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This version of the ESI published 10/02/2023 replaces the previous version published 19/01/2023. The yields of compounds 1a, 2a, 2b, 3a, and 4b in Section I.1 have been updated to include yields both before and after recrystallization.

BOINPYs: Facile Synthesis and Photothermal Properties Triggered by Photoinduced Nonadiabatic Decay

Lizhi Gai,‡[a] Ruijing Zhang,‡[bd] Xiuguang Shi,[a] Zhigang Ni,[a] Sisi Wang,[ac] Jun-Long Zhang,*[be] Hua Lu,*[a] Zijian Guo[c]

[a] College of Material, Chemistry and Chemical Engineering, Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, No. 2318, Yuhangtang Road, Hangzhou, 311121, P. R. China.

[b] Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China.

[c] State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, P. R. China.

[d] Spin-X Institute, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, China.

[e] Chemistry and Chemical Engineering, Guangdong Laboratory, Shantou 515031, China

These authors contributed equally

✉E-mail: hualu@hznu.edu.cn; zhangjunlong@pku.edu.cn

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I. Experimental Procedures

Methods

Materials

All reactions were carried out under a dry argon atmosphere by using Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. All air- and moisture-sensitive reactions were carried out under a nitrogen atmosphere. Glassware was dried in an oven at 100°C and cooled under a stream of inert gas before use. Dichloromethane was distilled over calcium hydride. The water used in this study was deionized with a Milli-QSP reagent water system (Millipore) to a specific resistivity of 18.2 MΩ cm^{-1}. All the solvents employed for the spectroscopic measurements were of spectroscopic grade.

Instrumentation

^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker DRX400 / 500 spectrometer and referenced to the residual proton signals of the solvent. HR-MS were recorded on a Bruker Daltonics microTOF-Q II spectrometer. UV-visible absorption spectra and fluorescence emission spectra were recorded on a commercial spectrophotometer (Shimadzu UV-1800 and Horiba JobinYvonFluorolog-3 spectrofluorimeter) at room temperature. Photothermal effects were determined using a UNI-T UT325 thermometer. Infrared (IR) thermal imaging was performed using a FLIR E53 thermal imaging camera.

I.1 Synthesis and Characterization

(Z)-2-(pyridin-2-ylmethylene)indolin-3-one

To a stirred solution of 1-acetylindolin-3-one (500 mg, 2.8 mmol) and picolinaldehyde (306 mg, 2.8 mmol) in DMF (10 mL) under argon atmosphere at room temperature, then triethylamine (0.4 ml) was added to the mixture and stirred vigorously overnight. The reaction mixture solution was added to distilled water and left to stand for a period of time when solid and liquid separate. The orange product (Z)-2-(pyridin-2-ylmethylene)indolin-3-one (602 mg, 95% yield) was obtained by filtering and drying. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 9.96 (s, 1 H), 8.66 (d, *J* = 4.0 Hz, 1 H), 7.70-7.66 (m, 2 H), 7.45 (t, *J* = 8.0 Hz, 1 H), 7.38 (d, *J* = 8.0 Hz, 1 H), 7.14 (t, *J* = 4.0 Hz, 1 H), 6.97 (d, *J* = 8.0 Hz, 1 H), 6.90 (t, *J* = .08 Hz, 1 H), 6.61 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 186.9, 155.9, 153.2, 149.3, 137.4, 136.6, 135.0, 127.5, 125.6, 122.2, 120.7, 120.1, 112.9, 105.2. HRMS-ESI: m/z: calcd for $[C_{14}H_{11}N_2O]^+$: 223.0866, found: 223.0857.

(Z)-2-(quinolin-2-ylmethylene)indolin-3-one

Prepared from (Z)-2-(pyridin-2-ylmethylene)indolin-3-one analogously to (Z)-2-(quinolin-2-ylmethylene)indolin-3-one (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 10.46 (s, 1 H), 8.07 (d, *J* = 12.0 Hz, 2 H), 7.77-7.69 (m, 3 H), 7.52-7.45 (m, 2 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.01 (d, *J* = 8.0 Hz, 1 H), 6.92 (t, *J* = 8.0 Hz, 1 H), 6.69 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 187.9, 156.6, 153.1, 148.7, 139.1, 136.6, 136.3, 123.0, 128.8, 126.6, 125.2, 124.1, 121.3, 120.4, 111.3, 104.6. HRMS-ESI: m/z: calcd for $[C_{18}H_{13}N_2O]^+$: 273.1022, found: 273.1026.

(Z)-2-(benzo[d]thiazol-2-ylmethylene)indolin-3-one

Prepared from (Z)-2-(pyridin-2-ylmethylene)indolin-3-one analogously to (Z)-2-(benzo[d]thiazol-2-ylmethylene)indolin-3-one (87% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.37 (s, 1H), 8.13 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.56 (m, 3H), 7.47 – 7.45 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 6.98 (t, *J* =8.0 Hz, 1H), 6.79 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 186.7, 163.5, 153.9, 153.7, 137.5, 137.1, 134.9, 126.8, 125.4, 124.4, 122.5, 122.3, 120.9, 119.7, 113.2, 97.4. HRMS-ESI: m/z: calcd for $[C_{16}H_{11}N_2OS]^+$: 279.0587, found: 279.0577.

6,6-difluoro-6l4,7l4-pyrido[1',2':1,6][1,3,2]diazaborinino[3,4-a]indol-13(6H)-one (1a)

(Z)-2-(pyridin-2-ylmethylene)indolin-3-one (450 mg, 2 mmol) was dissolved in dichloromethane (50 mL) and triethylamine (2 mL) was added under argon atmosphere at room temperature. After 10 minutes, boron trifluoride ether (2.5 mL) was added and the reaction was stopped when the raw material disappeared at TLC. Then extraction

with CH_2Cl_2, concentration in vacuo, and flash column chromatography employing gradient elution afforded the desired product **1a** (66% yield) and further recrystallization by CH_2Cl_2/hexane (~56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.68 (d, *J* = 8.0 Hz, 1 H), 7.97 (t, *J* = 8.0 Hz, 1 H), 7.66 (d, *J* = 8.0 Hz, 1 H), 7.53 (t, *J* = 8.0, 4.0 Hz, 1 H), 7.51 (s, 1 H), 7.44 (t, *J* = 8.0, 4.0 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.00 (t, *J* = 8.0 Hz, 1 H), 6.48 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 189.0, 155.2, 150.9, 142.9, 142.2, 141.2, 137.5, 125.9, 125.4, 122.2, 121.8, 121.7, 114.6, 94.2. HRMS-ESI: m/z: calcd for $[C_{14}H_9BF_2N_2NaO]^+$: 293.0671, found: 293.0674.

14,14-difluoro-14l4,15l4-indolo[1',2':3,4][1,3,2]diazaborinino[1,6-a]quinolin-8(14H)-one (2a)

2a was prepared analogously to **1a** (64% yield) and further recrystallization by CH_2Cl_2/hexane (~44%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm 8.90 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 8.0 Hz, 2H), 7.65 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J*=8.0 Hz, 1H), 6.47 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ ppm 153.1, 142.4, 137.7, 132.7, 129.6, 127.7, 127.6, 125.2, 124.3, 122.6, 121.0, 114.3, 95.4, 39.5. HRMS-ESI : m/z: calcd for $[C_{18}H_{12}BF_2N_2O]^+$: 321.1009, found: 321.0998.

6,6-difluoro-6l4,7l4-benzo[4',5']thiazolo[3',2':1,6][1,3,2]diazaborinino[3,4-a]indol-14(6H)-one (3a)

3a was prepared analogously to **1a** (71% yield) and further recrystallization by CH_2Cl_2/hexane (~51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.36 (d, *J* = 8.0 Hz, 1 H), 7.82 (d, *J* = 12.0 Hz, 1 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.63 (d, *J* = 8.0 Hz, 1 H), 7.57 (t, *J* = 8.0 Hz, 1 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.48 (t, *J* = 8.0 Hz, 1 H), 7.08 (t, *J* = 8.0, 4.0 Hz, 1 H), 6.59 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 187.8, 167.5, 154.9, 145.3, 142.9, 137.7, 129.6, 128.7, 126.7, 125.6, 123.9, 122.1, 121.6, 119.8, 115.8, 87.9. HRMS-ESI: m/z: calcd for $[C_{16}H_9BF_2N_2NaOS]^+$: 349.0392, found: 349.0395.

6,6-diphenyl-6l4,7l4-pyrido[1',2':1,6][1,3,2]diazaborinino[3,4-a]indol-13(6H)-one (1b)

To a stirred solution of (Z)-2-(pyridin-2-ylmethylene)indolin-3-one (450 mg, 2 mmol) and triphenylboron (500 mg, 2.1 mmol) in anhydrous solution of toluene under argon and the solution was heated to the reflux temperature for 3 h. The solvent was removed in vacuo and purified by column chromatography to yield (733 mg, 95%) of purple black solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.09 (d, *J* = 8.0 Hz, 1 H), 7.79 (t, *J* = 8.0 Hz, 1 H), 7.61 (d, *J* = 8.0 Hz, 1 H), 7.39 (d, *J* = 8.0 Hz, 1 H), 7.33-7.30 (m, 4 H), 7.28-7.26 (m, 6 H), 7.15 (t, *J* = 5.0 Hz, 1 H), 7.08 (t, *J* = 8.0 Hz, 1 H), 6.77 (t, *J* = 8.0 Hz, 1 H), 6.40 (s, 1 H), 6.09 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 189.7, 158.5, 151.8, 145.6, 144.8, 140.1, 136.8, 133.9, 127.9, 127.1, 125.3, 125.1, 122.1, 121.2, 120.1, 114.9, 96.3. HRMS-ESI: *m/z*: calcd for $[C_{26}H_{19}BN_2NaO]^+$: 409.1487, found: 409.1467.

14,14-diphenyl-14l4,15l4-indolo[1',2':3,4][1,3,2]diazaborinino[1,6-a]quinolin-8(14H)-one (2b)

2b was prepared analogously to **1b** (78% yield) and further recrystallization by CH_2Cl_2/hexane (~68%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 8.35 (d, *J* = 8.0 Hz, 1 H), 8.14 (d, *J* = 8.0 Hz, 1 H), 7.68-7.64 (m, 5 H), 7.53 (d, *J* = 8.0 Hz, 1 H), 7.45 (d, *J* = 8.0 Hz, 1 H), 7.31-7.24 (m, 4 H), 7.22 -7.19 (m, 4 H), 7.09 (t, *J* = 8.0 Hz, 1 H), 6.76 (t, *J* = 4.0 Hz, 1 H), 6.39 (s, 1 H), 6.34 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, CD_2Cl_2): *δ* ppm 189.7, 157.4, 153.9, 144.3, 142.2, 141.3, 136.6, 133.9, 130.6, 129.0, 128.9, 128.0, 126.8, 126.5, 126.3, 125.0, 124.3, 122.6, 121.0, 115.5, 95.4. HRMS-ESI: *m/z*: calcd for $[C_{30}H_{22}BN_2O]^+$: 437.1825, found: 437.1837.

6,6-diphenyl-6l4,7l4-benzo[4',5']thiazolo[3',2':1,6][1,3,2]diazaborinino[3,4-a]indol-14(6H)-one (3b)

3b was prepared analogously to **1b** (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.71 (d, *J* = 8.0 Hz, 1 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.56-7.54 (m, 4 H), 7.34 (d, *J* = 8.0 Hz, 1 H), 7.30-7.27 (m, 7 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 7.11 (t, *J* = 8.0 Hz, 1 H), 6.83 (t, *J* = 8.0 Hz, 1 H), 6.47 (s, 1 H), 6.29 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* ppm 189.4, 166.4, 157.9, 145.9, 145.7, 137.0, 133.9, 130.6, 128.0, 127.6, 127.1, 125.5, 125.2, 122.3, 121.9, 121.4, 121.3, 115.9, 89.1. HRMS-ESI: m/z: calcd for $[C_{28}H_{20}BN_2OS]^+$: 443.1389, found: 443.1375.

(Z)-2-((5-bromopyridin-2-yl)methylene)indolin-3-one

Prepared from (Z)-2-(pyridin-2-ylmethylene)indolin-3-one analogously to (Z)-2-((5-bromopyridin-2-yl)methylene)indolin-3-one (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.69 (s, 1H), 8.69 (d, *J* = 2.2 Hz, 1H), 7.78 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.26 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.92 (t, *J* =8.0 Hz, 1H), 6.52 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 187.72, 154.4, 153.1, 150.5, 139.3, 138.4, 136.7, 127.1, 125.3, 120.8, 120.5, 118.3, 111.7, 103.9. HRMS-ESI: *m/z*: calcd for $[C_{14}H_9BrN_2O+H]^+$300.9971, found: 300.9956.

9-bromo-6,6-diphenyl-6l4,7l4-pyrido[1',2':1,6][1,3,2]diazaborinino[3,4-a]indol-13(6H)-one (1c)

1c was prepared analogously to **1b** (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 8.10 (d, *J* = 4.0 Hz, 1 H), 7.85 (d, *J* = 4.0 Hz, 1 H), 7.60 (d, *J* = 4.0 Hz, 1 H), 7.32-7.28 (m, 10 H), 7.24 (d, *J* = 8.0 Hz, 1 H), 7.07 (t, *J* = 8.0 Hz, 1 H), 6.80 (t, *J* = 8.0, 4.0 Hz, 1 H), 6.32 (s, 1 H), 6.04 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* ppm 188.8, 158.5, 151.7, 146.9, 144.9, 142.7, 136.8, 132.0, 128.7, 127.3, 125.9, 125.1, 122.0, 120.5, 115.8, 114.9, 95.2. HRMS-ESI: *m/z*: calcd for $[C_{26}H_{19}BBrN_2O]^+$: 465.0773, found: 465.0780.

6,6,9-triphenyl-6l4,7l4-pyrido[1',2':1,6][1,3,2]diazaborinino[3,4-a]indol-13(6H)-one (4a)

Compound **1c** (150 mg, 0.32 mmol), $Pd(PPh_3)_4$ (37 mg, 0.032 mmol) and 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (80 μL, 0.38 mmol) in THF (15 mL) were mixed under an argon atmosphere, then degassed sodium carbonate aqueous solution (1 mL, 2 M in water) was added and the mixture was heated at reflux for 2 h. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2, then dried over anhydrous Na_2SO_4, and the solvent was evaporated. The residue was purified by column chromatography on silica gel and a product **4a** (123 mg, 83%) was found. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 8.31 (d, *J* = 8.0 Hz, 1 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.63 (d, *J* = 8.0 Hz, 1 H), 7.46-7.37 (m, 8 H), 7.34-7.27 (m, 8 H), 7.11 (t, *J* = 8.0 Hz, 1 H), 6.78 (t, *J* = 8.0 Hz, 1 H), 6.45 (s, 1 H), 6.15 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, CD_2Cl_2): *δ* ppm 189.5, 158.6, 150.0, 145.0, 144.1, 139.5, 136.7, 135.6, 135.1, 134.1, 129.8, 129.5, 128.1, 127.3, 126.9, 125.9, 125.0, 122.5, 120.3, 115.1, 96.2. HRMS-ESI: *m/z*: calcd for $[C_{32}H_{24}BN_2O]^+$: 463.1982, found: 463.1995.

(E)-6,6-diphenyl-9-styryl-6l4,7l4-pyrido[1',2':1,6][1,3,2]diazaborinino[3,4-a]indol-13(6H)-one (4b)

To a solution of ethynylbenzene (204 mg, 2.0 mmol) and catecholborane (0.26 mL, 2.4 mmol) in THF and the solution was heated to reflux under an argon atmosphere. After 1.5 h, catecholborane (0.2 mL, 1.8 mmol) was added again and stirred at the same temperature for 2h. Cooling to room temperature, the degassed solution of **1c** (600 mg, 1.3 mmol) and $Pd(PPh_3)_4$ (550 mg, 0.48 mmol) in THF (20 mL) was added dropwise and continued to react for half an hour. Then the degassed aqueous Na_2CO_3 (2 mL, 2 M in the water) was added and the mixture was heated to reflux for 10 h. After cooling to room temperature, extraction with CH_2Cl_2, concentration in vacuo, and flash column chromatography employing gradient elution afforded the desired product **4b** (482 mg, 76 % yield) and further recrystallization by CH_2Cl_2/hexane (~56%). ^{1}H NMR (400 MHz, CD_2Cl_2): *δ* ppm 8.08 (s, 1 H), 8.05 (d, *J* = 8.0 Hz, 1 H), 7.57 (d, *J* = 8.0 Hz, 1 H), 7.48-7.45 (m, 2 H), 7.42 (s, 1 H), 7.38-7.34 (m, 7 H), 7.32-7.27 (m, 6 H), 7.08 (d, *J* = 8.0 Hz, 1 H), 7.05 (s, 1 H), 6.86 (d, *J* = 16.0 Hz, 1 H), 6.78 (t, *J* = 8.0 Hz, 1 H), 6.41 (s, 1 H), 6.09 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, CD_2Cl_2): *δ* ppm 187.4, 170.7, 158.4, 150.1, 144.9, 144.5, 136.6, 136.3, 136.0, 134.2, 132.6, 129.3, 128.1, 127.3, 127.2, 125.9, 125.0, 123.0, 122.5, 120.3, 115.1, 96.6. HRMS-ESI: m/z: calcd for $[C_{34}H_{26}BN_2O]^+$: 489.2139, found: 489.2147.

6,6-diphenyl-9-(phenylethynyl)-6l4,7l4-pyrido[1',2':1,6][1,3,2]diazaborinino[3,4-a]indol-13(6H)-one (4c)

Compound **1c** (232 mg, 0.5 mmol), $PdCl_2(PPh_3)_2$ (105 mg, 0.15 mmol) and CuI (9.5 mg, 0.05 mmol) were dissolved in degassed solution of toluene/triethylamine (20 mL, 5:1, v/v) under an argon atmosphere, then ethynylbenzene (0.5 mL, 2.2 mmol) was added and the mixture was stirred at 60 ℃ for 10 h. The mixture was allowed to cool to

room temperature and then was washed with water and extracted with CH_2Cl_2, concentrated and chromatographed to afford a purple black solid (190 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.18 (d, *J* = 4.0 Hz, 1 H), 7.82 (d, *J* = 8.0 Hz, 1 H), 7.61 (d, *J* = 4.0 Hz, 1 H), 7.50-7.37 (m, 2 H), 7.35-7.31 (m, 8 H), 7.30-7.28 (m, 6 H), 7.09 (t, *J* = 8.0 Hz, 1 H), 6.80 (t, *J* = 8.0 Hz, 1 H), 6.37 (s, 1 H), 6.04 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ ppm 189.4, 157.8, 150.7, 148.0, 145.1, 142.4, 136.8, 134.2, 132.1, 129.8, 129.0, 128.2, 127.4, 125.4, 125.1, 122.5, 122.1, 120.7, 118.4, 114.1, 96.0, 95.5, 84.7. HRMS-ESI: m/z: calcd for $[C_{34}H_{24}BN_2O]^+$: 487.1982, found: 487.1985.

I.2 TD-DFT calculation

The ground state structures of compounds **1a-3b** and **4a-4c** are optimized using the density functional theory (DFT) method with the B3LYP functional and 6-31G(d) basis set. The absorption properties were predicted by the time-dependent (TD-DFT) method with the same basis set. The vertical excitation related calculations are based on the optimized ground-state geometry (S_0 state), while the emission related calculations were based on the optimized excited state (S_1 state) geometry at the B3LYP/6-31G (d, p) level. Anisotropy of the induced current density (ACID) plots were calculated by Herges's method.[S1] Nucleus independent chemical shifts (NICS) values were calculated using the standard gauge invariant atomic orbital (GIAO)[S2] method at the level of B3LYP/6-311G(d,p). All NICS values have been calculated at 1 Å above the center (NICS(1)) of each ring. All of the calculations were performed with the Gaussian09 program package.[S3]

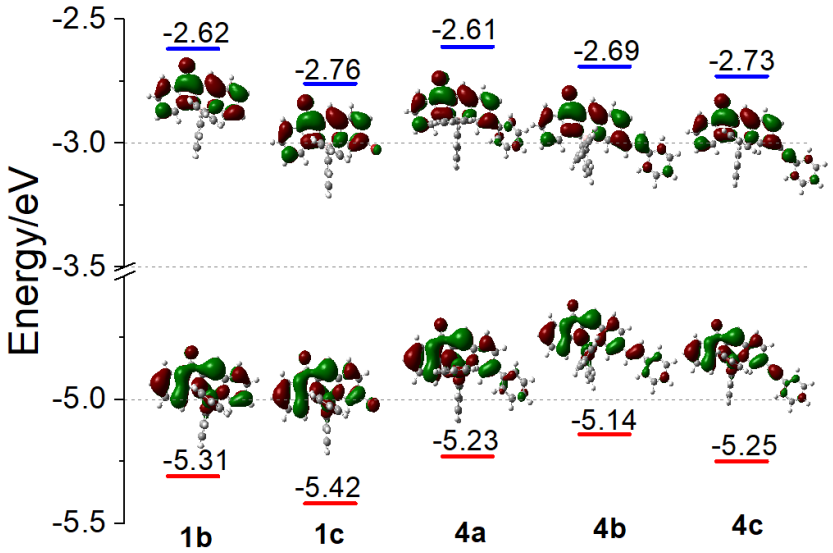


Fig. S1. Frontier orbital energy and nodal patterns of the frontier π MOs of the dyes **1b-4c** were calculated in dichloromethane with the PCM by using the B3LYP functional with the 6-31G (d, p) basis set.

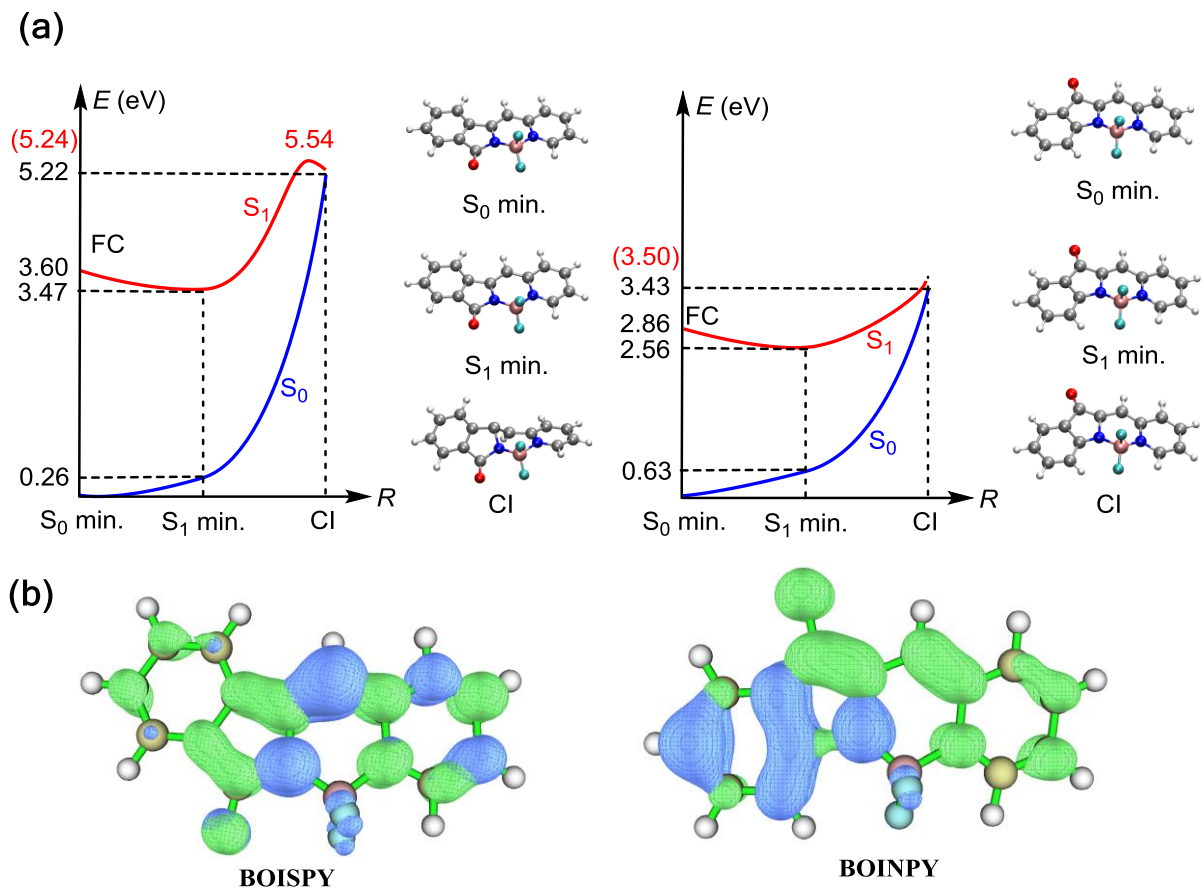


Fig. S2. (a) Potential energy curves (PECs) of the S_0 and S_1 states of BOISPY and BOINPY. (b) Isosurfaces (isovalue = 0.002) of hole and electron distributions for the S_1 state of BOISPY and BOINPY.[S4] The blue and green isosurfaces represent hole and electron distributions, respectively.

