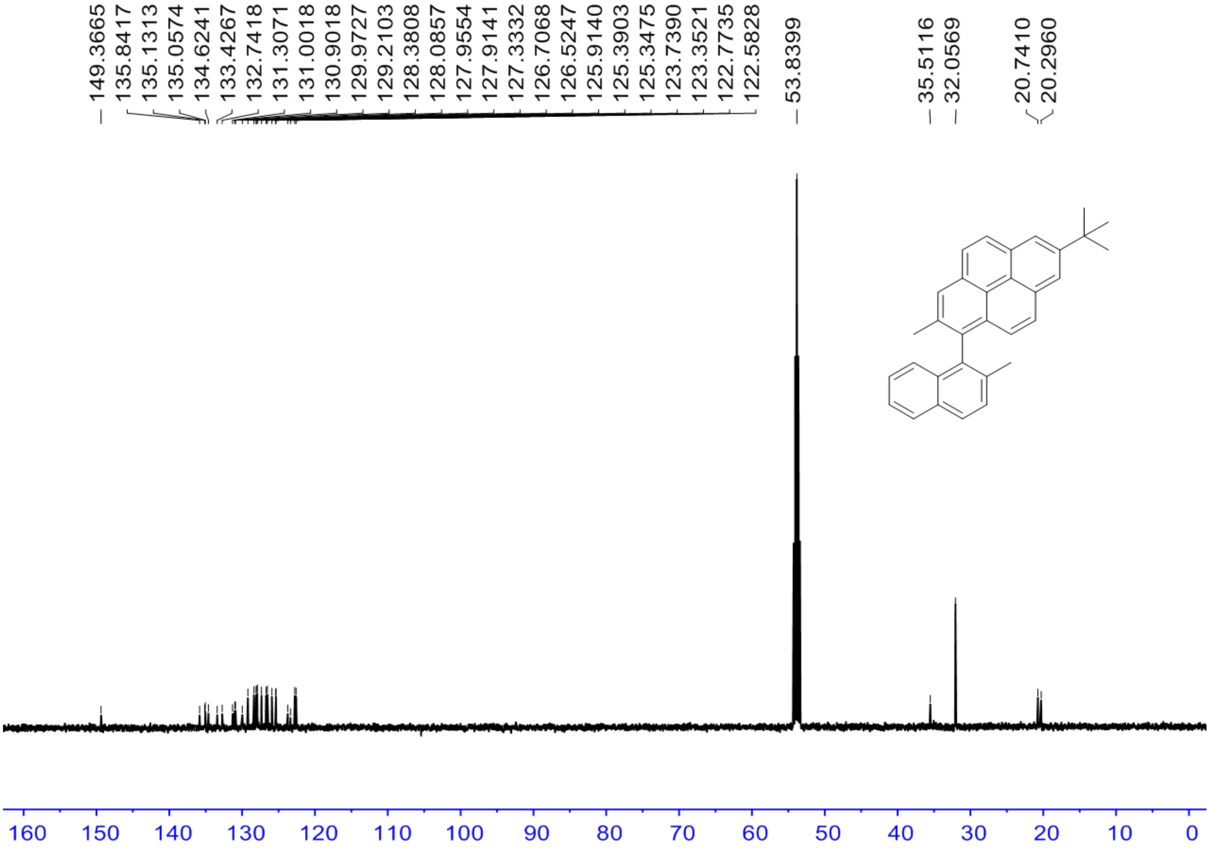
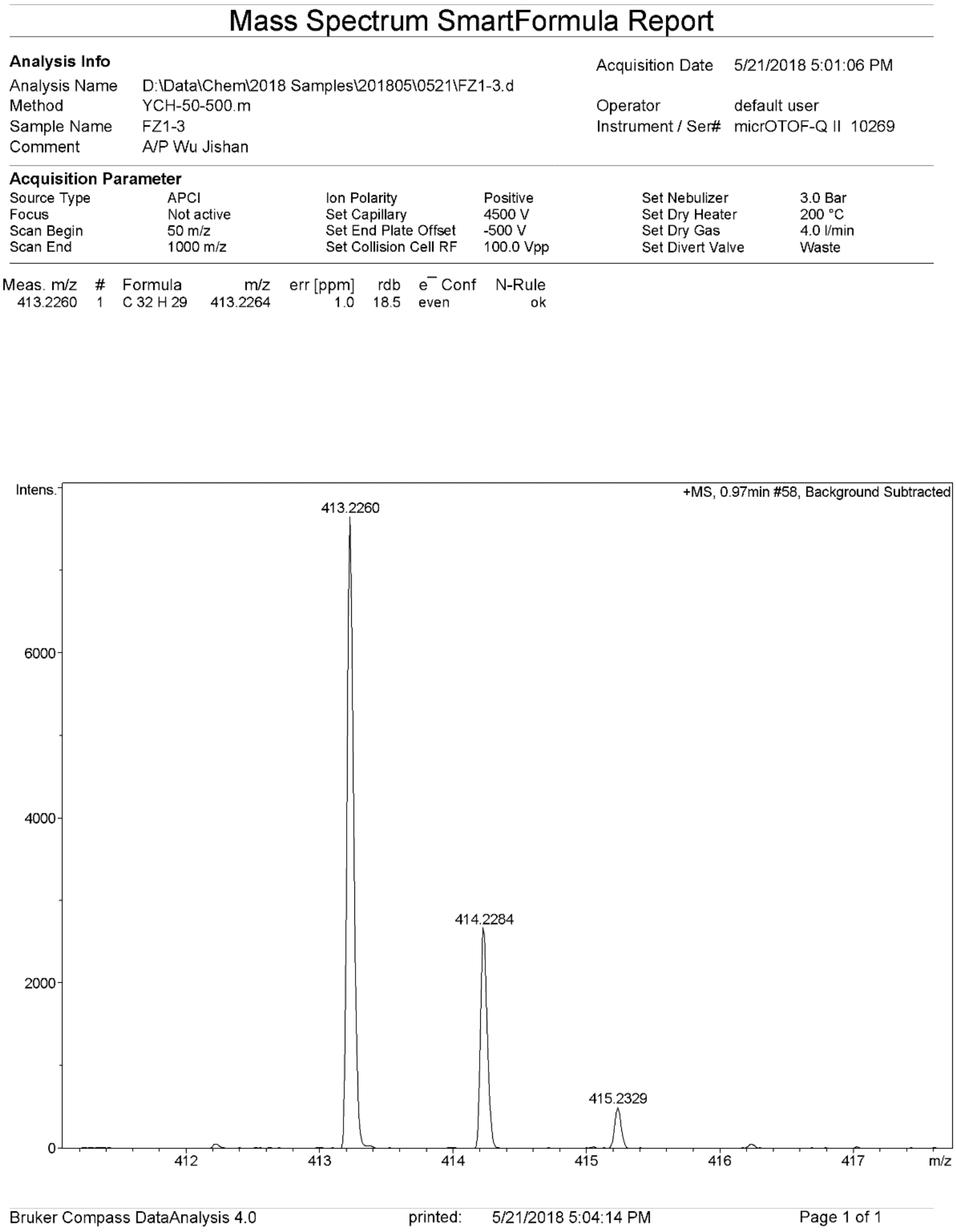


Fig. S26. ^{13}C NMR spectrum of compound **3** (126 MHz, Methylene Chloride-*d*$_2$).



Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	FZ1-3	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Wu Jishan		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
413.2260	1	C 32 H 29	413.2264	1.0	18.5	even	ok

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Fig. S27. HR APCI mass spectrum of compound [**3**+H]$^+$

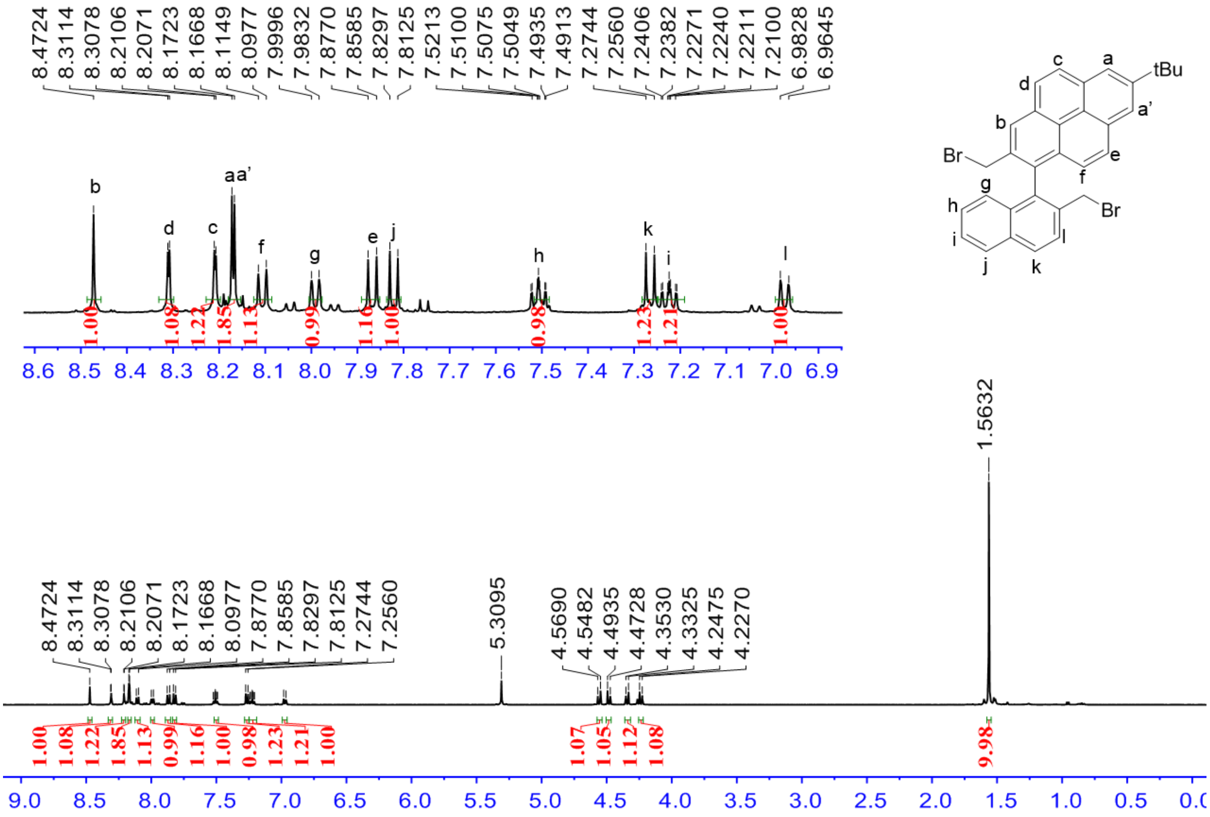


Fig. S28. ^{1}H NMR spectrum of compound **4** (500 MHz, Methylene Chloride-d_2).

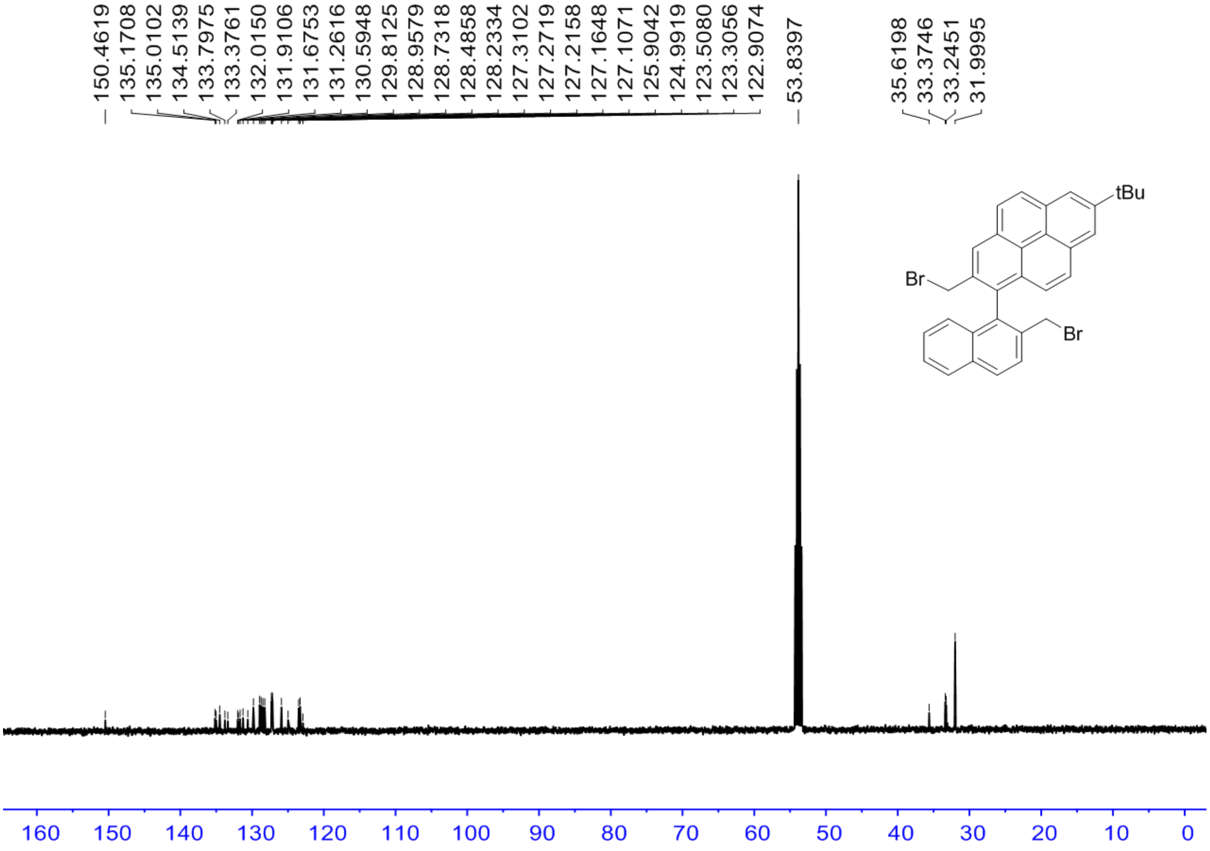
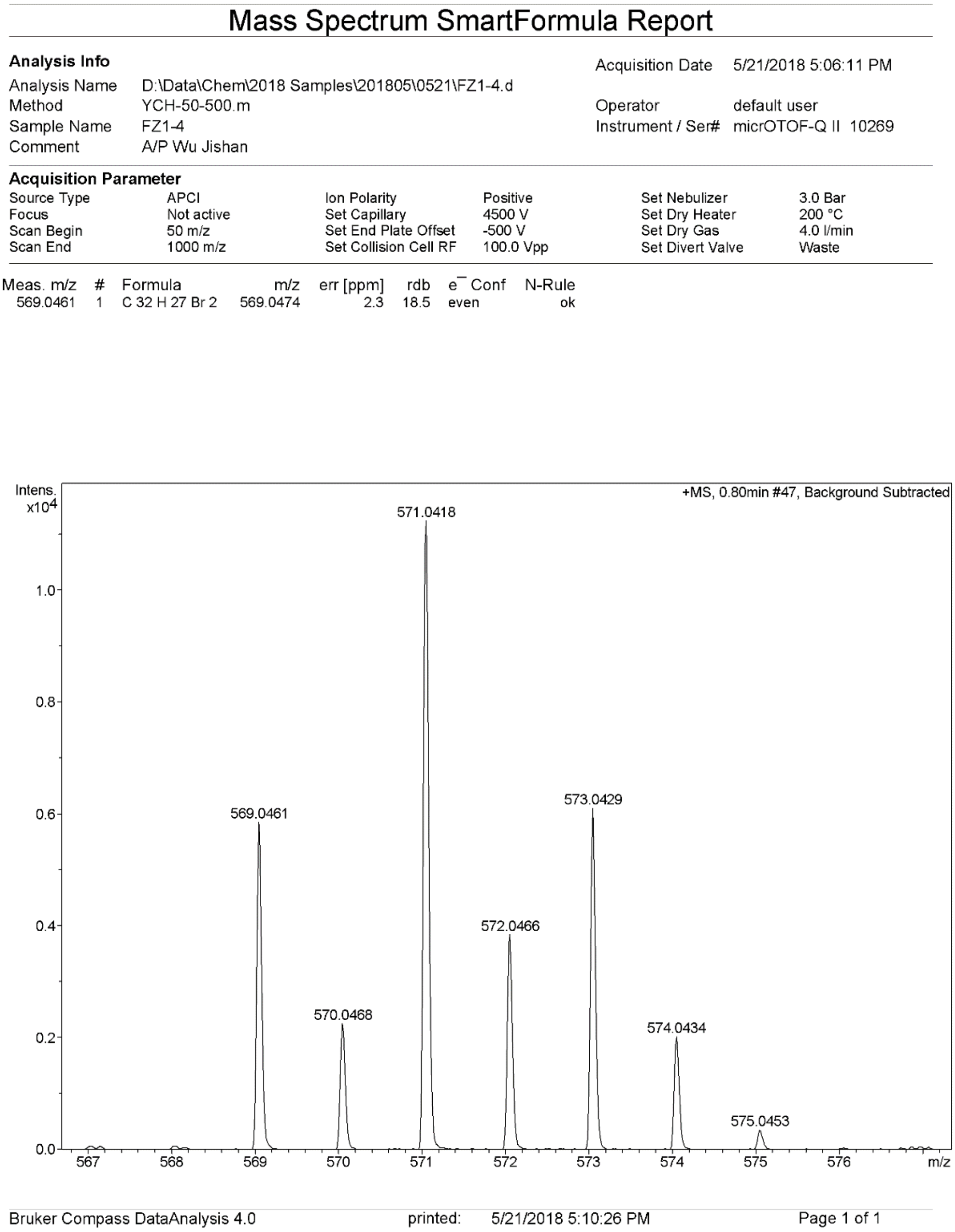


Fig. S29. ^{13}C NMR spectrum of compound **4** (126 MHz, Methylene Chloride-d_2).



