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Supplementary data

Influence of D–π–A System Through Linked Unit of Double and Triple Bonds in Triarylene Bridge for Dye-Sensitised Solar Cells

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1. Experimental

4-(N-(naphthalen-1-yl)-N-phenylamino)benzaldehyde **(2a)**

To a solution of **1a** (3.0 g, 8.04 mmol) in THF at -78 °C was added dropwise n-BuLi (7.5 mL, 12.06 mmol, 1.6 M in hexane). The mixture was stirred for 1 h, then to it was added DMF (0.93 mL, 12.06 mmol). The reaction was stirred with a magnetic bar for 6 h, then was quenched by adding water, then was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give the crude product. The product was purified by silica gel column chromatograph eluted with dichloromethane/hexane (1/1). Yellow solid of **2a** was obtained in 75% yield (1.95 g, 6.03 mmol). δ_H (400 MHz, $CDCl_3$) 9.80 (s, 1H), 7.90 (d, 1H, J = 8.6 Hz), 7.89 (d, 1H, J = 8.9 Hz), 7.83 (d, 1H, J = 8.2 Hz), 7.63 (d, 2H, J = 8.8 Hz), 7.46-7.50 (m, 2H), 7.37-7.40 (m, 2H), 7.23-7.30 (m, 4H), 7.10 (t, 2H, J = 6.7 Hz), 6.89 (d, 2H, J = 8.8 Hz). δ_C (100 MHz, $CDCl_3$) 190.3, 153.7, 146.2, 141.8, 135.2, 131.4, 130.8, 129.6, 128.6, 127.7, 127.5, 126.9, 126.4, 126.3, 124.8, 124.7, 123.6, 117.7. MS (FAB, 70 eV): m/z (relative intensity) 323 ($(M+H)^+$, 100); HRMS calcd for $C_{23}H_{17}NO$: 323.1310, found 323.1313.

4-(bis(4-(hexyloxy)phenyl)amino)benzaldehyde **(2b)**

Compound **2b** was synthesized in a way similar to that of **2a**, giving a yellow solid in 78%. δ_H (400 MHz, $CDCl_3$) δ_H (400 MHz, $CDCl_3$) 9.76 (s, 1H), 7.64 (d, 2H, J = 8.08 Hz), 7.13 (d, 4H, J = 7.96 Hz), 6.90 (d, 1H, J = 7.96 Hz), 6.86 (d, 2H, J = 8.08Hz), 3.97 (t, 4H, J = 6.04Hz), 1.79-1.82 (m, 4H), 1.37-1.49 (m, 12H), 0.93 (s, 6H). δ_C (100 MHz, $CDCl_3$) 190.2, 156.8, 154.0, 138.5, 131.3, 128.0, 127.9, 127.5, 116.6, 115.5, 115.4, 68.2, 31.5, 29.2, 25.7, 22.5, 14.0. MS (FAB, 70 eV): m/z (relative intensity) 473 ($(M+H)^+$, 100); HRMS calcd for $C_{31}H_{39}NO_3$: 473.2930, found 473.2928.

(E)-4-(4-(naphthalen-1-yl(phenyl)amino)styryl)benzaldehyde **(3a)**

A mixture of CH_3PPh_3I (6.46 g, 15.98 mmol), and NaH (60%) (0.96 g, 23.97 mmol) was placed in a three-necked flask under a nitrogen atmosphere and was stirred at 0 °C for 1.5 h. Added **2a** (2.58 g, 7.99 mmol) to the mixture slowly by dropwise, the stirred at 40°C for 0.5 h. After cooling, the reaction was quenched by adding water, and was extracted with methylene chloride. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under vacuum. The product was purified by silica gel column chromatograph eluted with hexane to obtain the white solid intermediate. A mixture of the white solid intermediate, $Pd(OAc)_2$ (71 mg, 0.32 mmol), tri(o-tolyl)phosphine (192 mg, 0.64 mmol), and 4-bromobenzaldehyde (1.55 g, 8.37 mmol) in 15 mL dry triethylamine and 10 mL dry THF was placed in a three-necked flask under a nitrogen atmosphere and was stirred at 70 °C for 16 h. After cooling, the reaction was quenched by adding $NaNH_4$, and was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under vacuum. The product was purified by silica gel column chromatograph eluted with EA/hexane (1/11). Orange solid of **3a** was obtained in 87% yield (2.95 g, 6.95 mmol). δ_H (400 MHz, $CDCl_3$) 9.99 (s, 1H), 7.93 (d, 2H, J = 7.6 Hz), 7.86 (d, 2H, *J* = 8.4 Hz), 7.82 (d, 1H, *J* = 8.4 Hz), 7.62 (d, 2H, *J* = 8.0 Hz), 7.47-7.53 (m, 2H), 7.36-7.41 (m, 4H), 7.18-7.28 (m, 3H), 7.14 (d, 2H, *J* = 8.8 Hz), 6.98-7.04 (m, 4H). δ_C (100 MHz, $CDCl_3$) 191.5, 148.8, 147.7, 143.9, 143.0, 135.3, 134.9, 131.8, 131.1, 130.2, 129.4, 129.2, 128.4, 127.8, 127.3, 126.8, 126.5, 126.3, 126.2, 124.9, 124.0, 122.8, 122.6, 120.7. MS (FAB, 70 eV): m/z (relative intensity) 425 (M^+, 100); HRMS calcd for $C_{31}H_{23}NO$: 425.1774, found 425.4765.

(E)-4-(4-(bis(4-(hexyloxy)phenyl)amino)styryl)benzaldehyde **(3b)**

Compound **3b** was synthesized in a way similar to that of **3a**, giving an orange liquid in 87%. δ_H (400 MHz, $CDCl_3$) 9.96 (s, 1H), 7.85 (d, 2H, *J* = 8.4 Hz), 7.62 (d, 2H, *J* = 8.0 Hz), 7.36 (d, 2H, *J* = 8.72 Hz), 7.20 (d, 1H, *J* = 16.24 Hz), 7.08 (d, 4H, *J* = 8.88 Hz), 6.97 (d, 1H, *J* = 16.2 Hz), 6.92 (d, 2H, *J* = 8.64 Hz), 6.85 (d, 4H, *J* = 8.88 Hz), 3.96 (t, 4H, *J* = 6.52 Hz), 1.76-1.82 (m, 4H), 1.47-1.50 (m, 4H), 1.35-1.39 (m, 8H), 0.93 (t, 6H, *J* = 7.04 Hz). δ_C (100 MHz, $CDCl_3$) 191.5, 155.8, 149.2, 144.2, 140.2, 134.8, 132.1, 130.3, 128.2, 127.8, 127, 126.5, 124.2, 119.7, 115.4, 68.3, 31.6, 29.4, 25.8, 22.6, 14.1. MS (FAB, 70 eV): m/z (relative intensity) 575 (M^+, 100); HRMS calcd for $C_{39}H_{45}O_3N$: 575.3399, found 575.3399.

5-((E)-4-((E)-4-(naphthalen-1-yl(phenyl)amino)styryl)styryl)thiophene-2-carbaldehyde **(4a)**

Compound **4a** was synthesized in a way similar to that of **3a**, giving a red solid in 80%. δ_H (400 MHz, $CDCl_3$) 9.83 (s, 1H), 7.89 (t, 2H, *J* = 9.6 Hz), 7.77 (d, 1H, *J* = 8.0 Hz), 7.63 (d, 1H, *J* = 3.2 Hz), 7.31-7.45 (m, 10H), 7.03-7.24 (m, 8H), 6.88-6.96 (m, 4H). δ_C (100 MHz, $CDCl_3$) 182.4, 152.6, 148.2, 147.9, 143.1, 141.4, 138.4, 137.1, 135.3, 134.6, 132.6, 131.1, 130.1, 129.1, 129.0, 128.4, 127.4, 127.2, 126.6, 126.4, 126.3, 126.1, 125.7, 124.7, 124.1, 122.5, 122.3, 121.1, 120.2, 117.7. MS (FAB, 70 eV): m/z (relative intensity) 533 (M^+, 100); HRMS calcd for $C_{37}H_{27}NOS$: 533.1808, found 533.1807.

5-((E)-4-((E)-4-(bis(4-(hexyloxy)phenyl)amino)styryl)styryl)thiophene-2-carbaldehyde **(4b)**

Compound **4b** was synthesized in a way similar to that of **3a**, giving a orange solid in 85%. δ_H (400 MHz, $CDCl_3$) 9.88 (s, 1H), 7.72 (d, 1H, *J* = 3.92 Hz), 7.53 (s, 4H), 7.37 (d, 2H, *J* = 8.72 Hz), 7.29 (d, 1H, *J* = 16.12 Hz), 7.18-7.23 (m, 2H), 7.13 (d, 1H, *J* = 16.32 Hz), 7.08 (d, 4H, *J* = 8.84 Hz), 6.98 (d, 1H, *J* = 16.32 Hz), 6.88-6.91 (m, 6H), 3.97 (t, 4H, *J* = 6.44 Hz), 1.77-1.84 (m, 4H), 1.47-1.53 (m, 4H), 1.36-1.41 (m, 8H), 0.95 (t, 6H, *J* = 6.92 Hz). δ_C (100 MHz, $CDCl_3$) 182.4, 155.8, 152.3, 148.7, 141.5, 140.2, 138.5, 137.3, 134.6, 132.4, 129.0, 128.8, 127.2, 126.8, 126.6, 126.5, 124.8, 120.2, 119.7, 115.2, 68.3, 31.5, 29.2, 25.7, 22.6, 13.7. MS (FAB, 70 eV): m/z (relative intensity) 683 (M^+, 100); HRMS calcd for $C_{45}H_{49}NO_3S$: 683.3433, found 683.3436.

4-((E)-4-((E)-4-(naphthalen-1-yl(phenyl)amino)styryl)styryl)benzaldehyde **(5a)**

Compound **5a** was synthesized in a way similar to that of **3a**, giving a red solid in 85%. δ_H (400 MHz, $CDCl_3$) 10.01 (s, 1H), 7.95 (d, 1H, *J* = 8.52 Hz), 7.92 (d, 1H, *J* = 8.36 Hz), 7.89 (d, 2H, *J* = 8.16 Hz), 7.81 (d, 1H, *J* = 8.24 Hz), 7.67 (d, 1H, *J* = 8.12 Hz), 7.47-7.54 (m, 6H), 7.36-7.41 (m, 4H), 7.17-7.29 (m, 4H), 7.08-7.12 (m, 3H), 6.95-7.01 (m, 4H). δ_C (100 MHz, $CDCl_3$) 191.5, 148.2, 147.9, 143.5, 143.2, 138.0, 135.4, 135.3, 135.2, 131.8, 131.2, 130.2, 129.1, 128.8, 128.4, 128.0, 127.4, 127.2, 126.8, 126.6, 126.4, 126.3, 126.2, 125.8, 124.7, 122.5, 122.2, 121.2. MS (ESI, 70 eV): m/z (relative intensity) 527 (M^+, 100); HRMS calcd for $C_{39}H_{29}NO$: 527.2249, found 527.2252.

4-((E)-4-((E)-4-(bis(4-(hexyloxy)phenyl)amino)styryl)styryl)benzaldehyde **(5b)**

Compound **5b** was synthesized in a way similar to that of **3a**, giving a orange solid in 83%. δ_H (400 MHz, $CDCl_3$) 10.01 (s, 1H), 7.88 (d, 2H, *J* = 7.88 Hz), 7.66 (d, 2H, *J* = 7.84 Hz), 7.51 (d, 4H, *J* = 8.88 Hz), 7.36 (d, 2H, *J* = 8.24 Hz), 7.27 (d, 1H, *J* = 15.84 Hz), 7.14 (d, 1H, *J* = 16.72 Hz), 7.09 (d, 4H, *J* = 8.44 Hz), 6.86-6.98 (m, 7H), 3.97 (t, 4H, *J* = 6.28 Hz), 1.78-1.83 (m, 4H), 1.47-1.51 (m, 4H), 1.36-1.41 (m, 8H), 0.96 (t, 6H, *J* = 6.24 Hz). δ_C (100 MHz, $CDCl_3$) 191.5, 155.6, 148.6, 143.5, 140.4, 138.2, 135.2, 131.9, 130.2, 129.1, 129.0, 127.4, 127.3, 126.8, 126.7, 126.6, 126.5, 125.1, 120.1, 115.3, 68.2, 31.6, 29.3, 25.8, 22.6, 14.1. MS (ESI, 70 eV): m/z (relative intensity) 677 (M^+, 100); HRMS calcd for $C_{47}H_{51}NO_3$: 677.3869, found 677.3860.