Table S1. Selected transition energies and wave functions of **dyes** calculated using the TD-DFT method with the B3LYP functional and 6-31G (d, *p*) basis set.

Dyes	State [a]	Energy [eV]	λ_{abs} [nm]	f [b]	Orbitals (coefficient)[c]
1a	S1	2.48	500	0.21	H→L (96%)
1b	S1	2.22	559	0.14	H→L (98%)
2a	S1	2.36	527	0.29	H→L (97%)
2b	S1	2.04	607	0.19	H→L (99%)
3a	S1	2.44	509	0.27	H→L (96%)
3b	S1	2.13	582	0.18	H→L (98%)
1a-Br	S1	2.45	506	0.26	H→L (97%)
1c	S1	2.18	568	0.17	H→L (98%)
4a	S1	2.16	573	0.22	H→L (98%)
4b	S1	2.08	597	0.40	H→L (97%)
4c	S1	2.12	585	0.34	H→L (97%)

[a]Excited state. [b]Oscillator strength. [c]MOs involved in the transitions with H and L denoting the HOMO and LUMO, respectively.

I.3 X-ray analysis

Crystals of dyes **1a**, **3a** and **2b** suitable for X-ray analysis were obtained by slow diffusion of hexane into their dichloromethane solutions about a week period at room temperature. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were collected using a diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. The determination of unit cell parameters and data collections were performed with Mo Kα radiation (λ) at 0.71073 Å. The structure was solved by the direct method using the SHELXS-974 program and refined by the least-squares method on F^2, SHELXL-97, incorporated in SHELXTL V5.10.

Crystallographic Data for compound **1a**: $C_{14}H_9BF_2N_2O$, M_w=270.04, monoclinic, space group P 21/c, a = 7.7662(11) Å, b = 20.908(3) Å, c = 7.2899(11) Å, α = 90.00 °, β = 90.463(3)°, γ = 90.00 °, V = 1183.7(3) $Å^3$, Z = 4, F(000) = 552.0, ρ = 1.515 Mg m^{-3}, $R1$ [I>2σ(I)] = 0.0733, w$R2$ [all data] = 0.2239, GOF = 1.023. CCDC 2142887.

Crystallographic Data for compound **2b**: $C_{30}H_{21}BN_2O$, M_w= 436.30, tetragonal, space group I 41/a, a = 17.675(3) Å, b = 17.675(3) Å, c = 29.023(5) Å, α = 90.00 °, β = 90.00°, γ = 90.00 °, V = 9067(3) $Å^3$, Z = 16, F(000) = 3648.0, ρ = 1.278 Mg m^{-3}, $R1$ [I>2σ(I)] = 0.0643, w$R2$ [all data] = 0.2155, GOF = 1.018. CCDC 2142890.

Crystallographic Data for compound **3a**: $C_{16}H_9BF_2N_2OS$, M_w= 326.12, monoclinic, space group P 21/c, a = 7.763(3) Å, b = 24.877(10) Å, c = 7.273(3) Å, α = 90.00 °, β = 90.525(12)°, γ = 90.00 °, V = 1404.5(10) $Å^3$, Z = 4, F(000) = 664.0, ρ = 1.542 Mg m^{-3}, $R1$ [I>2σ(I)] = 0.0807, w$R2$ [all data] = 0.2198, GOF = 1.125. CCDC 2142888.

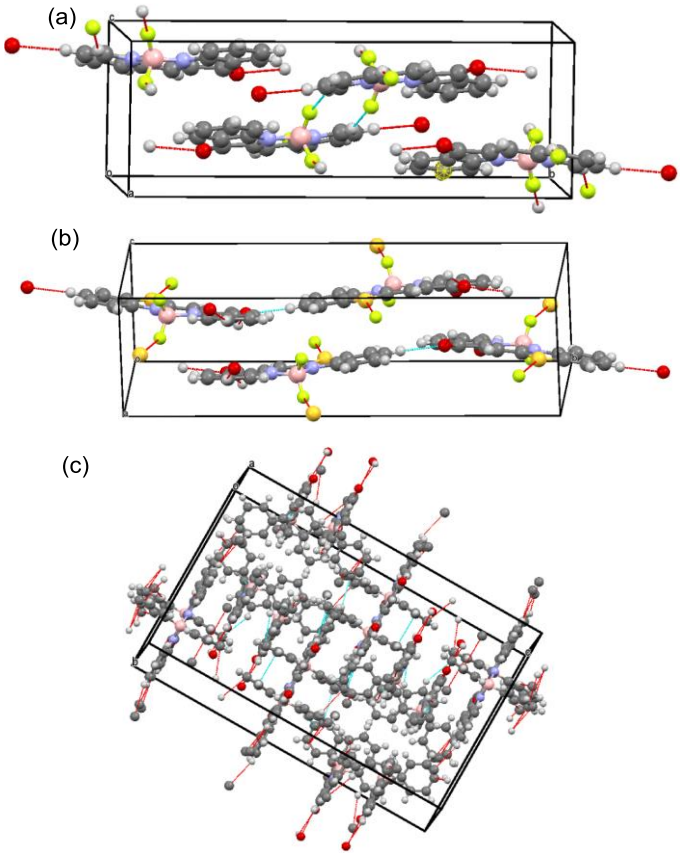


Fig. S3. Packing diagram (right) views of the molecular structures of **1a** (a), **3a** (b), and **2b**(c) with the thermal ellipsoids set at 50% probability. Green for F atom, red for O atom, blue for N atom, black for C atom, pink for B atom, grey for H, yellow for S.

I.4 Spectroscopic measurements

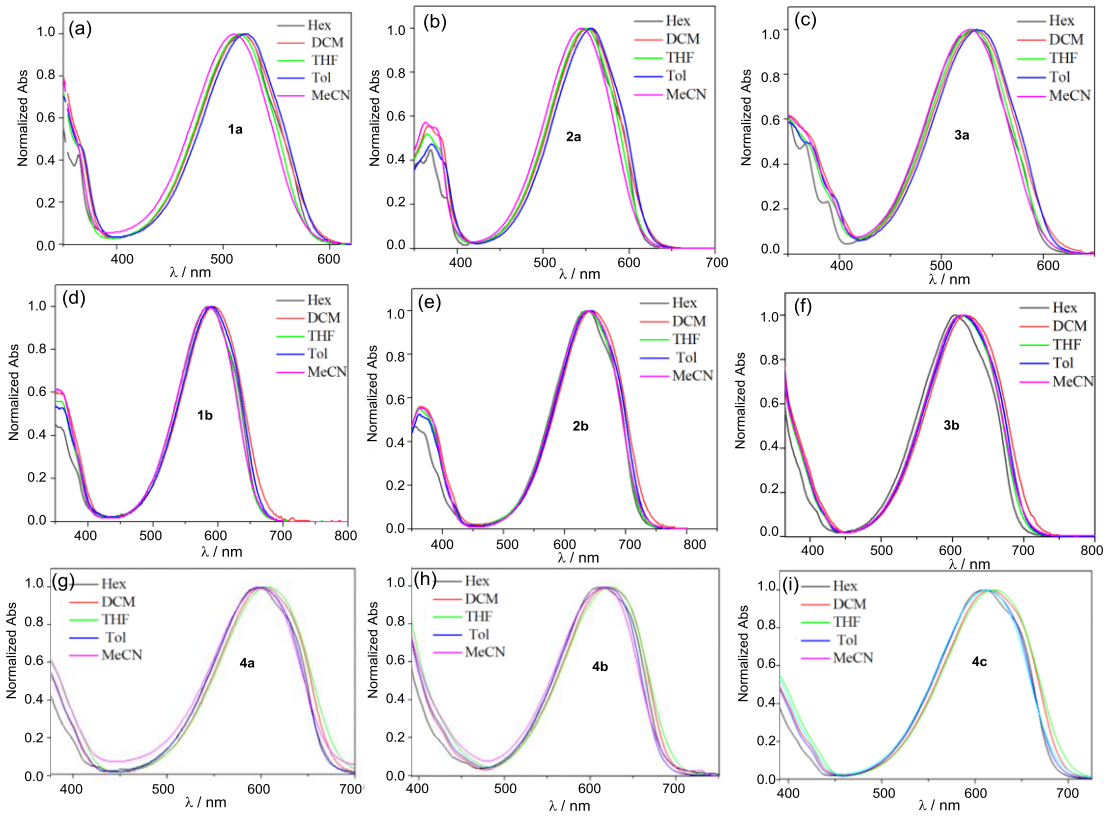


Fig. S4 The absorption spectra of **1a-4c** in different solvents.

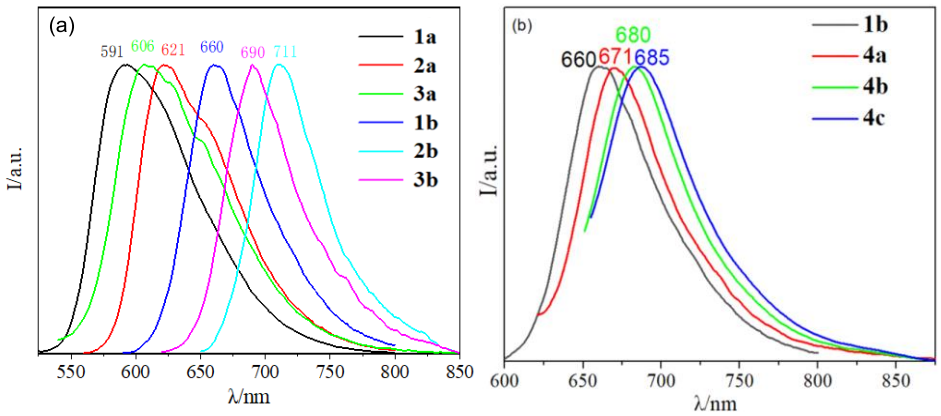


Fig. S5 (a) The emission of **1a-3b** in 2-Methyltetrahydrofuran solution at room temperature. (b) The emission of **1b**, and **4a-4c** in 2-Methyltetrahydrofuran solution at room temperature.

Table S2 The absorption of **1a-3b** and **4a-4c** in various solvents and the film at 298 K

	solvent	λ_{abs} [nm]	ε_{abs} [M^{-1} cm^{-1}]	Film [nm]		λ_{abs} [nm]	ε_{abs} [M^{-1} cm^{-1}]	Film [nm]
1a	Hexane	518	26500		**1b**	586	18400	
	Toluene	521	25800			590	18300	
	CH_2Cl_2	518	24900	527		593	16900	644
	THF	515	26100			585	16800	
	CH_3CN	510	25900			585	16800	
2a	Hexane	552	13500		**2b**	636	25400	
	Toluene	556	48200			641	24600	
	CH_2Cl_2	552	52200	567		644	24500	720
	THF	550	52600			637	23900	
	CH_3CN	545	50800			638	23700	
3a	Hexane	531	32800		**3b**	604	24300	
	Toluene	534	30900			613	24800	
	CH_2Cl_2	534	30700	576		618	24100	672
	THF	531	30900			611	23800	
	CH_3CN	528	31100			615	24000	
4a	Hexane	598	16000		**4b**	618	23600	
	Toluene	604	16200			618	20600	
	CH_2Cl_2	608	15400	645		625	24500	660
	THF	599	16200			612	26200	
	CH_3CN	599	14800			620	25200	
4c	Hexane	613	78000					
	Toluene	612	76400					
	CH_2Cl_2	621	72200	639				
	THF	611	74300					
	CH_3CN	617	72300					

I.5 Singlet oxygen generation

Singlet oxygen quantum yields of the photosensitizers were calculated by monitoring the photooxidation of 1,3-diphenyl isobenzofuran (DPBF), a known singlet oxygen scavenger, using Rose Bengal (RB) for **1a-3a** (Φ_Δ(RB) =0.75 in methanol) and using MB for **1b-3b** and **4a-4c**(Φ_Δ(MB) =0.57 in DCM).[S5] The mixture of photosensitizer and DPBF was irradiated with a 635 nm laser beam at a power of 100 mW/cm^2 at 50 s intervals. The absorbance was measured after each irradiation and a decrease in the absorption band intensity for DPBF at 411 nm was observed. The following equation was used to calculate the singlet oxygen quantum yield of the sensitizer:

$$\Phi_{\Delta(x)} = \Phi_{\Delta(\mathrm{std})}\left(\frac{S_x}{S_{\mathrm{std}}}\right)\left(\frac{F_{\mathrm{std}}}{F_x}\right)$$

where $\Phi_{\Delta(x)}$ is the singlet oxygen quantum yield of the sample, the 'χ' and 'std' subscripts denote the sample and MB standard, respectively, S denotes the slope of a plot of the change in absorbance for DPBF at 414 nm vs the irradiation time, and *F* is the absorption correction factor, which is given by $F = 1-10^{-OD}$ (where OD represents the optical density of sample and MB at the irradiation wavelength).

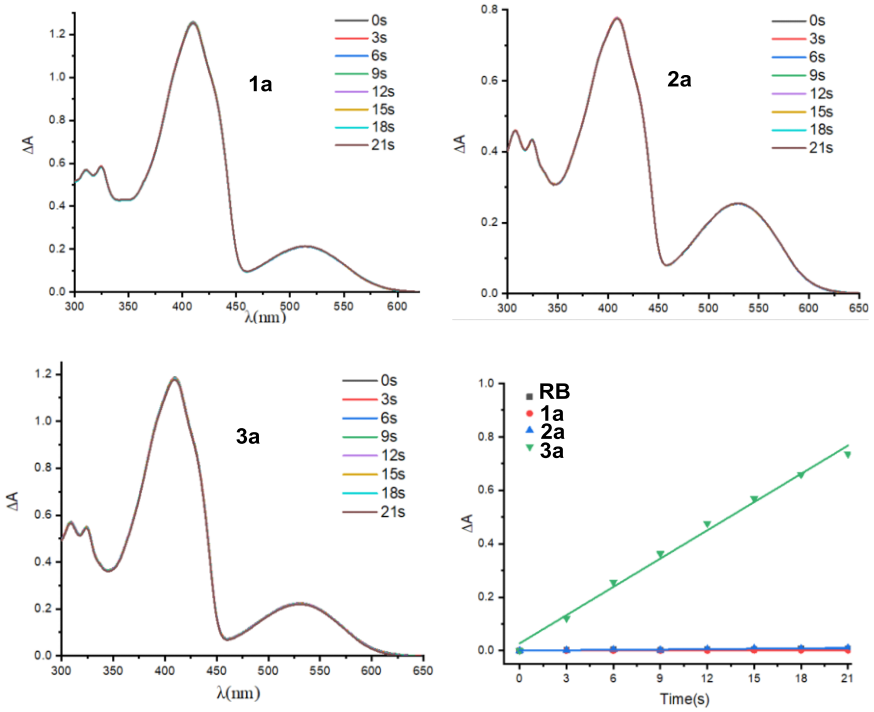


Fig. S6. Absorbance decrease at 414 nm of DPBF in the presence of **1a-3a**, **RB** under irradiation of 525 nm laser. The single oxygen generation is based on a plot of changes in absorbance by DPBF at 414 nm against irradiation time (λ_{irr} = 525 nm) in the presence of RB, or photosensitizer in dichloromethane.

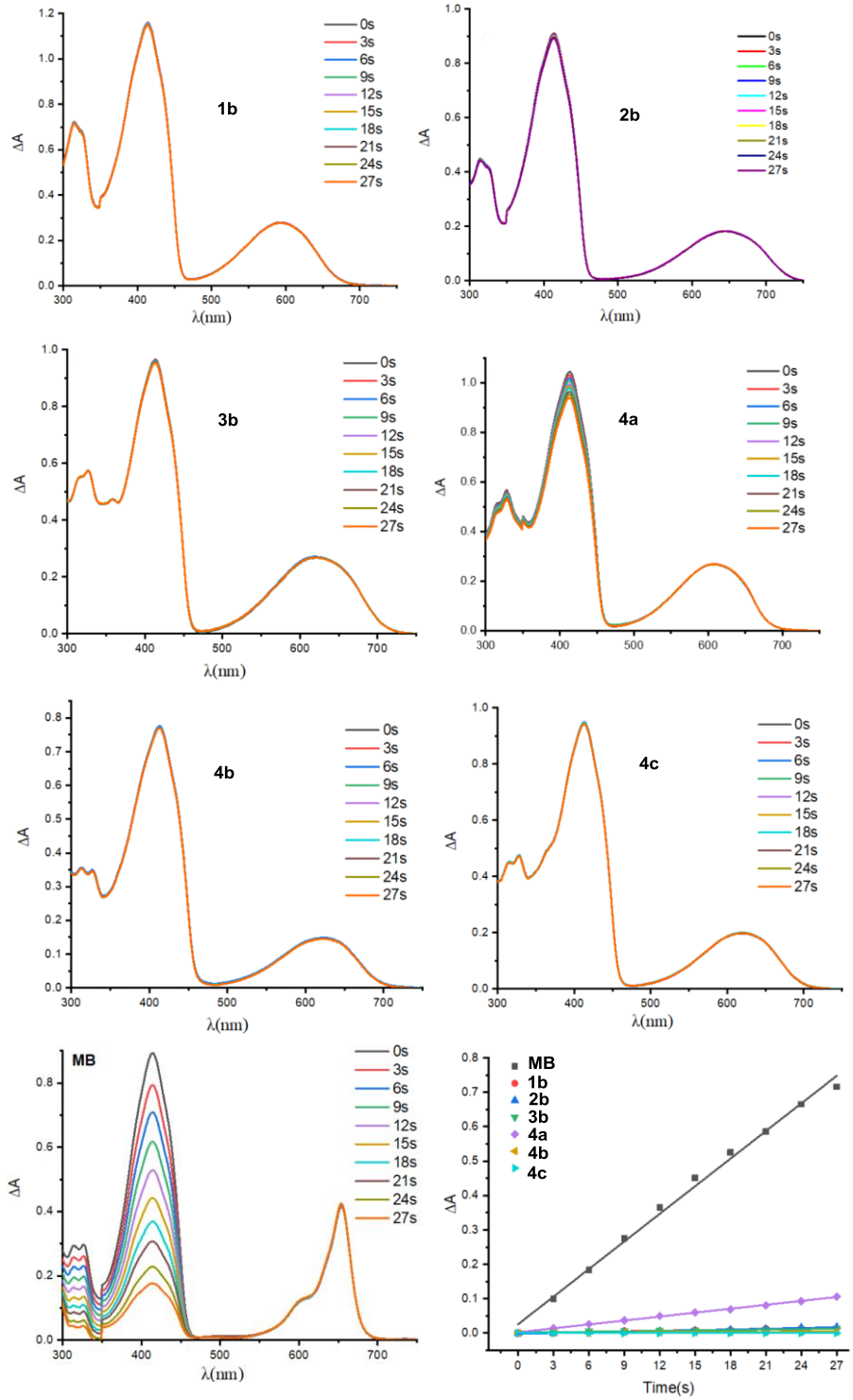


Fig. S7. Absorbance decrease at 414 nm of DPBF in the presence of **1b-3b** and **4a-4c**, **MB** under irradiation of 635 nm laser. The single oxygen generation is based on a plot of changes in absorbance by DPBF at 414 nm against irradiation time (λ_{irr} = 635 nm) in the presence of MB, or photosensitizer in dichloromethane

I.6 PTT properties of dyes

Photothermal property of BOINPYs 2b and 4a-4c

The photothermal effect of dye in DMF was examined under 650 nm laser irradiationy recording the temperature of the samples as the irradiation time increases. At the same time, pure DMF was used as a negative control group. (1) With a 650 nm laser irradiation (0.8 W cm^{-2}) for 15 min, the temperature-rising curve of dye with different concerntration (12.5, 25, 50, and 100 μmol/L) and pure DMF were recorded. (2) dye (50 μmol/L) were irradiated by a 650 nm laser with different laser intensity (0.2, 0.4, 0.8, and 1.0 W cm^{-2}) for 15 min. (3) dye sample was circulatively irradiated at power density of 0.8 W/cm^2 for four times, consisting of irradiation period of 15 min and cooling progress until the sample temperature decreased to room temperature.

Photothermal Conversion Efficiency of BOINPYs 2b, 4a-4c and 2b@F127

2b or 4a-4c in DMF or **2b**@F127 NPs in water were irradiation by 650 nm laser for 15 min and then cooled to room temperature, and the temperature of samples were recorded by an infrared camera, relatively. At the same time, pure DMF or water were used as the negative control group.

The photothermal conversion efficiencies (*η*) was measured and calculated according to these equations (1-4):

$$\eta = \frac{hS(T_{\max} - T_{\text{surr}}) - Q_s}{I(1-10^{-A})} \qquad (1)$$

$$\theta = \frac{\Delta T}{\Delta T_{\max}} = \frac{T - T_{surr}}{T_{max} - T_{\text{surr}}} \qquad (2)$$

$$t = -\tau ln\theta \qquad (3)$$

$$hS = \frac{mC_p}{\tau} \qquad (4)$$

where *h* is the heat transfer coefficient, **S** is the surface area of the container. The T_{max} and T_{surr} are the maximum temperature of the solution and the ambient temperature, respectively, *I* is the laser power, *A* is the absorbance of the sample at 650 nm and Q_s expresses the heat associated with light absorption by the solvent. *m* and C_p are the mass and heat capacity of the system, respectively, *τ* is the heat transfer time constant, which can be determined by the linear relationship of *t* versus -lnθ through the natural cooling curve of the sample.