Mass Spectrum SmartFormula Report

Analysis Info

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Method	YCH-50-500.m	Operator	default user
Sample Name	FZ1-4	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Wu Jishan		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
569.0461	1	C 32 H 27 Br 2	569.0474	2.3	18.5	even	ok

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Fig. S30. HR APCI mass spectrum of compound [**4**+H]$^+$

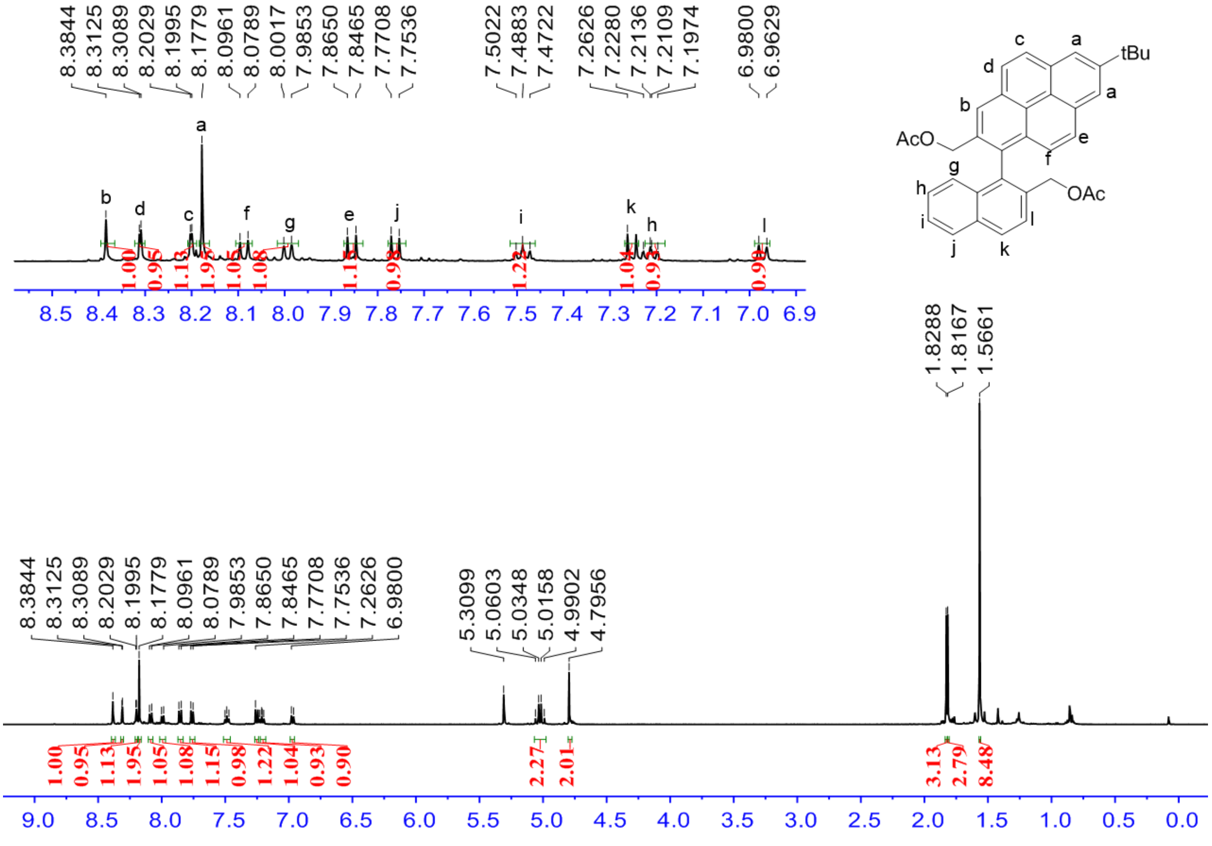


Fig. S31. ^{1}H NMR spectrum of compound **5** (500 MHz, Methylene Chloride-d_2).

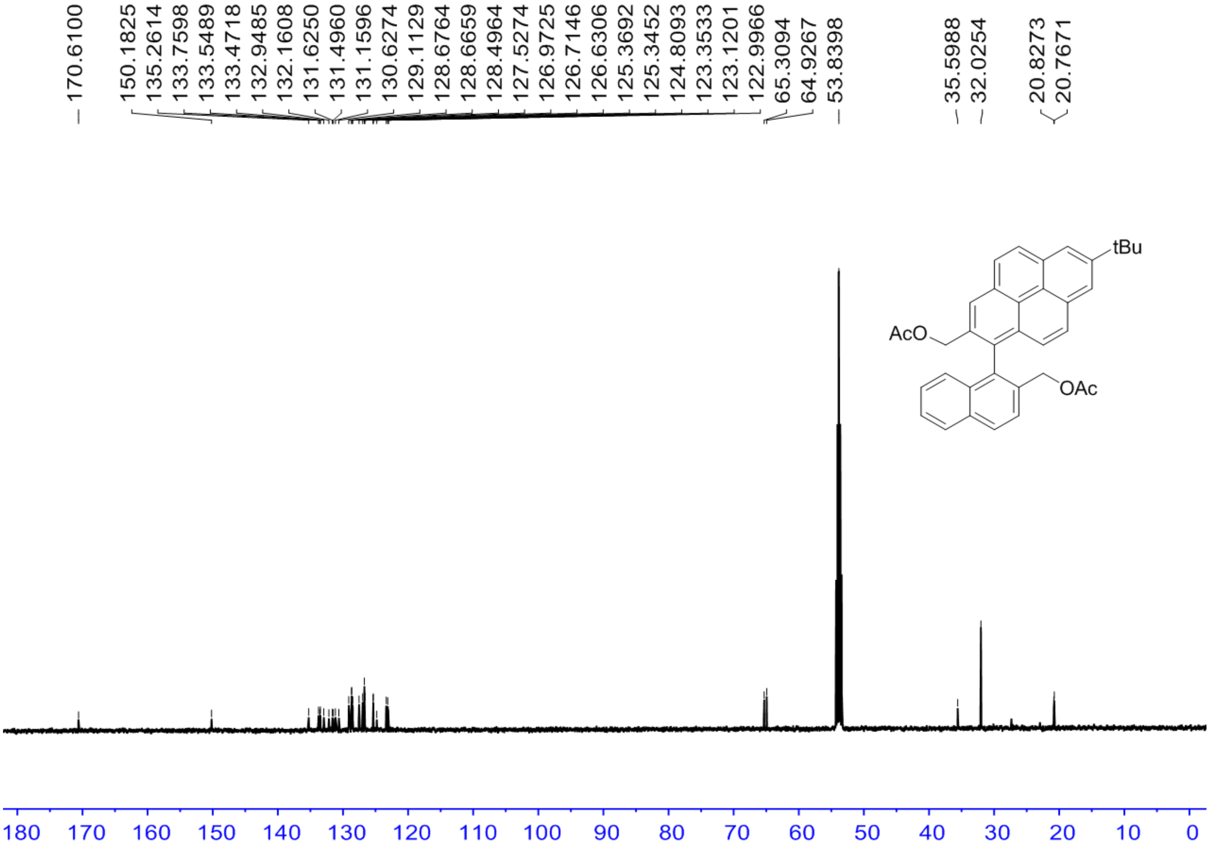
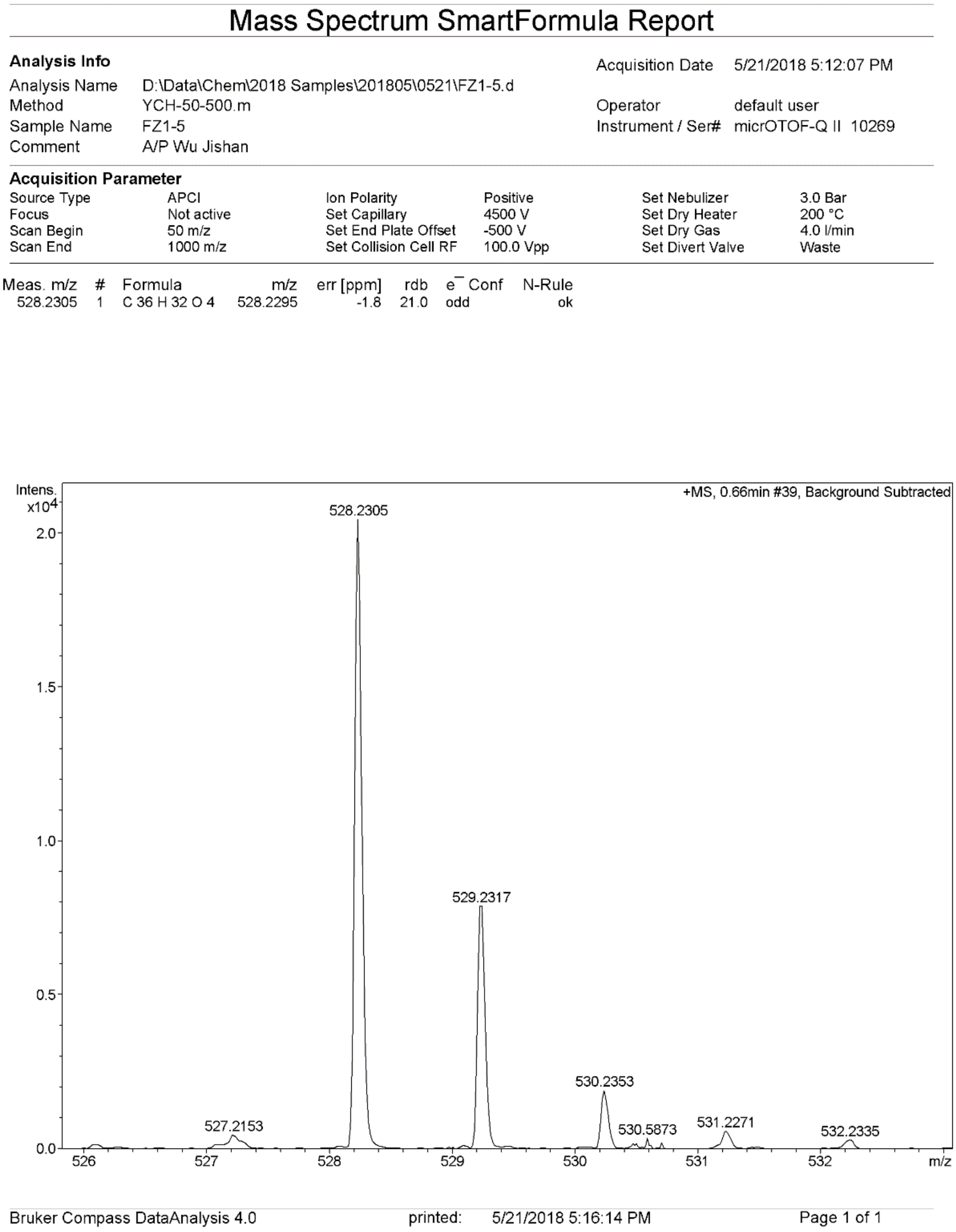


Fig. S32. ^{13}C NMR spectrum of compound **5** (126 MHz, Methylene Chloride-d_2).



Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	FZ1-5	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Wu Jishan		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
528.2305	1	C 36 H 32 O 4	528.2295	-1.8	21.0	odd	ok

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Fig. S33. HR APCI mass spectrum of compound [**5**+H]$^+$

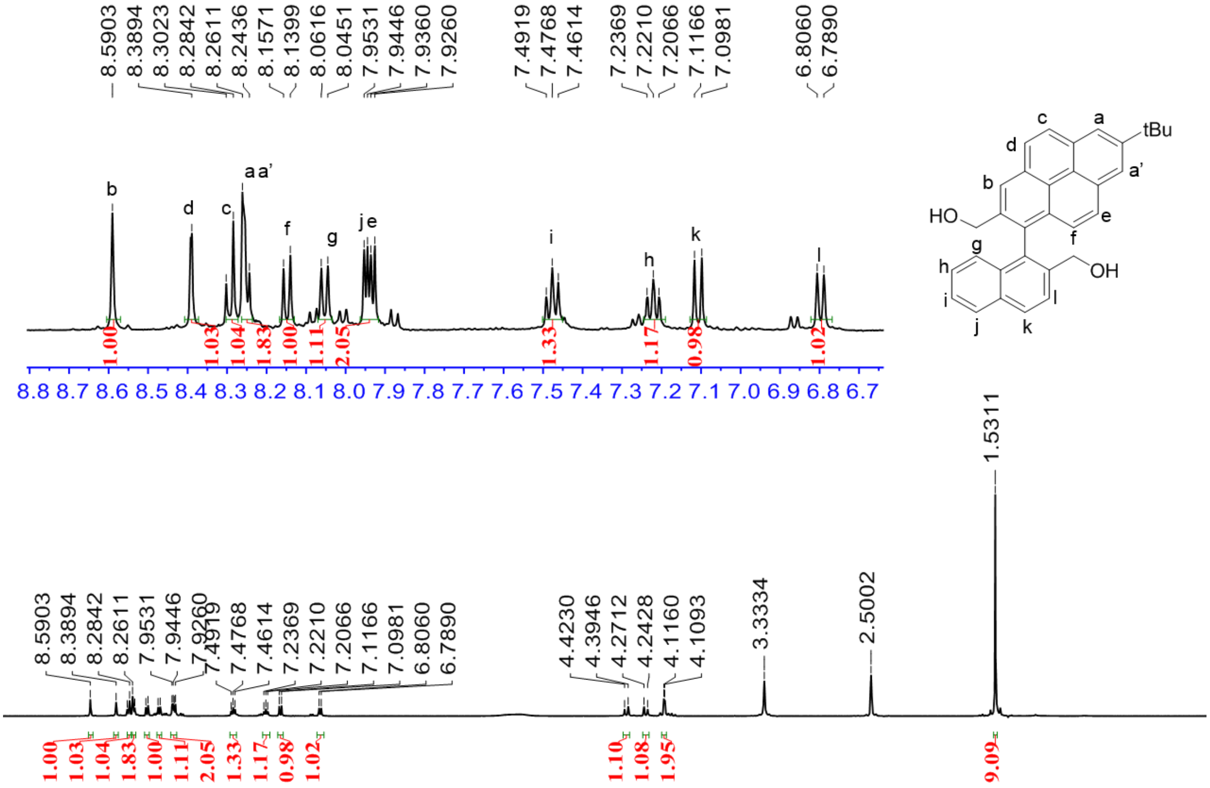


Fig. S34. ^{1}H NMR spectrum of compound **6** (500 MHz, DMSO-d_6).

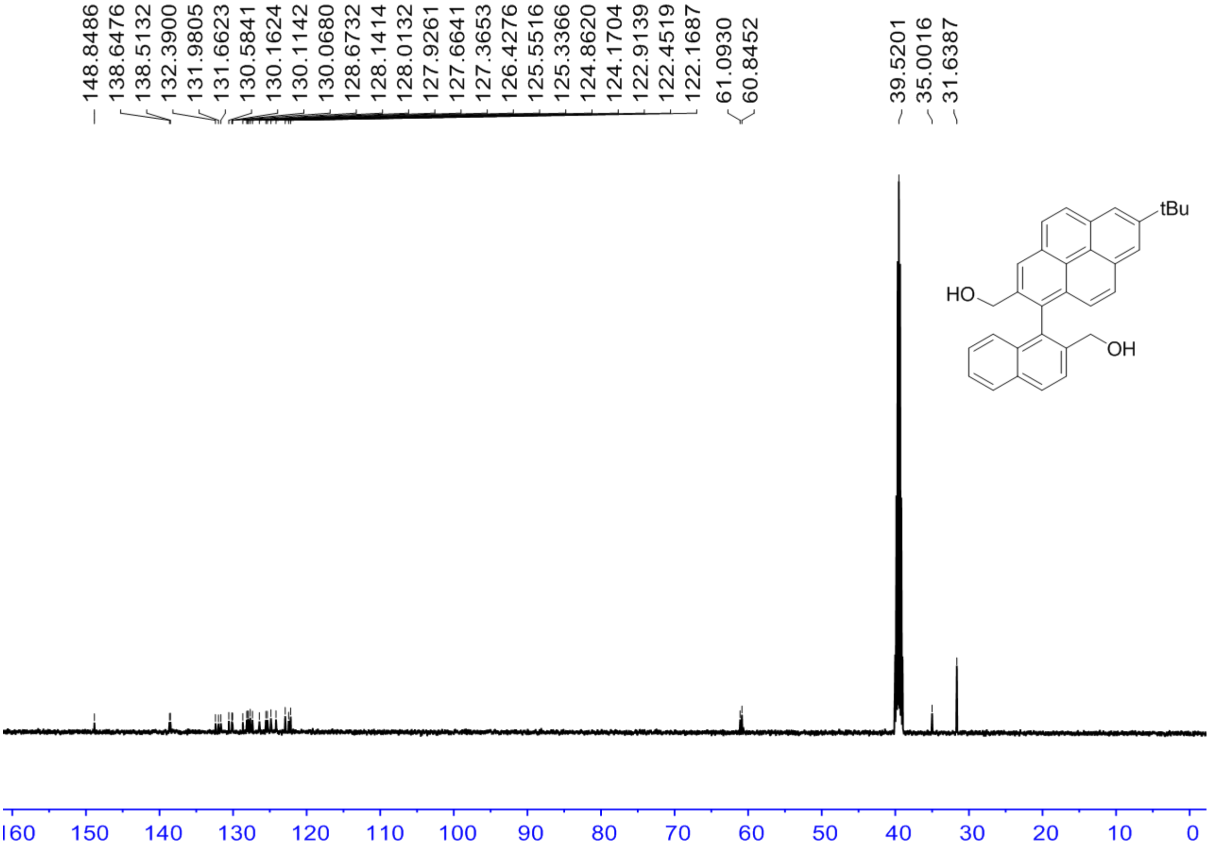
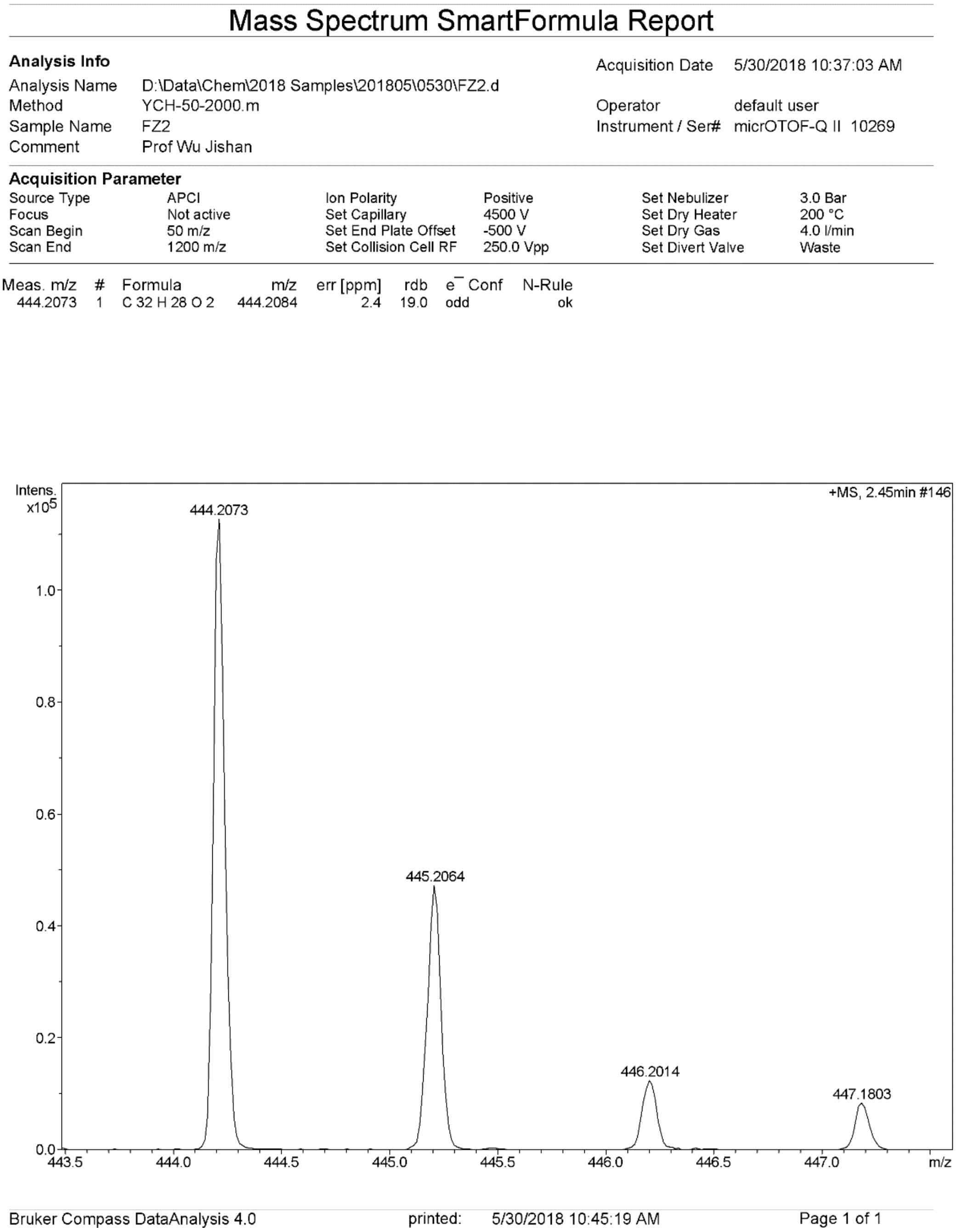