4-((trimethylsilyl)ethynyl)benzaldehyde **(6)**

A mixture of 4-bromobenzaldehyde (3.52 g, 19 mmol), $PdCl_2(PPh_3)_2$ (267 mg, 0.38 mmol), and CuI (144 mg, 0.76 mmol) was placed in a three-necked flask with 25 mL trimethylamine under a nitrogen atmosphere, and stirred at room temperature for 10 minutes. Added trimethylsilylacetylene (2.8 g, 28.6 mmol) to the mixture slowly by dropwise, the stirred at 50°C for 2 h. After cooling, the reaction was quenched by adding $NaNH_4$, and was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under vacuum. The product was purified by silica gel column chromatograph eluted with EA/hexane (1/9). Yellow solid of **6** was obtained in 99% yield (3.79 g, 18.81 mmol). δ_H (400 MHz, $CDCl_3$) 10.01 (s, 1H), 7.83 (d, 2H, *J* = 8.16 Hz), 7.62 (d, 2H, *J* = 8.28 Hz), 0.28 (s, 9H). δ_C (100 MHz, $CDCl_3$) 191.3, 135.6, 132.4, 129.4, 129.3, 103.8, 99.0, 0.2. MS (FAB, 70 eV): m/z (relative intensity) 203 ($(M+H)^+$, 100); HRMS calcd for $C_{12}H_{15}OSi$: 203.0892, found 203.0892.

4-((4-bromophenyl)ethynyl)benzaldehyde **(7)**

A mixture of **6** (3.83 g, 19 mmol) in 15 mL THF and 25 mL methanol, added K_2CO_3 (1.3 g, 9.5 mmol) was placed in a three-necked flask and stirred at 25 °C. After 1 hr, the reaction was quenched by adding water, and was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under vacuum, to obtain the intermediate. A mixture of the intermediate, CuI (144 mg, 0.76 mmol), $PdCl_2(PPh_3)_2$ (267 mg, 0.38 mmol), and 1-bromo-4-iodobenzene (5.6 g, 20 mmol) in 25 mL dry triethylamine and 10 mL dry THF was placed in a three-necked flask under a nitrogen atmosphere and was stirred at 70 °C for 2 h. After cooling, the reaction was quenched by adding $NaNH_4$, and was extracted with methylene chloride. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under vacuum. The product was purified by silica gel column chromatograph eluted with EA/hexane (1/10). Yellow solid of **7** was obtained in 96% yield (5.16 g, 18.24 mmol). δ_H (400 MHz, $CDCl_3$) 10.0 (s, 1H), 7.89 (d, 2H, *J* = 8.28 Hz), 7.69 (d, 2H, *J* = 8.16 Hz), 7.54 (d, 2H, *J* = 8.4 Hz), 7.43 (d, 2H, *J* = 8.52 Hz). δ_C (100 MHz, $CDCl_3$) 191.3, 135.6, 133.1, 132.1, 129.6, 129.2, 123.3, 121.4, 92.2, 89.5. MS (EI, 70 eV): m/z (relative intensity) 283 (M$^+$, 100); HRMS calcd for $C_{15}H_9BrO$: 283.9837, found 283.9837.

5-((trimethylsilyl)ethynyl)thiophene-2-carbaldehyde **(8)**

Compound **8** was synthesized in a way similar to that of **6**, giving a yellow solid in 98%. δ_H (400 MHz, $CDCl_3$) 9.86 (s, 1H), 7.63 (d, 1H, *J* = 3.92 Hz), 7.26 (d, 1H, *J* = 3.92 Hz), 0.28 (s, 9H). δ_C (100 MHz, $CDCl_3$) 182.4, 143.8, 135.7, 133.1, 132.5, 104.6, 96.4, 0.39. MS (FAB, 70 eV): m/z (relative intensity) 208 (M$^+$, 100); HRMS calcd for $C_{10}H_{12}OSSi$: 208.0378, found 208.0382.

5-((4-bromophenyl)ethynyl)thiophene-2-carbaldehyde **(9)**

Compound **9** was synthesized in a way similar to that of **7**, giving a yellow solid in 96%.δ_H (400 MHz, $CDCl_3$) 9.9 (s, 1H), 7.69 (d, 1H, *J* = 3.88 Hz), 7.54 (d, 2H, *J* = 8.36 Hz), 7.42 (d, 2H, *J* = 8.36 Hz), 7.34 (d, 1H, *J* = 3.92 Hz), 7.28 (s, 2H). δ_C (100 MHz, $CDCl_3$) 182.3, 144.1, 135.9, 133.0, 132.7, 132.3, 131.8, 123.8, 120.8, 96.6, 83.0. MS (EI, 70 eV): m/z (relative intensity) 289 (M$^+$, 100); HRMS calcd for $C_{13}H_7BrOS$: 289.9401, found 289.9398.

5-((4-((4-(naphthalen-1-yl(phenyl)amino)phenyl)ethynyl)phenyl)ethynyl)thiophene-2-carbaldehyde **(10a)**

Compound **10a** was synthesized according to the same procedure as that of **7**. Orange solid of **10a** was obtained in 80%. δ_H (400 MHz, $CDCl_3$) 9.85 (s, 1H), 7.87 (dd, 2H, *J* = 8.24, 3.0 Hz), 7.78 (d, 1H, *J* = 8.2 Hz), 7.65 (d, 1H, *J* = 3.96 Hz), 743-7.48 (m, 6H), 7.28-7.37 (m, 5H), 7.21 (d, 2H, *J* = 7.32 Hz), 7.10 (d, 2H, *J* = 7.56 Hz), 6.99 (t, 1H, *J* = 7.32 Hz), 6.87 (d, 2H, *J* = 8.8 Hz). δ_C (100 MHz, $CDCl_3$) 182.3, 148.8, 147.3, 143.9, 142.7, 135.9, 135.2, 132.6, 132.5, 131.5, 131.4, 131.0, 129.3, 128.4, 127.3, 126.9, 126.6, 126.3, 126.2, 124.8, 123.9, 123.2, 123.0, 120.9, 119.9, 114.4, 97.7, 92.6, 87.9, 83.5. MS (EI, 70 eV): m/z (relative intensity) 529 (M$^+$, 100); HRMS calcd for $C_{37}H_{23}NOS$: 529.1495, found 529.1481.

5-((4-((4-(bis(4-(hexyloxy)phenyl)amino)phenyl)ethynyl)phenyl)ethynyl)thiophene-2-carbaldehyde **(10b)**

Compound **10b** was synthesized according to the same procedure as that of **7**. Orange solid of **10b** was obtained in 76%. δ_H (400 MHz, $CDCl_3$) 9.87 (s, 1H), 7.67 (d, 1H, *J* = 3.84 Hz), 7.48 (s, 4H), 7.26-7.31 (m, 3H), 7.06 (d, 4H, *J* = 8.64 Hz), 6.83 (d, 6H, *J* = 8.6 Hz), 3.9 (t, 4H, *J* = 6.52 Hz), 1.75-1.79 (m, 4H), 1.41-1.47 (m, 4H), 1.25-1.35 (m, 8H), 0.9 (t, 6H, *J* = 6.68 Hz). δ_C (100 MHz, $CDCl_3$) 182.3, 156.1, 149.2, 144, 139.8, 136, 132.8, 132.5, 132.5, 131.5, 131.4, 127.2, 125.1, 120.8, 118.8, 115.4, 113.1, 97.8, 93.1, 87.7, 83.5, 68.3, 31.6, 29.3, 25.7, 22.6, 14.0. MS (EI, 70 eV): m/z (relative intensity) 679 (M$^+$, 100); HRMS calcd for $C_{45}H_{45}NO_3S$: 679.3120, found 679.3118.

4-((4-((4-(naphthalen-1-yl(phenyl)amino)phenyl)ethynyl)phenyl)ethynyl)benzaldehyde **(11a)**

Compound **11a** was synthesized according to the same procedure as that of **7**. Yellow solid of **11a** was obtained in 82%. δ_H (400 MHz, $CDCl_3$) 10.04 (s, 1H), 7.88-7.93 (m, 4H), 7.82 (d, 1H, *J* = 8.2 Hz), 7.69 (d, 2H, *J* = 8.16 Hz), 7.47-7.53 (m, 6H), 7.34-7.41 (m, 4H), 7.25 (d, 2H, *J* = 7.48 Hz), 7.15 (d, 2H, *J* = 7.72 Hz), 7.03 (t, 1H, *J* = 7.28 Hz), 6.93 (d, 2H, *J* = 8.76 Hz). δ_C (100 MHz, $CDCl_3$) 191.3, 148.8, 147.4, 142.7, 135.5, 135.3, 132.6, 132.0, 131.6, 131.4, 131.1, 129.5, 129.4, 129.3, 128.4, 127.3, 126.9, 126.6, 126.3, 126.2, 124.4, 124.0, 123.2, 123.0, 121.6, 119.9, 114.5, 93.2, 92.3, 90.0, 88.0. MS (EI, 70 eV): m/z (relative intensity) 523 (M^+, 100); HRMS calcd for $C_{39}H_{25}NO$: 523.1936, found 523.1938.

4-((4-((4-(bis(4-(hexyloxy)phenyl)amino)phenyl)ethynyl)phenyl)ethynyl)benzaldehyde **(11b)**

Compound **11b** was synthesized according to the same procedure as that of **7**. Yellow solid of **11b** was obtained in 85%. δ_H (400 MHz, $CDCl_3$) 10.04 (s, 1H), 7.88 (d, 2H, *J* = 8.2 Hz), 7.69 (d, 2H, *J* = 8.2 Hz), 7.49-7.54 (m, 4H), 7.32 (d, 2H, *J* = 8.4 Hz), 7.08 (d, 4H, *J* = 8.96 Hz), 6.86 (d, 6H, *J* = 8.96 Hz), 3.95 (t, 4H, *J* = 6.52 Hz), 1.76-1.83 (m, 4H), 1.45-1.50 (m, 4H), 1.35-1.38 (m, 8H), 0.94 (t, 6H, *J* = 6.92 Hz). δ_C (100 MHz, $CDCl_3$) 191.3, 156.0, 149.1, 139.8, 135.4, 132.4, 132.1, 131.6, 131.3, 129.6, 129.4, 127.2, 124.6, 121.5, 118.8, 115.3, 113.1, 93.3, 92.8, 90.0, 87.7, 68.2, 31.6, 29.3, 25.7, 22.6, 14.0. MS (EI, 70 eV): m/z (relative intensity) 673 (M^+, 100); HRMS calcd for $C_{47}H_{47}NO_3$: 673.3556, found 673.3560.