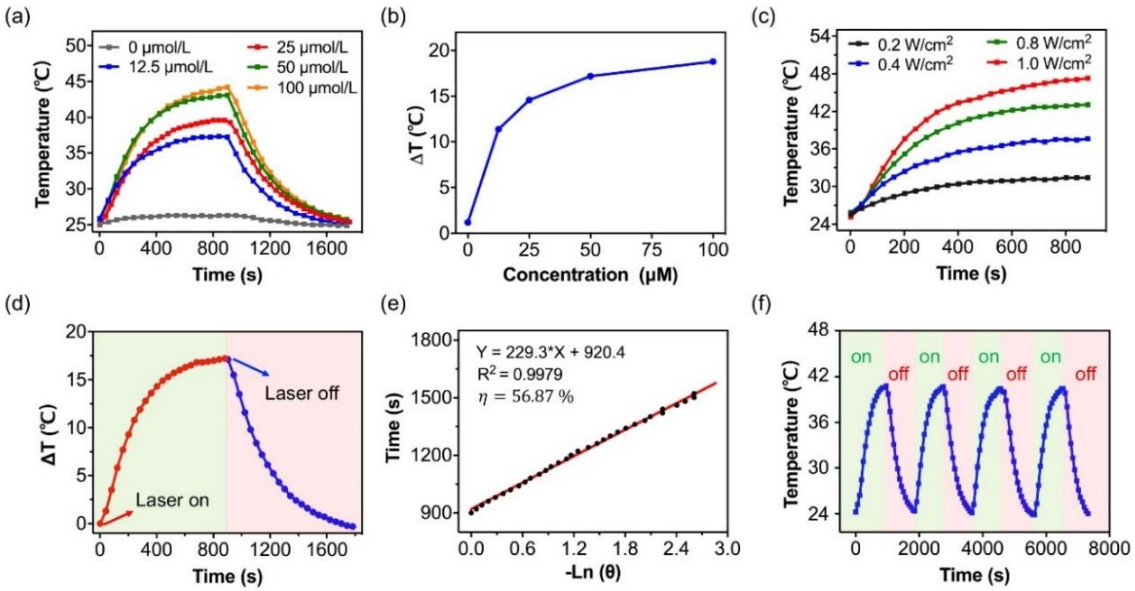


Fig. S8. (a) Photothermal conversion and (b) temperature changes of **2b** at different concentrations in DMF upon irradiation of 650 nm laser (0.8 W cm^{-2}). (c) Photothermal heating curves of **2b** (50 μM) upon 650 nm laser irradiation with different power intensities. (d) Temperature-change curves of **2b** with or without laser irradiation (650 nm, 0.8 W·cm^{-2}). (e) Linear fitting of the time vs -Ln(θ) plot of **2b**. θ is a dimensionless parameter, known as the driving force temperature. (f) Photothermal stability of **2b** for four heating and cooling cycles.

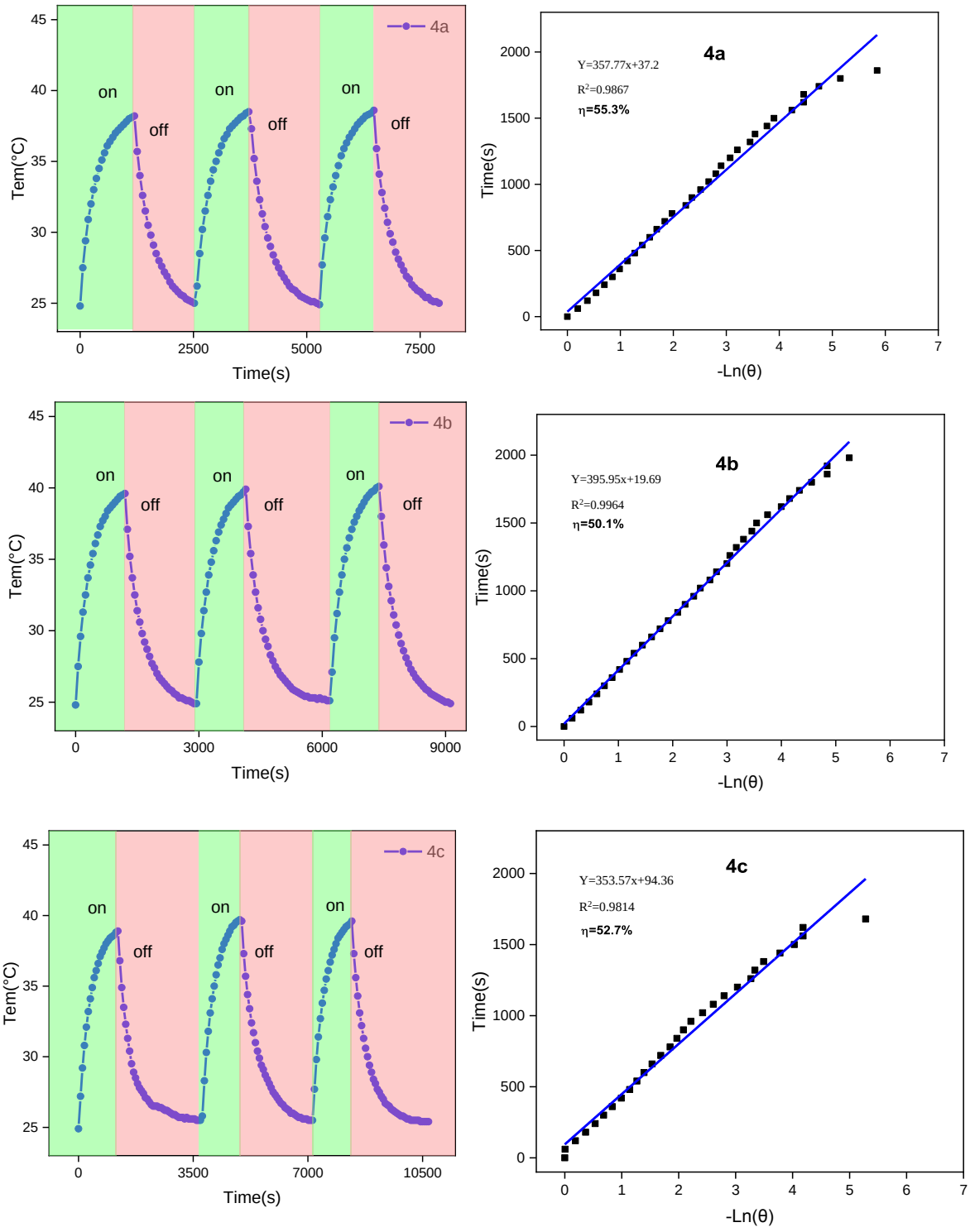


Fig. S9. (a) Photothermal conversion and (b) temperature changes of **4a-4c** at different concentrations in DMF upon irradiation of 650 nm laser (0.8 W cm^{-2}), linear fitting of the time vs -Ln(θ) plot of **4a-4c**. θ is a dimensionless parameter, known as the driving force temperature. (f) Photothermal stability of **4a-4c** for three heating and cooling cycles.

I.7 Preparation of 2b@F127 nanoparticle

2b (2 mg) and Poloxamer F127 (6 mg) was completely dissolved in THF (3 mL) and then 10 mL deionized water was added dropwise into the above solution. After stirring for 24 hours at room temperature, the organic solvent THF was dialyzed against PBS buffer (pH 7.4) for 48 h. **2b**@F127 were stored at 4 ^{o}C for further use.

I.8 General animals culture

Cell culture

HeLa cells were cultured in Dulbecco's modified Eagle medium (DMEM, Corning) supplemented with 10 % fetal bovine serum (FBS), 1 % penicillin and streptomycin in an atmosphere of 5 % CO_2 and 95 % air at 37 °C.

ROS detection

ROS generation in live cells was determined using 2',7'-dichlorodihydrofluorescein diacetate (DCFH-DA), an indicator that reacts with cellular ROS to provide an increase in green fluorescence (DCF). HeLa cells were seeded into confocal dishes. **2b**@F127 (100 μM) was then added. After 24 h, DCFH-DA (10 μM) was added and incubated for another 30 min. The cells subject to different treatment conditions (control, Laser, **2b**@F127, and **2b**@F127 + Laser) were then imaged by means of confocal fluorescence microscopy (Ex_{488} / Em_{525}).

Cytotoxicity testing

CCK 8 assay was carried out to evaluate the dark toxicity and phototoxicity of **2b**@F127. HepG2 cells were first seeded in two 96-well plates, which were incubated at 37 °C for 24 h. After removal of the medium and rinsing with PBS, HepG2 were pretreated with **2b@**F127 (final concentration contains 0, 10, 20, 30, 40, 50, 75 or 100 μM) solutions for 24 h. One plate was kept in the dark for studying dark toxicity, and another plate was irradiated using the 650 nm laser at a power of 0.5 W cm^{-2} for 10 min. The cells were incubated for 24 h, followed by addition of CCK 8 (10 μL) for additional 1 h incubation. The absorbance at 450 nm was measured using a Microplate Reader.

Dead/live cell co-staining

To demonstrate visually the killing effect of **2b**@F127, HeLa cells were incubated on confocal plates for 24 h and then treated under different conditions (control, Laser, **2b**@F127, and **2b**@F127 + Laser). After incubation for 24 h, each plate was incubated with 1 mL of dye solution (2 μM calcein AM and 4 μM PI), co-stained for 30 min at 37 °C, and imaged using a confocal fluorescence microscope.

***In vivo* phototherapy**

Nude mice bearing subcutaneous HeLa tumors (~ 100 mm^3) were divided into four groups randomly (5 mice for each group): Control, **2b**@F127, Laser, **2b** @F127 + Laser. All samples were injected intratumorally with concentration of 200 μM. The 650 nm laser irradiation was applied in corresponding groups with powder density of 0.5 W cm^{-2} for 10 min. After treatment of all the mice on the first day, tumor growth was measured by vernier caliper every two days for 2 weeks and tumor volume (V) was calculated as V = (tumor length) × (tumor width)^2/2. The body weight of each mouse was monitored every other day using a digital balance during the treatment. Finally, the tumor issue and main organs (heart, liver, spleen, lung and kidney) of each group after treatment were extracted and fixed with 4% paraformaldehyde for hematoxylin and eosin (H&E) staining. TUNEL analysis of the tumors were also carried out.

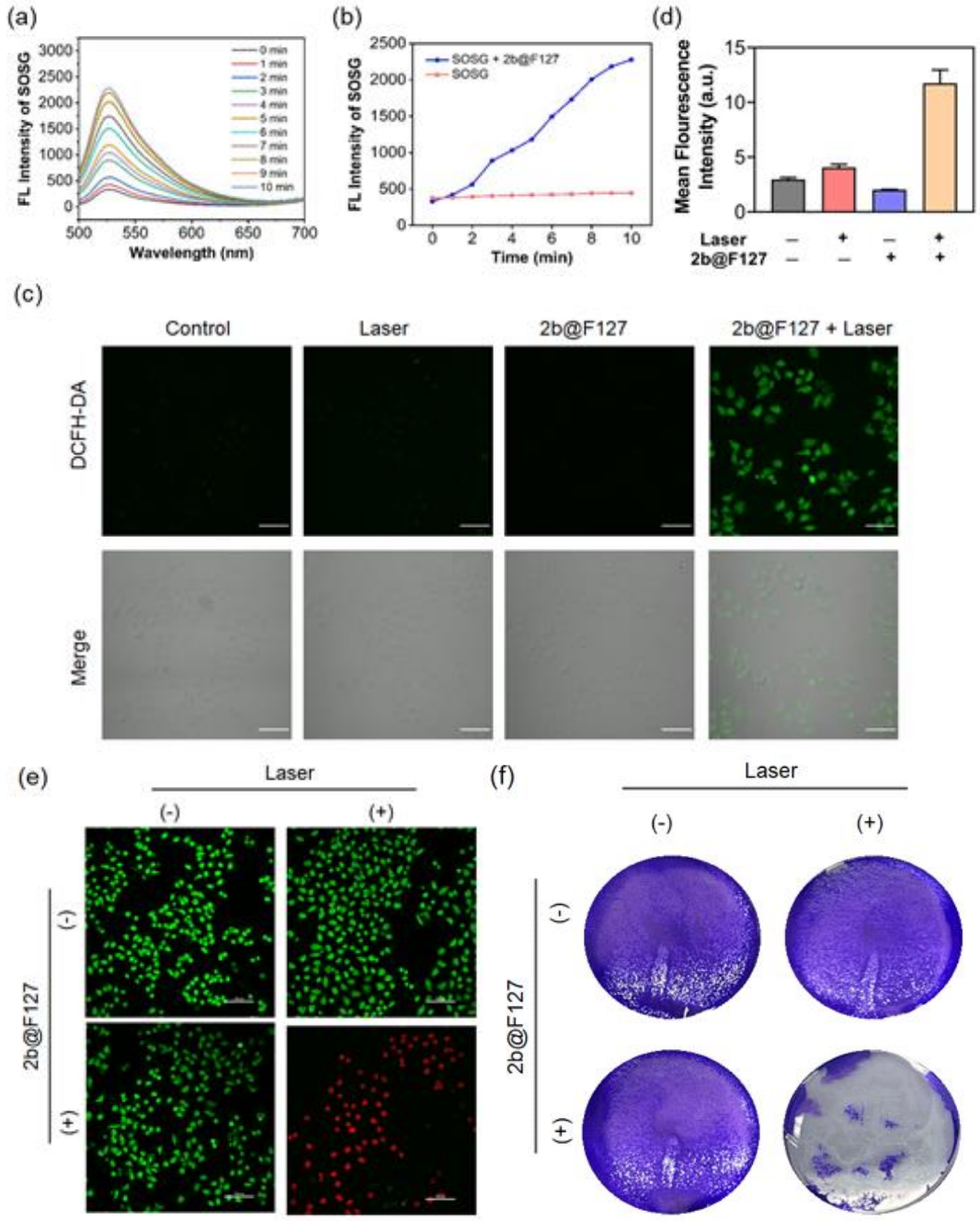


Fig. S10 (a) Time-dependent fluorescence spectral changes observed for PBS 7.4 of **2b**@F127 upon light irradiation at 650 nm. (b) Fluorescence changes of SOSG in **2b**@F127 under irradiation (650 nm, 0.2 W cm^{-2}) as a function of time. (c) Intracellular ROS level of HeLa cells under different conditions (control without any treatment, Laser, **2b**@F127 and **2b**@F127 + Laser). (d) Corresponding quantification of CLSM images using the green mean fluorescence intensity of DCFH-DA. (e) Fluorescence images of calcein AM (green fluorescence; live cells) and PI (red fluorescence; dead cells) co-stained HeLa cells under different conditions. (f) Typical photographs of colony formation of cancer cells treated with various treatments. Scale bars: 100 μm.

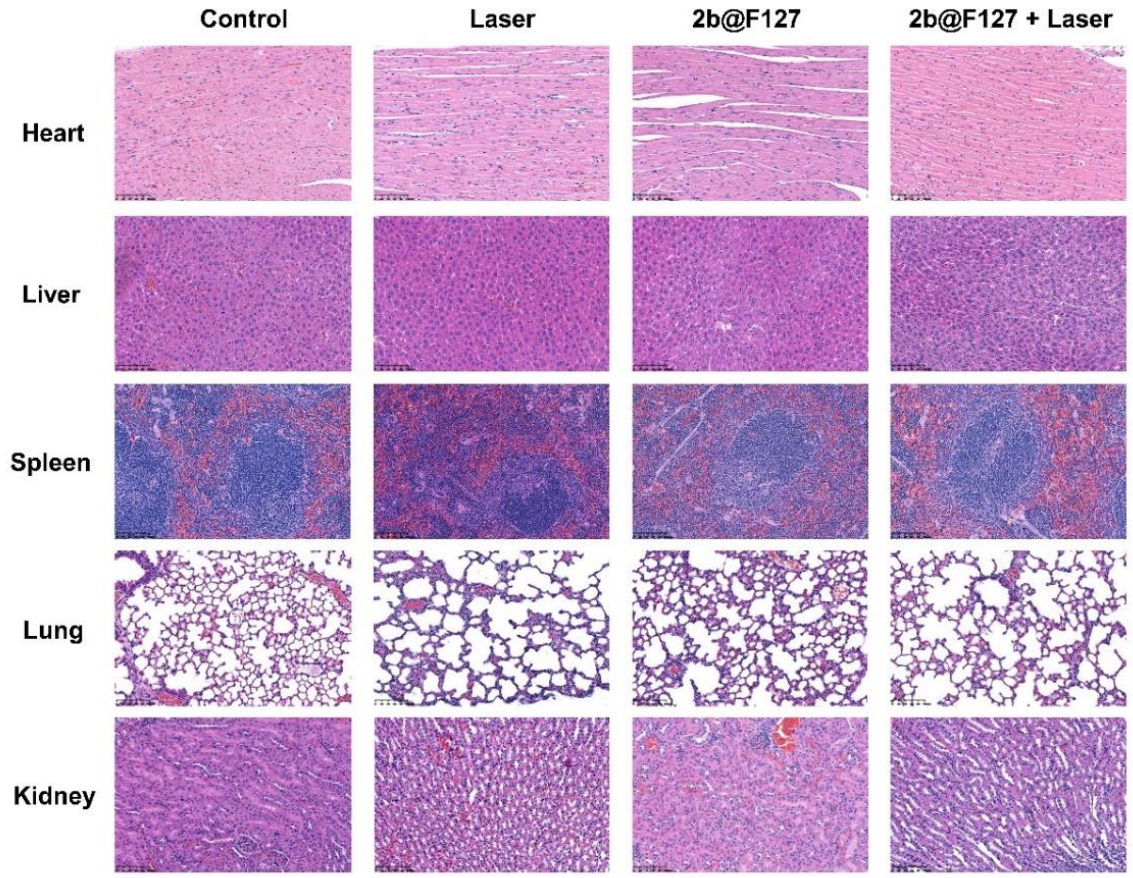
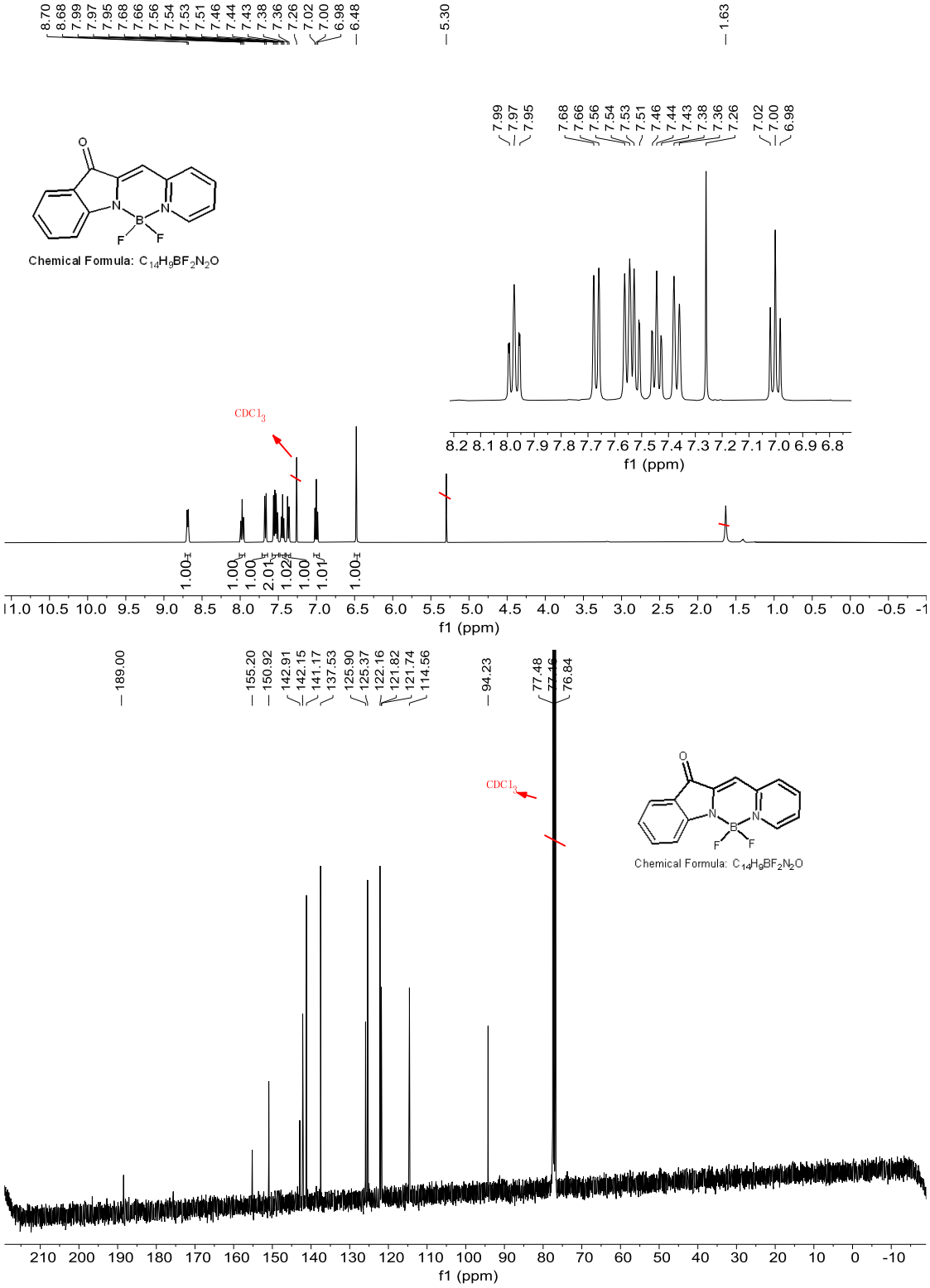
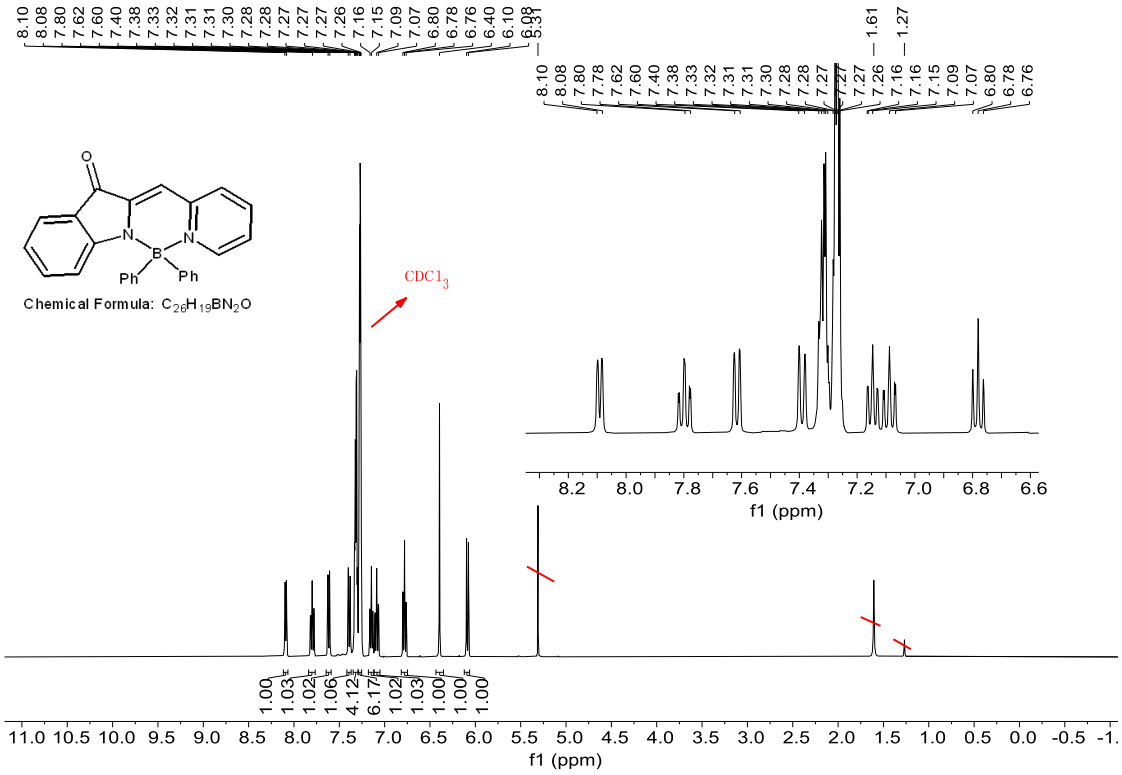


Fig. S11 H&E images of the heart, liver, spleen, lung and kidney under different treatments. Scale bar: 100 μm.