Fig. S35. ^{13}C NMR spectrum of compound **6** (126 MHz, DMSO-d_6).



Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	FZ2	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Prof Wu Jishan		

Acquisition Parameter

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Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	250.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
444.2073	1	C 32 H 28 O 2	444.2084	2.4	19.0	odd	ok

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Fig. S36. HR APCI mass spectrum of compound [**6**+H]$^+$

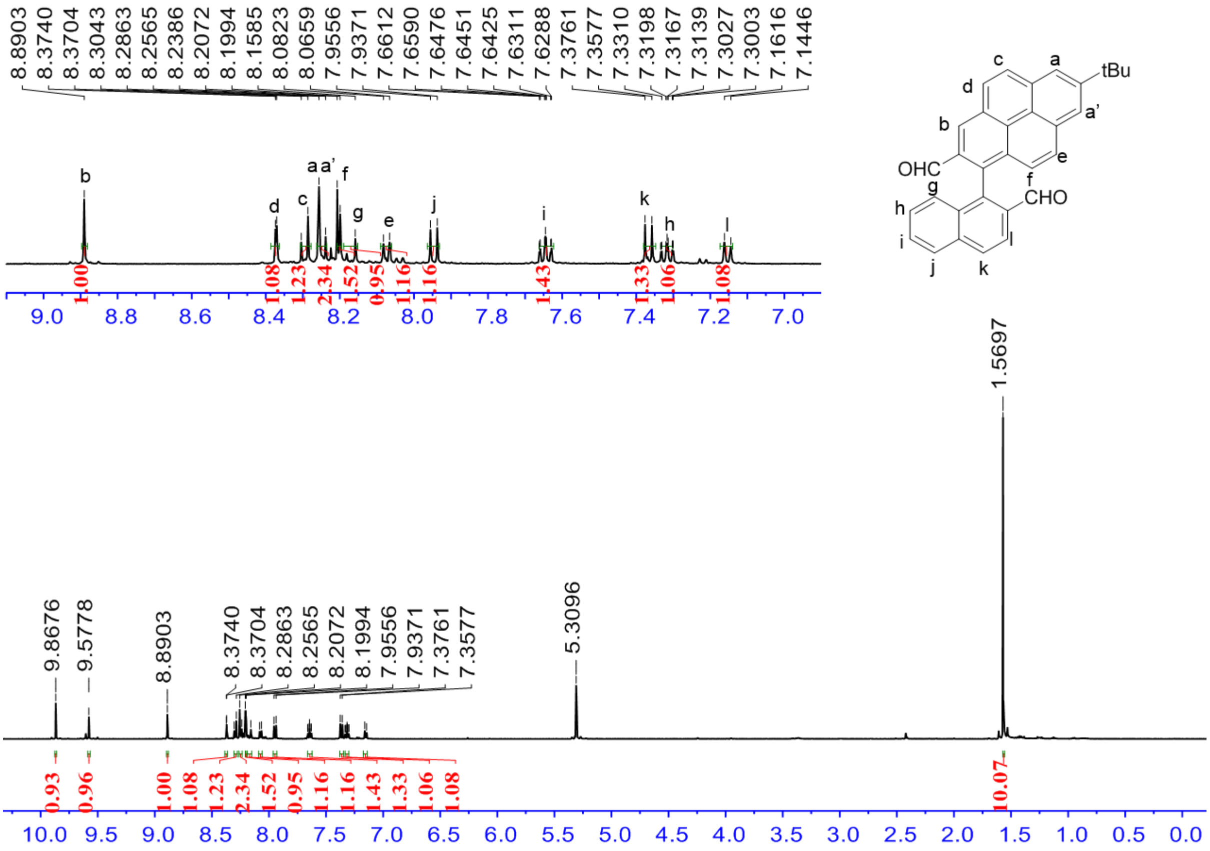


Fig. S37. ^{1}H NMR spectrum of compound **7** (500 MHz, Methylene Chloride-d_2).

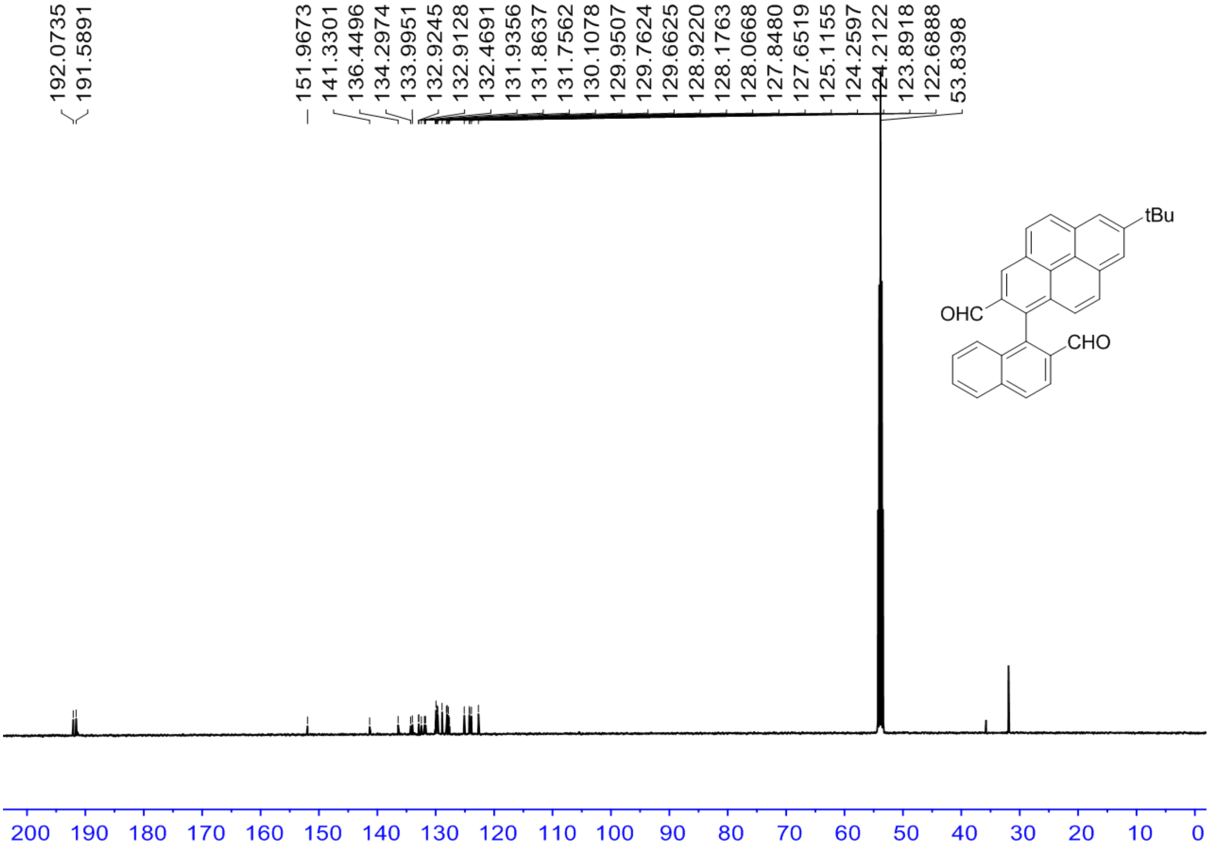
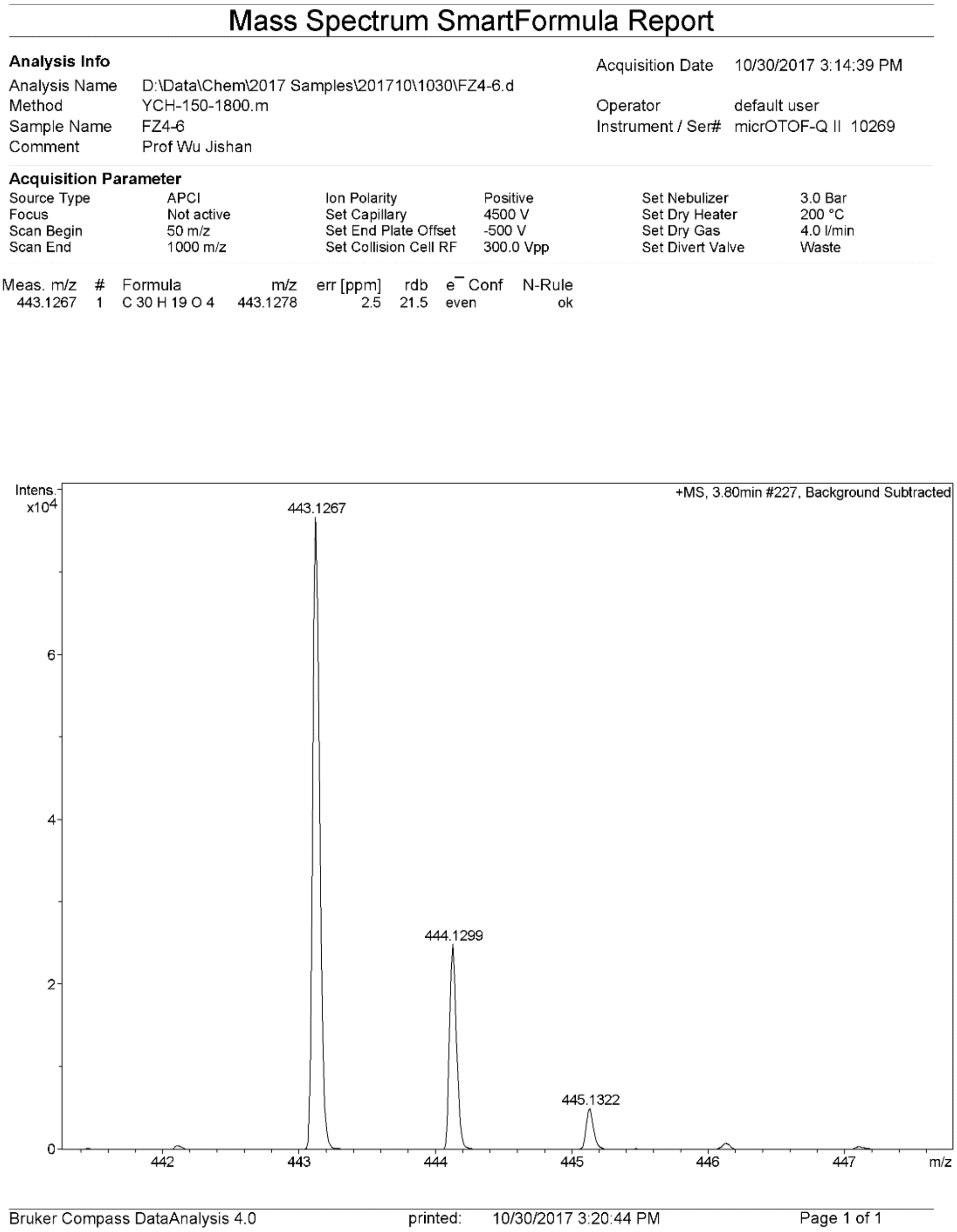


Fig. S38. ^{13}C NMR spectrum of compound **7** (126 MHz, Methylene Chloride-d_2).



Mass Spectrum SmartFormula Report

Analysis Info

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Comment	Prof Wu Jishan		

Acquisition Parameter

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Scan End	1000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
443.1267	1	C 30 H 19 O 4	443.1278	2.5	21.5	even	ok

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Fig. S39. HR APCI mass spectrum of compound [**7**+H]$^+$

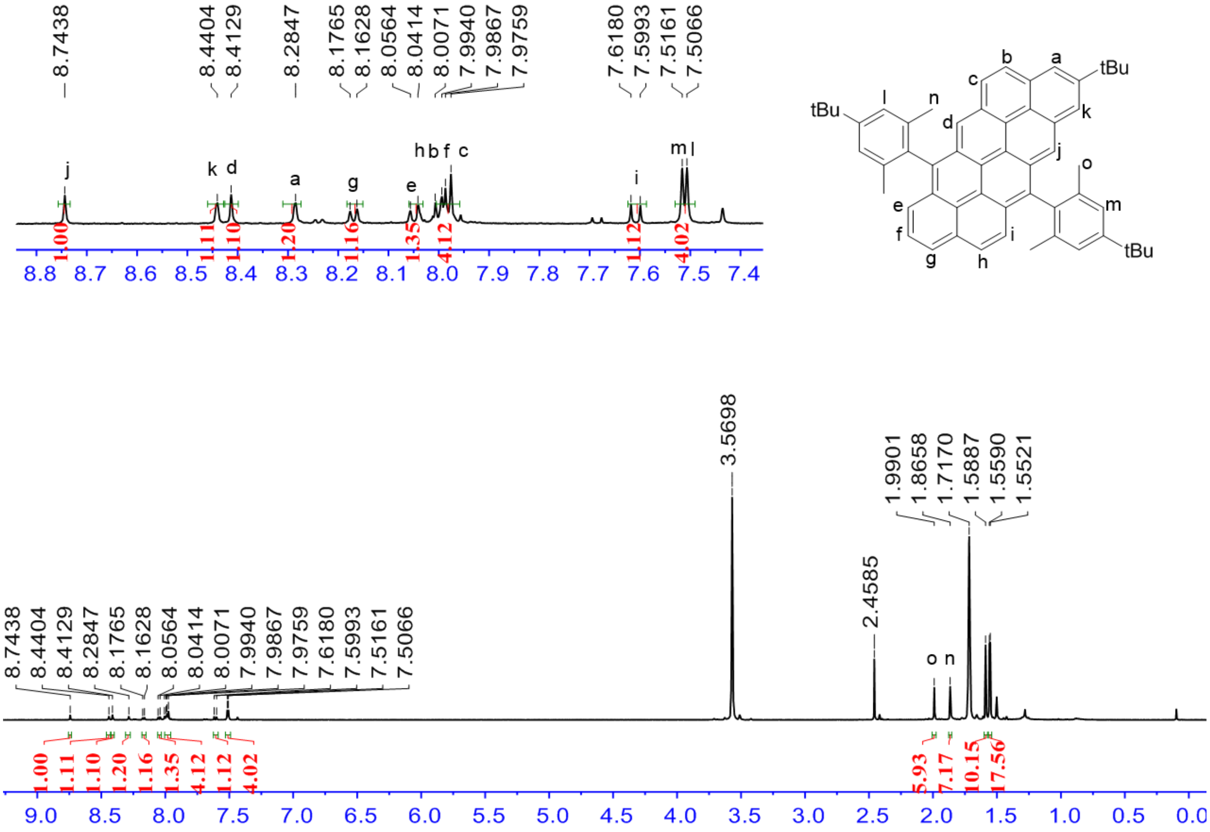


Fig. S40. ^{1}H NMR spectrum of compound **TT-Ar** (500 MHz, THF-d_8).