2. ^{1}H and ^{13}C NMR spectra

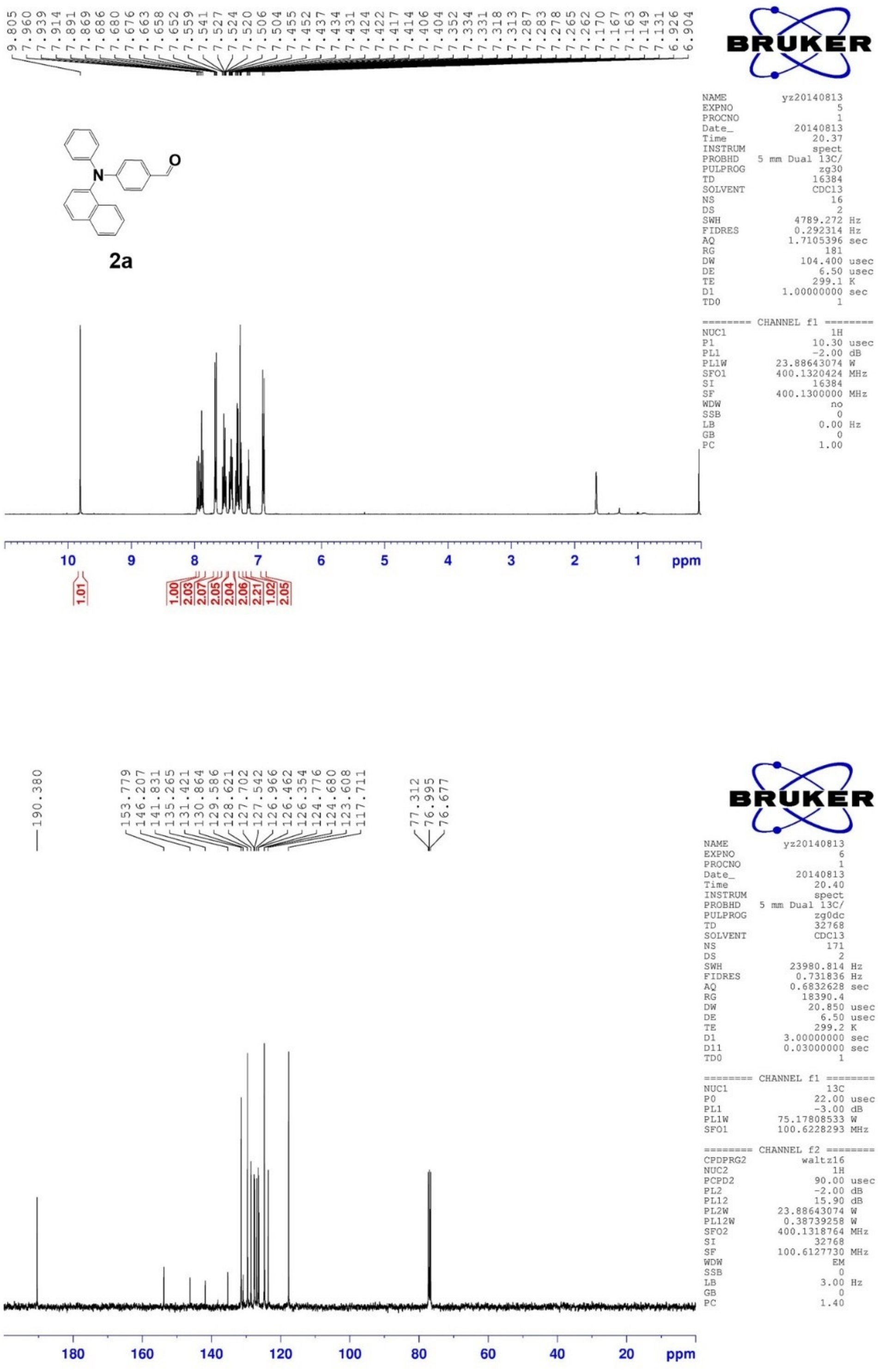

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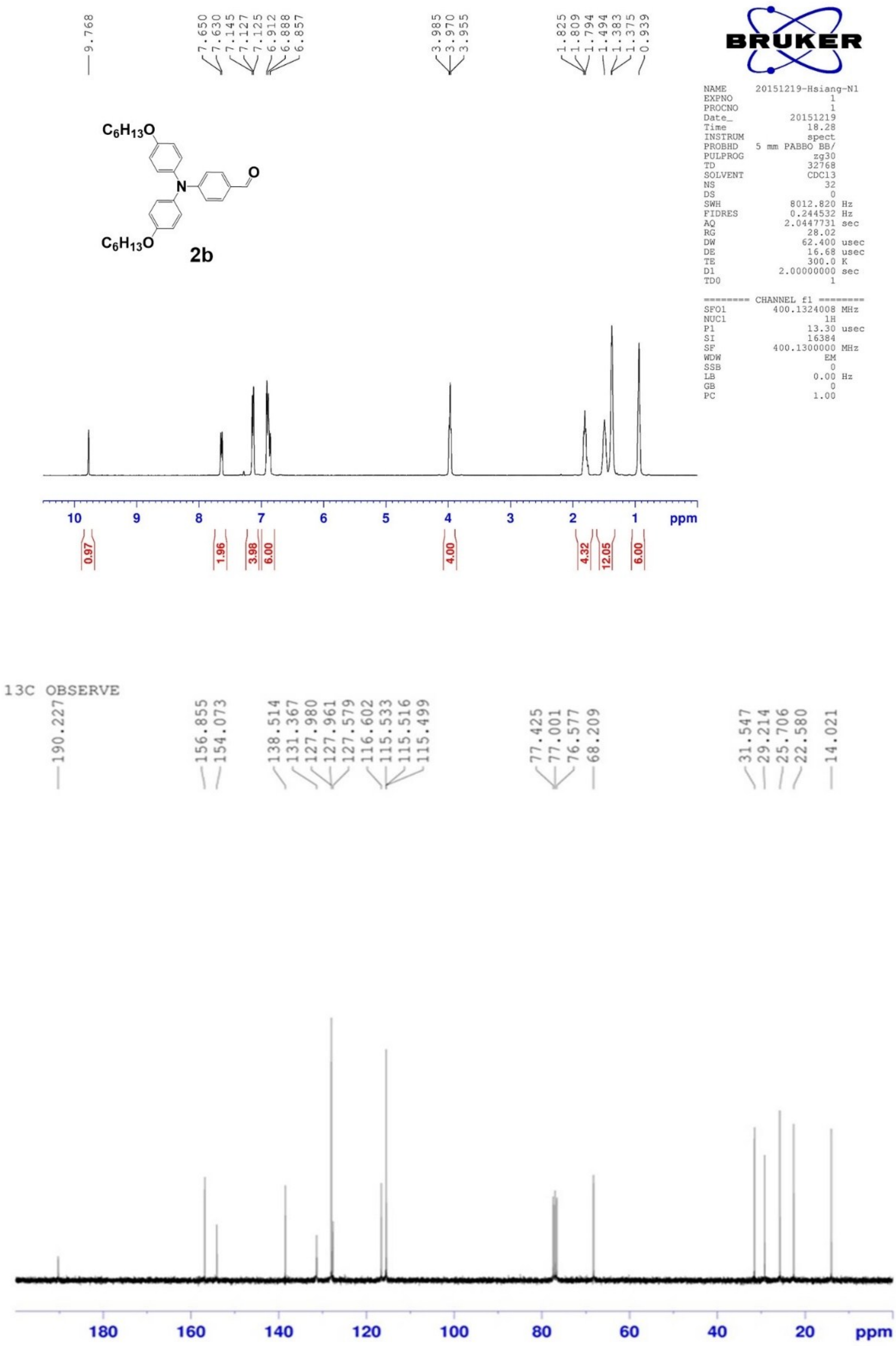
Fig. S1. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **2a** in $CDCl_3$.



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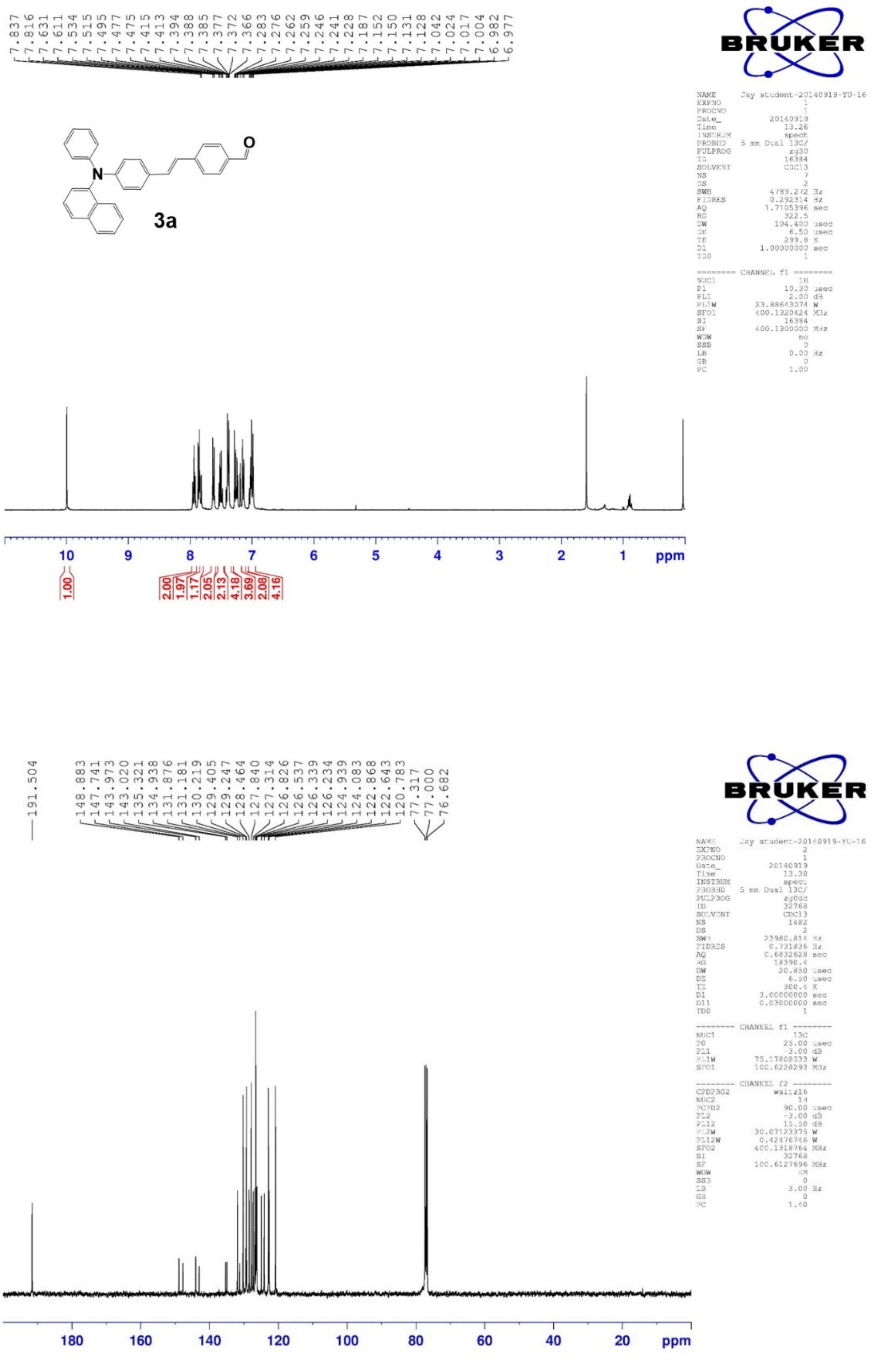
PROBHD   5 mm PABBO BB/
PULPROG                  zg30
TD                      32768
SOLVENT                 CDCl3
NS                         32
DS                          0
SWH                  8012.820 Hz
FIDRES               0.244532 Hz
AQ                  2.0447731 sec
RG                      28.02
DW                     62.400 usec
DE                      16.68 usec
TE                      300.0 K
D1                 2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              400.1324008 MHz
NUC1                       1H
P1                      13.30 usec
SI                      16384
SF                400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.00
```

Fig. S2. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **2b** in $CDCl_3$.