II. ^{1}H, ^{13}C NMR spectra and HRMS-ESI

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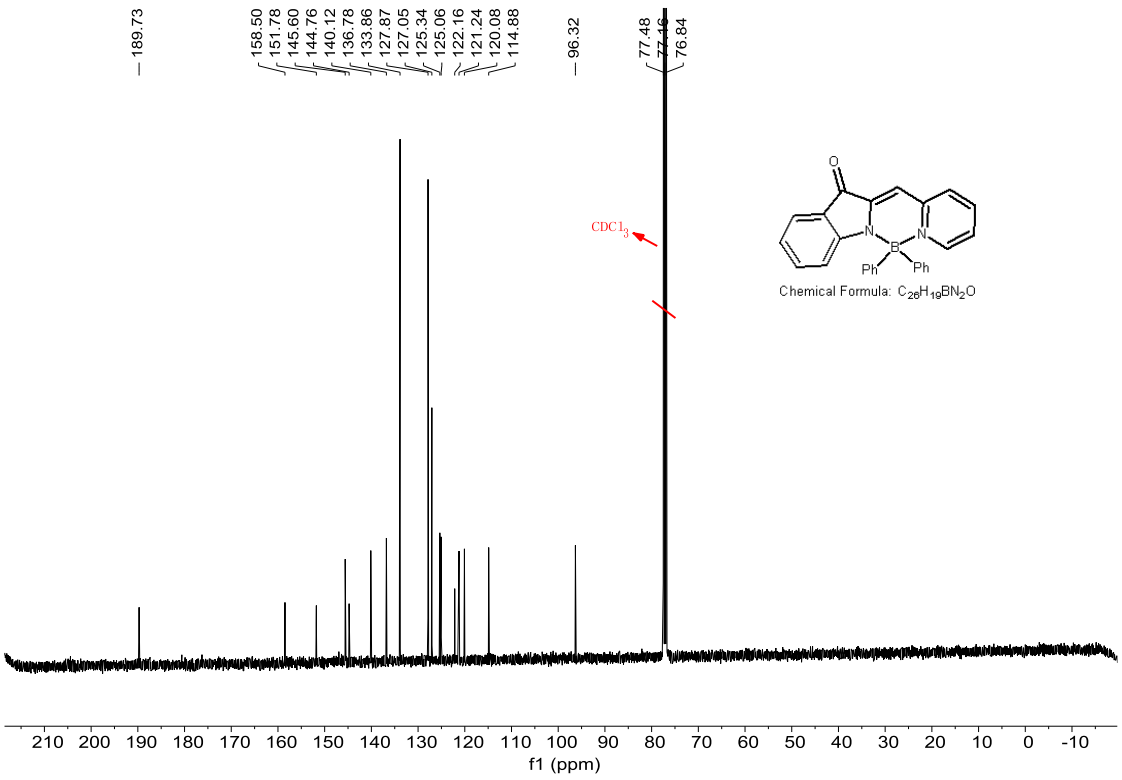
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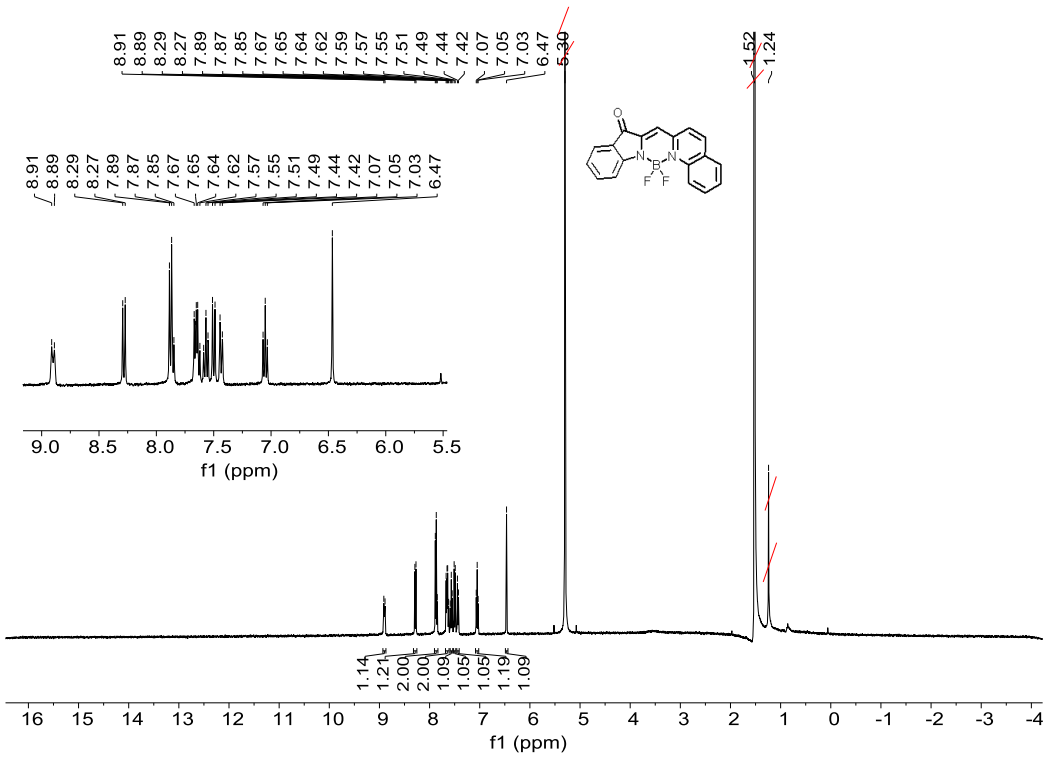
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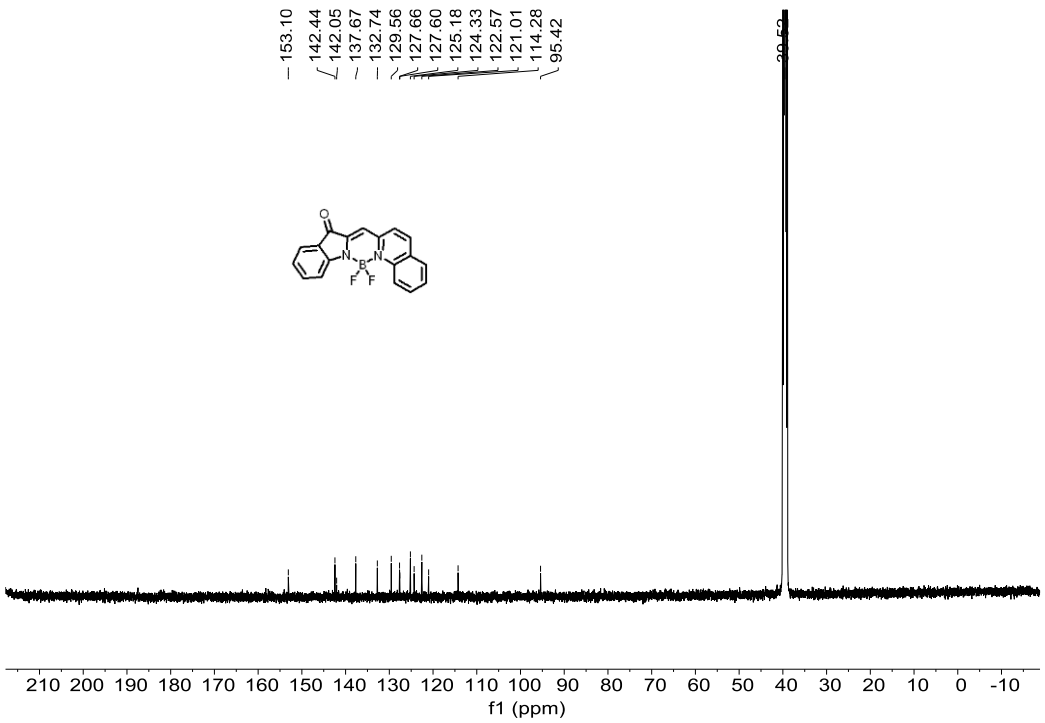
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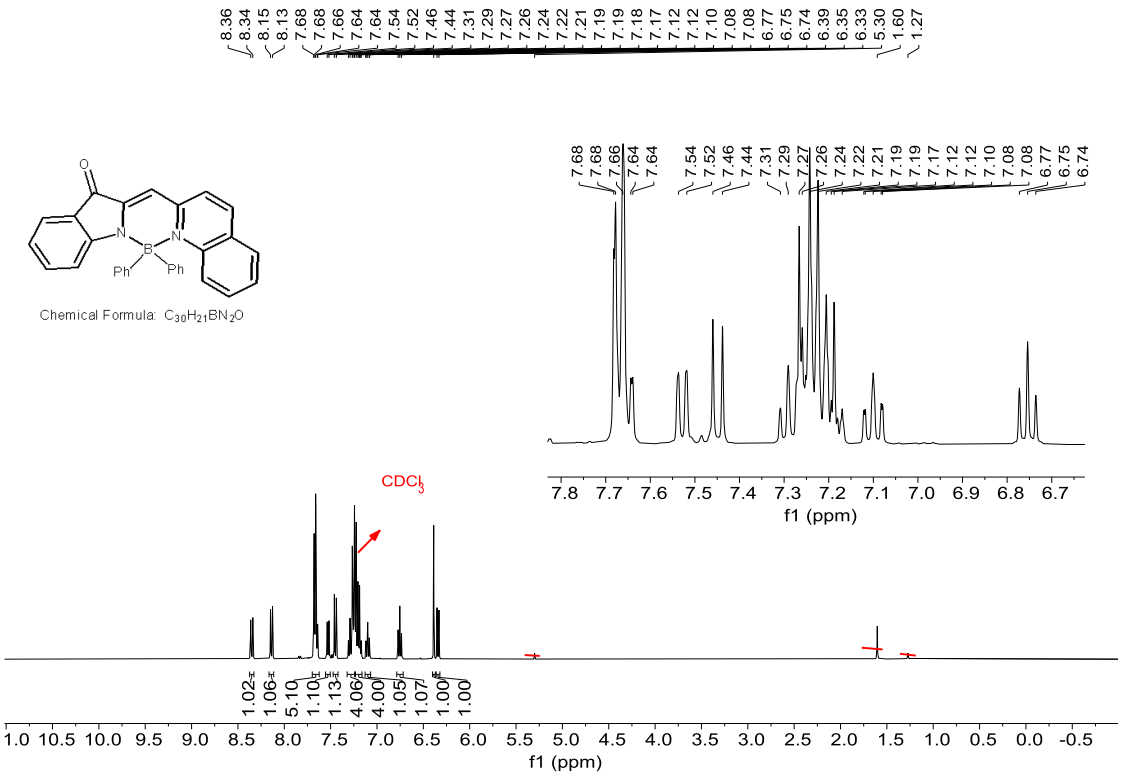
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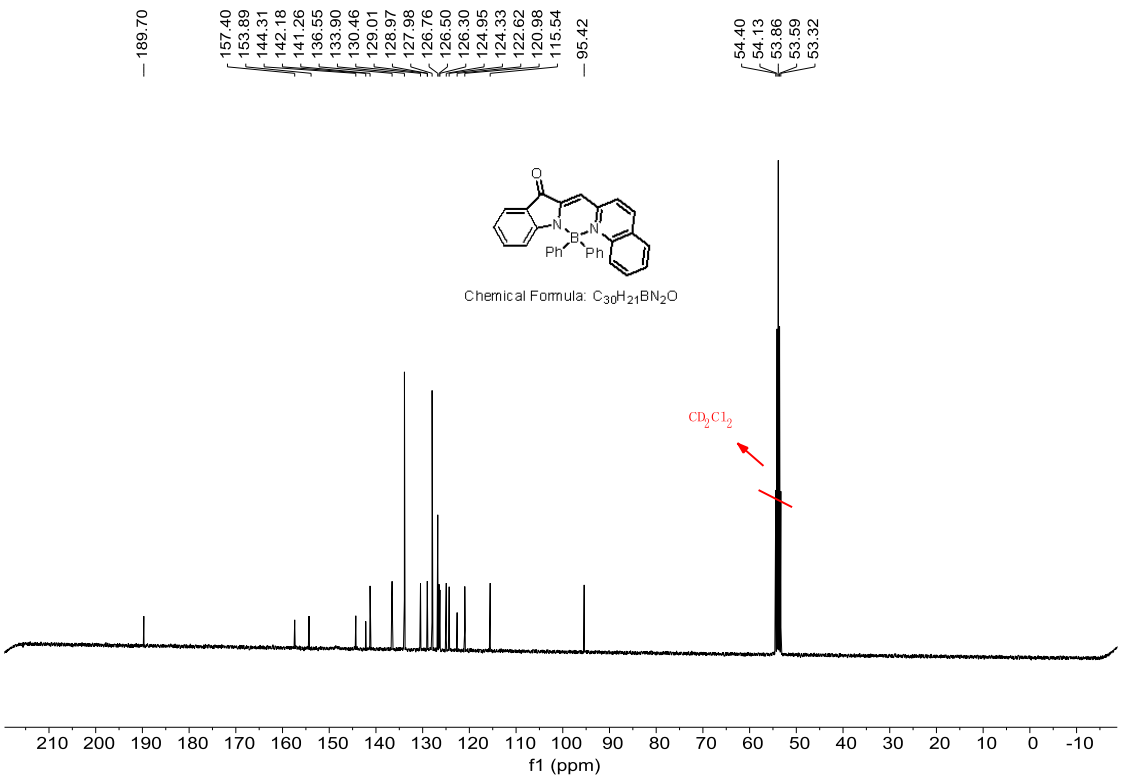
f1 (ppm)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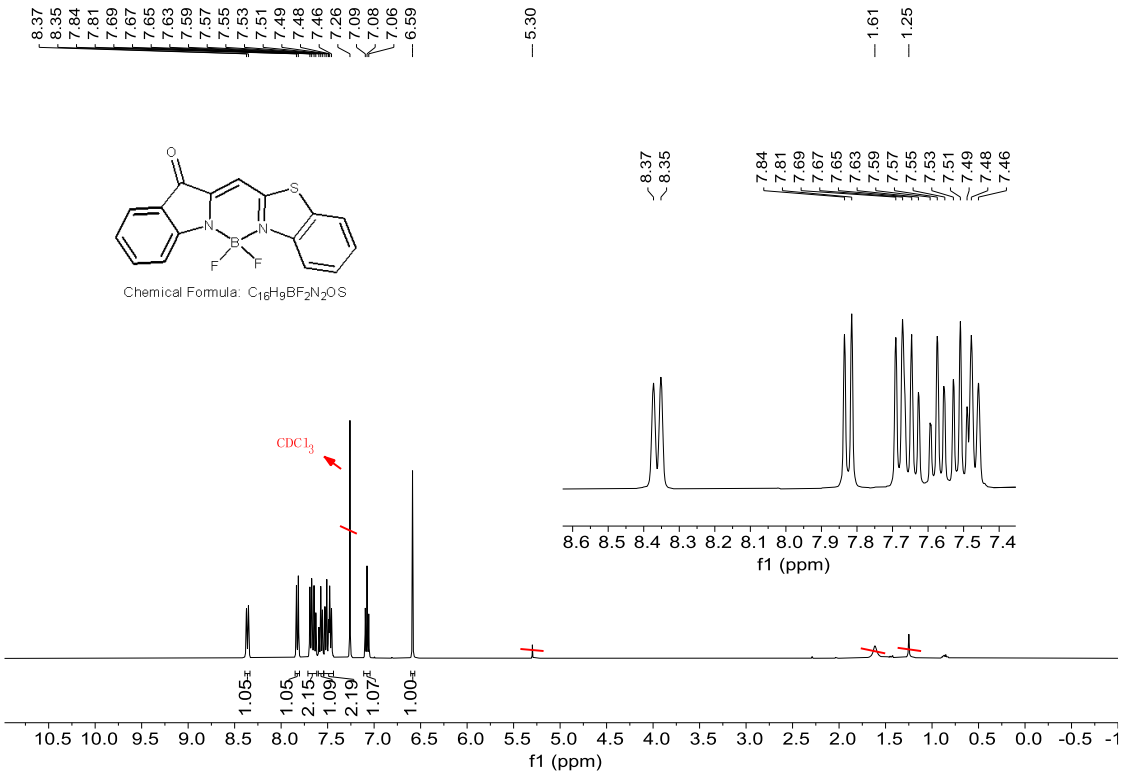
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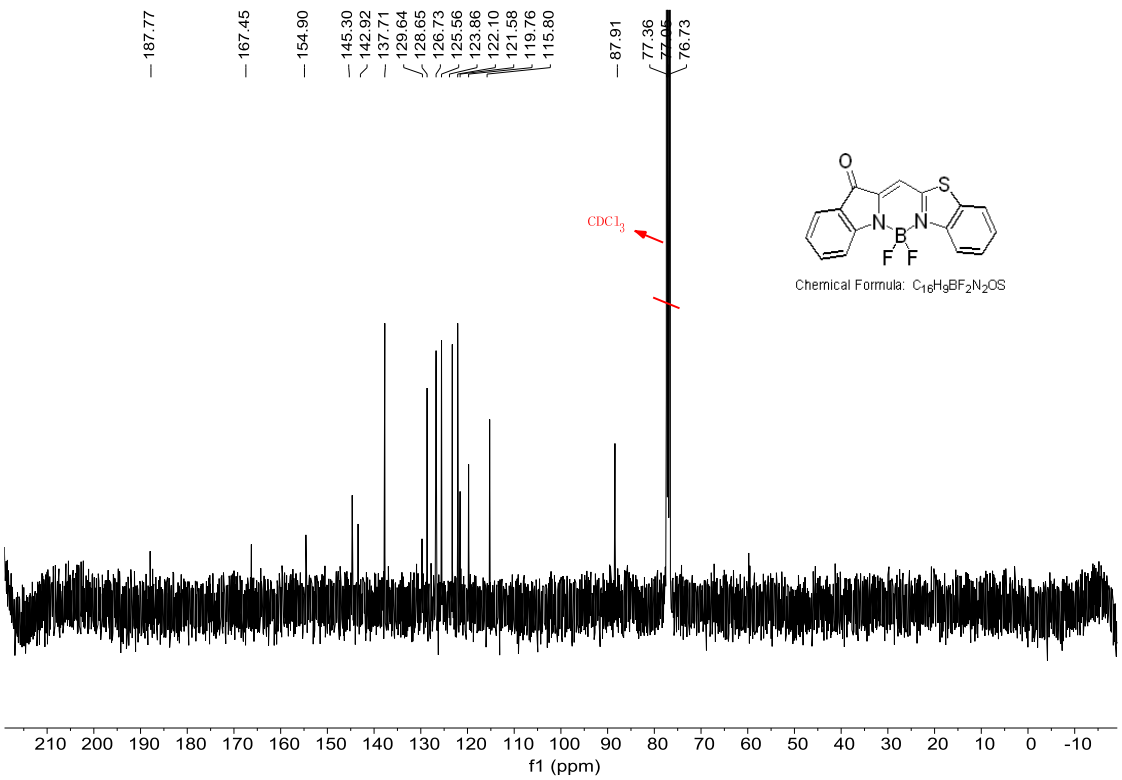
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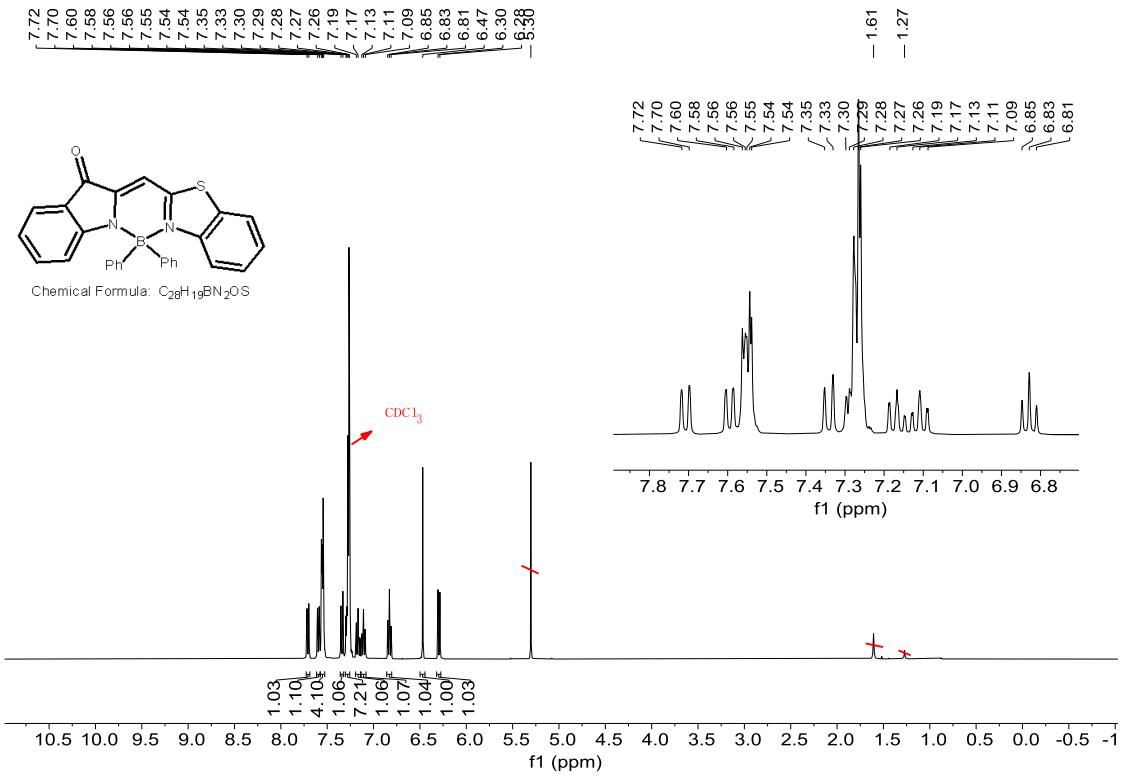
f1 (ppm)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1.61 1.27
O
S
N
B
N
Ph
Ph
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CDCl3
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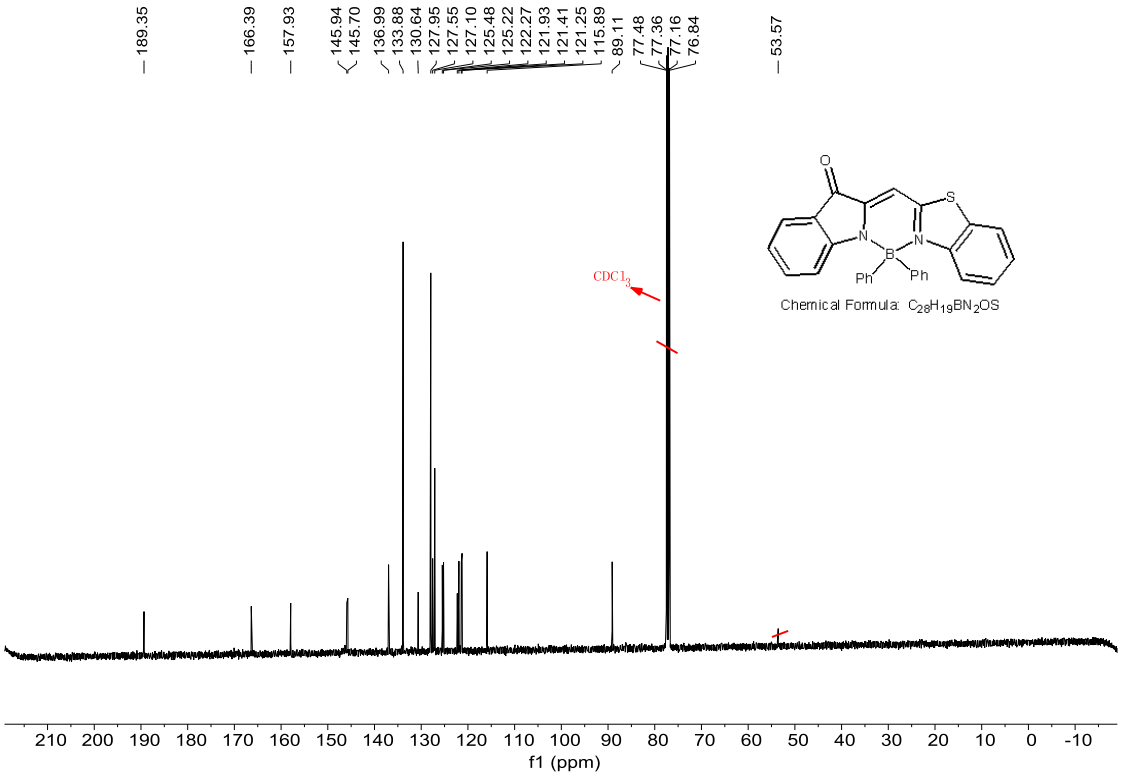
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O
S
N
B
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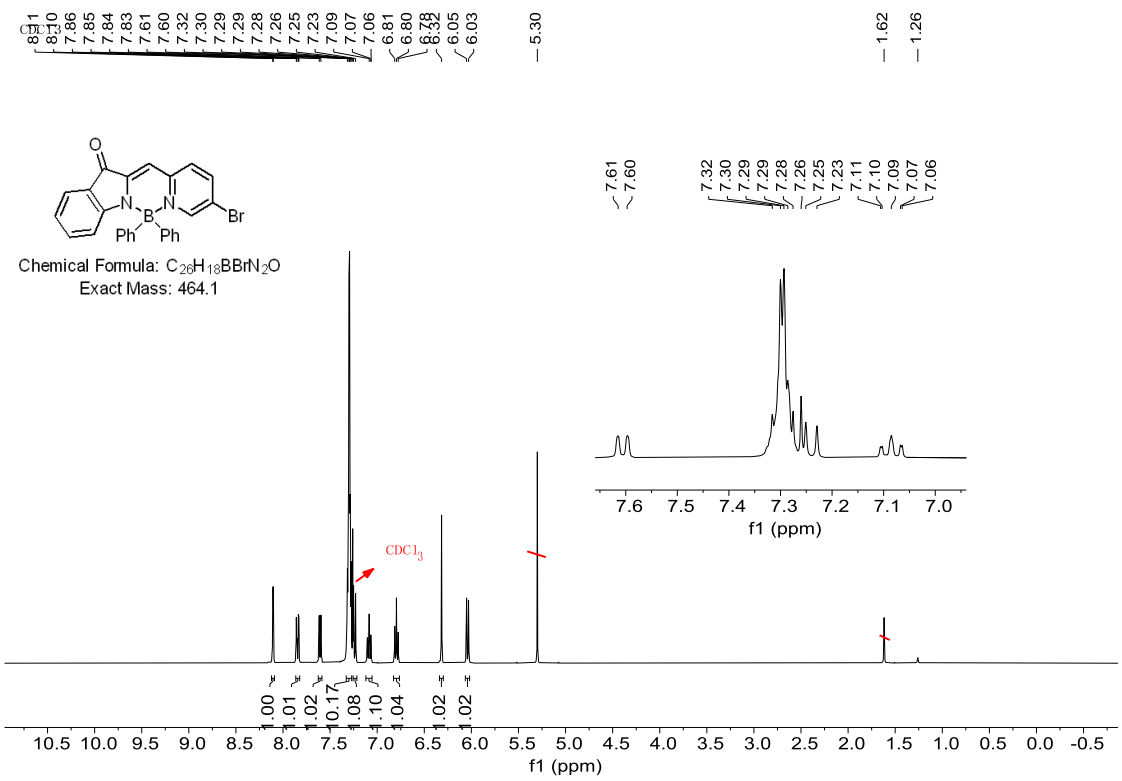
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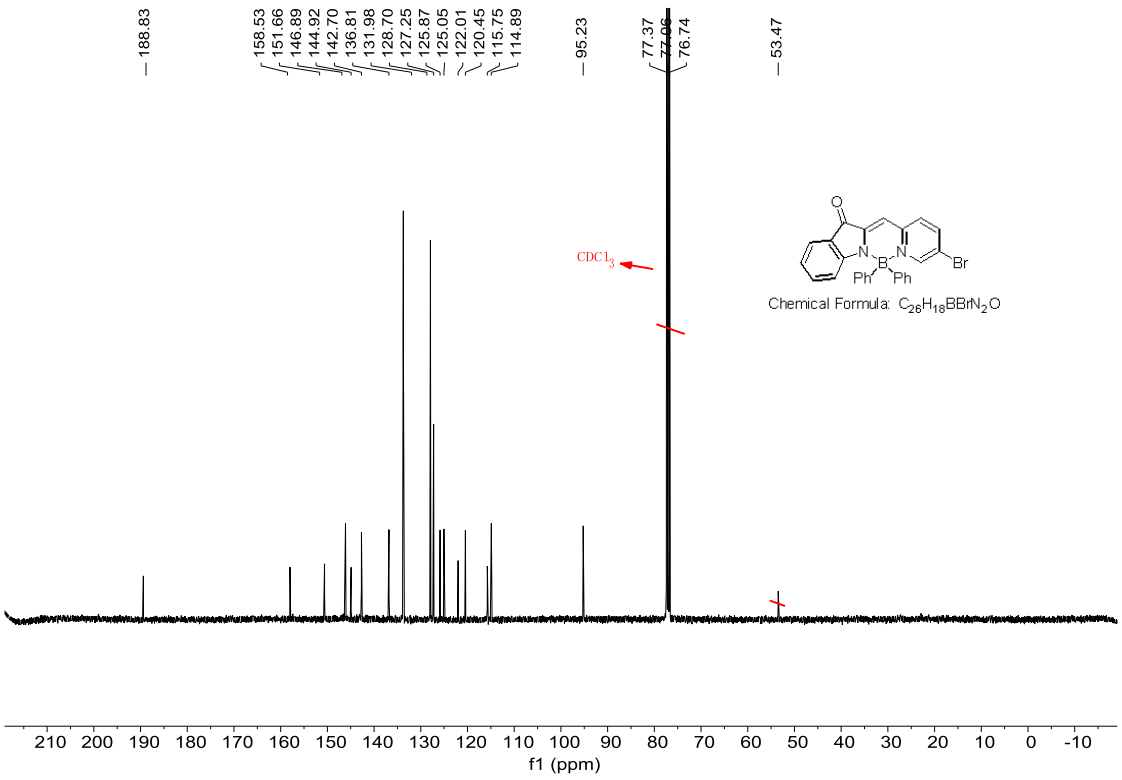
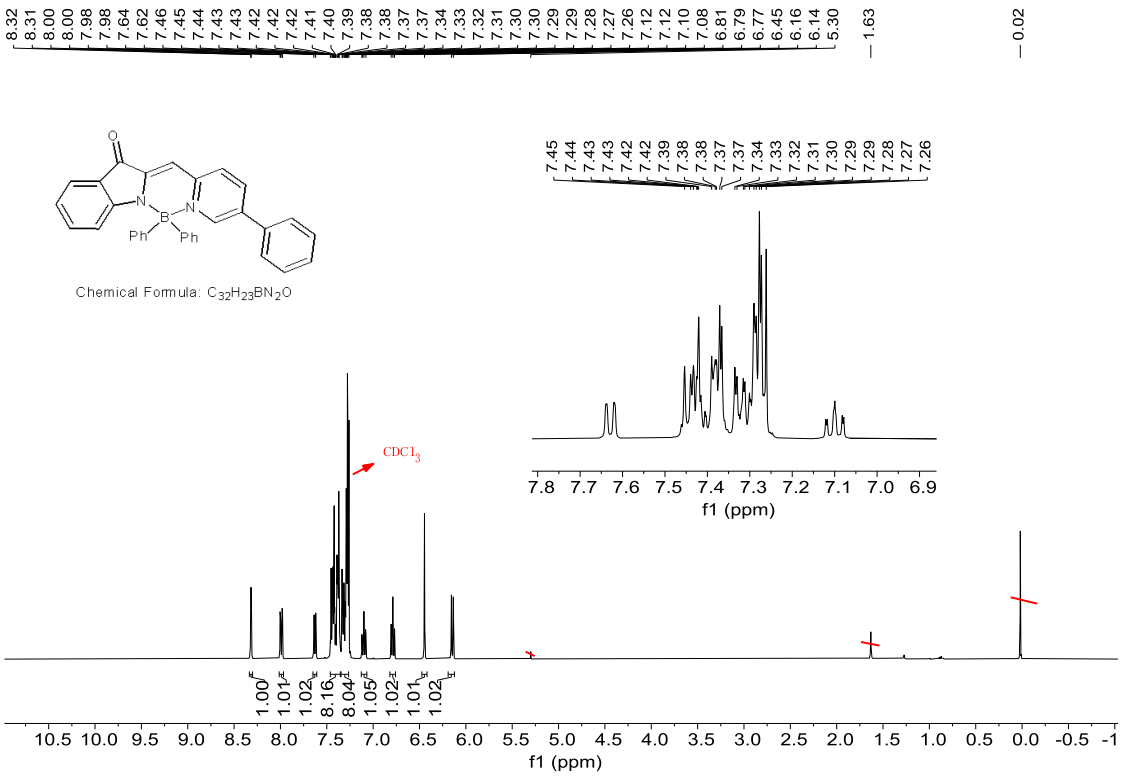
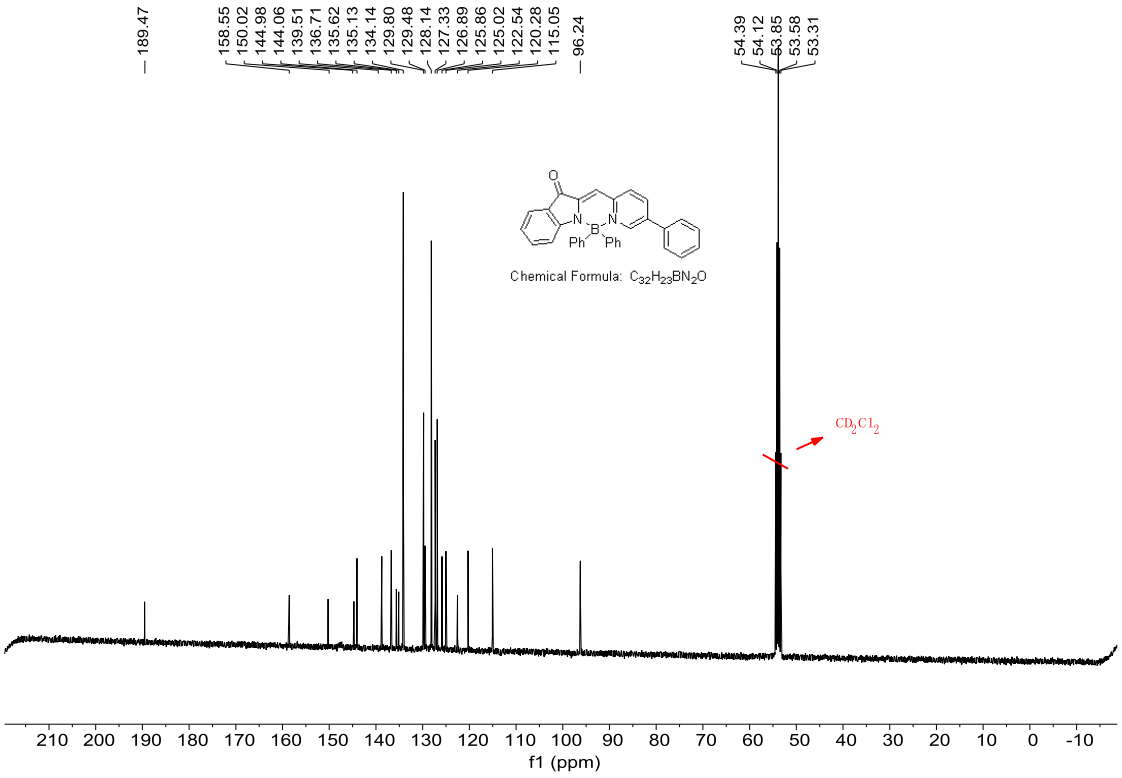
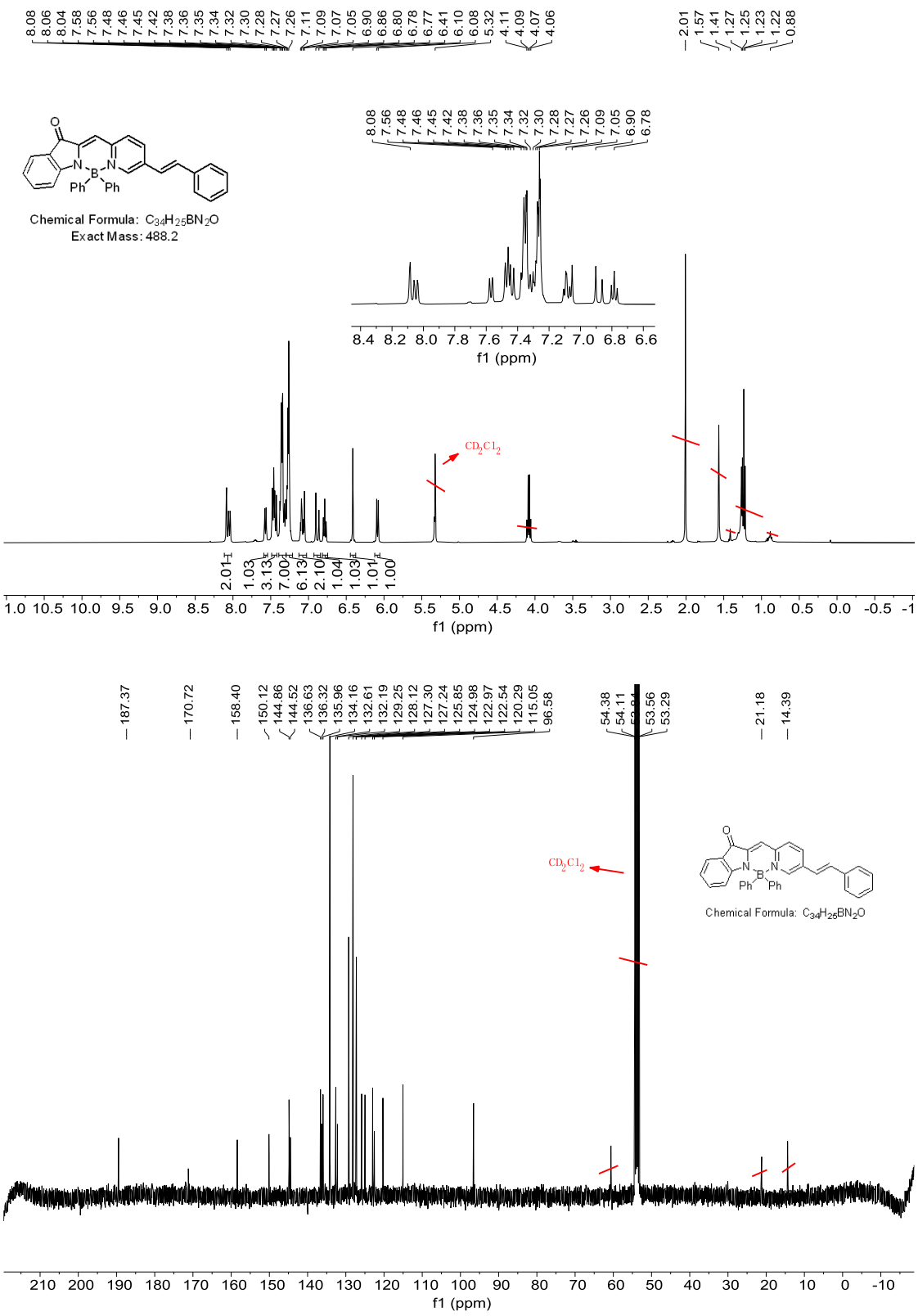
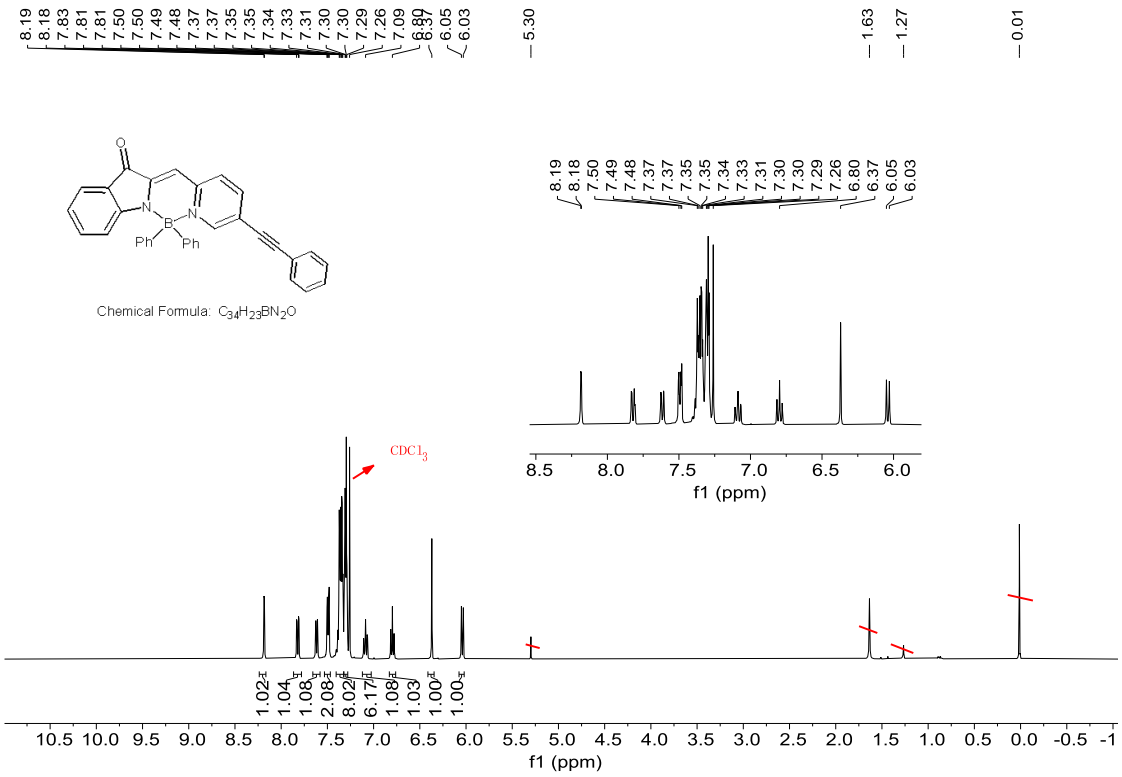
1.62
1.26
Chemical Formula: C26H18BBrN2O
Exact Mass: 464.1
7.61
7.60
7.32
7.30
7.29
7.29
7.28
7.26
7.25
7.23
7.11
7.10
7.09
7.07
7.06
7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
CDCl3
1.00
1.01
1.02
10.17
1.08
1.10
1.04
1.02
1.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