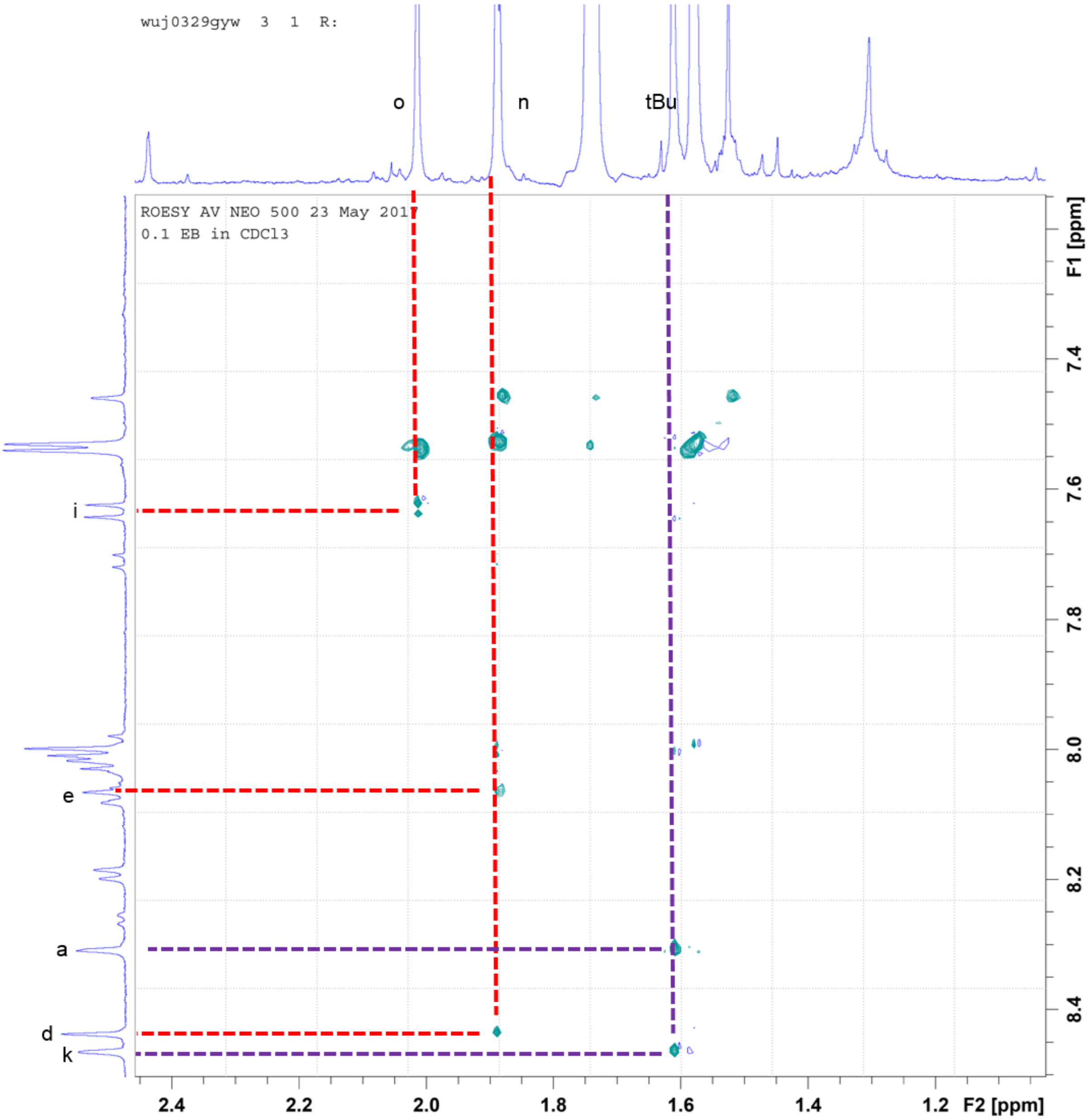


Fig. S41. 2D ROESY NMR spectrum of compound **TT-Ar** (500 MHz, THF-d_8).

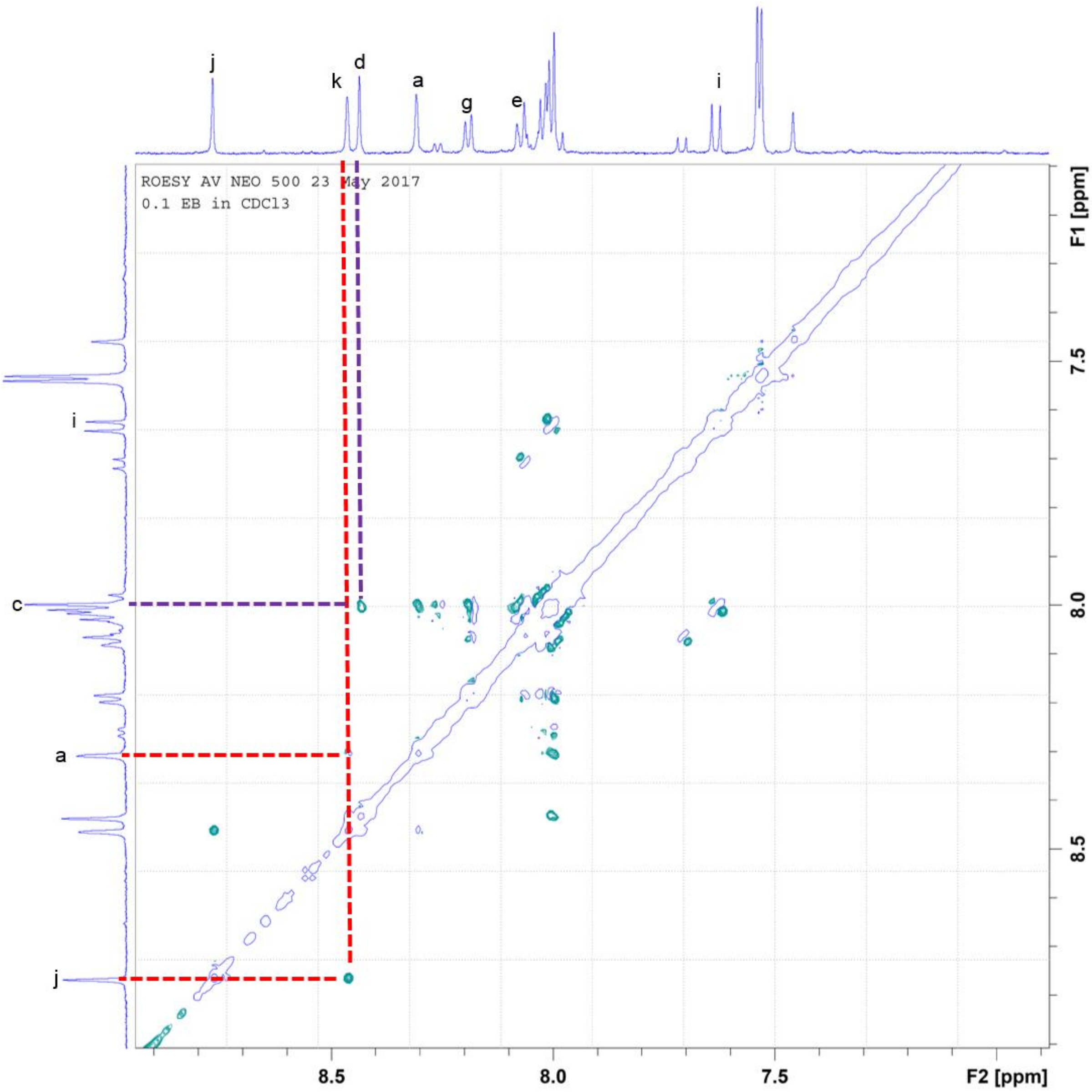
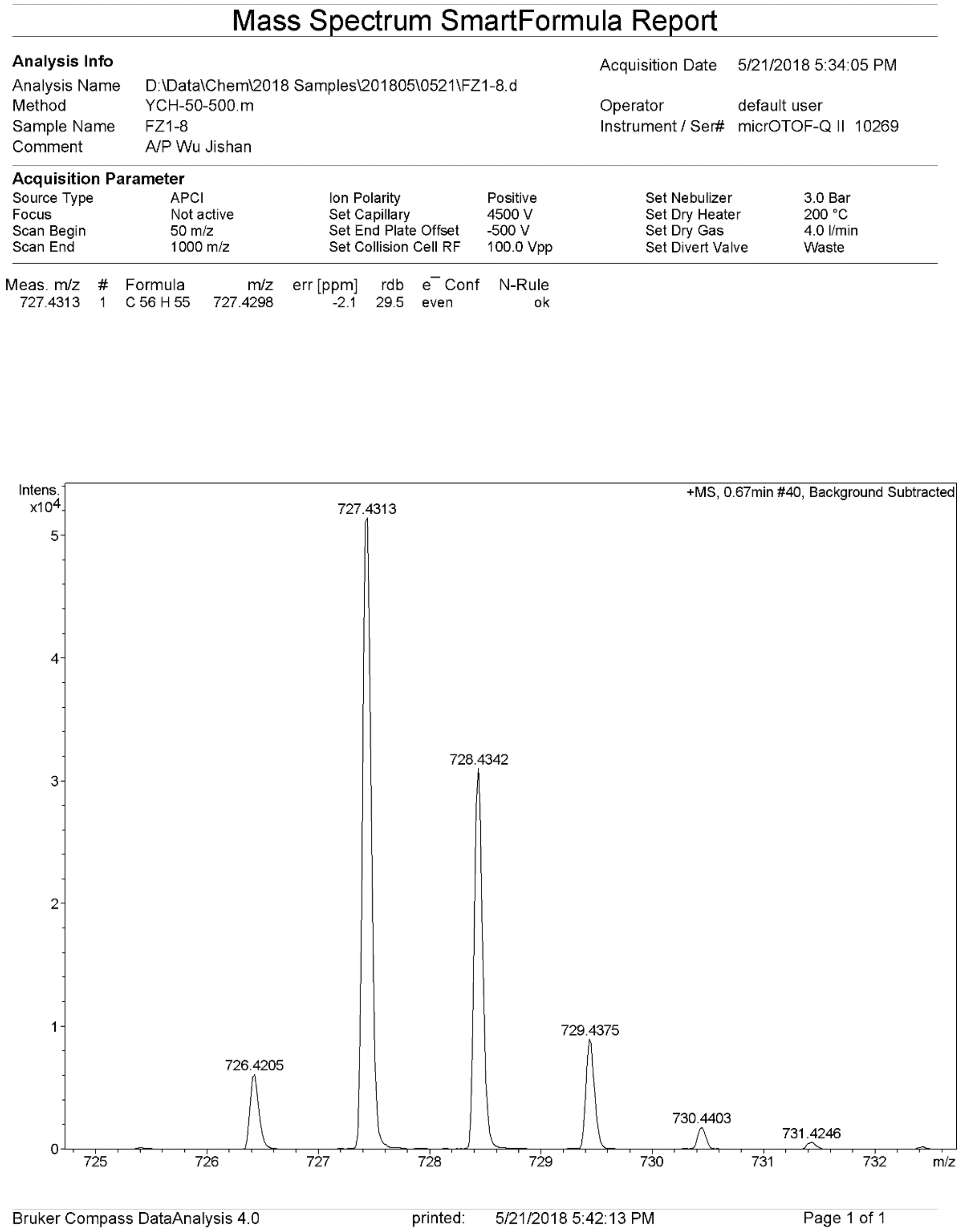


Fig. S42. 2D ROESY NMR spectrum of compound **TT-Ar** (500 MHz, THF-d_8).



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201805\0521\FZ1-8.d	Acquisition Date	5/21/2018 5:34:05 PM
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Sample Name	FZ1-8	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Wu Jishan		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
727.4313	1	C 56 H 55	727.4298	-2.1	29.5	even	ok

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Fig. S43. HR APCI mass spectrum of compound [**TT-Ar**+H]$^+$.

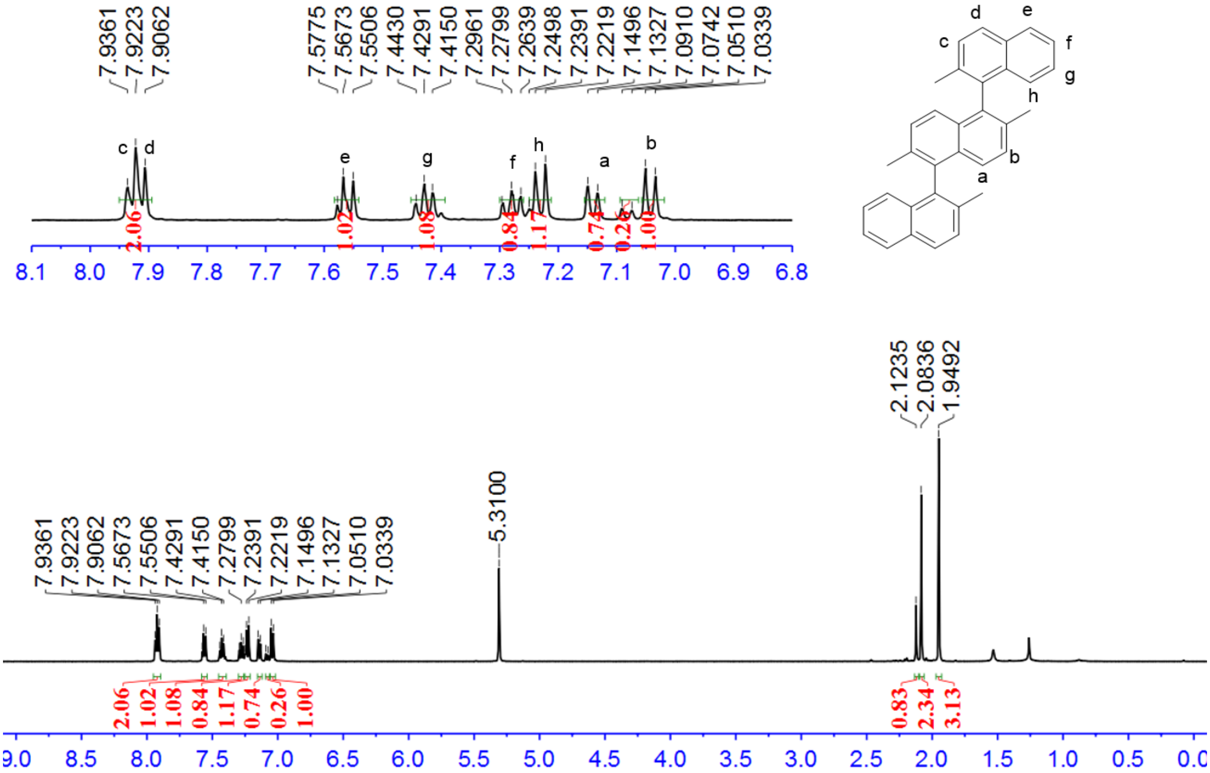


Fig. S44. ^{1}H NMR spectrum of compound **10** (500 MHz, Methylene Chloride-*d*$_2$).