```
NAME      Jay student-20140919-YU-16
EXPNO                    1
PROCNO                   1
Date_             20140919
Time                 13.26
INSTRUM              spect
PROBHD    5 mm Dual 13C/
PULPROG               zg30
TD                   16384
SOLVENT              CDCl3
NS                       7
DS                       2
SWH               4789.272 Hz
FIDRES            0.292314 Hz
AQ               1.7105396 sec
RG                   322.5
DW                 104.400 usec
DE                    6.50 usec
TE                   299.8 K
D1              1.00000000 sec
TD0                      1

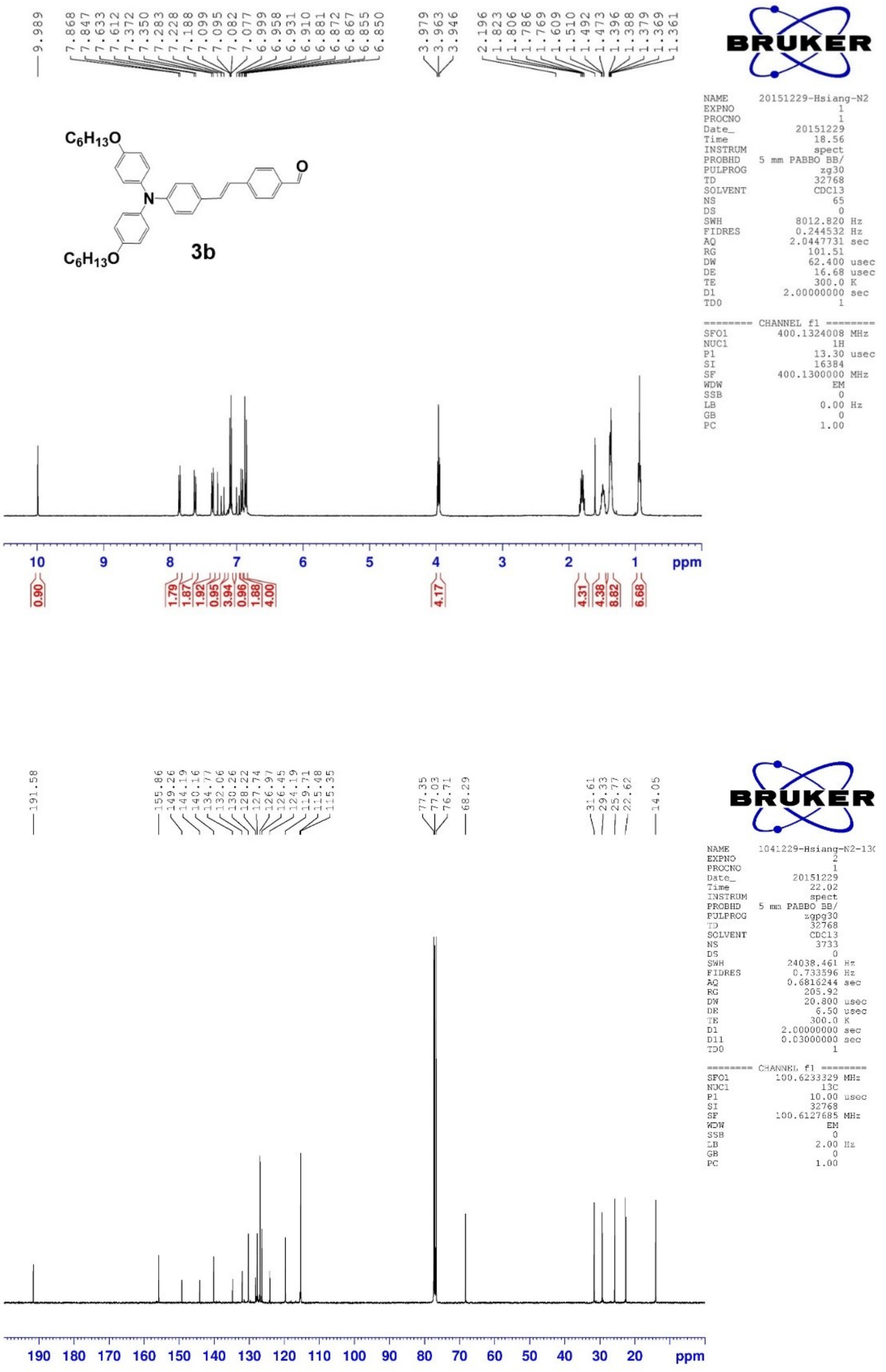
======== CHANNEL f1 ========
NUC1                    1H
P1                   10.30 usec
PL1                  -2.00 dB
PL1W           23.88643074 W
SFO1           400.1320424 MHz
SI                   16384
SF             400.1300000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

```
NAME      Jay student-20140919-YU-16
EXPNO                    2
PROCNO                   1
Date_             20140919
Time                 13.30
INSTRUM              spect
PROBHD    5 mm Dual 13C/
PULPROG             zg0dc
TD                   32768
SOLVENT              CDCl3
NS                    1482
DS                       2
SWH              23980.814 Hz
FIDRES            0.731836 Hz
AQ               0.6832628 sec
RG                 18390.4
DW                  20.850 usec
DE                    6.50 usec
TE                   300.4 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P0                   25.00 usec
PL1                  -3.00 dB
PL1W           75.17808533 W
SFO1           100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -3.00 dB
PL12                 15.50 dB
PL2W           30.07123375 W
PL12W           0.42476746 W
SFO2           400.1318764 MHz
SI                   32768
SF             100.6127696 MHz
WDW                     EM
SSB                      0
LB                    3.00 Hz
GB                       0
PC                    1.40
```

Fig. S3. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **3a** in $CDCl_3$.



```
NAME      20151229-Hsiang-N2
EXPNO                    1
PROCNO                   1
Date_             20151229
Time                 18.56
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      65
DS                       0
SWH               8012.820 Hz
FIDRES            0.244532 Hz
AQ               2.0447731 sec
RG                  101.51
DW                  62.400 usec
DE                   16.68 usec
TE                   300.0 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1324008 MHz
NUC1                    1H
P1                   13.30 usec
SI                   16384
SF             400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

```
NAME      1041229-Hsiang-N2-13C
EXPNO                    2
PROCNO                   1
Date_             20151229
Time                 22.02
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                    3733
DS                       0
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ               0.6816244 sec
RG                  205.92
DW                  20.800 usec
DE                    6.50 usec
TE                   300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           100.6233329 MHz
NUC1                   13C
P1                   10.00 usec
SI                   32768
SF             100.6127685 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.00
```

Fig. S4. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **3b** in $CDCl_3$.

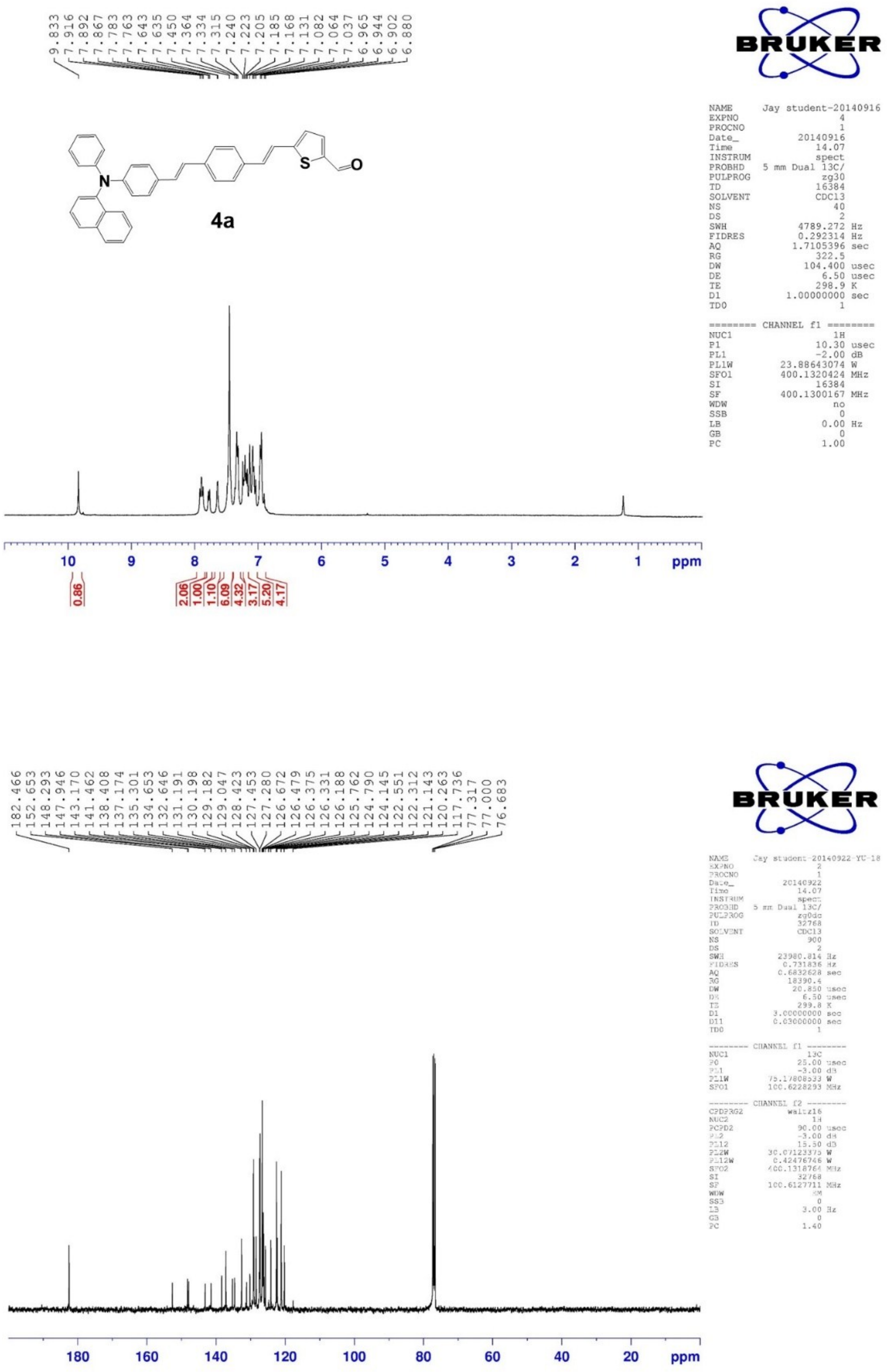
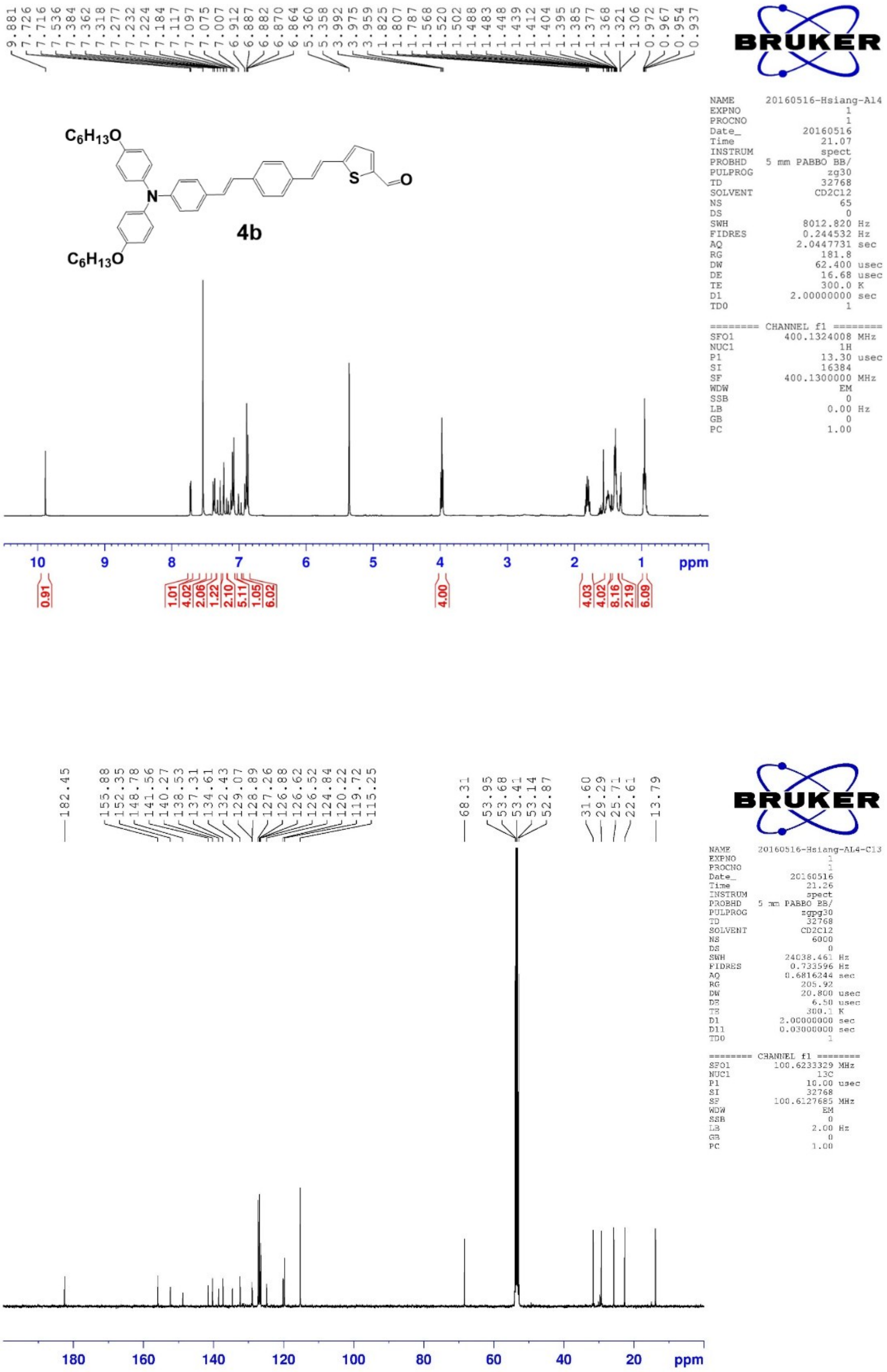


Fig. S5. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **4a** in $CDCl_3$.