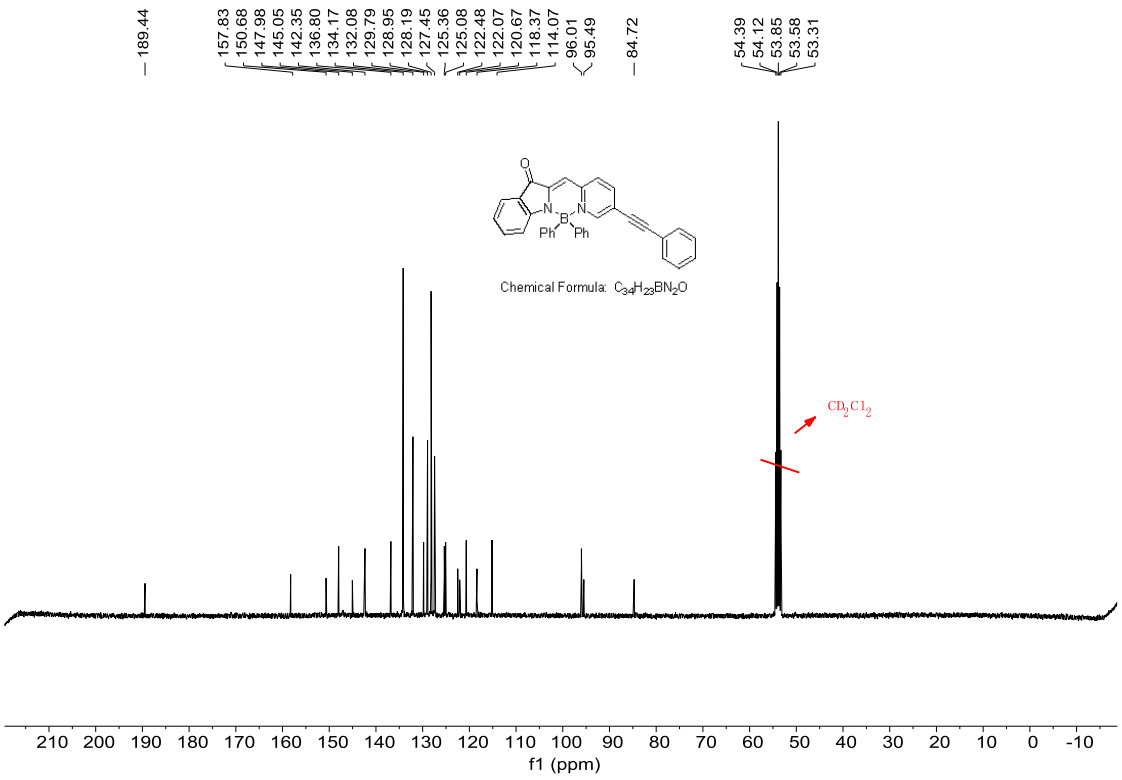

188.83
158.53
151.66
146.89
144.92
142.70
136.81
131.98
128.70
127.25
125.87
125.05
122.01
120.45
115.75
114.89
95.23
77.37
77.06
76.74
53.47
CDCl3
Chemical Formula: C26H18BBrN2O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