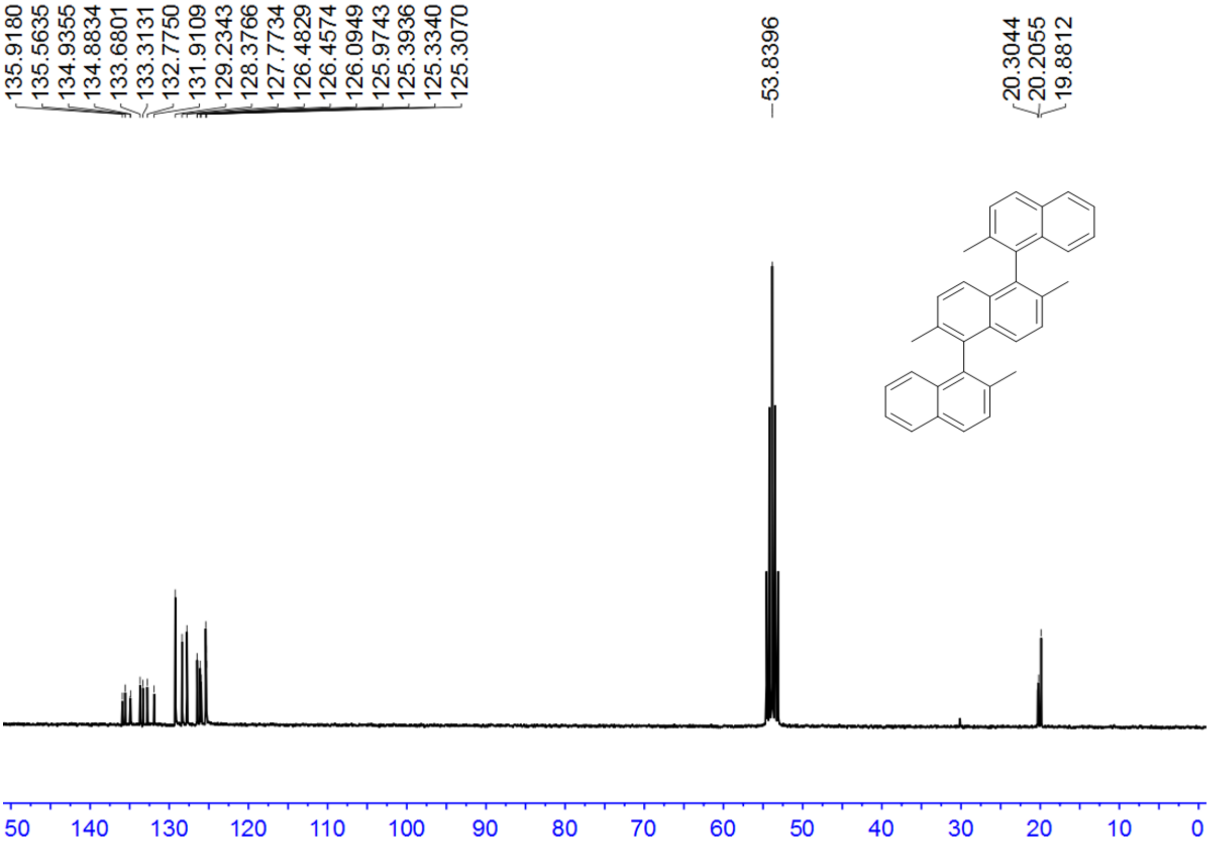
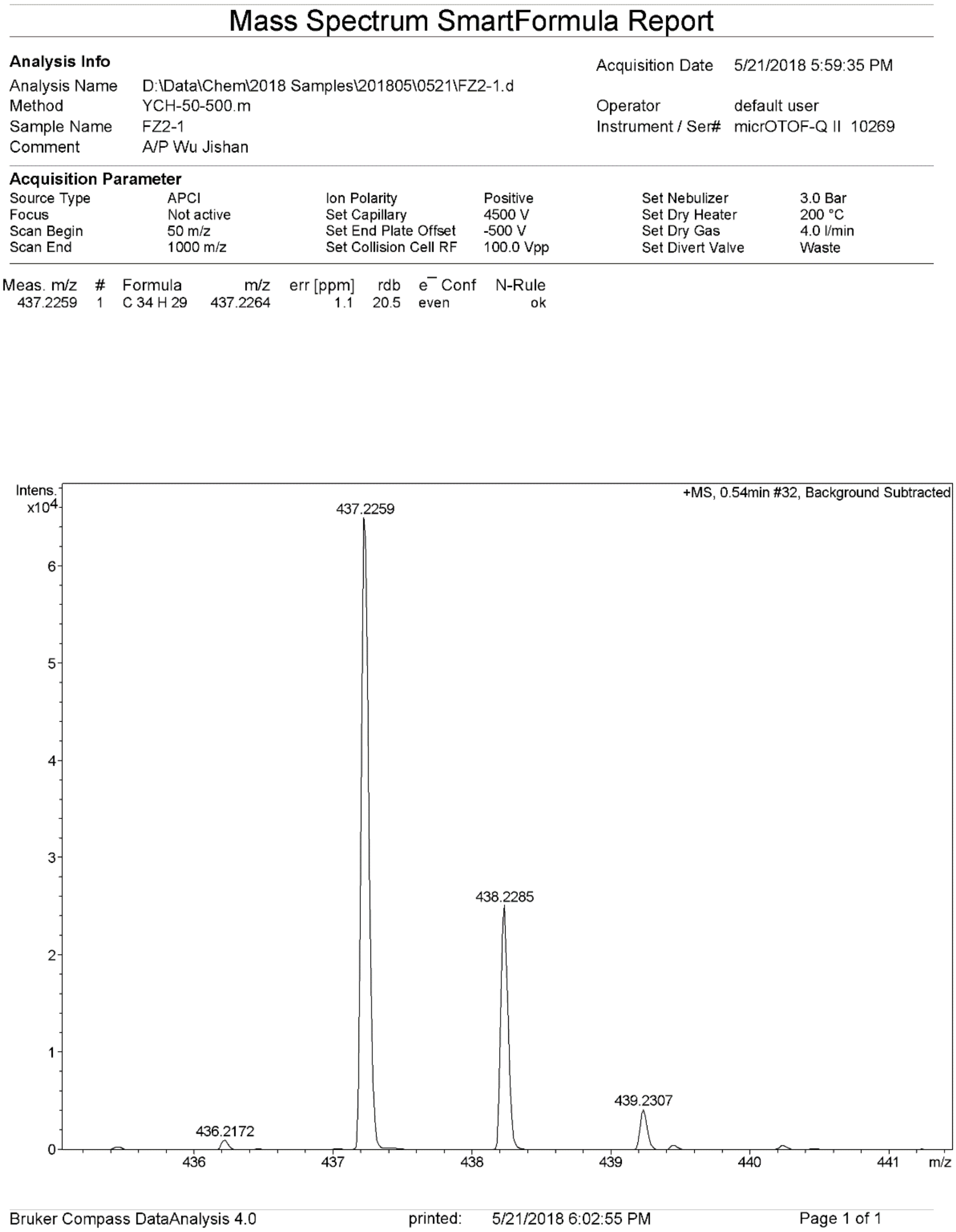


Fig. S45. ^{13}C NMR spectrum of compound **10** (75 MHz, Methylene Chloride-*d*$_2$).



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\Chem\2018 Samples\201805\0521\FZ2-1.d
Method YCH-50-500.m
Sample Name FZ2-1
Comment A/P Wu Jishan

Acquisition Date 5/21/2018 5:59:35 PM
Operator default user
Instrument / Ser# micrOTOF-Q II 10269

Acquisition Parameter

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Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	1000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
437.2259	1	C 34 H 29	437.2264	1.1	20.5	even	ok

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Fig. S46. HR APCI mass spectrum of compound [**10**+H]$^+$

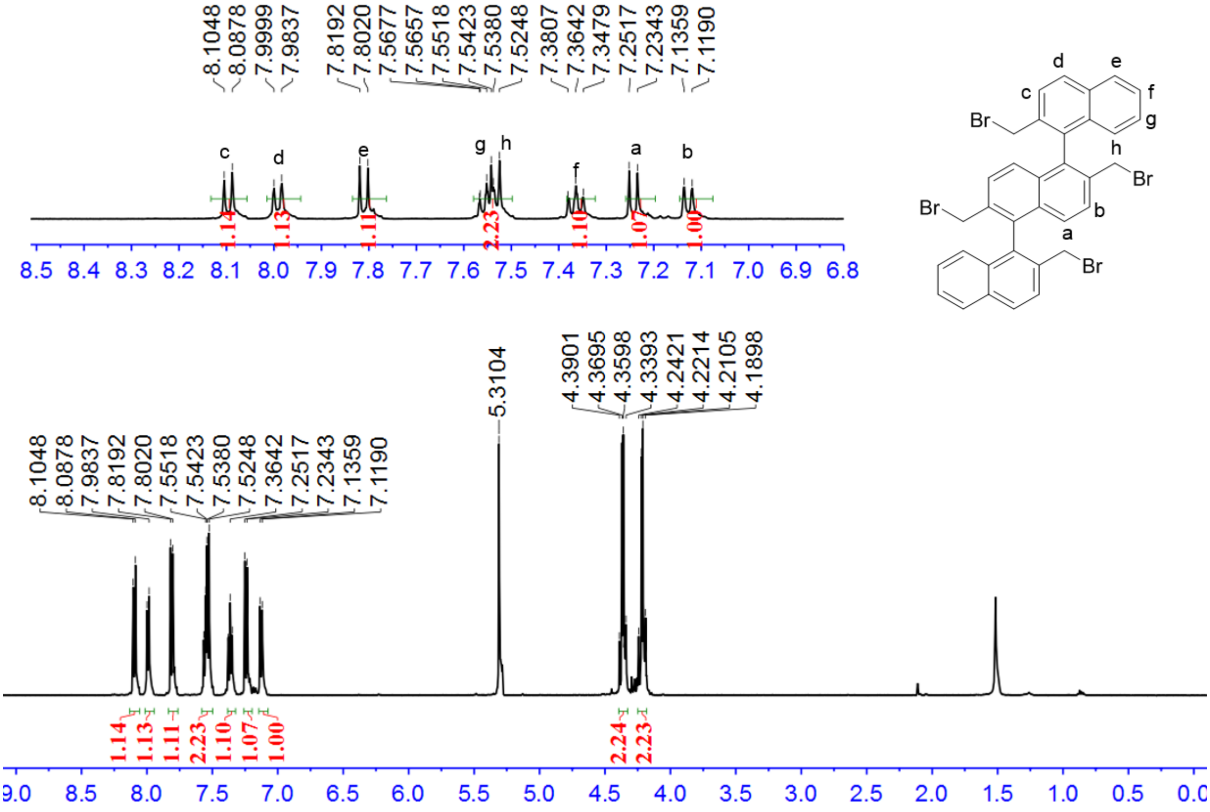


Fig. S47. ^{1}H NMR spectrum of compound **11** (500 MHz, Methylene Chloride-d_2).

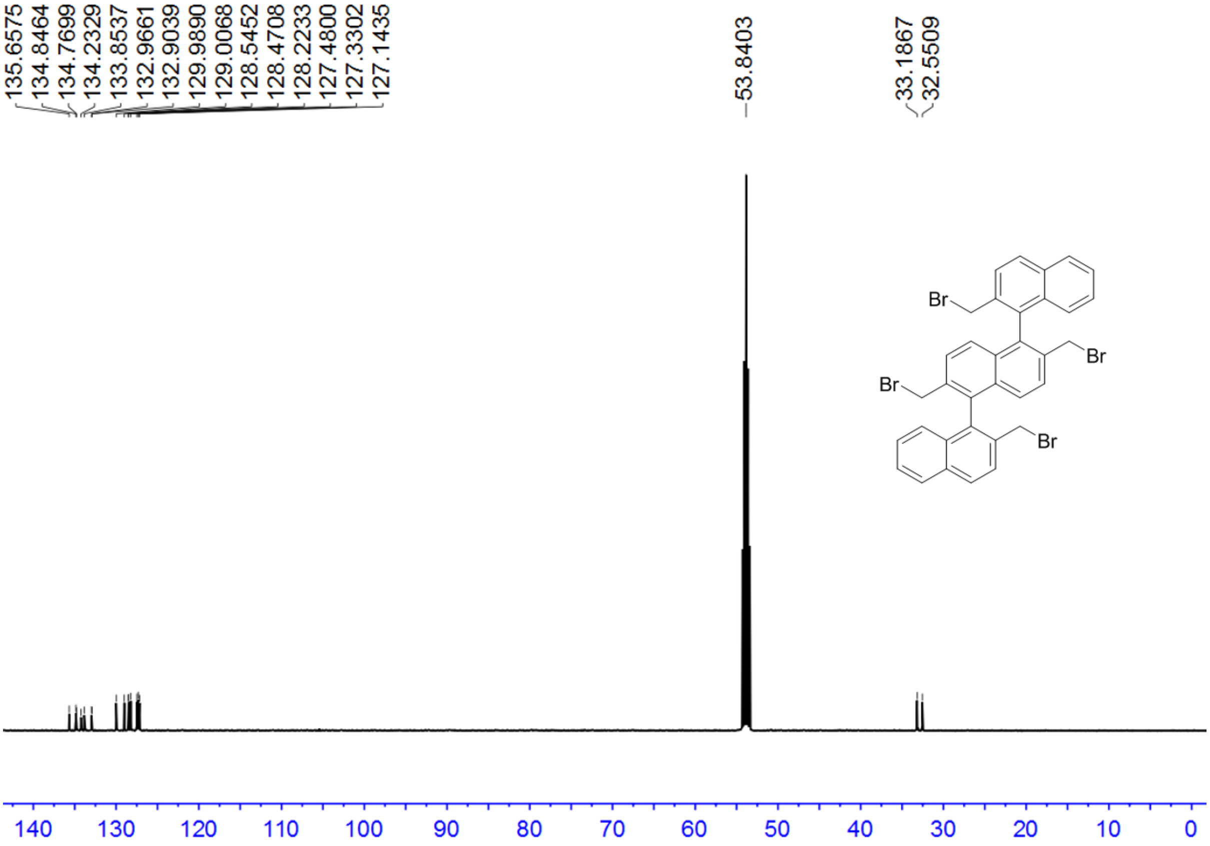
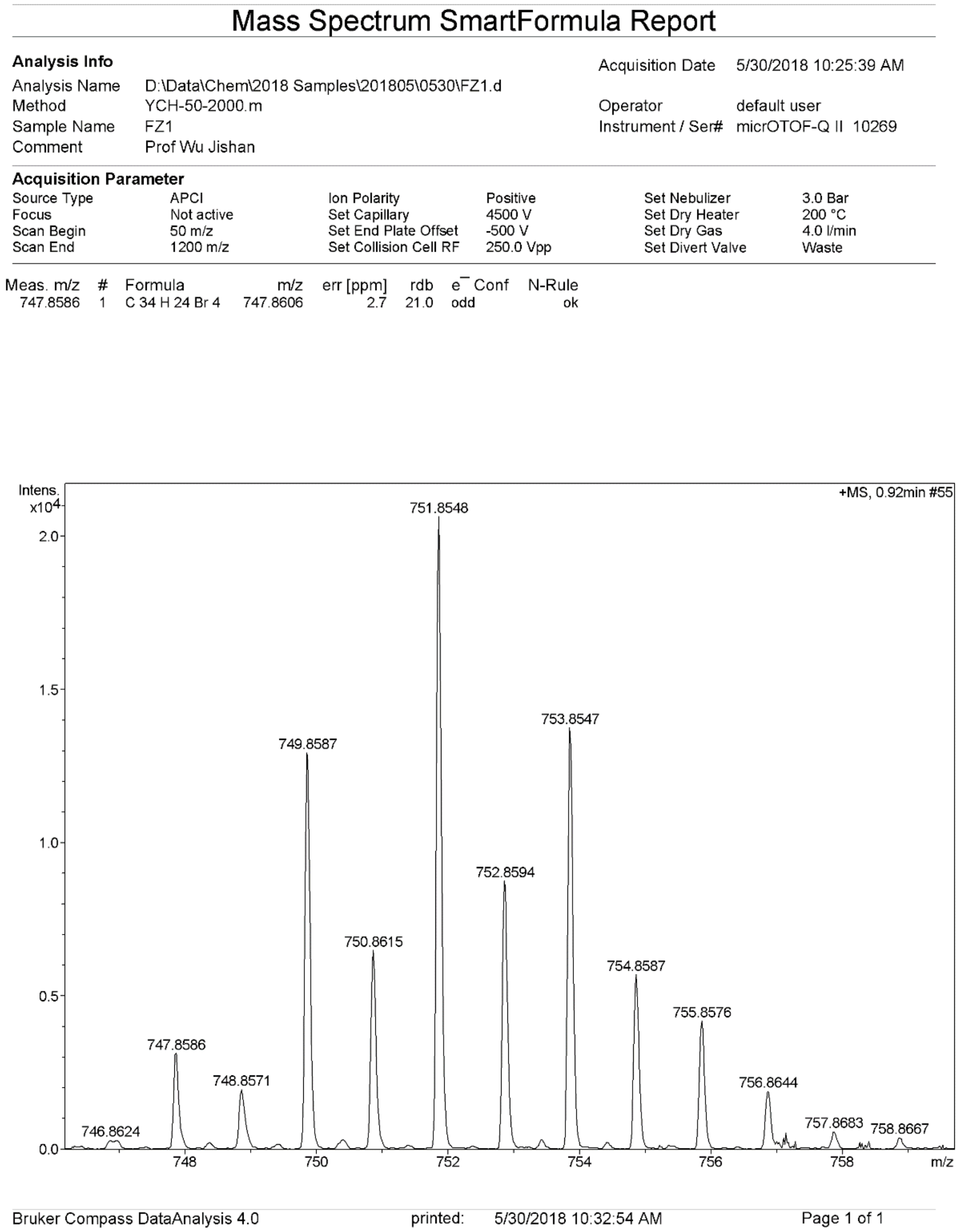


Fig. S48. ^{13}C NMR spectrum of compound **11** (126 MHz, Methylene Chloride-d_2).



Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	FZ1	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Prof Wu Jishan		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	250.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
747.8586	1	C 34 H 24 Br 4	747.8606	2.7	21.0	odd	ok

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Fig. S49. HR APCI mass spectrum of compound [**11**+H]$^+$

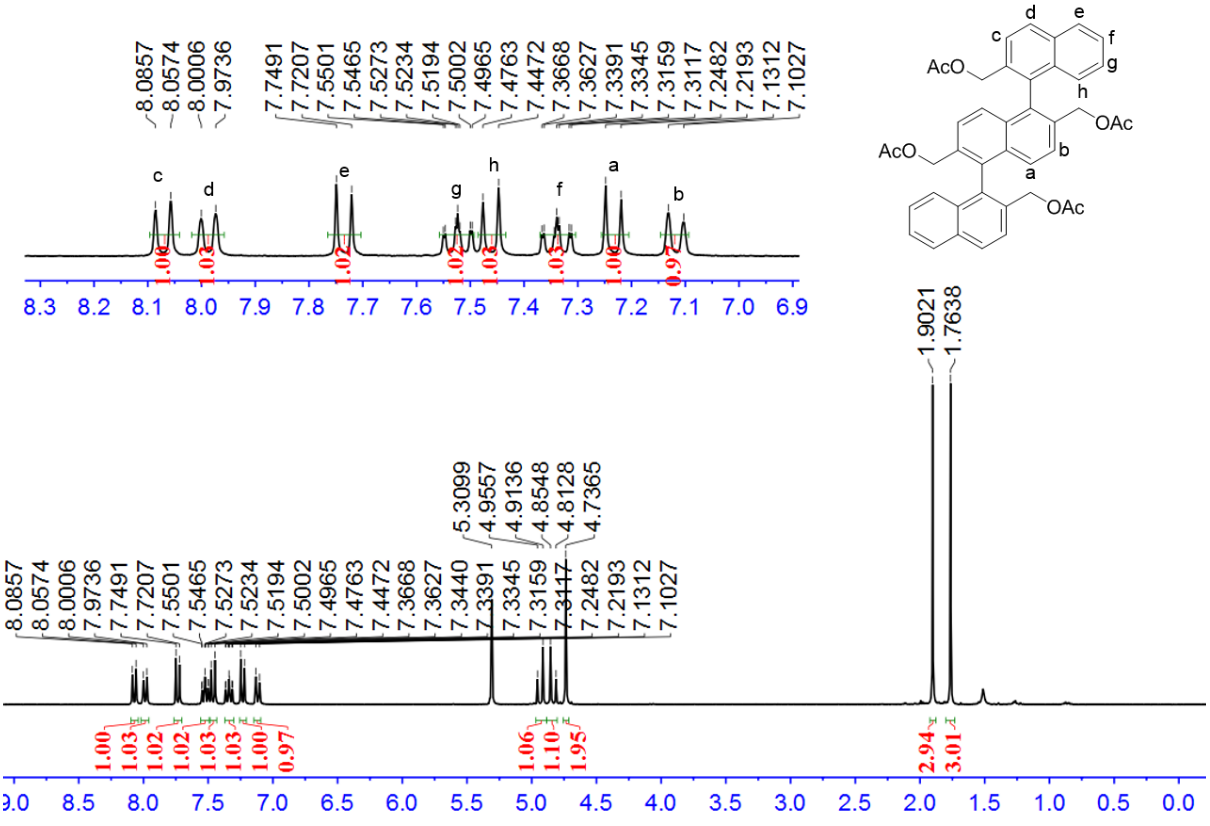


Fig. S50. ^{1}H NMR spectrum of compound **11-a** (300 MHz, Methylene Chloride-d_2).