```
NAME       20160516-Hsiang-A14
EXPNO                    1
PROCNO                   1
Date_             20160516
Time                 21.07
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   32768
SOLVENT             CD2C12
NS                      65
DS                       0
SWH               8012.820 Hz
FIDRES            0.244532 Hz
AQ               2.0447731 sec
RG                   181.8
DW                  62.400 usec
DE                   16.68 usec
TE                   300.0 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1324008 MHz
NUC1                    1H
P1                   13.30 usec
SI                   16384
SF             400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

```
NAME       20160516-Hsiang-AL4-C13
EXPNO                    1
PROCNO                   1
Date_             20160516
Time                 21.26
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   32768
SOLVENT             CD2C12
NS                    6000
DS                       0
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ               0.6816244 sec
RG                  205.92
DW                  20.800 usec
DE                    6.50 usec
TE                   300.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           100.6233329 MHz
NUC1                   13C
P1                   10.00 usec
SI                   32768
SF             100.6127685 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.00
```

Fig. S6. ^1H NMR (upper) and ^{13}C NMR (lower) spectra of **4b** in $CDCl_3$.

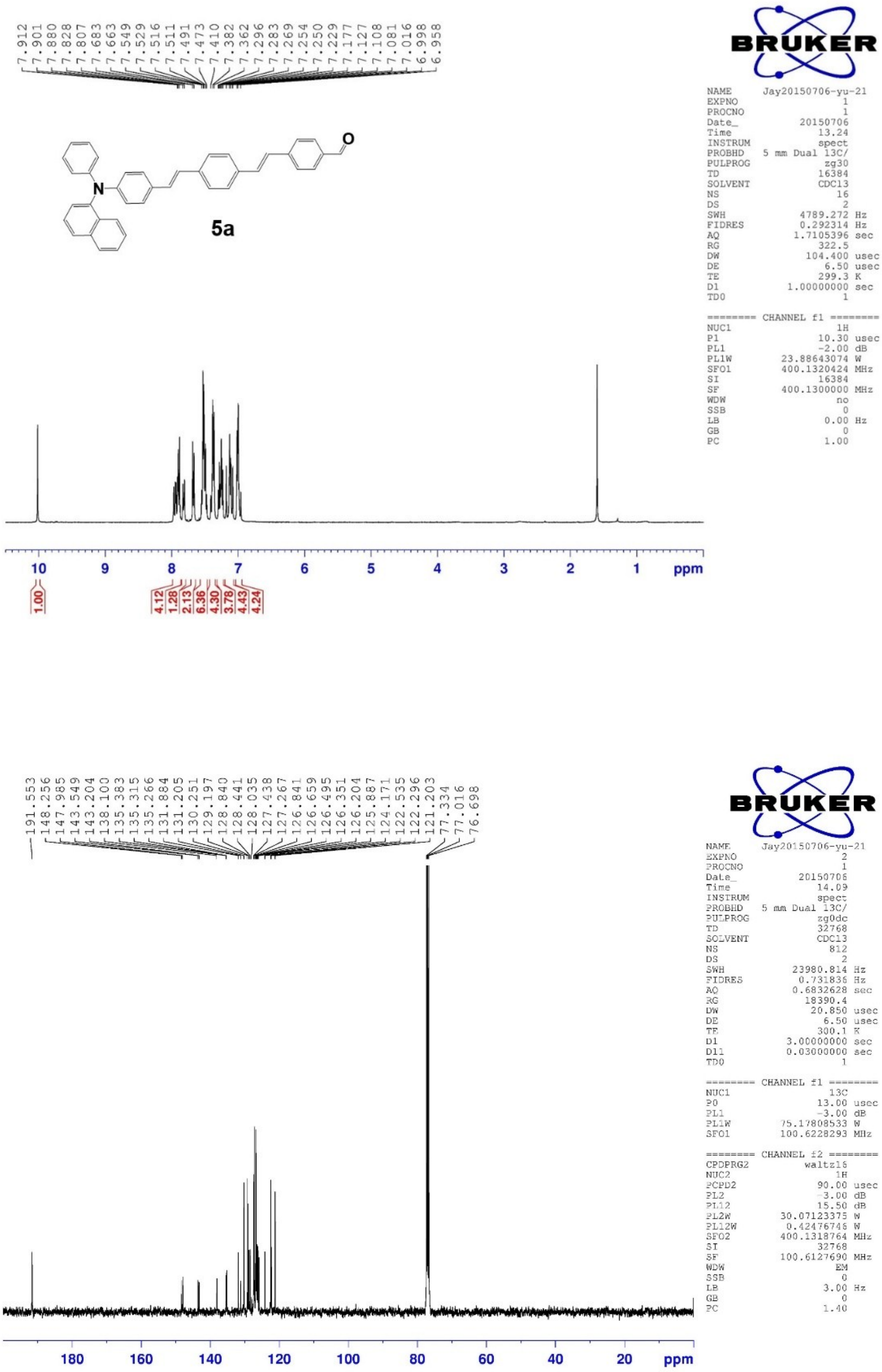
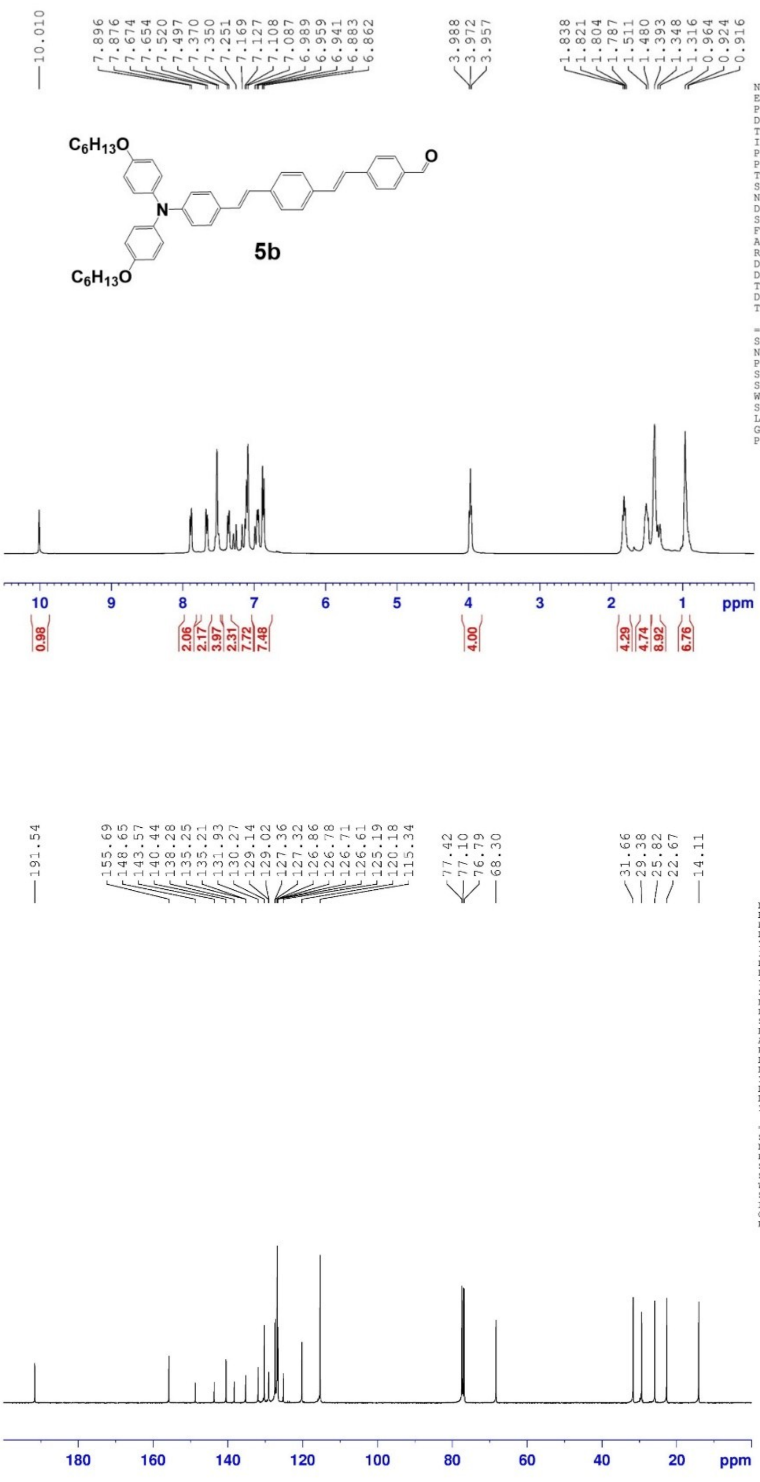


Fig. S7. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **5a** in $CDCl_3$.



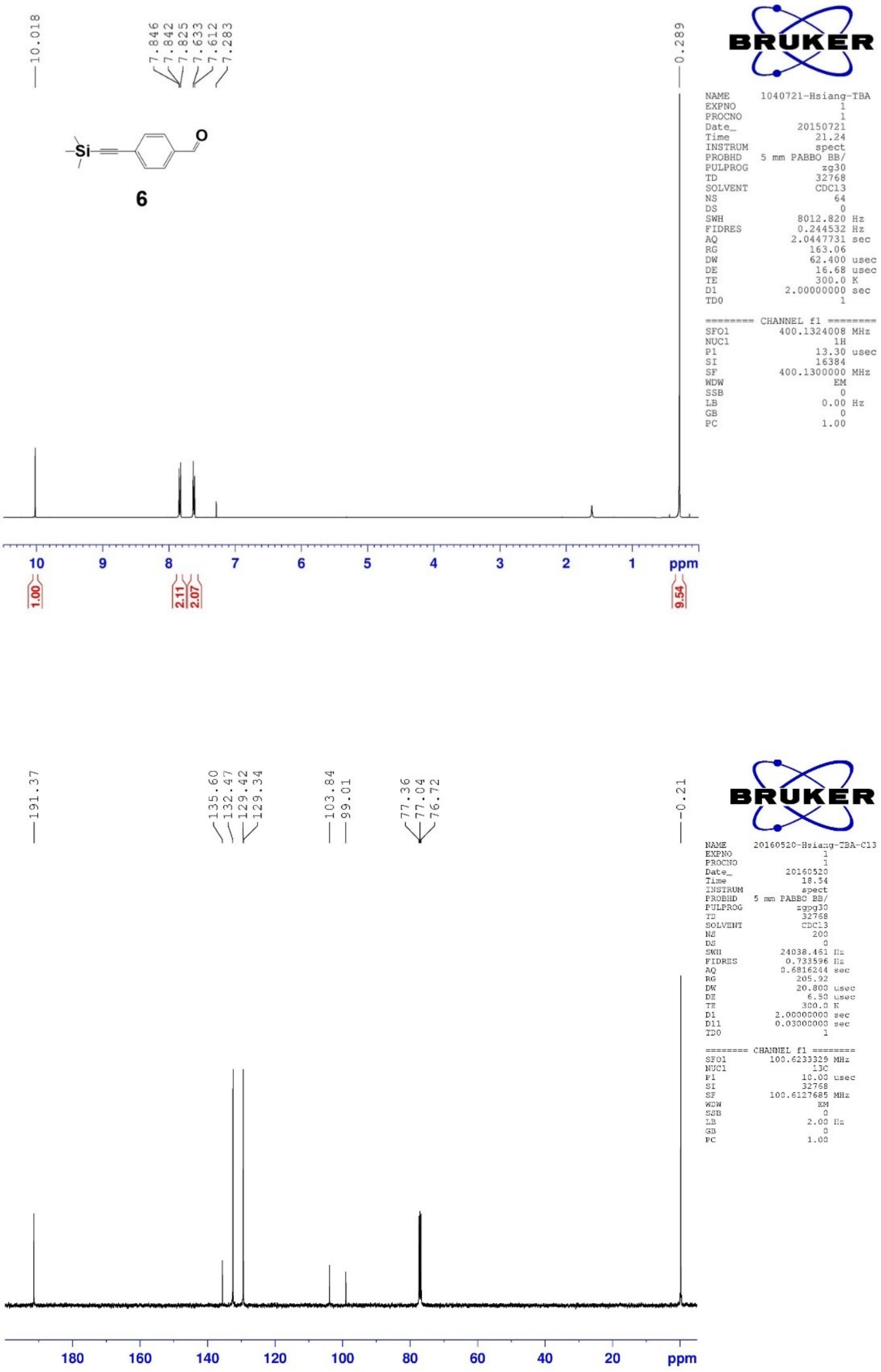
```
NAME       20151126-Hsiang-A13
EXPNO                    1
PROCNO                   1
Date_             20151127
Time                  7.46
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      32
DS                       0
SWH               8012.820 Hz
FIDRES            0.244532 Hz
AQ               2.0447731 sec
RG                   28.02
DW                  62.400 usec
DE                   16.68 usec
TE                   300.1 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                    1H
P1                   13.30 usec
SI                   16384
SF           400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