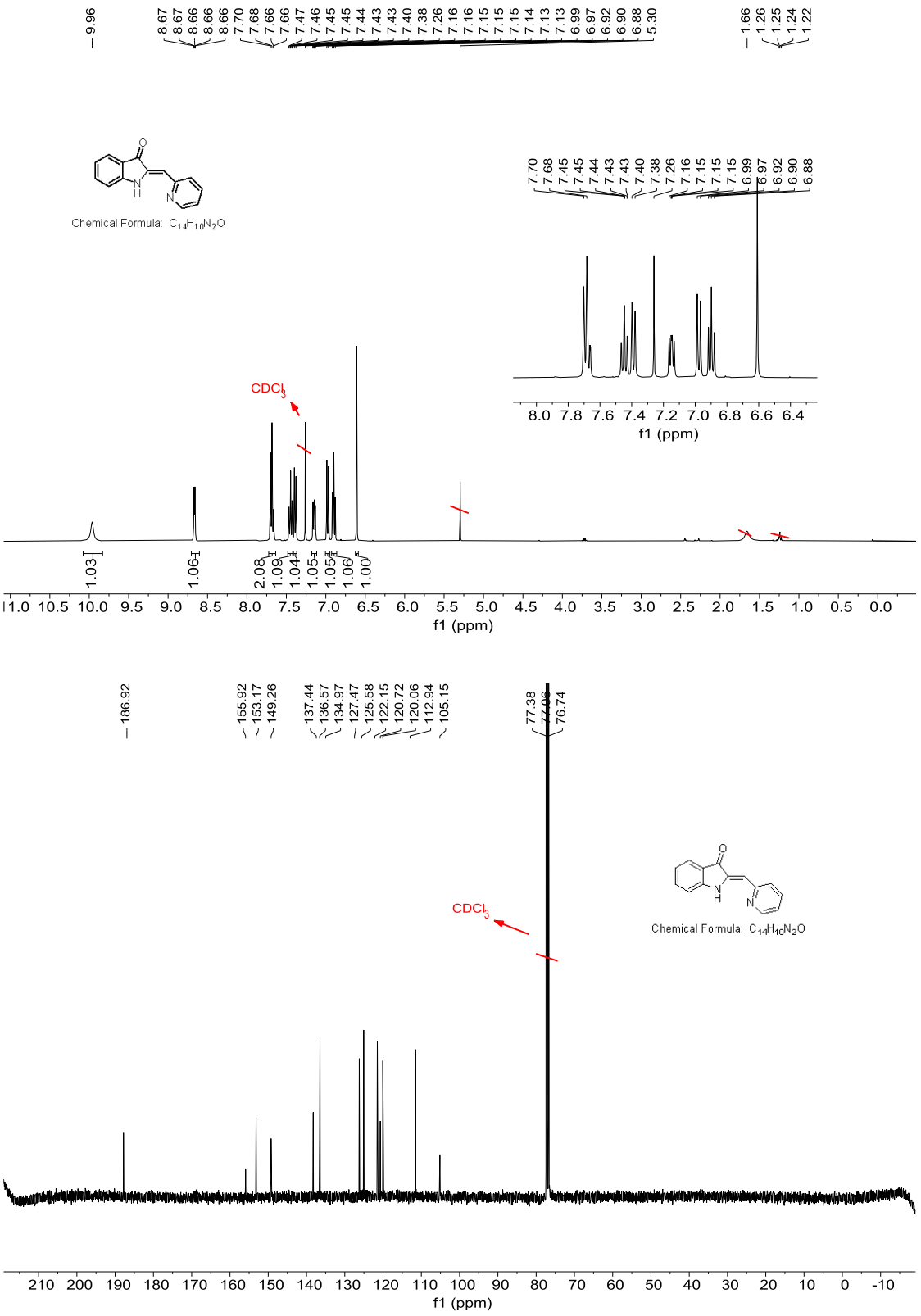

8.32 8.31 8.00 8.00 7.98 7.98 7.64 7.62 7.46 7.45 7.44 7.43 7.43 7.42 7.42 7.42 7.41 7.40 7.39 7.38 7.38 7.37 7.37 7.34 7.33 7.32 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.26 7.12 7.12 7.10 7.08 6.81 6.79 6.77 6.45 6.16 6.14 5.30
1.63
0.02
Chemical Formula: C32H23BN2O
7.45 7.44 7.43 7.43 7.42 7.42 7.39 7.38 7.38 7.37 7.37 7.34 7.33 7.32 7.31 7.30 7.29 7.29 7.28 7.27 7.26
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
CDCl3
1.00 1.01 1.02 8.16 8.04 1.05 1.02 1.01 1.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

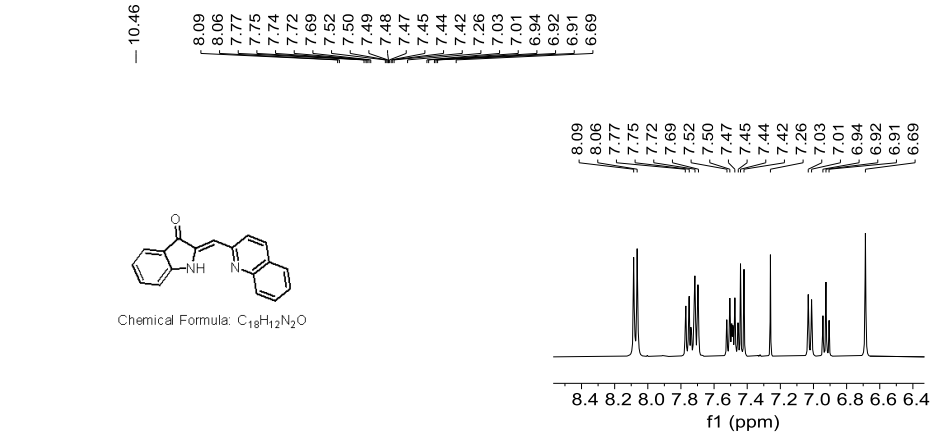

189.47
158.55 150.02 144.98 144.06 139.51 136.71 135.62 135.13 134.14 129.80 129.48 128.14 127.33 126.89 125.86 125.02 122.54 120.28 115.05
96.24
54.39 54.12 53.85 53.58 53.31
Chemical Formula: C32H23BN2O
CD2Cl2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

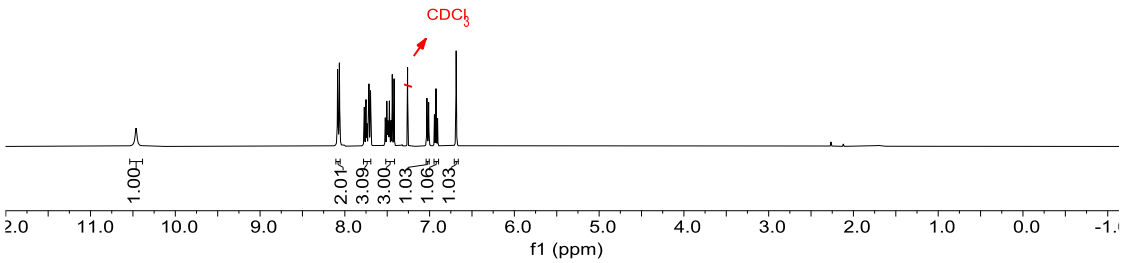

8.08 8.06 8.04 7.58 7.56 7.48 7.46 7.45 7.42 7.38 7.36 7.35 7.34 7.32 7.30 7.28 7.27 7.26 7.11 7.09 7.07 7.05 6.90 6.86 6.80 6.78 6.77 6.41 6.10 6.08 5.32 4.11 4.09 4.07 4.06
2.01 1.57 1.41 1.27 1.25 1.23 1.22 0.88
Chemical Formula: C34H25BN2O
Exact Mass: 488.2
f1 (ppm)
CD2Cl2
2.01 1.03 3.13 7.00 6.13 2.10 1.04 1.03 1.01 1.00
f1 (ppm)
187.37 170.72 158.40 150.12 144.86 144.52 136.63 136.32 135.96 134.16 132.61 132.19 129.25 128.12 127.30 127.24 125.85 124.98 122.97 122.54 120.29 115.05 96.58
54.38 54.11 53.84 53.56 53.29
21.18 14.39
CD2Cl2
Chemical Formula: C34H25BN2O
f1 (ppm)

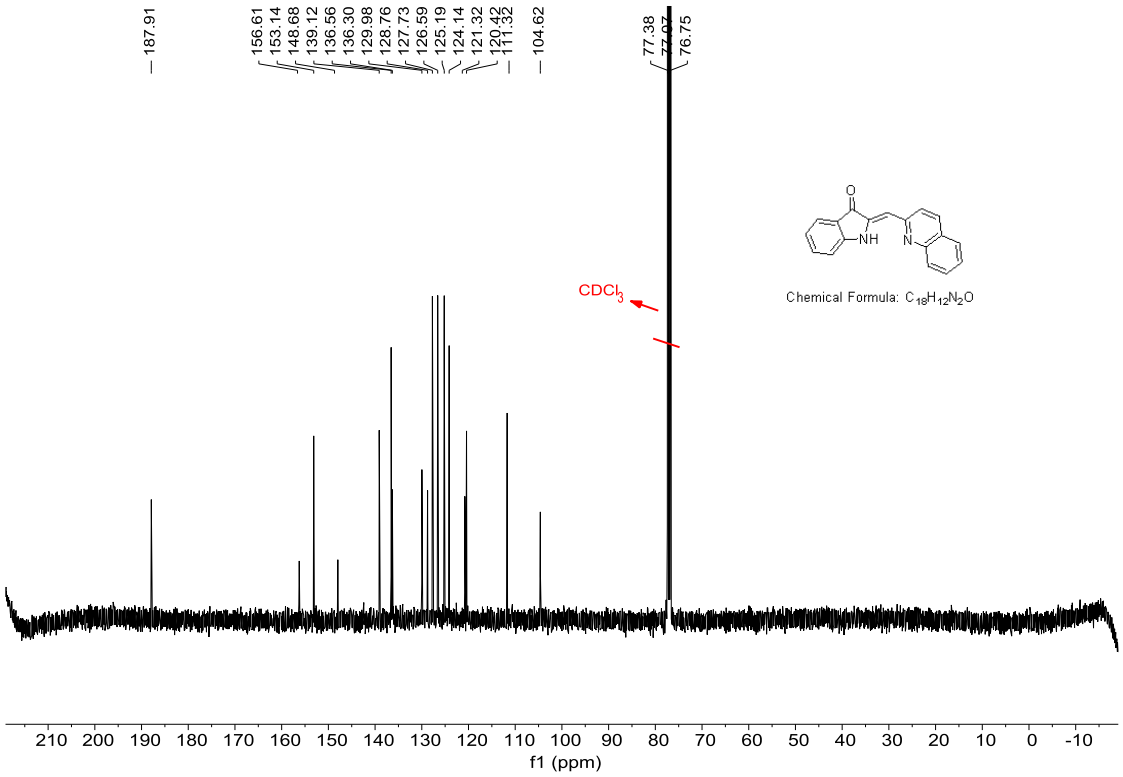

8.19
8.18
7.83
7.81
7.81
7.50
7.50
7.49
7.48
7.37
7.37
7.35
7.35
7.34
7.33
7.31
7.30
7.30
7.29
7.26
7.09
6.80
6.37
6.05
6.03
5.30
1.63
1.27
0.01
Chemical Formula: C34H23BN2O
CDCl3
1.02
1.04
1.08
2.08
8.02
6.17
1.08
1.03
1.00
1.00
f1 (ppm)

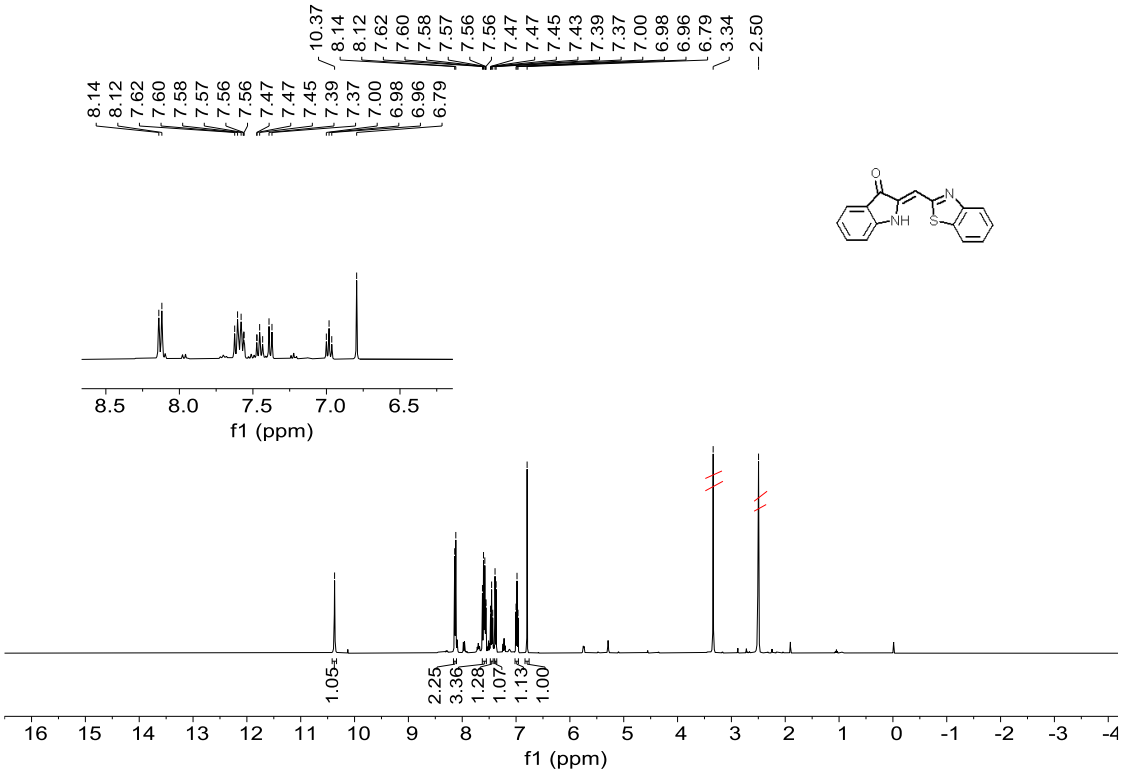

189.44
157.83
150.68
147.98
145.05
142.35
136.80
134.17
132.08
129.79
128.95
128.19
127.45
125.36
125.08
122.48
122.07
120.67
118.37
114.07
96.01
95.49
84.72
54.39
54.12
53.85
53.58
53.31
Chemical Formula: C34H23BN2O
CD2Cl2
f1 (ppm)

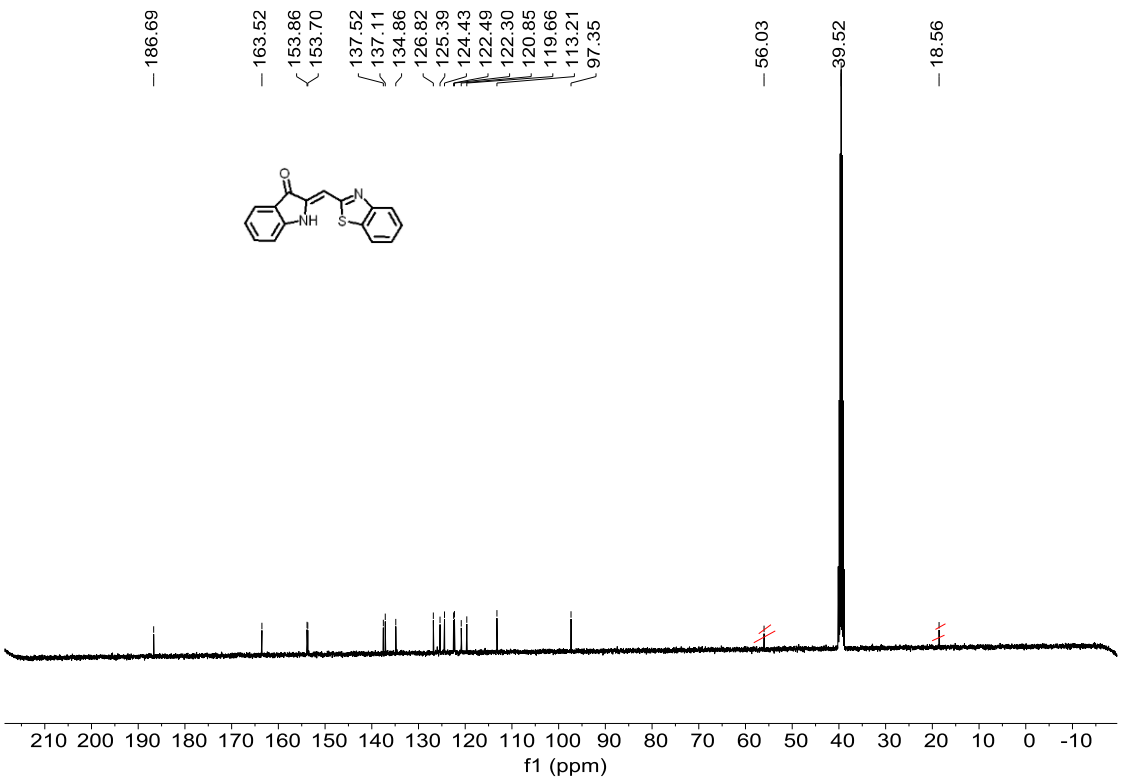

9.96
8.67
8.67
8.66
8.66
8.66
7.70
7.68
7.66
7.66
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.40
7.38
7.26
7.16
7.16
7.15
7.15
7.15
7.14
7.13
7.13
6.99
6.97
6.92
6.90
6.88
5.30
1.66
1.26
1.25
1.24
1.22
Chemical Formula: C14H10N2O
CDCl3
1.03
1.06
2.08
1.09
1.04
1.05
1.05
1.06
1.00
f1 (ppm)
186.92
155.92
153.17
149.26
137.44
136.57
134.97
127.47
125.58
122.15
120.72
120.06
112.94
105.15
77.38
77.06
76.74
CDCl3
Chemical Formula: C14H10N2O
f1 (ppm)

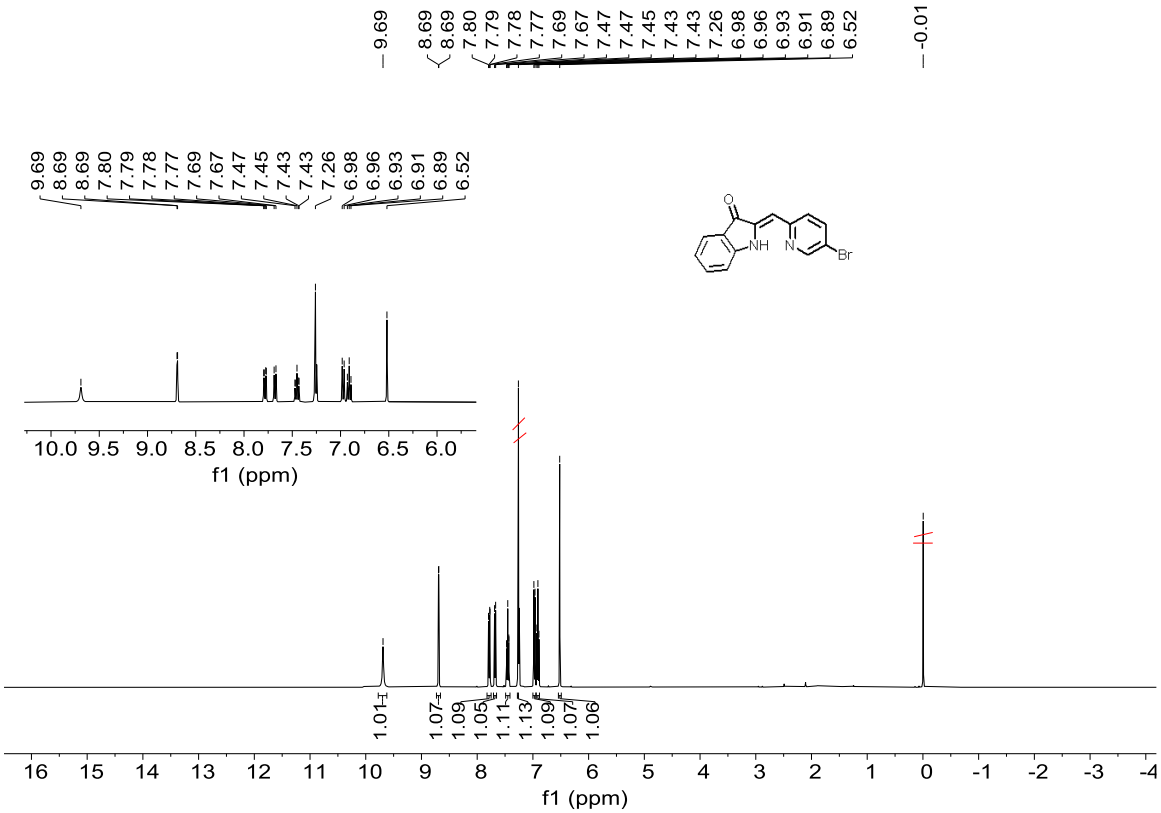

10.46
8.09
8.06
7.77
7.75
7.74
7.72
7.69
7.52
7.50
7.49
7.48
7.47
7.45
7.44
7.42
7.26
7.03
7.01
6.94
6.92
6.91
6.69
NH
N
Chemical Formula: C18H12N2O
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4
f1 (ppm)

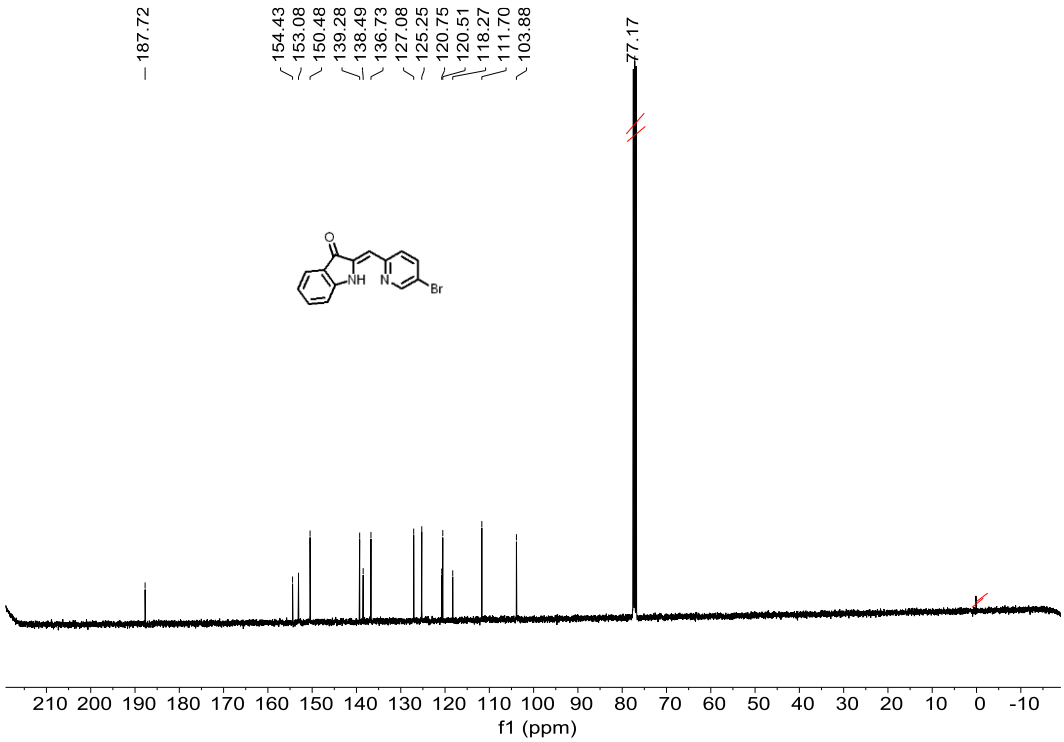

CDCl3
1.00
2.01
3.09
3.00
1.03
1.06
1.03
2.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


187.91
156.61
153.14
148.68
139.12
136.56
136.30
129.98
128.76
127.73
126.59
125.19
124.14
121.32
120.42
111.32
104.62
77.38
77.07
76.75
CDCl3
NH
N
Chemical Formula: C18H12N2O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


10.37
8.14
8.12
7.62
7.60
7.58
7.57
7.56
7.56
7.47
7.47
7.45
7.43
7.39
7.37
7.00
6.98
6.96
6.79
3.34
2.50
O
N
NH
S
8.5
8.0
7.5
7.0
6.5
f1 (ppm)
1.05
2.25
3.36
1.28
1.07
1.13
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