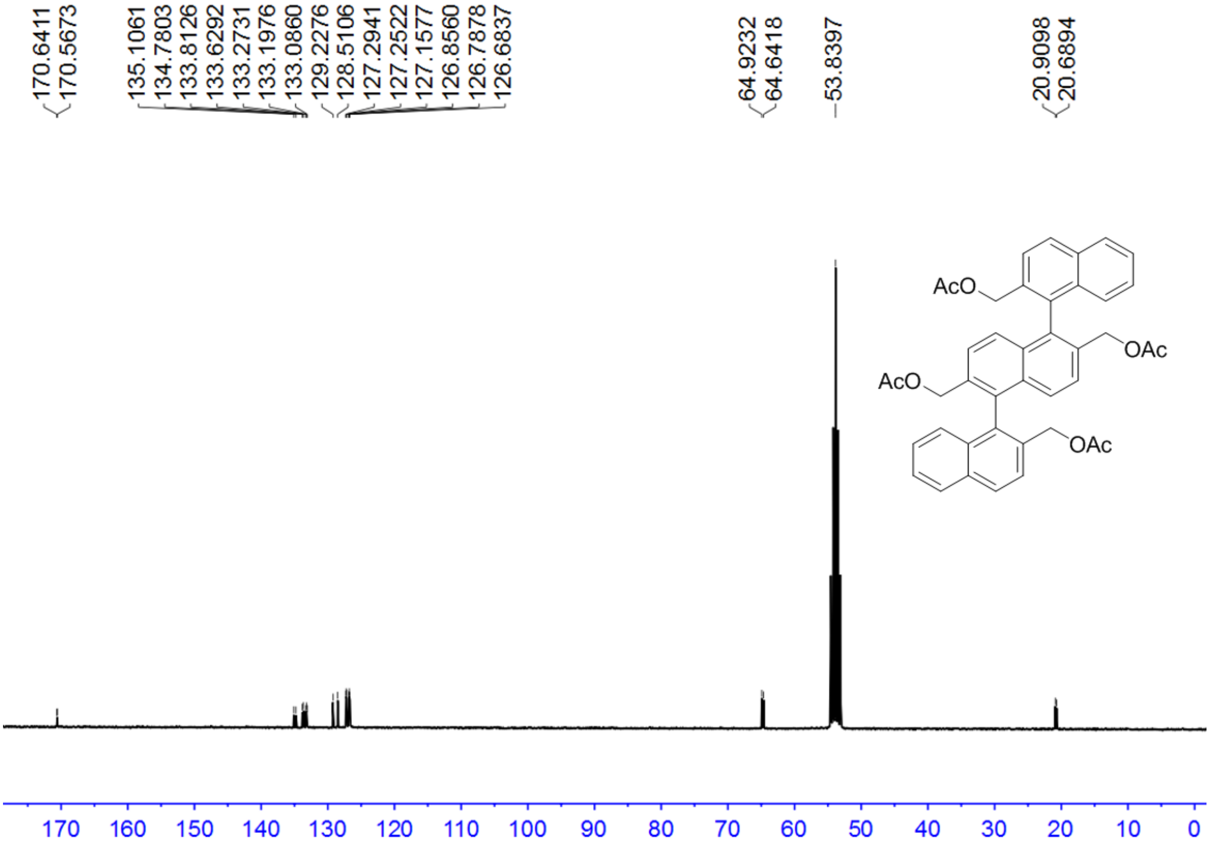
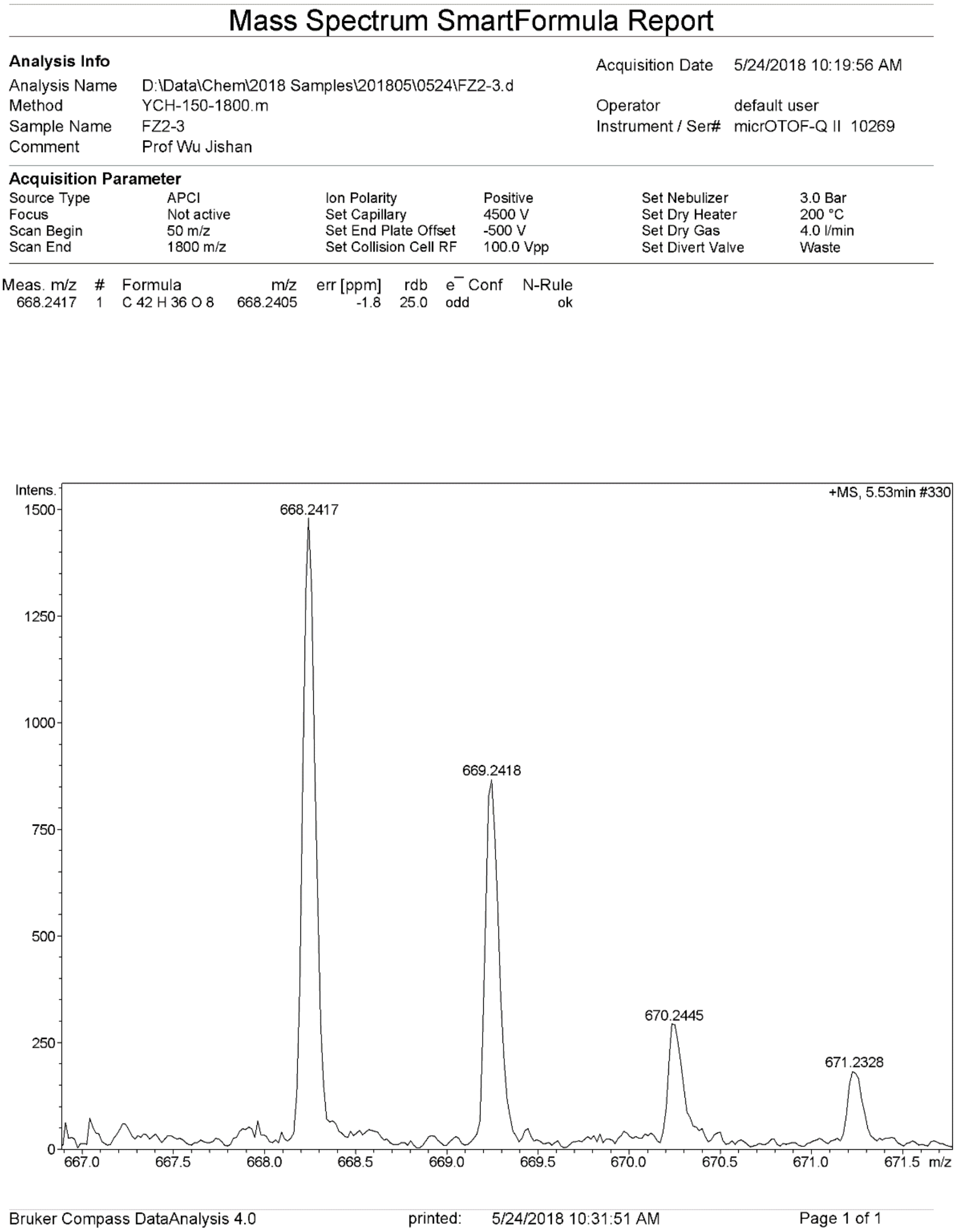


Fig. S51. ^{13}C NMR spectrum of compound **11-a** (75 MHz, Methylene Chloride-d_2).



Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	FZ2-3	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Prof Wu Jishan		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	1800 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
668.2417	1	C 42 H 36 O 8	668.2405	-1.8	25.0	odd	ok

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Fig. S52. HR APCI mass spectrum of compound [**11-a**+H]$^+$

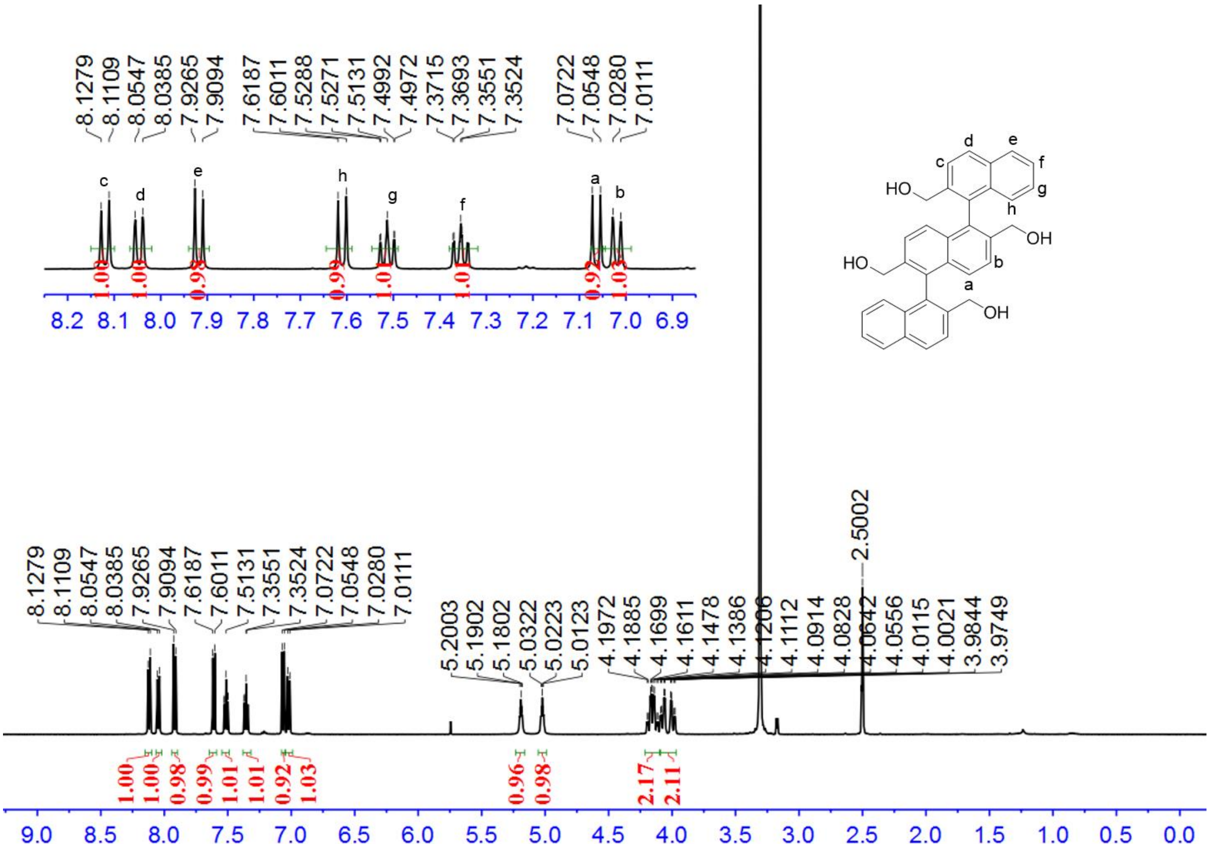

Fig. S53. ^{1}H NMR spectrum of compound **11-b** (500 MHz, DMSO-d_6).

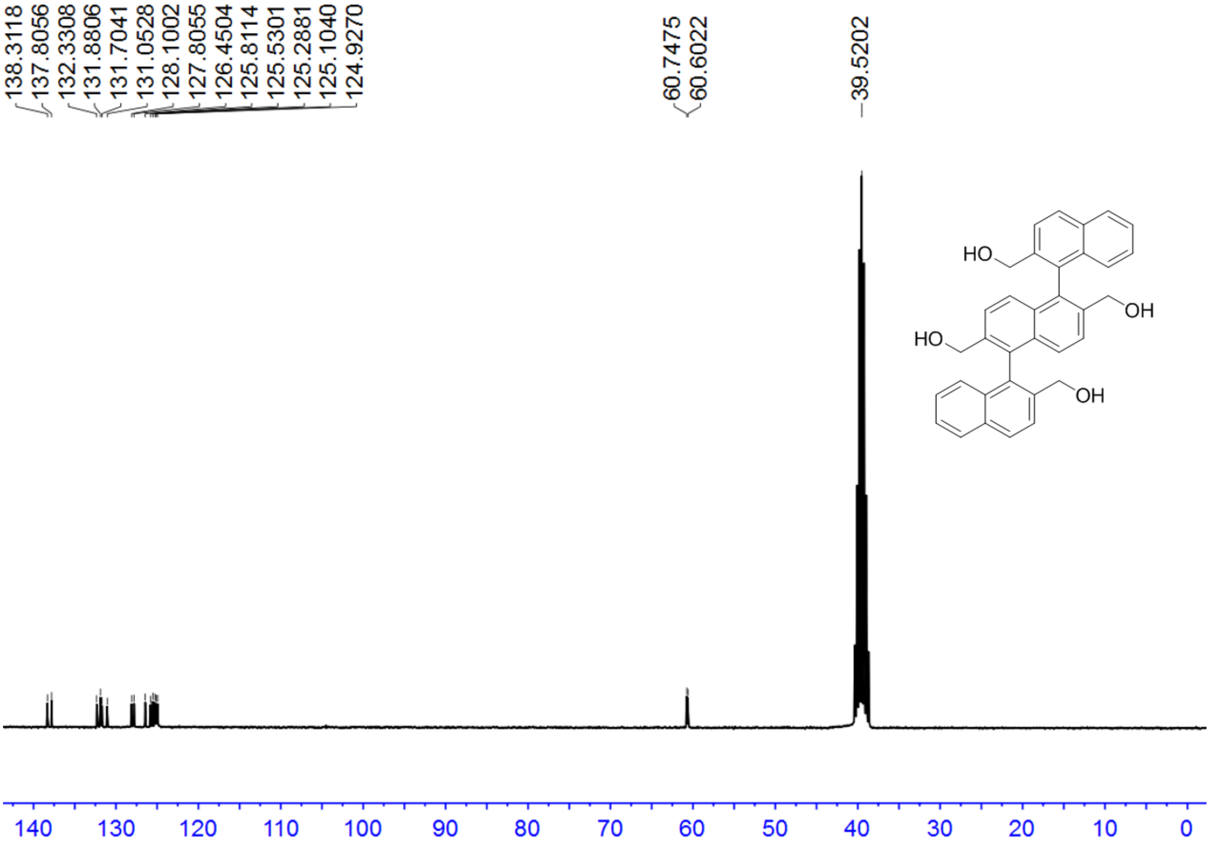

Fig. S54. ^{13}C NMR spectrum of compound **11-b** (75 MHz, DMSO-d_6).

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201805\0524\FZ2-4.d	Acquisition Date	5/24/2018 10:35:22 AM
Method	YCH-150-1800.m	Operator	default user
Sample Name	FZ2-4	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Prof Wu Jishan		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
500.1981	1	C 34 H 28 O 4	500.1982	0.2	21.0	odd	ok

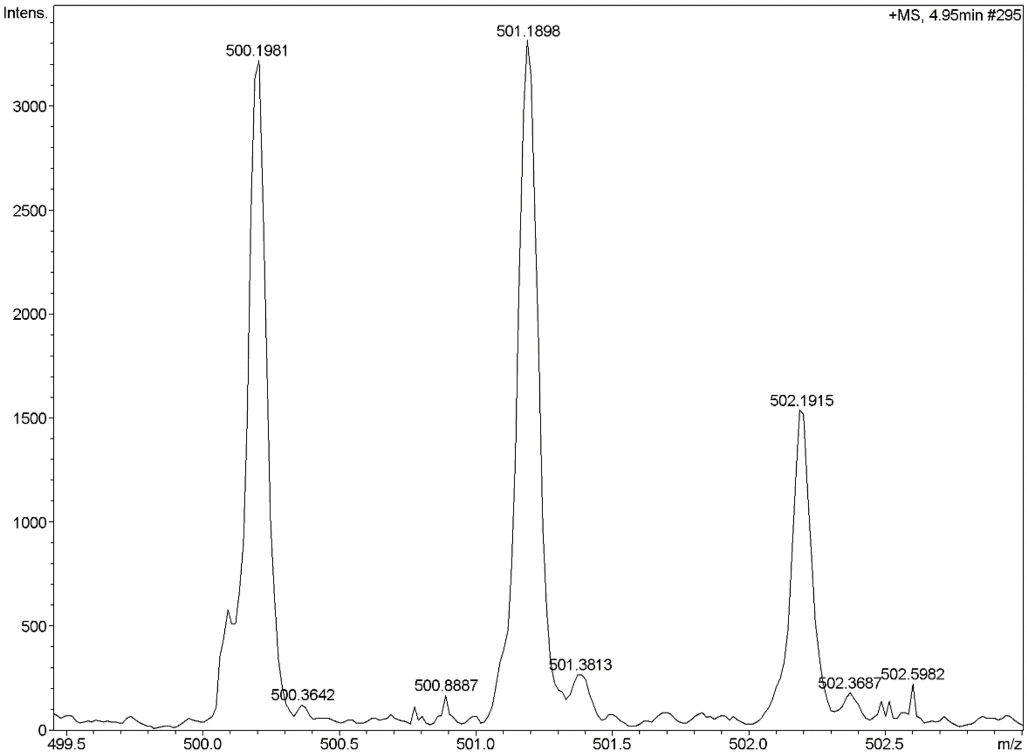

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Fig. S55. HR APCI mass spectrum of compound [**11-b**+H]$^+$

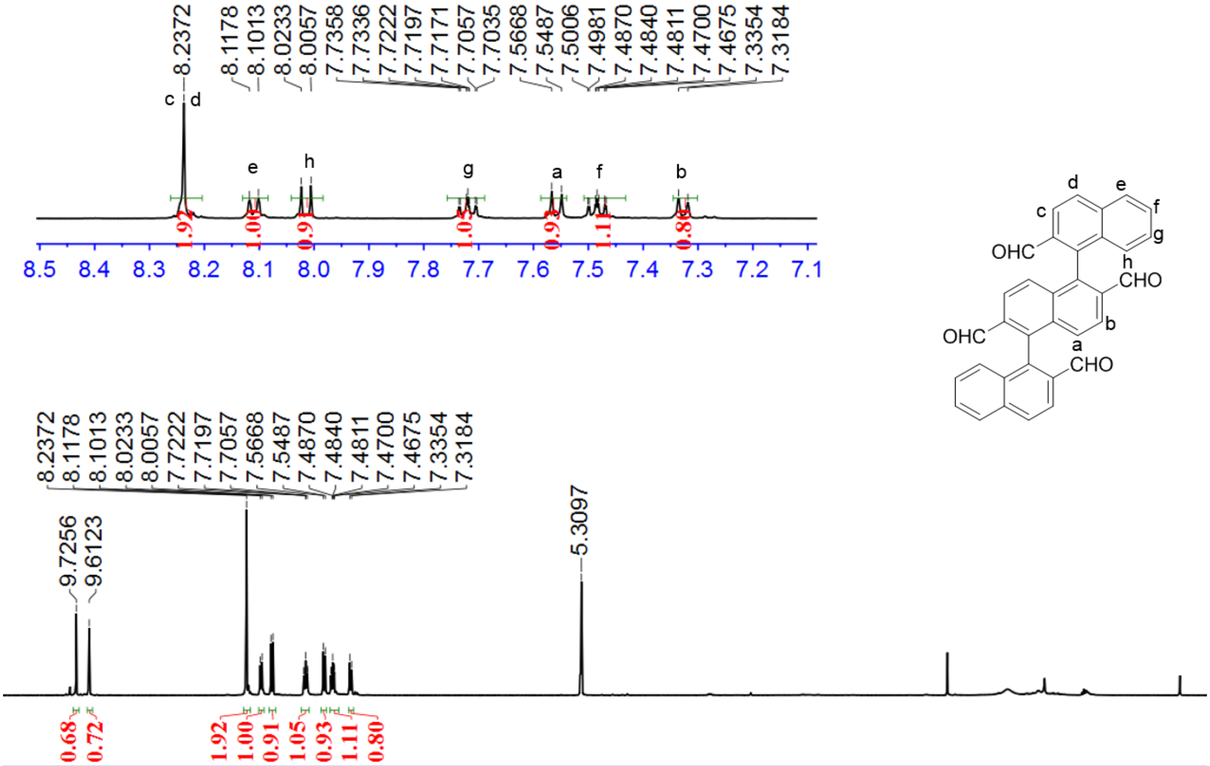


Fig. S56. ^{1}H NMR spectrum of compound **12** (500 MHz, Methylene Chloride-*d*$_2$).