```
NAME       20151127-Hsiang-A13-C13
EXPNO                    1
PROCNO                   1
Date_             20151128
Time                  2.40
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                    8000
DS                       0
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ               0.6816244 sec
RG                  205.92
DW                  20.800 usec
DE                    6.50 usec
TE                   300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         100.6233329 MHz
NUC1                   13C
P1                   10.00 usec
SI                   32768
SF           100.6127685 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.00
```

Fig. S8. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **5b** in $CDCl_3$.



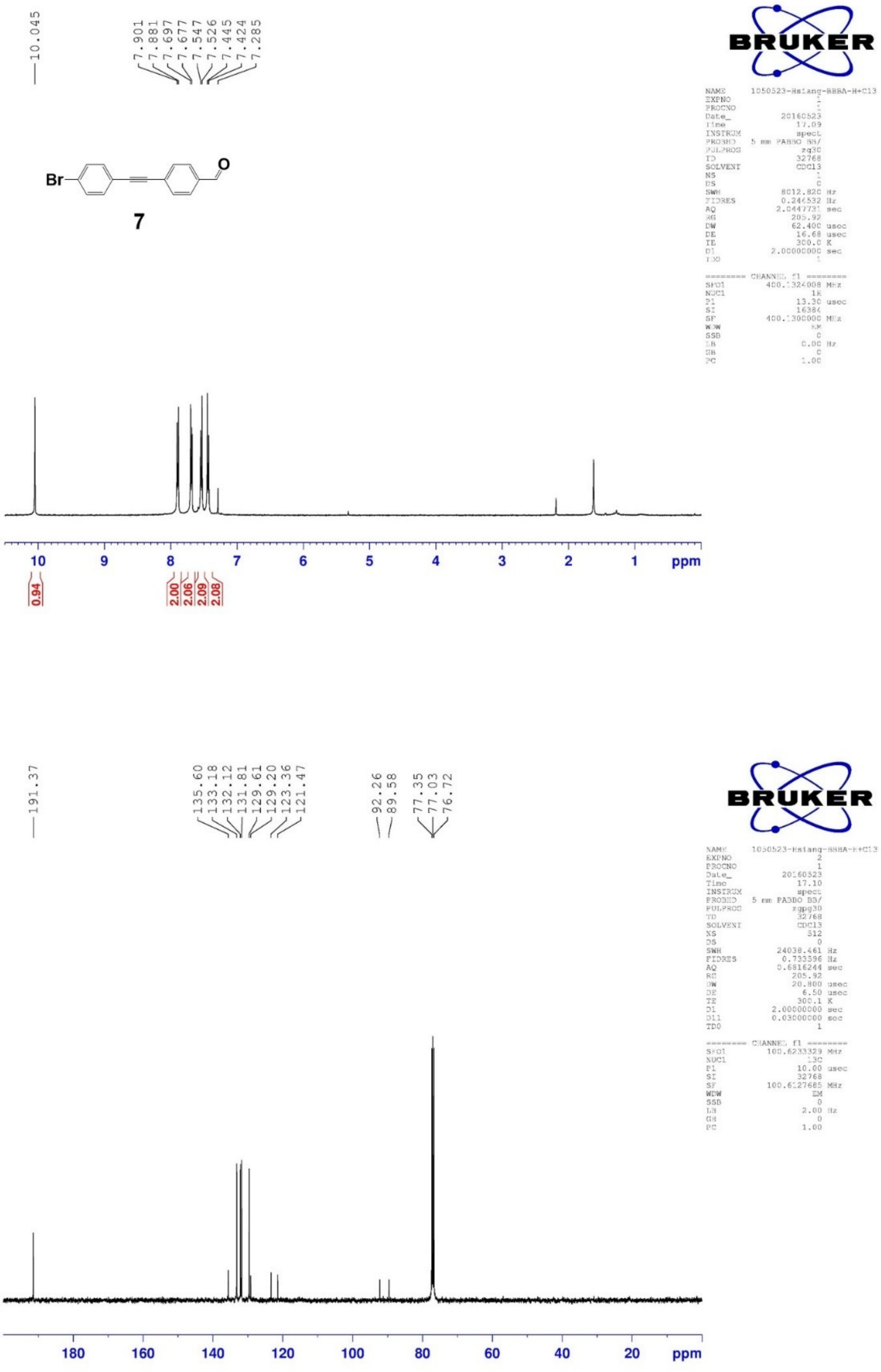
```
NAME       1040721-Hsiang-TBA
EXPNO                       1
PROCNO                      1
Date_                20150721
Time                    21.24
INSTRUM                 spect
PROBHD     5 mm PABBO BB/
PULPROG                  zg30
TD                      32768
SOLVENT                 CDCl3
NS                         64
DS                          0
SWH                  8012.820 Hz
FIDRES               0.244532 Hz
AQ                  2.0447731 sec
RG                     163.06
DW                     62.400 usec
DE                      16.68 usec
TE                      300.0 K
D1                 2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              400.1324008 MHz
NUC1                       1H
P1                      13.30 usec
SI                      16384
SF                400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.00
```

```
NAME       20160520-Hsiang-TBA-C13
EXPNO                       1
PROCNO                      1
Date_                20160520
Time                    18.54
INSTRUM                 spect
PROBHD     5 mm PABBO BB/
PULPROG               zgpg30
TD                      32768
SOLVENT                 CDCl3
NS                        200
DS                          0
SWH                 24038.461 Hz
FIDRES               0.733596 Hz
AQ                  0.6816244 sec
RG                     205.92
DW                     20.800 usec
DE                       6.50 usec
TE                      300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              100.6233329 MHz
NUC1                      13C
P1                      10.00 usec
SI                      32768
SF                100.6127685 MHz
WDW                        EM
SSB                         0
LB                       2.00 Hz
GB                          0
PC                       1.00
```

Fig. S9. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **6** in $CDCl_3$.



7

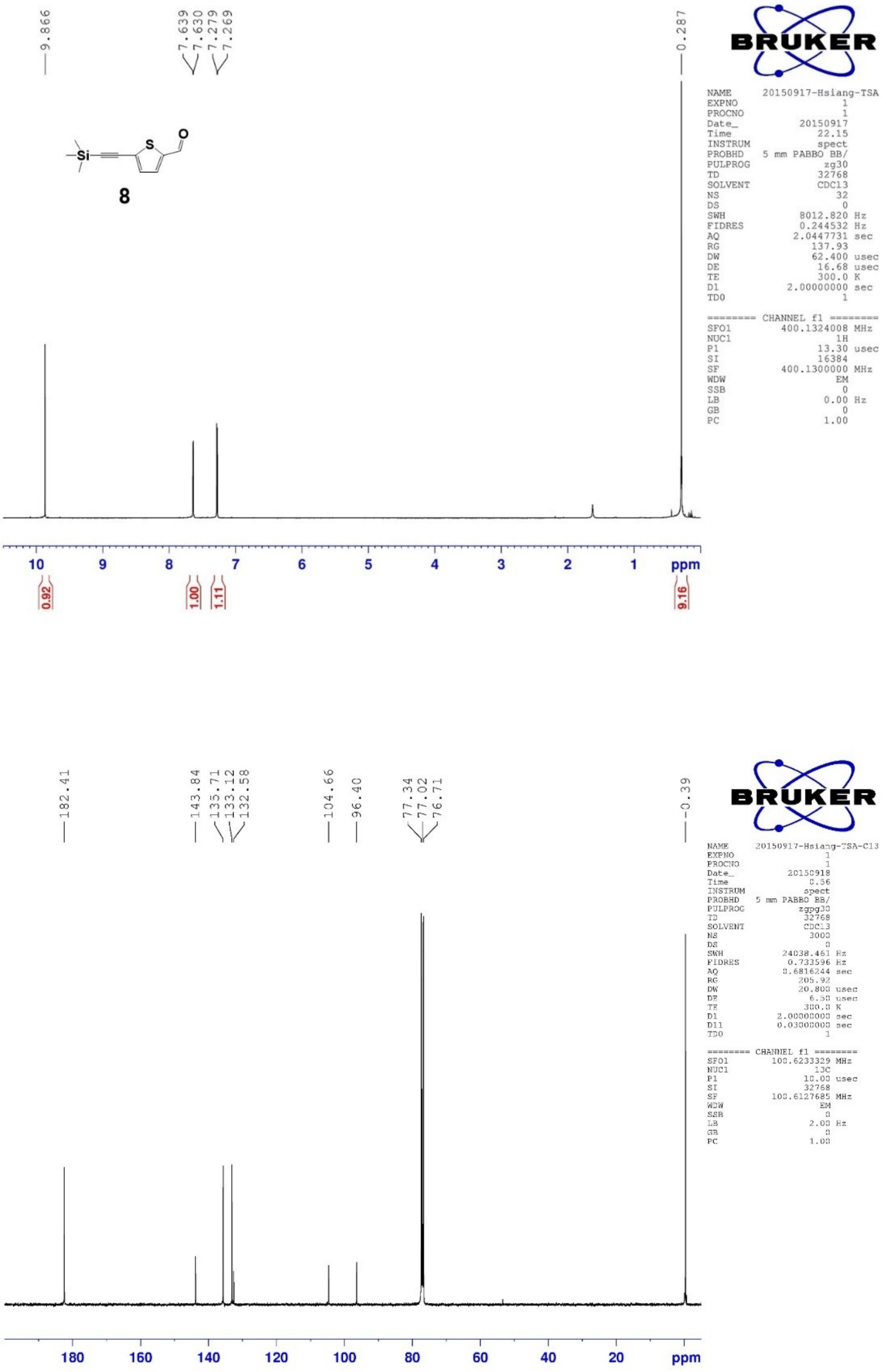
```
NAME       1050523-Hsiang-BBBA-H+C13
EXPNO                      1
PROCNO                     1
Date_               20160523
Time                   17.09
INSTRUM                spect
PROBHD     5 mm PABBO BB/
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                         1
DS                         0
SWH                 8012.820 Hz
FIDRES              0.244532 Hz
AQ                 2.0447731 sec
RG                    205.92
DW                    62.400 usec
DE                     16.68 usec
TE                     300.0 K
D1                2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             400.1324008 MHz
NUC1                      1H
P1                     13.30 usec
SI                     16384
SF               400.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.00
```