186.69
163.52
153.86
153.70
137.52
137.11
134.86
126.82
125.39
124.43
122.49
122.30
120.85
119.66
113.21
97.35
56.03
39.52
18.56
O
N
NH
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.69
8.69
8.69
7.80
7.79
7.78
7.77
7.69
7.67
7.47
7.47
7.45
7.43
7.43
7.26
6.98
6.96
6.93
6.91
6.89
6.52
-0.01
NH
N
Br
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0
f1 (ppm)
1.01
1.07
1.09
1.05
1.11
1.13
1.09
1.07
1.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


187.72
154.43
153.08
150.48
139.28
138.49
136.73
127.08
125.25
120.75
120.51
118.27
111.70
103.88
77.17
NH
N
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

HRMS Spectra

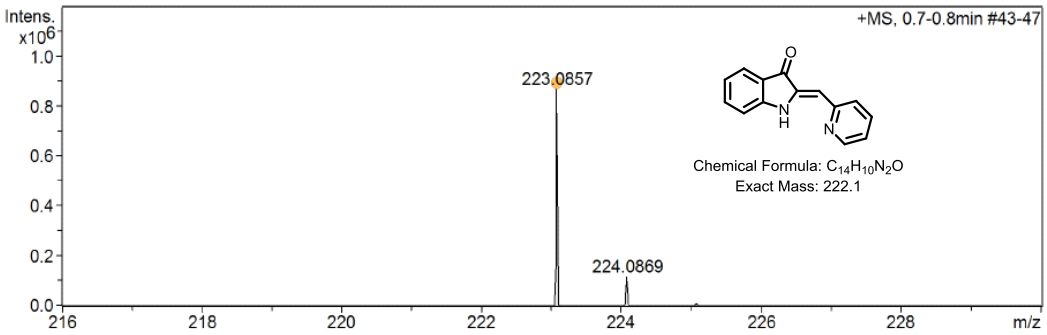
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-1_01.d	Acquisition Date	1/8/2021 2:13:01 PM
Method	ESI+100-800-201112.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
223.0857	1	C14H11N2O	223.0866	3.8	15.9	1	100.00	10.5	even	ok

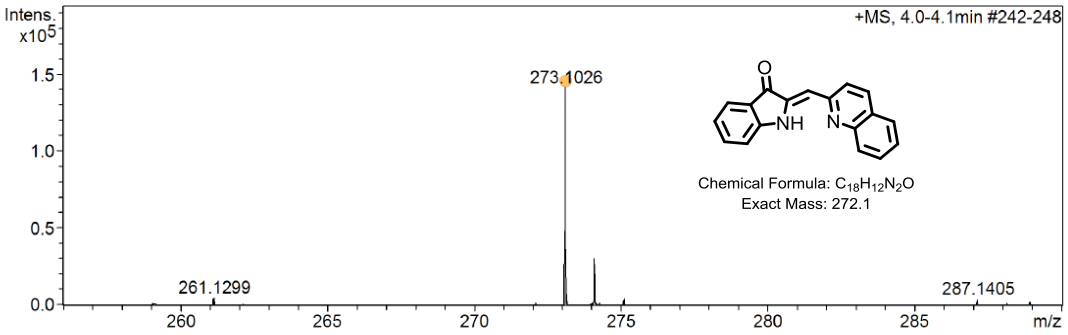
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-2_01.d	Acquisition Date	1/8/2021 2:14:29 PM
Method	ESI+100-800-201112.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
273.1026	1	C18H13N2O	273.1022	-1.3	8.9	1	100.00	13.5	even	ok

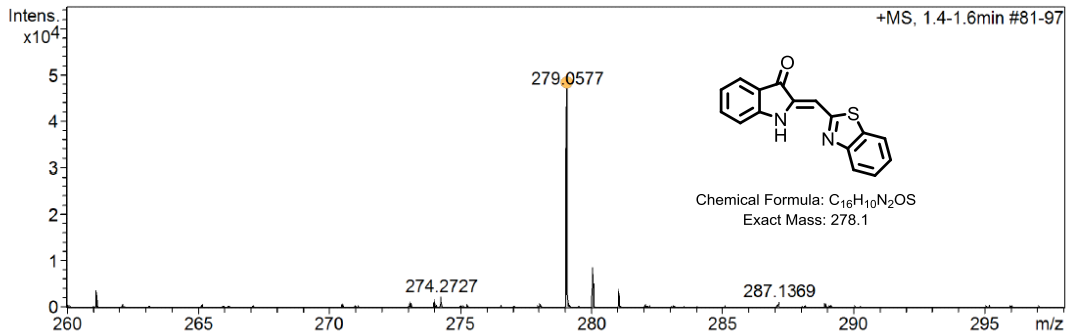
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-3_01.d	Acquisition Date	1/8/2021 2:21:20 PM
Method	ESI+100-800-201112.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
279.0577	1	C16H11N2OS	279.0587	3.5	3.7	1	100.00	12.5	even	ok

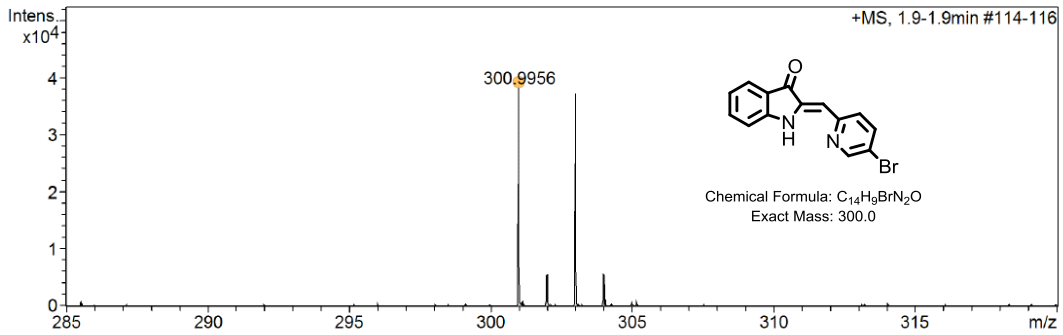
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-4_01.d	Acquisition Date	1/8/2021 2:23:18 PM
Method	ESI+100-800-201112.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
300.9956	1	C14H10BrN2O	300.9971	-5.0	9.0	1	100.00	10.5	even	ok

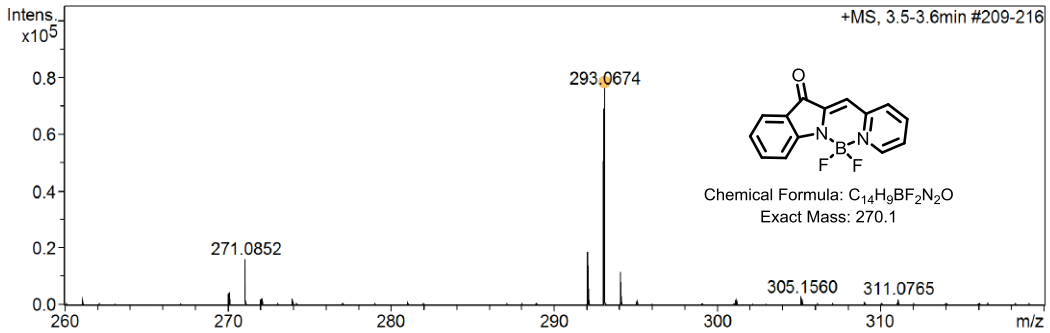
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-5_01.d	Acquisition Date	1/8/2021 2:25:24 PM
Method	ESI+100-800-201112.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
293.0674	1	C14H9BF2N2NaO	293.0671	1.2	4.3	1	100.00	10.5	even	ok

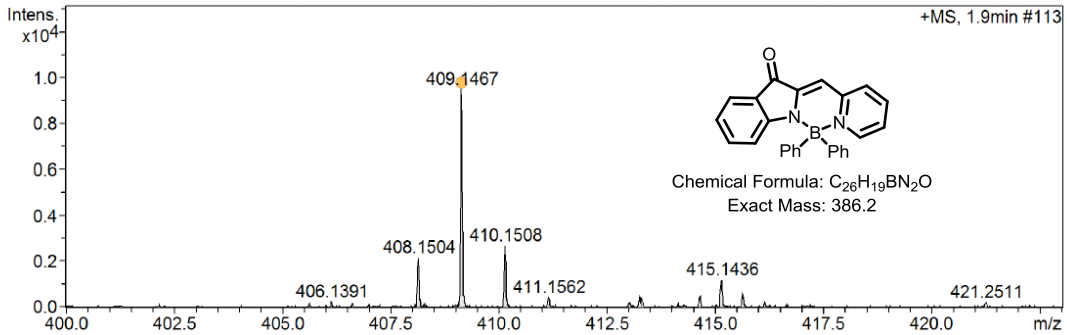
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-6_01.d	Acquisition Date	1/8/2021 2:29:24 PM
Method	ESI+100-800-201112.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
409.1467	1	C26H19BN2NaO	409.1487	-4.9	3.1	1	100.00	18.5	even	ok

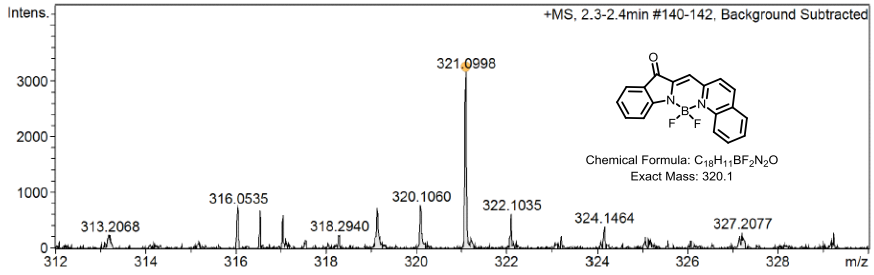
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-7_01.d	Acquisition Date	1/8/2021 2:31:26 PM
Method	ESI+100-800-201112.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
321.0998	1	C18H12BF2N2O	321.1009	-3.3	11.8	1	100.00	13.5	even	ok

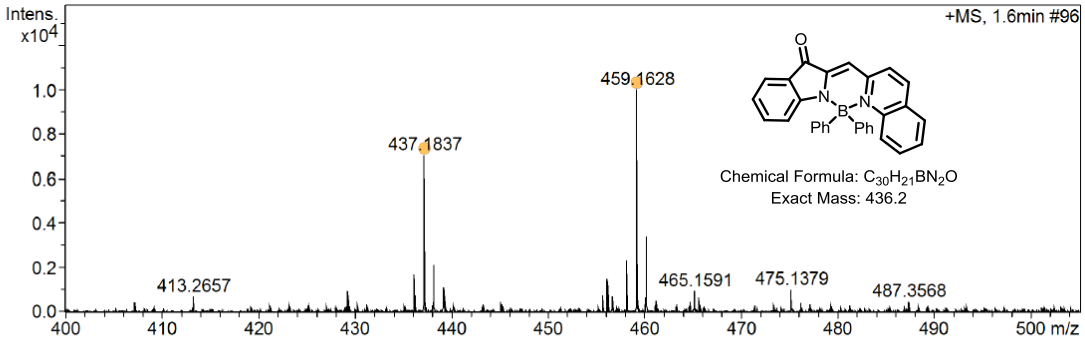
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-8_01.d	Acquisition Date	1/8/2021 2:34:01 PM
Method	ESI+100-800-201112.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
437.1837	1	C30H22BN2O	437.1825	2.7	26.0	1	100.00	21.5	even	ok
459.1628	1	C30H21BN2NaO	459.1644	-3.6	9.5	1	100.00	21.5	even	ok

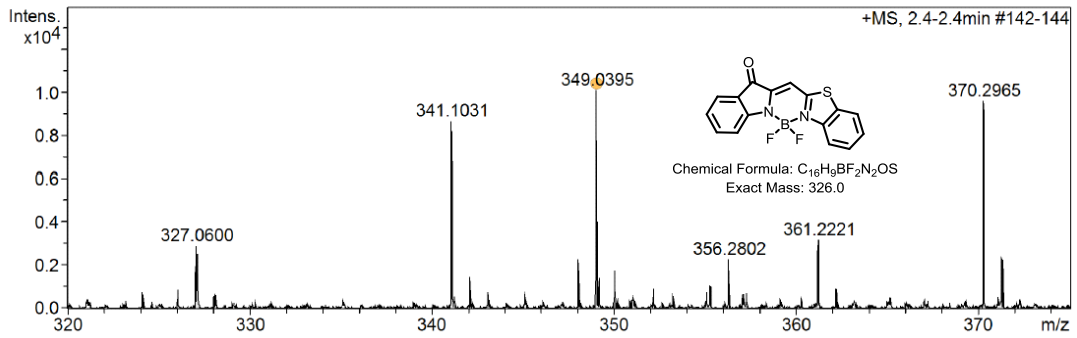
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-9_01.d	Acquisition Date	1/8/2021 2:36:03 PM
Method	ESI+100-800-201112.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
349.0395	1	C16H9BF2N2NaOS	349.0392	0.9	15.7	1	100.00	12.5	even	ok

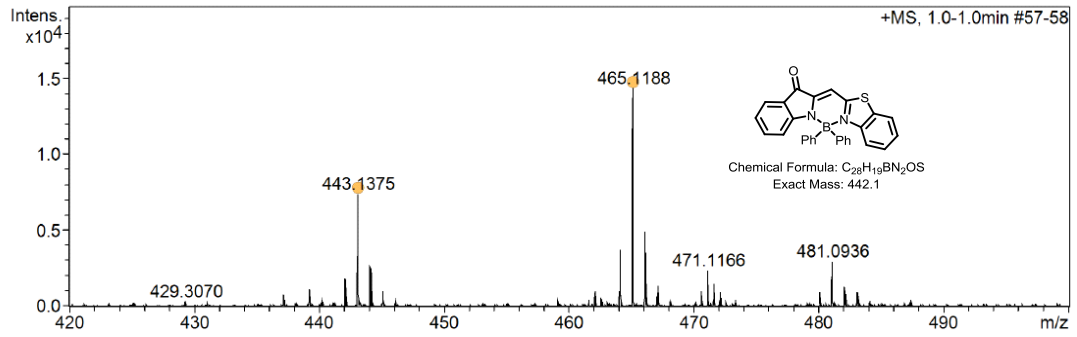
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-10_01.d	Acquisition Date	1/8/2021 2:40:11 PM
Method	ESI+100-800-201112.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
443.1375	1	C28H20BN2OS	443.1389	3.2	27.7	1	100.00	20.5	even	ok
465.1188	1	C28H19BN2NaOS	465.1208	-4.4	19.5	1	100.00	20.5	even	ok

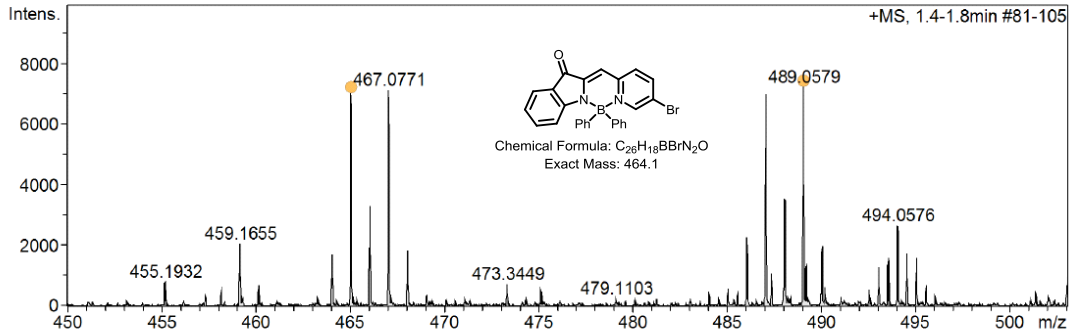
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-11_01.d	Acquisition Date	1/8/2021 2:41:16 PM
Method	ESI+100-800-201112.m		
Sample Name		Operator	BDAL@DE
Comment		Instrument / Ser#	microTOF-Q II 228888.10 324

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
465.0780	1	C26H19BBrN2O	465.0773	1.5	15.6	1	100.00	18.5	even	ok
489.0579	1	C26H18BBrN2NaO	487.0592	0.8	34.8	1	100.00	18.5	even	ok

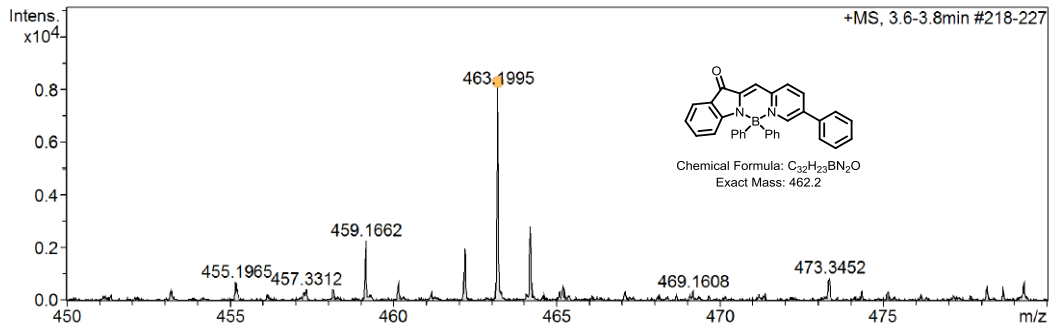
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-12_01.d	Acquisition Date	1/8/2021 2:43:45 PM
Method	ESI+100-800-201112.m		
Sample Name		Operator	BDAL@DE
Comment		Instrument / Ser#	microTOF-Q II 228888.10 324

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
463.1995	1	C32H24BN2O	463.1982	-2.9	11.3	1	100.00	22.5	even	ok

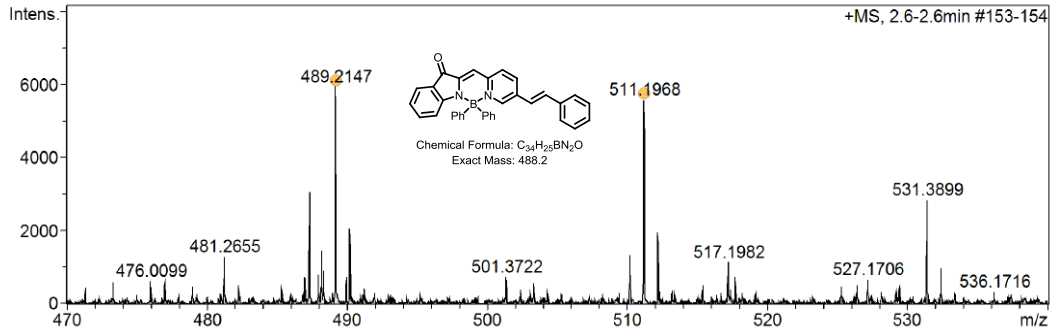
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-13_01.d	Acquisition Date	1/8/2021 2:47:50 PM
Method	ESI+100-800-201112.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
489.2147	1	C34H26BN2O	489.2139	-1.7	13.0	1	100.00	23.5	even	ok
511.1968	1	C34H25BN2NaO	511.1958	2.0	8.2	1	100.00	23.5	even	ok

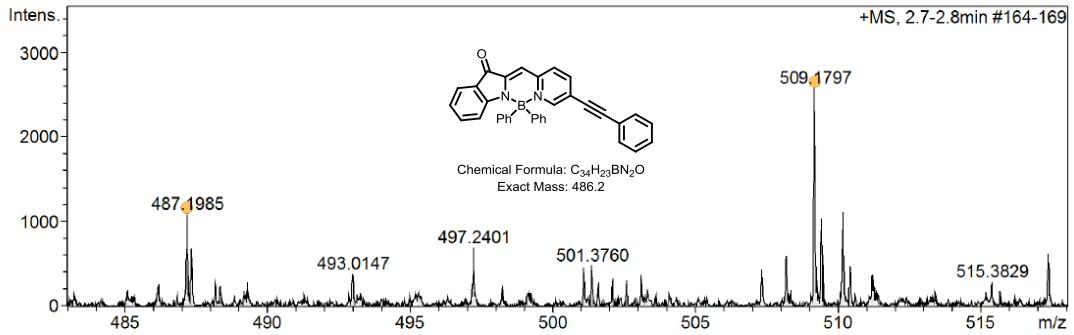
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LUH-210106-SXG-14_01.d	Acquisition Date	1/8/2021 2:50:35 PM
Method	ESI+100-800-201112.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	750 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
487.1985	1	C34H24BN2O	487.1982	-0.6	58.0	1	100.00	24.5	even	ok
509.1797	1	C34H23BN2NaO	509.1802	-0.8	46.9	1	100.00	24.5	even	ok

III Cartesian coordinates

DFT optimized S_0 state geometry of compound **1a**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.938819	0.808442	-0.147487
2	6	0	4.606962	-0.411304	-0.261219
3	6	0	3.880491	-1.611351	-0.283583
4	6	0	2.484693	-1.638686	-0.193140
5	6	0	1.830359	-0.416429	-0.072082
6	6	0	2.549155	0.794704	-0.054181
7	7	0	0.445451	-0.177637	0.033373
8	6	0	0.230717	1.163288	0.108251
9	6	0	1.568269	1.886537	0.066994
10	8	0	1.724685	3.094685	0.115891
11	5	0	-0.661092	-1.192309	0.320420
12	7	0	-2.045285	-0.428136	-0.026637
13	6	0	-2.179566	0.936853	0.022301
14	6	0	-1.004942	1.738963	0.155312
15	6	0	-3.119616	-1.217080	-0.256495
16	6	0	-4.390040	-0.705879	-0.416055
17	6	0	-4.564461	0.686334	-0.335569
18	6	0	-3.468369	1.497688	-0.122541
19	9	0	-0.572797	-2.308542	-0.495643
20	9	0	-0.720963	-1.545893	1.655954
21	1	0	4.474776	1.752523	-0.129984
22	1	0	5.689246	-0.435778	-0.335709
23	1	0	4.416192	-2.551770	-0.377375
24	1	0	1.928605	-2.567682	-0.224997
25	1	0	-1.087013	2.817193	0.205201
26	1	0	-2.902947	-2.277148	-0.301488
27	1	0	-5.223627	-1.374350	-0.593639
28	1	0	-5.552127	1.122563	-0.448144
29	1	0	-3.567265	2.576356	-0.076077

SCF done: -948.38292093 Hartree
No imaginary Frequency.