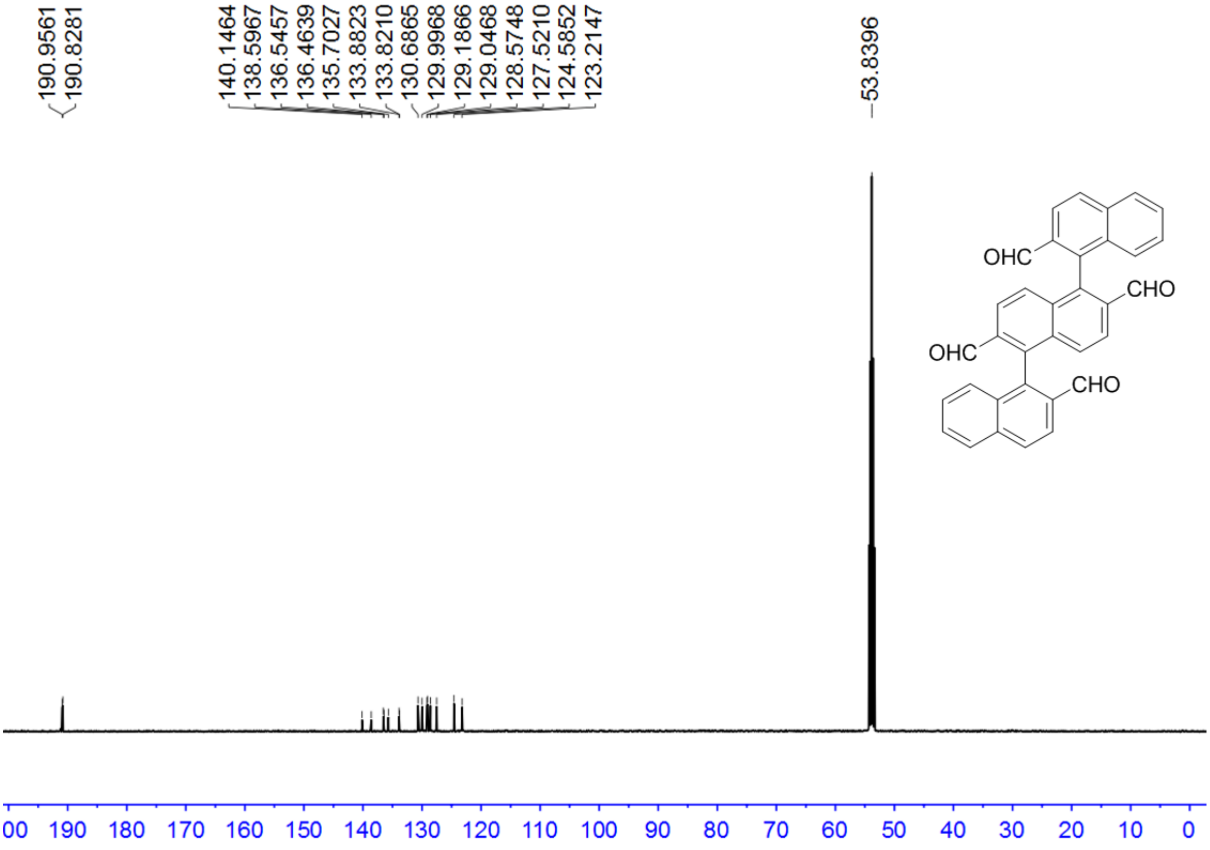
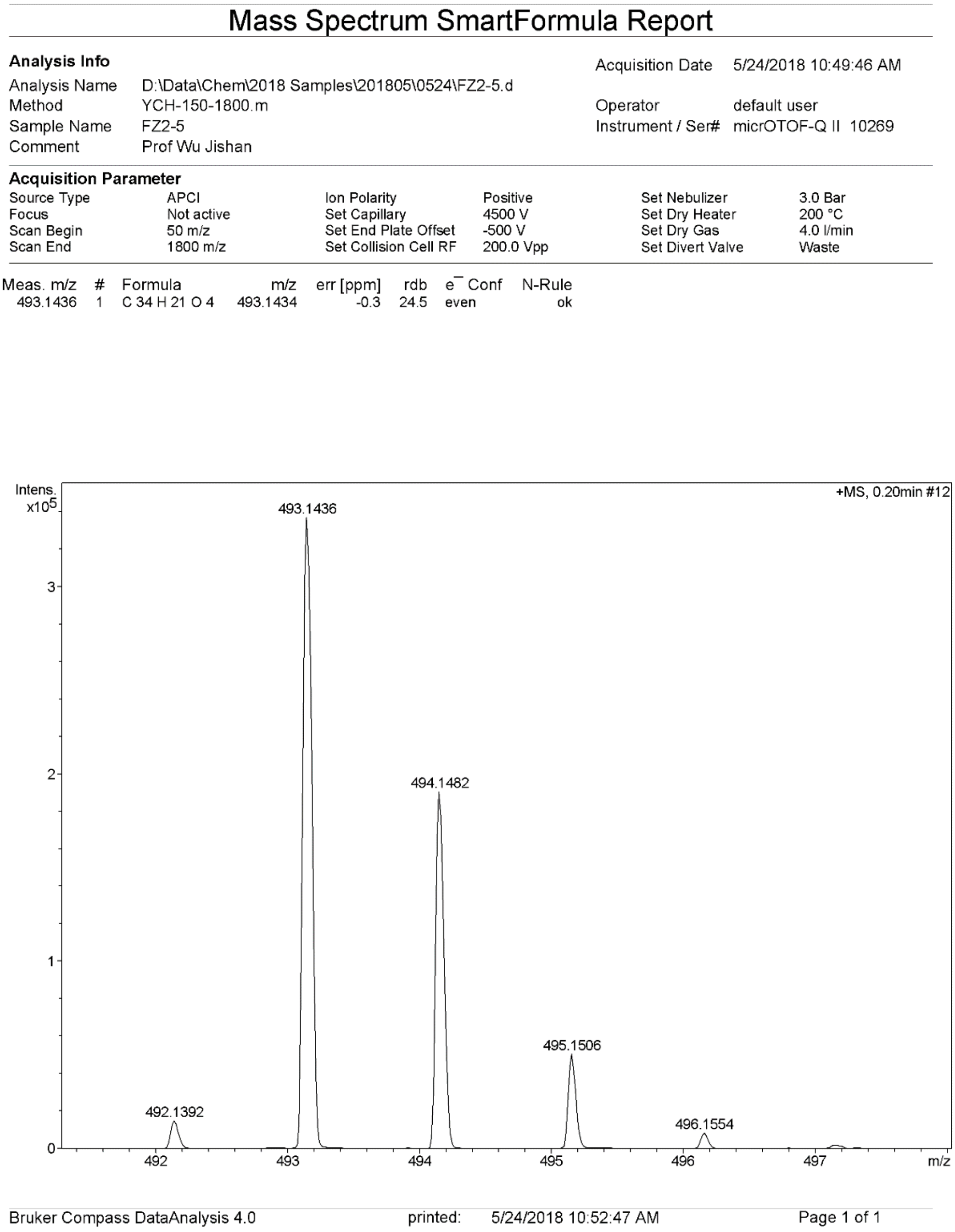


Fig. S57. ^{13}C NMR spectrum of compound **12** (126 MHz, Methylene Chloride-*d*$_2$).



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201805\0524\FZ2-5.d	Acquisition Date	5/24/2018 10:49:46 AM
Method	YCH-150-1800.m	Operator	default user
Sample Name	FZ2-5	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Prof Wu Jishan		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
493.1436	1	C 34 H 21 O 4	493.1434	-0.3	24.5	even	ok

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Fig. S58. HR APCI mass spectrum of compound [**12**+H]$^+$.

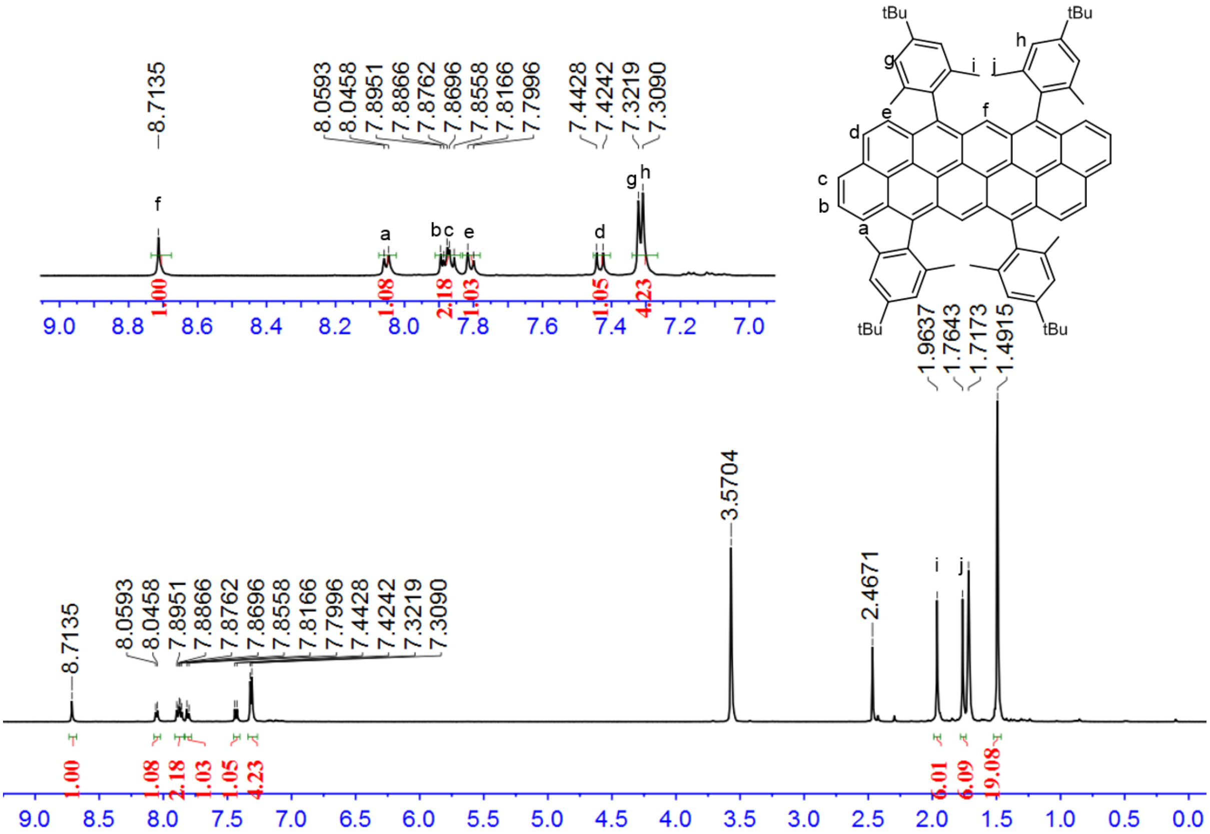


Fig. S59. ^{1}H NMR spectrum of compound **PP-Ar** (500 MHz, THF-d_8).

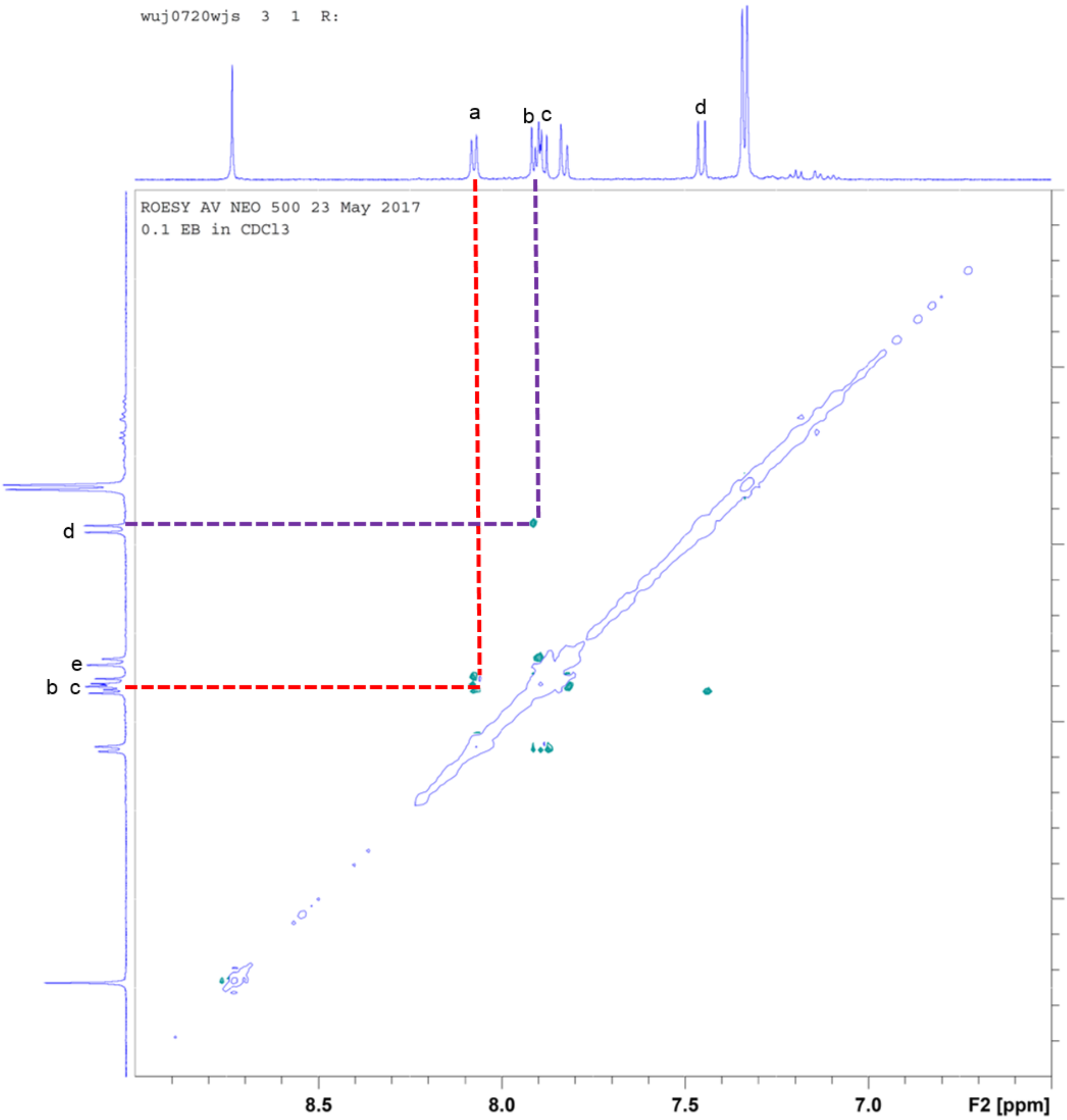


Fig. S60. 2D ROESY NMR spectrum of compound **PP-Ar** (500 MHz, THF-d_8).