```
NAME       1050523-Hsiang-BBBA-H+C13
EXPNO                      2
PROCNO                     1
Date_               20160523
Time                   17.10
INSTRUM                spect
PROBHD     5 mm PABBO BB/
PULPROG              zgpg30
TD                     32768
SOLVENT                CDCl3
NS                       512
DS                         0
SWH                24038.461 Hz
FIDRES              0.733596 Hz
AQ                 0.6816244 sec
RG                    205.92
DW                    20.800 usec
DE                      6.50 usec
TE                     300.1 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             100.6233329 MHz
NUC1                     13C
P1                     10.00 usec
SI                     32768
SF               100.6127685 MHz
WDW                       EM
SSB                        0
LB                      2.00 Hz
GB                         0
PC                      1.00
```

Fig. S10. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **7** in $CDCl_3$.



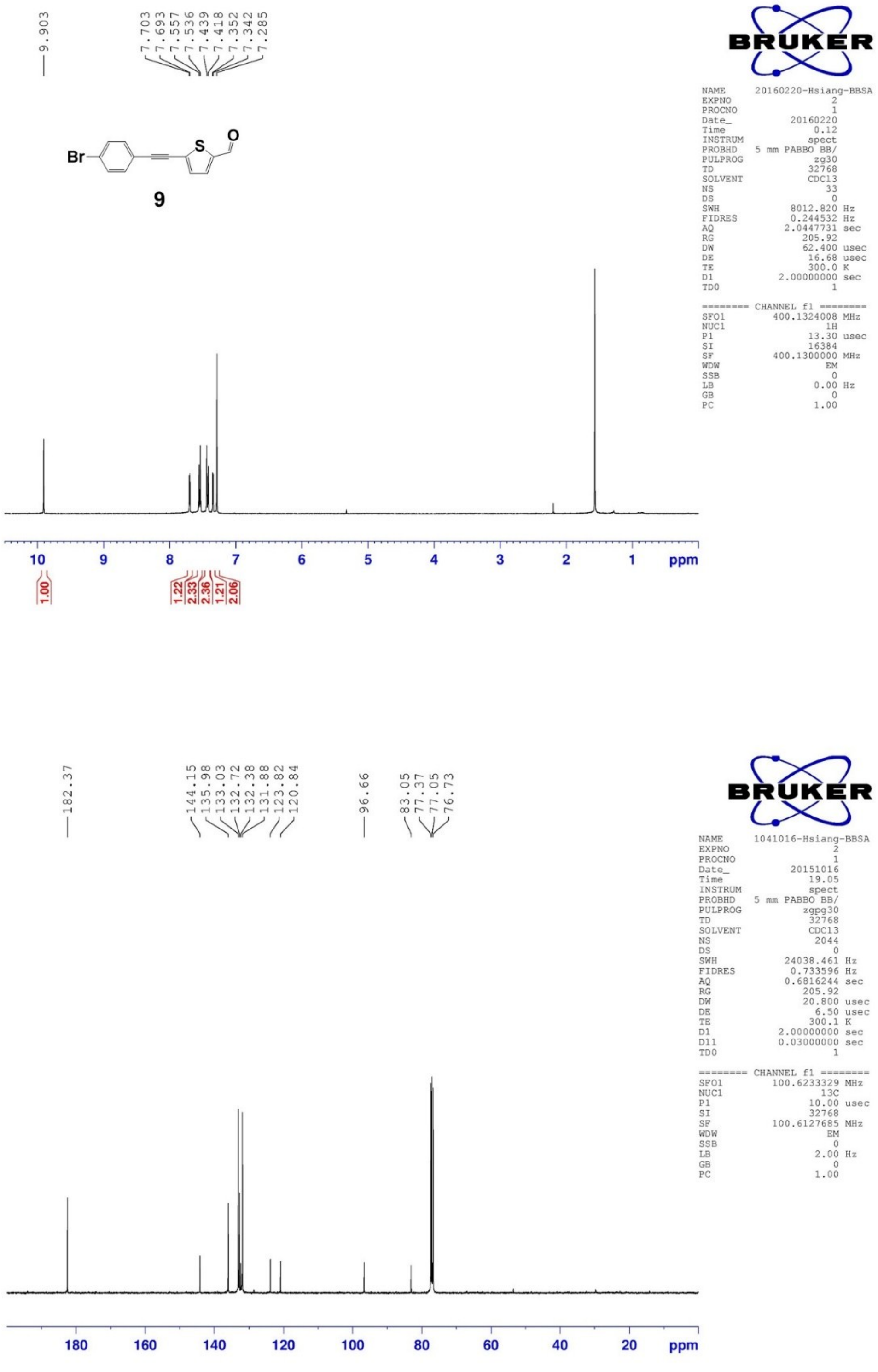
```
NAME      20150917-Hsiang-TSA
EXPNO                       1
PROCNO                      1
Date_                20150917
Time                    22.15
INSTRUM                 spect
PROBHD    5 mm PABBO BB/
PULPROG                  zg30
TD                      32768
SOLVENT                 CDCl3
NS                         32
DS                          0
SWH                  8012.820 Hz
FIDRES               0.244532 Hz
AQ                  2.0447731 sec
RG                     137.93
DW                     62.400 usec
DE                      16.68 usec
TE                      300.0 K
D1                 2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              400.1324008 MHz
NUC1                       1H
P1                      13.30 usec
SI                      16384
SF                400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.00
```

```
NAME      20150917-Hsiang-TSA-C13
EXPNO                       1
PROCNO                      1
Date_                20150918
Time                     0.56
INSTRUM                 spect
PROBHD    5 mm PABBO BB/
PULPROG                zgpg30
TD                      32768
SOLVENT                 CDCl3
NS                       3000
DS                          0
SWH                 24038.461 Hz
FIDRES               0.733596 Hz
AQ                  0.6816244 sec
RG                     205.92
DW                     20.800 usec
DE                       6.50 usec
TE                      300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              100.6233329 MHz
NUC1                      13C
P1                      10.00 usec
SI                      32768
SF                100.6127685 MHz
WDW                        EM
SSB                         0
LB                       2.00 Hz
GB                          0
PC                       1.00
```

Fig. S11. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **8** in $CDCl_3$.



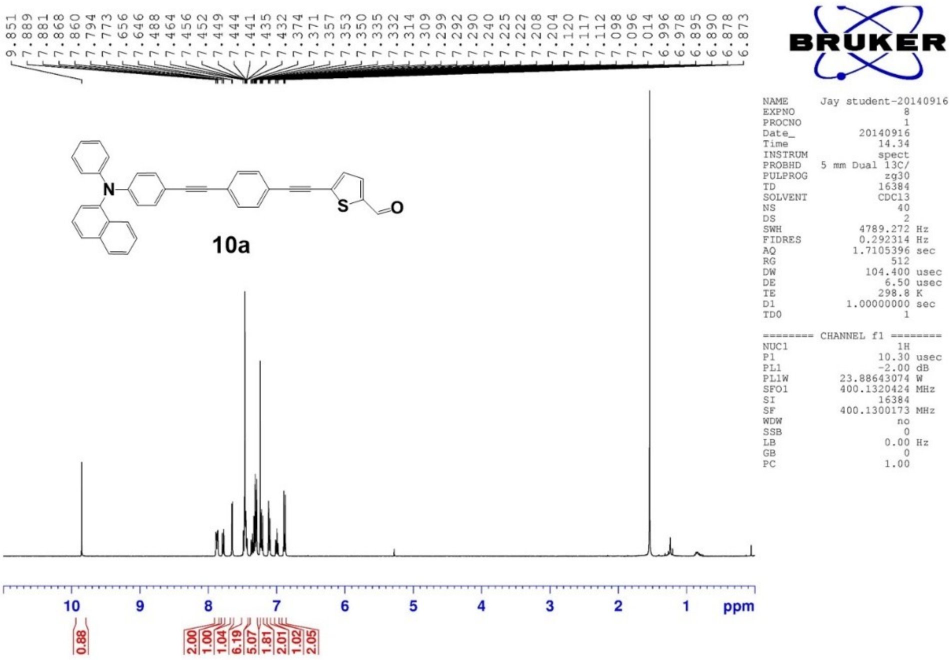
```
NAME       20160220-Hsiang-BBSA
EXPNO                         2
PROCNO                        1
Date_                  20160220
Time                       0.12
INSTRUM                   spect
PROBHD     5 mm PABBO BB/
PULPROG                    zg30
TD                        32768
SOLVENT                   CDCl3
NS                           33
DS                            0
SWH                    8012.820 Hz
FIDRES                 0.244532 Hz
AQ                    2.0447731 sec
RG                       205.92
DW                       62.400 usec
DE                        16.68 usec
TE                        300.0 K
D1                   2.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1               400.1324008 MHz
NUC1                         1H
P1                        13.30 usec
SI                        16384
SF                 400.1300000 MHz
WDW                          EM
SSB                           0
LB                         0.00 Hz
GB                            0
PC                         1.00
```