DFT optimized S_0 state geometry of compound **1b**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.485069	-0.686828	-0.237753
2	6	0	4.885867	0.592481	0.144891
3	6	0	3.919244	1.579690	0.384645
4	6	0	2.548472	1.336209	0.247859
5	6	0	2.151866	0.058354	-0.148533
6	6	0	3.123279	-0.941006	-0.380054
7	7	0	0.848621	-0.447532	-0.354042
8	6	0	0.950475	-1.760570	-0.702171
9	6	0	2.410546	-2.172781	-0.739106
10	8	0	2.830710	-3.284335	-1.018015
11	5	0	-0.530264	0.179386	0.034896
12	7	0	-1.621523	-0.691624	-0.873530
13	6	0	-1.408001	-2.008238	-1.201521
14	6	0	-0.101249	-2.559723	-1.033237
15	6	0	-2.812839	-0.122765	-1.162351
16	6	0	-3.861782	-0.816525	-1.735698
17	6	0	-3.680580	-2.173677	-2.034667
18	6	0	-2.457078	-2.759011	-1.774580
19	6	0	-0.899725	-0.113614	1.595739
20	6	0	0.043551	-0.639006	2.496282
21	6	0	-0.263700	-0.882808	3.837159
22	6	0	-1.540761	-0.609720	4.324635
23	6	0	-2.502840	-0.090299	3.456749
24	6	0	-2.180329	0.150110	2.120875
25	6	0	-0.621090	1.729742	-0.443047
26	6	0	-0.977864	2.784551	0.414784
27	6	0	-1.028889	4.109967	-0.029456
28	6	0	-0.723329	4.416820	-1.354740
29	6	0	-0.363662	3.389324	-2.230801
30	6	0	-0.313849	2.072531	-1.775742
31	1	0	5.203078	-1.480511	-0.421136
32	1	0	5.938985	0.825813	0.262990
33	1	0	4.240739	2.571750	0.689420
34	1	0	1.825232	2.117038	0.441930
35	1	0	0.086587	-3.593234	-1.295537
36	1	0	-2.895013	0.926765	-0.911470
37	1	0	-4.796490	-0.306726	-1.935542

38	1	0	-4.484339	-2.755132	-2.475535
39	1	0	-2.267123	-3.798231	-2.018665
40	1	0	1.047110	-0.865289	2.149142
41	1	0	0.496367	-1.289942	4.498914
42	1	0	-1.785439	-0.800128	5.365960
43	1	0	-3.504198	0.126788	3.819861
44	1	0	-2.956254	0.554730	1.474541
45	1	0	-1.212157	2.567482	1.452754
46	1	0	-1.305699	4.901318	0.662333
47	1	0	-0.761096	5.445386	-1.702977
48	1	0	-0.117595	3.616921	-3.264776
49	1	0	-0.021543	1.287781	-2.470544

SCF done: -1211.89501613 Hartree
No imaginary Frequency.

DFT optimized S_0 state geometry of compound **2a**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.254005	-1.168877	-0.001682
2	6	0	4.283210	-2.181173	-0.001912
3	6	0	2.912697	-1.898508	-0.001336
4	6	0	2.538857	-0.558758	-0.000386
5	6	0	3.505323	0.465477	-0.000291
6	6	0	4.866425	0.171844	-0.000920
7	7	0	1.236549	-0.015032	0.000375
8	6	0	1.318866	1.333174	0.000595
9	6	0	2.783194	1.749268	0.000319
10	8	0	3.195747	2.895849	0.000471
11	5	0	-0.078440	-0.804962	0.002050
12	7	0	-1.296134	0.268287	0.000219
13	6	0	-1.089690	1.615219	0.000106
14	6	0	0.229361	2.152723	0.000675
15	6	0	-2.597473	-0.238292	-0.000286
16	6	0	-3.716616	0.646215	-0.001177
17	6	0	-3.474001	2.047914	-0.001428
18	6	0	-2.196767	2.516580	-0.000756
19	9	0	-0.177355	-1.588539	-1.138686
20	9	0	-0.177766	-1.584256	1.145610
21	6	0	-2.843672	-1.632815	0.000197
22	6	0	-4.140187	-2.108789	-0.000218
23	6	0	-5.246829	-1.236408	-0.001173
24	6	0	-5.030930	0.123812	-0.001649
25	1	0	6.306625	-1.432465	-0.002172
26	1	0	4.602213	-3.219572	-0.002623
27	1	0	2.171322	-2.688397	-0.001780
28	1	0	5.595840	0.976064	-0.000830
29	1	0	0.371271	3.225537	0.000722
30	1	0	-4.318557	2.731278	-0.002101
31	1	0	-1.981469	3.578809	-0.000871
32	1	0	-2.018011	-2.326867	0.000781
33	1	0	-4.304290	-3.182003	0.000180
34	1	0	-6.256254	-1.634770	-0.001517
35	1	0	-5.863924	0.821134	-0.002353

SCF done: -1102.02861162 Hartree
No imaginary Frequency.

DFT optimized S_0 state geometry of compound **2b**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.363900	0.471190	-0.351870
2	6	0	-4.423060	1.494129	-0.174846
3	6	0	-3.046254	1.246478	-0.129989
4	6	0	-2.615585	-0.072899	-0.262035
5	6	0	-3.562481	-1.101425	-0.461033
6	6	0	-4.929583	-0.845514	-0.503705
7	7	0	-1.297715	-0.593213	-0.258480
8	6	0	-1.368281	-1.920133	-0.501438
9	6	0	-2.817470	-2.353996	-0.628654
10	8	0	-3.203523	-3.491694	-0.839676
11	5	0	0.042744	0.152266	0.138471
12	7	0	1.276808	-0.911503	-0.277301
13	6	0	1.034988	-2.195043	-0.665941
14	6	0	-0.284588	-2.724411	-0.685157
15	6	0	2.599937	-0.465037	-0.220221
16	6	0	3.673322	-1.283598	-0.690320
17	6	0	3.377671	-2.597590	-1.143138
18	6	0	2.096398	-3.048539	-1.097667
19	6	0	2.933488	0.790583	0.338883
20	6	0	4.244190	1.226917	0.370089
21	6	0	5.292686	0.441007	-0.144322

22	6	0	5.003071	-0.803990	-0.657734
23	6	0	0.166122	1.464494	-0.831285
24	6	0	0.400041	2.783753	-0.403050
25	6	0	0.459325	3.856099	-1.297051
26	6	0	0.293750	3.638261	-2.664483
27	6	0	0.066483	2.339961	-3.123760
28	6	0	0.000470	1.281332	-2.217894
29	6	0	0.061441	0.336741	1.760621
30	6	0	-0.625573	1.379309	2.414865
31	6	0	-0.687455	1.475805	3.806832
32	6	0	-0.059653	0.520771	4.605139
33	6	0	0.621357	-0.530768	3.991867
34	6	0	0.674002	-0.614947	2.600045
35	1	0	-6.422602	0.707281	-0.379853
36	1	0	-4.768069	2.519321	-0.073641
37	1	0	-2.344755	2.062537	-0.025935
38	1	0	-5.626433	-1.663888	-0.657432
39	1	0	-0.441017	-3.767281	-0.928365
40	1	0	4.184236	-3.233030	-1.497926
41	1	0	1.835997	-4.054016	-1.407338
42	1	0	2.164540	1.407078	0.770367
43	1	0	4.463038	2.195369	0.809190
44	1	0	6.314664	0.804883	-0.118292
45	1	0	5.791738	-1.448900	-1.035008
46	1	0	0.542757	2.987820	0.654672
47	1	0	0.638118	4.861098	-0.923352
48	1	0	0.340706	4.468623	-3.363592
49	1	0	-0.064407	2.153301	-4.186526
50	1	0	-0.191030	0.281250	-2.600843
51	1	0	-1.136524	2.137892	1.832078
52	1	0	-1.228742	2.299183	4.265737
53	1	0	-0.103665	0.592176	5.688361
54	1	0	1.112133	-1.288738	4.597060
55	1	0	1.210985	-1.450361	2.159675

SCF done: -1365.53167113 Hartree
No imaginary Frequency.

DFT optimized S_0 state geometry of compound **3a**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.352300	-0.957340	-0.001466
2	6	0	-4.454583	-2.034332	-0.001246
3	6	0	-3.066956	-1.847126	-0.000633
4	6	0	-2.602773	-0.537110	-0.000189
5	6	0	-3.494687	0.551214	-0.000477
6	6	0	-4.873000	0.353785	-0.001103
7	7	0	-1.261154	-0.087207	0.000509
8	6	0	-1.250268	1.263418	0.000473
9	6	0	-2.683920	1.780033	-0.000051
10	8	0	-3.011259	2.953177	-0.000143
11	5	0	-0.005528	-0.986936	0.001812
12	7	0	1.236877	0.025425	0.000377
13	6	0	1.128053	1.362801	0.000373
14	6	0	-0.113232	2.031005	0.000634
15	9	0	0.059370	-1.767572	1.142239
16	9	0	0.059249	-1.770867	-1.136393
17	6	0	2.559704	-0.421696	-0.000255
18	6	0	3.502566	0.623605	-0.000592
19	16	0	2.679151	2.179417	-0.000239
20	6	0	2.987134	-1.755641	-0.000600
21	6	0	4.354092	-2.006796	-0.001134
22	6	0	5.290147	-0.960323	-0.001389
23	6	0	4.873715	0.368210	-0.001149
24	1	0	-6.420620	-1.147177	-0.001954
25	1	0	-4.844569	-3.048073	-0.001592
26	1	0	-2.382455	-2.686887	-0.000612
27	1	0	-5.544898	1.206501	-0.001307
28	1	0	-0.185305	3.110051	0.000577
29	1	0	2.261642	-2.558653	-0.000576
30	1	0	4.702857	-3.034465	-0.001401
31	1	0	6.351538	-1.186504	-0.001820
32	1	0	5.593319	1.179964	-0.001398

SCF done: -1422.79638570 Hartree
No imaginary Frequency.

DFT optimized S_0 state geometry of compound **3b**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.402418	0.119209	-0.699282
2	6	0	-4.563613	1.220664	-0.488232
3	6	0	-3.176666	1.090951	-0.342819
4	6	0	-2.630857	-0.190061	-0.410472
5	6	0	-3.475230	-1.298849	-0.633473
6	6	0	-4.852498	-1.160477	-0.775428
7	7	0	-1.274038	-0.599903	-0.300378
8	6	0	-1.225781	-1.937654	-0.484258
9	6	0	-2.624766	-2.492670	-0.688802
10	8	0	-2.902598	-3.665959	-0.868291
11	5	0	-0.014155	0.242049	0.202047
12	7	0	1.263873	-0.662733	-0.309860
13	6	0	1.152360	-1.979533	-0.549144
14	6	0	-0.072874	-2.673280	-0.561968
15	6	0	2.592080	-0.216033	-0.395777
16	6	0	3.508154	-1.235309	-0.733034
17	16	0	2.670107	-2.764940	-0.926786
18	6	0	3.077230	1.077920	-0.154544
19	6	0	4.441455	1.317201	-0.277358
20	6	0	5.337609	0.297963	-0.629149
21	6	0	4.875755	-0.994688	-0.856477
22	6	0	0.004466	1.671655	-0.572858
23	6	0	0.057591	2.912689	0.086941
24	6	0	0.056878	4.121288	-0.616185
25	6	0	0.007036	4.120288	-2.010279
26	6	0	-0.042868	2.902601	-2.692412
27	6	0	-0.045637	1.703867	-1.979400
28	6	0	0.010220	0.284703	1.830004
29	6	0	1.004875	-0.336550	2.606392
30	6	0	0.984101	-0.315413	4.003221
31	6	0	-0.048519	0.331912	4.679017
32	6	0	-1.056396	0.953750	3.940516
33	6	0	-1.021082	0.928083	2.546183
34	1	0	-6.472233	0.264747	-0.806736
35	1	0	-4.997462	2.215346	-0.437967
36	1	0	-2.555510	1.964742	-0.199805
37	1	0	-5.468012	-2.039078	-0.942975
38	1	0	-0.123626	-3.739638	-0.735760
39	1	0	2.400368	1.874819	0.115851
40	1	0	4.815882	2.319257	-0.094076
41	1	0	6.397338	0.513519	-0.719579
42	1	0	5.558531	-1.795806	-1.119402
43	1	0	0.101205	2.934624	1.172258
44	1	0	0.096483	5.062445	-0.073764
45	1	0	0.006877	5.057224	-2.560419
46	1	0	-0.081962	2.888788	-3.778516
47	1	0	-0.092306	0.766746	-2.530220
48	1	0	1.824657	-0.856464	2.119395
49	1	0	1.775624	-0.808936	4.561339
50	1	0	-0.070567	0.349967	5.765120
51	1	0	-1.872414	1.459478	4.450330
52	1	0	-1.825515	1.417770	2.005727

SCF done: -1686.30505803 Hartree
No imaginary Frequency.

DFT optimized S_0 state geometry of compound **1c**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.703385	-1.061808	-0.000992
2	6	0	-4.779307	-2.117118	-0.000792
3	6	0	-3.397508	-1.896466	-0.000375
4	6	0	-2.963785	-0.574853	-0.000133
5	6	0	-3.882426	0.491742	-0.000366
6	6	0	-5.255757	0.259815	-0.000790
7	7	0	-1.636897	-0.093226	0.000319
8	6	0	-1.658249	1.263383	0.000281
9	6	0	-3.103807	1.740959	-0.000095
10	8	0	-3.464417	2.905097	-0.000193
11	5	0	-0.363110	-0.939718	0.001130
12	7	0	0.876959	0.111733	0.000389
13	6	0	0.753810	1.477754	0.000346
14	6	0	-0.548005	2.056204	0.000430
15	6	0	2.096815	-0.473065	0.000074
16	6	0	3.257450	0.269420	-0.000201
17	6	0	3.175607	1.672548	-0.000173
18	6	0	1.931202	2.263001	0.000089
19	9	0	-0.243469	-1.713247	1.140712
20	9	0	-0.243316	-1.715125	-1.137164
21	35	0	4.940054	-0.605583	-0.000611
22	1	0	-6.766774	-1.277667	-0.001321
23	1	0	-5.144703	-3.140046	-0.000984
24	1	0	-2.693357	-2.720112	-0.000296
25	1	0	-5.947913	1.096252	-0.000958

26	1	0	-0.665311	3.132204	0.000369
27	1	0	2.102666	-1.555299	0.000047
28	1	0	4.078875	2.272187	-0.000376
29	1	0	1.830214	3.342389	0.000070

SCF done: -3519.47989163 Hartree
No imaginary Frequency.

DFT optimized S_0 state geometry of compound **4a**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.797586	1.037363	-1.103789
2	6	0	4.860110	1.916436	-0.543282
3	6	0	3.531344	1.546167	-0.308615
4	6	0	3.144113	0.250096	-0.655656
5	6	0	4.089765	-0.637907	-1.215675
6	6	0	5.410182	-0.258626	-1.441746
7	7	0	1.882333	-0.372258	-0.526785
8	6	0	1.988145	-1.647327	-0.995881
9	6	0	3.407227	-1.914230	-1.454435
10	8	0	3.819330	-2.957040	-1.917974
11	5	0	0.614285	0.064814	0.290774
12	7	0	-0.607308	-0.811205	-0.399269
13	6	0	-0.394102	-2.069714	-0.904766
14	6	0	0.945079	-2.515854	-1.114580
15	6	0	-1.863666	-0.327264	-0.318514
16	6	0	-2.997968	-1.035515	-0.706142
17	6	0	-2.787468	-2.344374	-1.189025
18	6	0	-1.507808	-2.847901	-1.285289
19	6	0	-4.344599	-0.430603	-0.596553
20	6	0	-5.459171	-1.215248	-0.255040
21	6	0	-6.727373	-0.646867	-0.155520
22	6	0	-6.906571	0.717038	-0.392274
23	6	0	-5.807452	1.507915	-0.731438
24	6	0	-4.539107	0.940897	-0.835982
25	6	0	0.729847	-0.404848	1.848914
26	6	0	1.919407	-0.168952	2.567164
27	6	0	2.058583	-0.519966	3.910117
28	6	0	1.001481	-1.127222	4.590014
29	6	0	-0.188725	-1.374954	3.908550
30	6	0	-0.314677	-1.017922	2.563361
31	6	0	0.278536	1.638003	0.065952
32	6	0	0.011068	2.517593	1.128840
33	6	0	-0.297013	3.864361	0.909666
34	6	0	-0.349974	4.367754	-0.389605
35	6	0	-0.091476	3.515672	-1.467073
36	6	0	0.217464	2.175633	-1.235918
37	1	0	6.818189	1.366721	-1.268968
38	1	0	5.170616	2.923602	-0.279323
39	1	0	2.830693	2.247682	0.124450
40	1	0	6.108549	-0.971135	-1.870359
41	1	0	1.129168	-3.507887	-1.507323
42	1	0	-1.943835	0.665205	0.104576
43	1	0	-3.631846	-2.943615	-1.514681
44	1	0	-1.327025	-3.839136	-1.685945
45	1	0	-5.327993	-2.271383	-0.038473
46	1	0	-7.574819	-1.268727	0.117261
47	1	0	-7.894769	1.159836	-0.313347
48	1	0	-5.938030	2.568263	-0.925558
49	1	0	-3.697460	1.560919	-1.130118
50	1	0	2.763432	0.298403	2.067876
51	1	0	2.994895	-0.321409	4.425371
52	1	0	1.106057	-1.404909	5.635216
53	1	0	-1.021211	-1.850843	4.420692
54	1	0	-1.257701	-1.234348	2.067928
55	1	0	0.049557	2.142103	2.147396
56	1	0	-0.495479	4.518153	1.754959
57	1	0	-0.587970	5.413591	-0.563755
58	1	0	-0.125308	3.898500	-2.483878
59	1	0	0.424328	1.529108	-2.086386

SCF done: -1442.95876114 Hartree
No imaginary Frequency.

DFT optimized S_0 state geometry of compound **4b**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.663387	0.441713	0.315683
2	6	0	5.734501	1.475961	-0.131797
3	6	0	4.355306	1.244891	-0.097790
4	6	0	3.911789	-0.068028	-0.250610
5	6	0	4.844623	-1.109973	-0.443134
6	6	0	6.215525	-0.869005	-0.476561
7	7	0	2.589433	-0.562254	-0.260081
8	6	0	2.640009	-1.905491	-0.460461

9	6	0	4.082414	-2.353160	-0.591640
10	8	0	4.451912	-3.487812	-0.781613
11	5	0	1.274118	0.228593	0.081231
12	7	0	0.049094	-0.872737	-0.197306
13	6	0	0.235370	-2.207056	-0.454516
14	6	0	1.556437	-2.726802	-0.551997
15	6	0	-1.203341	-0.384305	-0.110165
16	6	0	-2.362432	-1.143626	-0.263845
17	6	0	-2.173077	-2.521393	-0.531088
18	6	0	-0.901396	-3.033172	-0.622758
19	6	0	-3.656682	-0.484495	-0.140665
20	6	0	-4.867681	-1.071057	-0.249535
21	6	0	-6.176518	-0.426612	-0.130561
22	6	0	-7.332091	-1.218216	-0.270359
23	6	0	-8.605539	-0.663608	-0.167061
24	6	0	-8.754849	0.701332	0.079315
25	6	0	-7.618266	1.503714	0.220746
26	6	0	-6.347021	0.950171	0.117597
27	6	0	1.238507	0.588614	1.670993
28	6	0	1.669527	1.827514	2.182406
29	6	0	1.718638	2.091323	3.553161
30	6	0	1.333424	1.113092	4.469030
31	6	0	0.905412	-0.128455	3.997166
32	6	0	0.863831	-0.378321	2.625249
33	6	0	1.043790	1.451271	-0.968327
34	6	0	0.312314	2.613821	-0.656763
35	6	0	0.069443	3.613913	-1.602039
36	6	0	0.558788	3.481135	-2.901163
37	6	0	1.286636	2.339882	-3.242752
38	6	0	1.518458	1.347438	-2.290050
39	1	0	7.725008	0.665307	-0.335420
40	1	0	6.093236	2.494640	-0.013776
41	1	0	3.660894	2.064121	0.029641
42	1	0	6.904789	-1.694540	-0.626045
43	1	0	1.712865	-3.783268	-0.729197
44	1	0	-1.269974	0.677340	0.090642
45	1	0	-3.025951	-3.178196	-0.665945
46	1	0	-0.737840	-4.085178	-0.829022
47	1	0	-3.601338	0.583346	0.058361
48	1	0	-4.914591	-2.140842	-0.446471
49	1	0	-7.222708	-2.282609	-0.462385
50	1	0	-9.480401	-1.297237	-0.278957
51	1	0	-9.745451	1.138333	0.160633
52	1	0	-7.725654	2.567346	0.412387
53	1	0	-5.480508	1.593906	0.230412
54	1	0	1.970467	2.614004	1.496848
55	1	0	2.056645	3.063040	3.903962
56	1	0	1.367259	1.314138	5.536230
57	1	0	0.604908	-0.903393	4.697684
58	1	0	0.530146	-1.358648	2.293781
59	1	0	-0.071203	2.749403	0.351377
60	1	0	-0.497273	4.497959	-1.321070
61	1	0	0.376552	4.257570	-3.639058
62	1	0	1.673136	2.223026	-4.251882
63	1	0	2.085984	0.466848	-2.580345

SCF done: -1520.36558722 Hartree
No imaginary Frequency.

DFT optimized S_0 state geometry of compound **4c**.

-Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.330414	1.409227	-1.049813
2	6	0	5.315130	2.216515	-0.517408
3	6	0	4.017521	1.741888	-0.297308
4	6	0	3.745678	0.415204	-0.632985
5	6	0	4.769566	-0.403297	-1.159394
6	6	0	6.058125	0.080047	-1.371240
7	7	0	2.536984	-0.307499	-0.508645
8	6	0	2.756889	-1.582671	-0.930976
9	6	0	4.199431	-1.739163	-1.372589
10	8	0	4.706477	-2.762645	-1.803286
11	5	0	1.229395	0.073629	0.260458
12	7	0	0.090956	-0.969945	-0.372342
13	6	0	0.426804	-2.233781	-0.799333
14	6	0	1.799735	-2.550918	-1.007772
15	6	0	-1.202734	-0.608696	-0.313630
16	6	0	-2.260977	-1.469969	-0.618419
17	6	0	-1.926745	-2.788907	-1.009284
18	6	0	-0.603006	-3.152208	-1.102518
19	6	0	-3.602785	-1.021887	-0.524720
20	6	0	-4.755776	-0.640344	-0.448612
21	6	0	-6.102095	-0.186206	-0.357453
22	6	0	-7.173100	-1.060555	-0.631659
23	6	0	-8.486566	-0.610294	-0.540972
24	6	0	-8.754892	0.711682	-0.177539
25	6	0	-7.699931	1.585721	0.096080
26	6	0	-6.382739	1.145897	0.008423
27	6	0	1.343630	-0.288382	1.845483

28	6	0	2.569789	-0.629866	2.442662
29	6	0	2.676431	-0.927701	3.803421
30	6	0	1.545889	-0.897245	4.618321
31	6	0	0.311793	-0.564858	4.056908
32	6	0	0.221263	-0.267365	2.696886
33	6	0	0.761739	1.587095	-0.096698
34	6	0	0.480459	2.558696	0.879259
35	6	0	0.097574	3.859053	0.534378
36	6	0	-0.016766	4.223132	-0.806649
37	6	0	0.257146	3.278677	-1.799363
38	6	0	0.640804	1.986589	-1.443429
39	1	0	7.323143	1.819213	-1.204248
40	1	0	5.538629	3.248908	-0.263281
41	1	0	3.254601	2.387224	0.117263
42	1	0	6.821074	-0.578964	-1.774582
43	1	0	2.079231	-3.537299	-1.356100
44	1	0	-1.392949	0.411359	-0.007639
45	1	0	-2.716058	-3.494963	-1.243723
46	1	0	-0.320098	-4.146861	-1.428539
47	1	0	-6.960502	-2.086561	-0.913420
48	1	0	-9.303983	-1.292500	-0.754331
49	1	0	-9.781235	1.059085	-0.107909
50	1	0	-7.904632	2.613958	0.378690
51	1	0	-5.560399	1.821435	0.219496
52	1	0	3.469778	-0.665215	1.836284
53	1	0	3.644437	-1.187145	4.224167
54	1	0	1.623077	-1.131086	5.676547
55	1	0	-0.580303	-0.538512	4.677408
56	1	0	-0.757481	-0.013619	2.295361
57	1	0	0.570311	2.296568	1.929282
58	1	0	-0.109230	4.586315	1.315239
59	1	0	-0.313302	5.232589	-1.078168
60	1	0	0.176042	3.552174	-2.848151
61	1	0	0.859298	1.268376	-2.231089

SCF done: -1519.11441293 Hartree

No imaginary Frequency

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