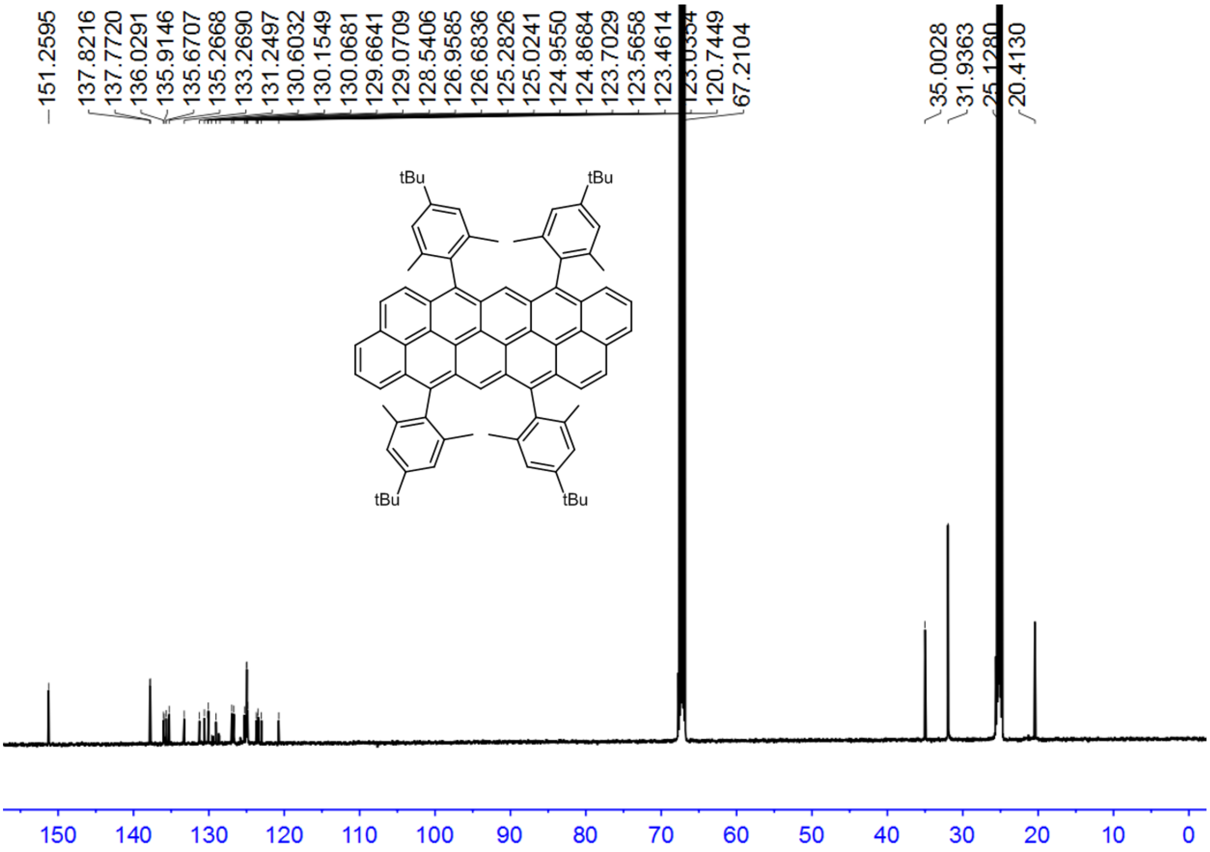
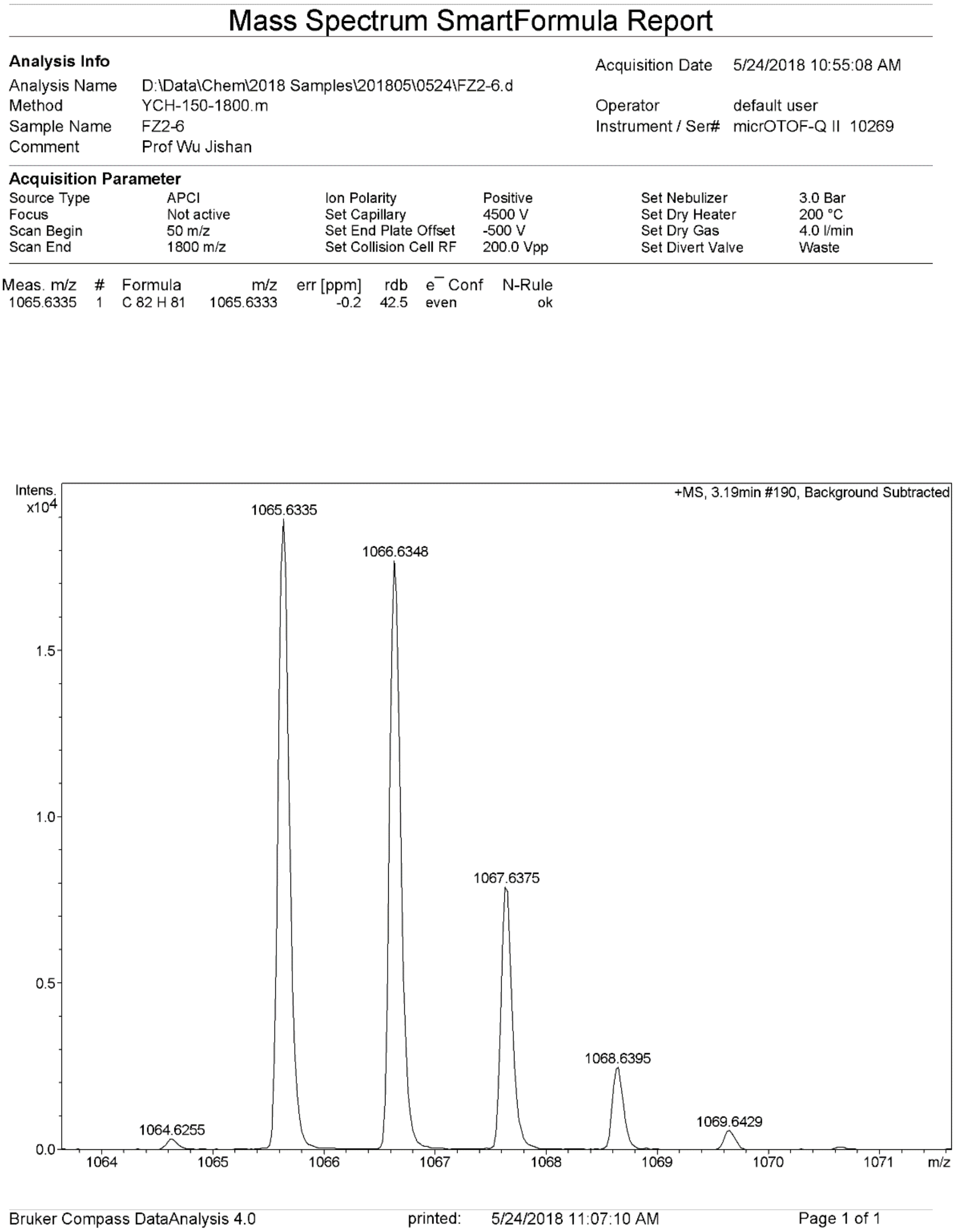


Fig. S61. ^{13}C NMR spectrum of compound **PP-Ar** (126 MHz, THF-d_8).



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201805\0524\FZ2-6.d	Acquisition Date	5/24/2018 10:55:08 AM
Method	YCH-150-1800.m	Operator	default user
Sample Name	FZ2-6	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Prof Wu Jishan		

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
1065.6335	1	C 82 H 81	1065.6333	-0.2	42.5	even	ok

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Fig. S62. HR APCI mass spectrum of compound [**PP-Ar**+H]$^+$

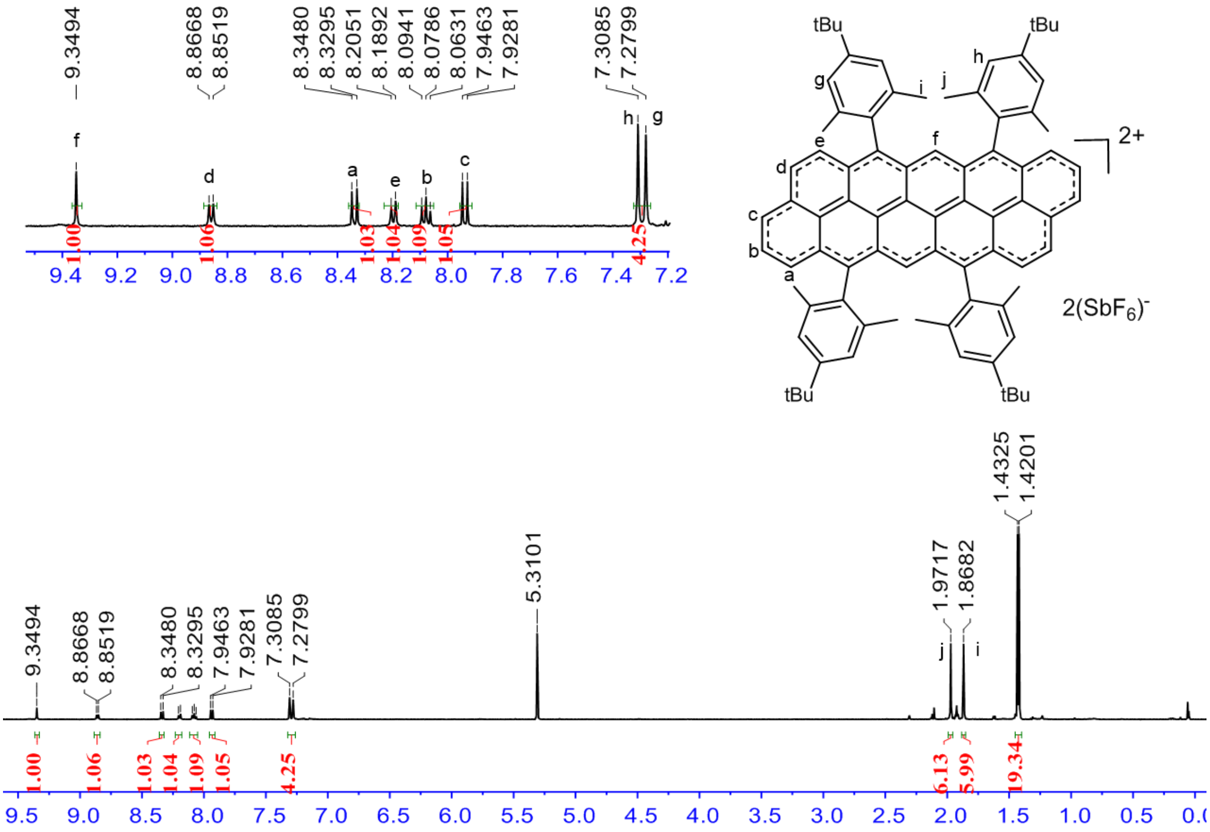

Fig. S63. ^{1}H NMR spectrum of compound **PP-Ar^{2+}** (500 MHz, Methylene Chloride-d_2, 298K, containing 10% CD$_3$CN).

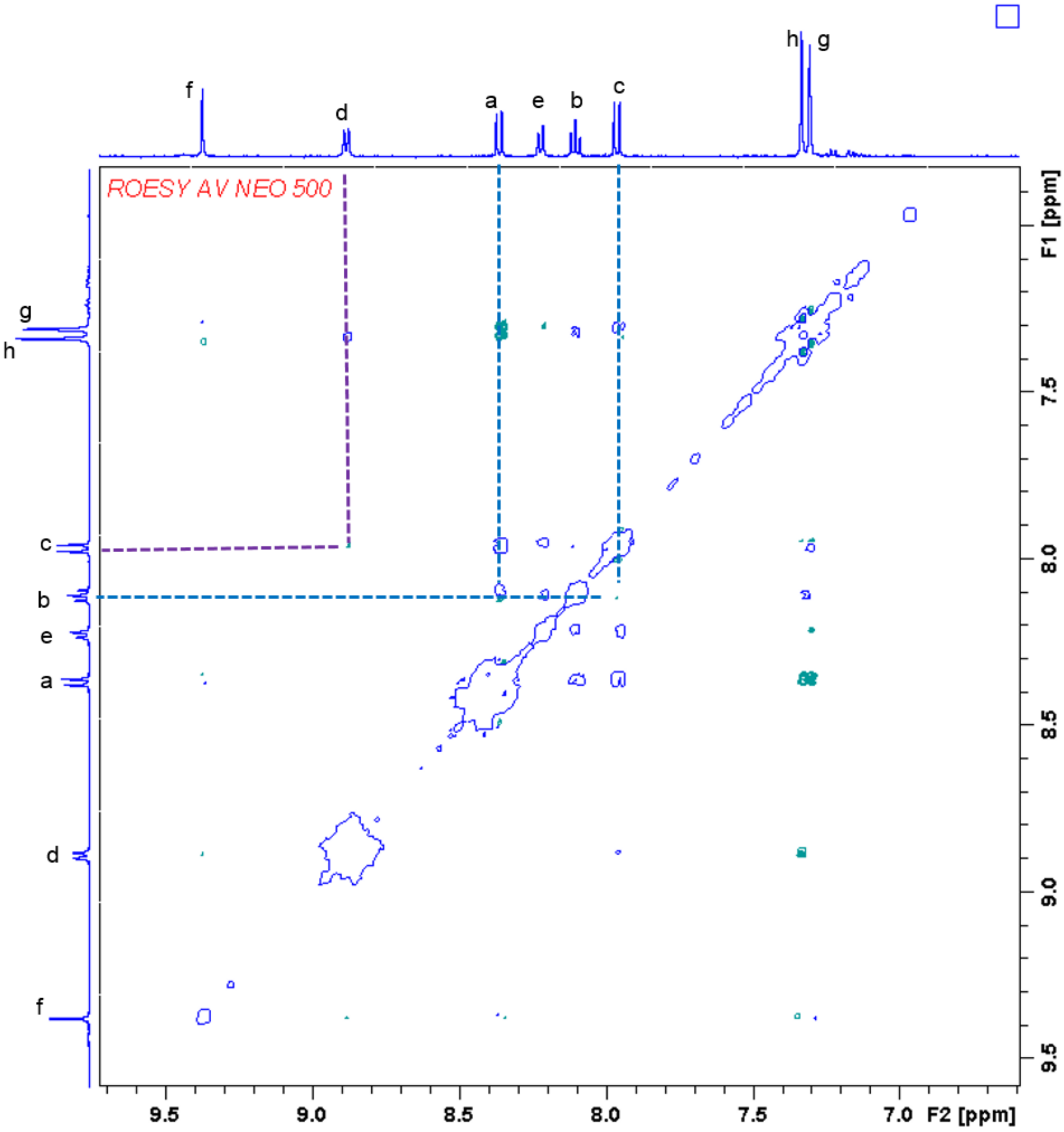

Fig. S64. 2D ROESY NMR spectrum of compound **PP-Ar**$^{2+}$ (500 MHz, Methylene Chloride-d_2, 298K, containing 10% CD_3CN).

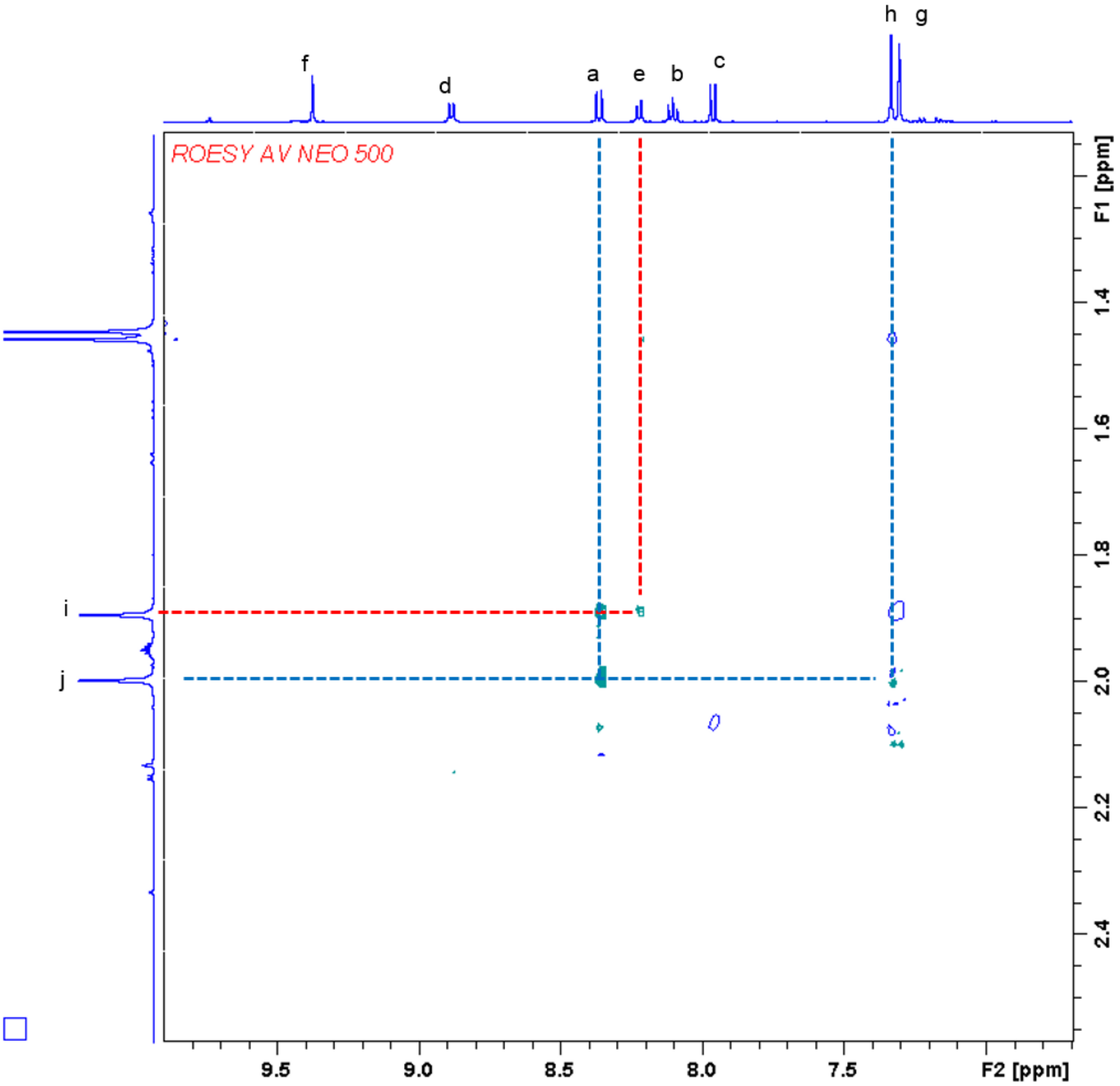

Fig. S65. 2D ROESY NMR spectrum of compound **PP-Ar^{2+}** (500 MHz, Methylene Chloride-d_2, 298K, containing 10% CD_3CN).

8. References

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