```
NAME       1041016-Hsiang-BBSA
EXPNO                         2
PROCNO                        1
Date_                  20151016
Time                      19.05
INSTRUM                   spect
PROBHD     5 mm PABBO BB/
PULPROG                 zgpg30
TD                        32768
SOLVENT                   CDCl3
NS                         2044
DS                            0
SWH                   24038.461 Hz
FIDRES                 0.733596 Hz
AQ                    0.6816244 sec
RG                       205.92
DW                       20.800 usec
DE                         6.50 usec
TE                        300.1 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1               100.6233329 MHz
NUC1                        13C
P1                        10.00 usec
SI                        32768
SF                 100.6127685 MHz
WDW                          EM
SSB                           0
LB                         2.00 Hz
GB                            0
PC                         1.00
```

Fig. S12. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **9** in $CDCl_3$.



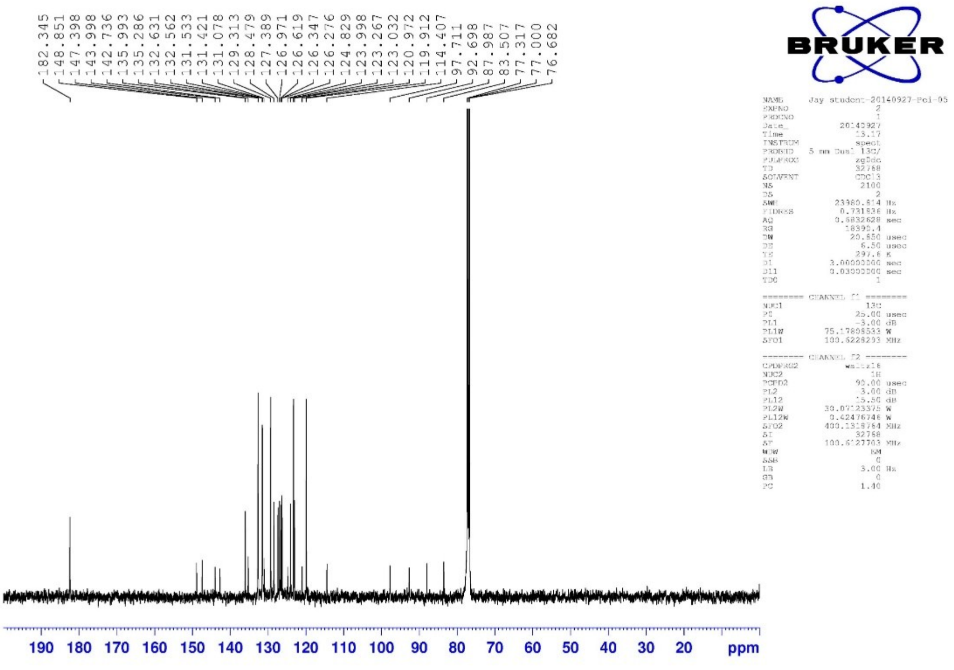
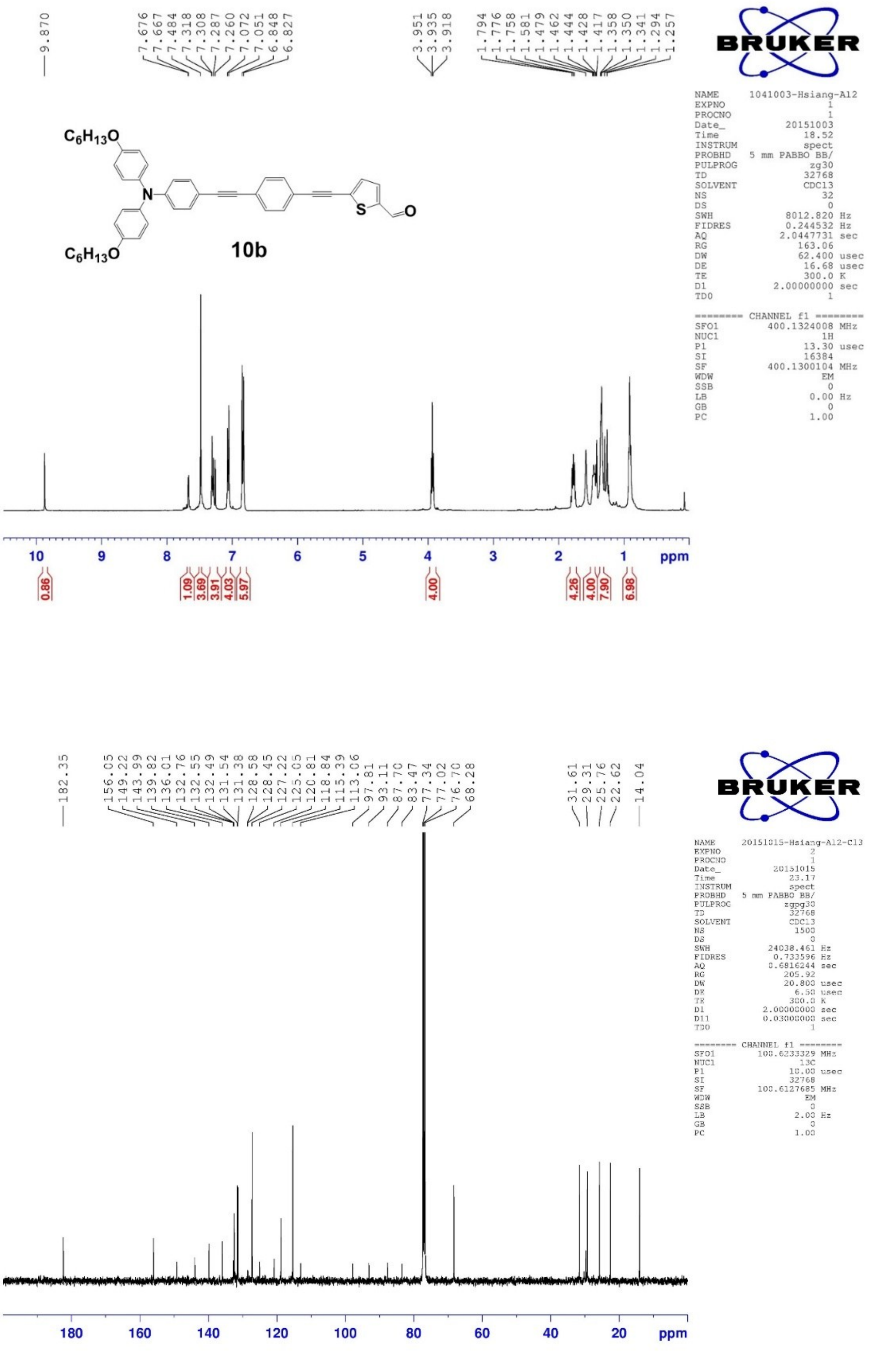


Fig. S13. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **10a** in $CDCl_3$.



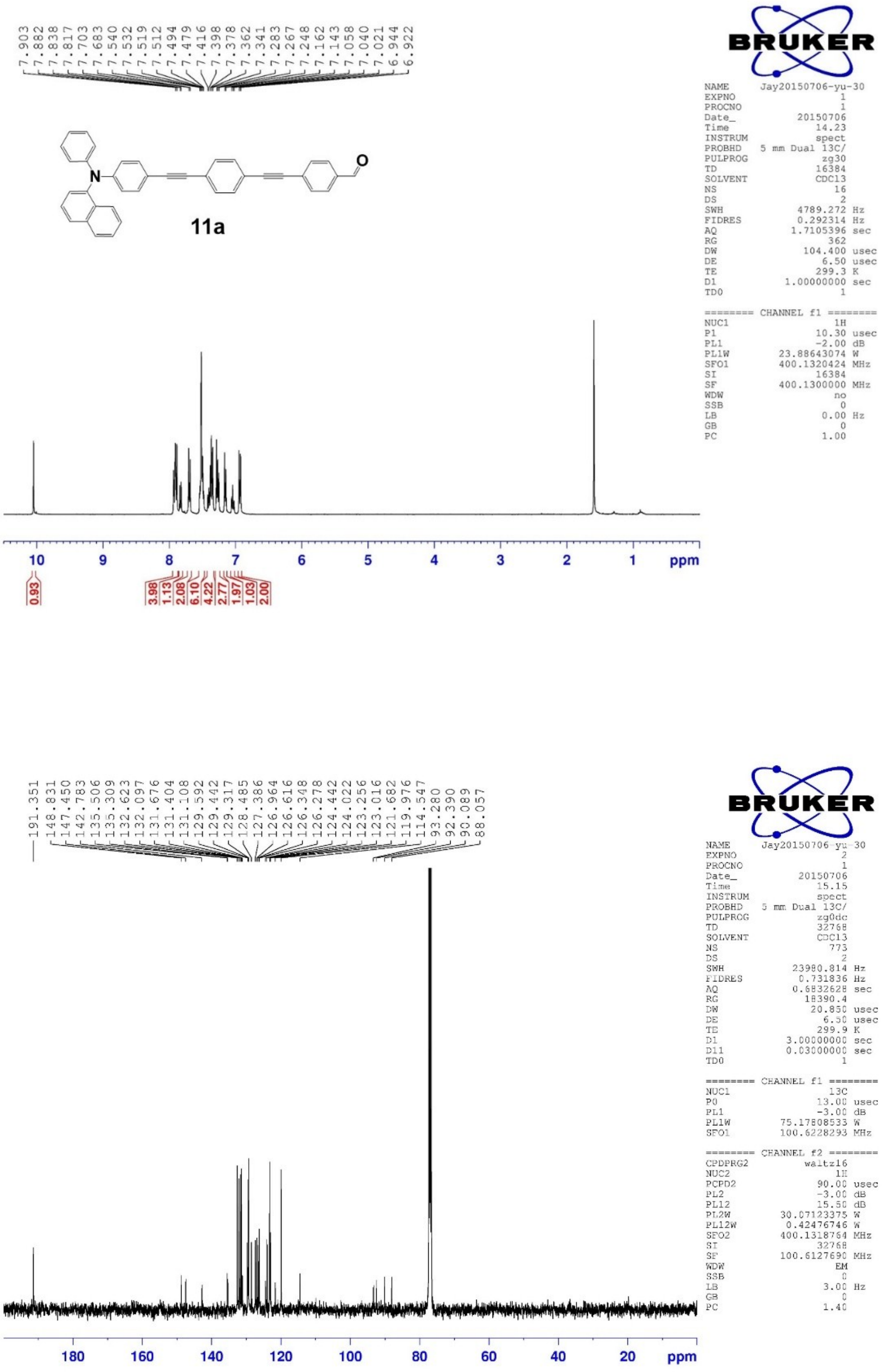
```
NAME        1041003-Hsiang-A12
EXPNO                      1
PROCNO                     1
Date_               20151003
Time                   18.52
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        32
DS                         0
SWH                 8012.820 Hz
FIDRES              0.244532 Hz
AQ                 2.0447731 sec
RG                    163.06
DW                    62.400 usec
DE                     16.68 usec
TE                     300.0 K
D1                2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             400.1324008 MHz
NUC1                      1H
P1                     13.30 usec
SI                     16384
SF               400.1300104 MHz
WDW                       EM
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.00
```

```
NAME       20151015-Hsiang-A12-C13
EXPNO                      2
PROCNO                     1
Date_               20151015
Time                   23.17
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG               zgpg30
TD                     32768
SOLVENT                CDCl3
NS                      1500
DS                         0
SWH                24038.461 Hz
FIDRES              0.733596 Hz
AQ                 0.6816244 sec
RG                    205.92
DW                    20.800 usec
DE                      6.50 usec
TE                     300.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             100.6233329 MHz
NUC1                     13C
P1                     10.00 usec
SI                     32768
SF               100.6127685 MHz
WDW                       EM
SSB                        0
LB                      2.00 Hz
GB                         0
PC                      1.00
```

Fig. S14. ^1H NMR (upper) and ^{13}C NMR (lower) spectra of **10b** in $CDCl_3$.



```
NAME       Jay20150706-yu-30
EXPNO                      1
PROCNO                     1
Date_               20150706
Time                   14.23
INSTRUM                spect
PROBHD    5 mm Dual 13C/
PULPROG                 zg30
TD                     16384
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 4789.272 Hz
FIDRES              0.292314 Hz
AQ                 1.7105396 sec
RG                       362
DW                   104.400 usec
DE                      6.50 usec
TE                     299.3 K
D1                1.00000000 sec
TD0                        1

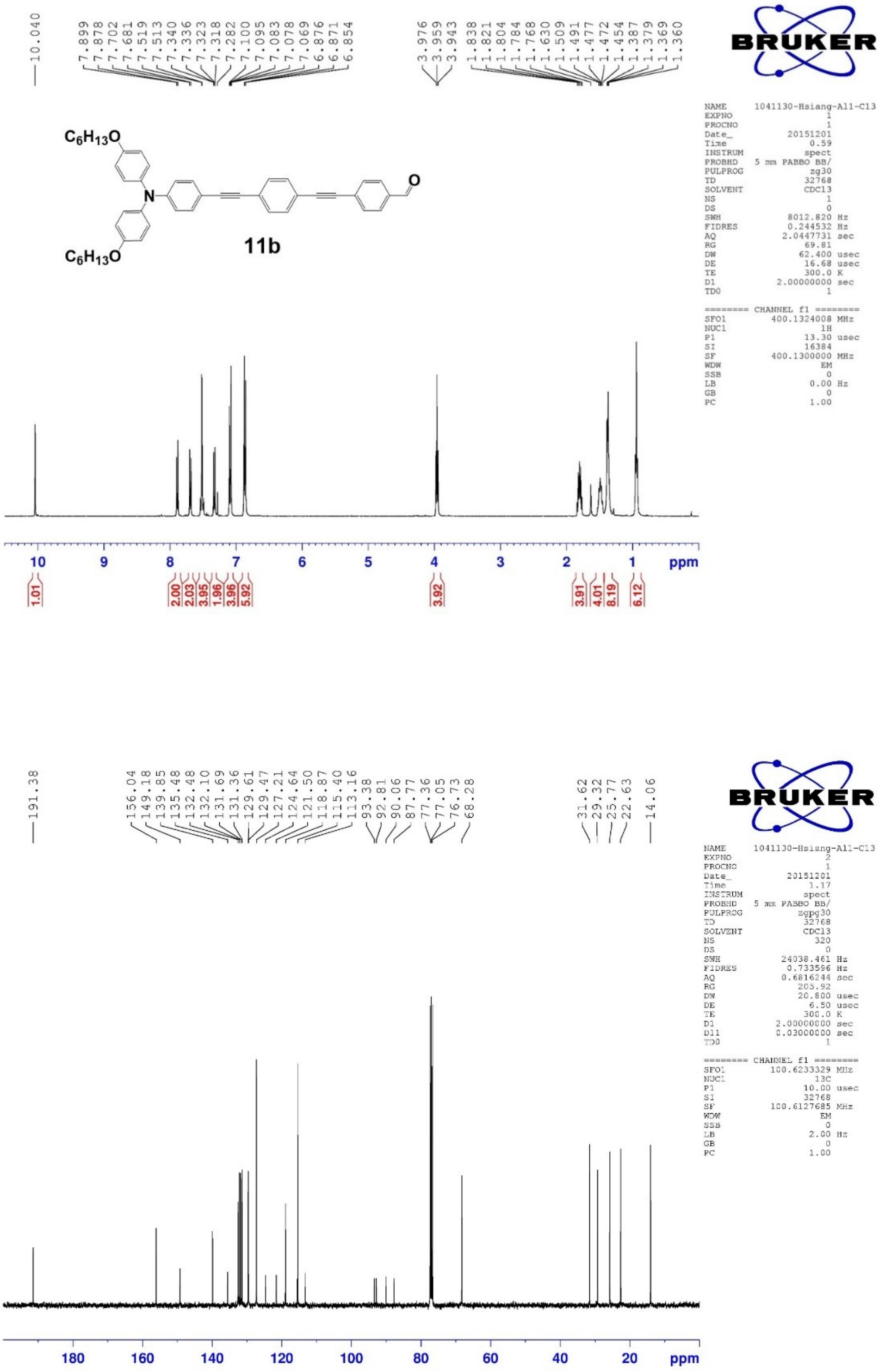
======== CHANNEL f1 ========
NUC1                      1H
P1                     10.30 usec
PL1                    -2.00 dB
PL1W             23.88643074 W
SFO1             400.1320424 MHz
SI                     16384
SF               400.1300000 MHz
WDW                       no
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.00
```

```
NAME       Jay20150706-yu-30
EXPNO                      2
PROCNO                     1
Date_               20150706
Time                   15.15
INSTRUM                spect
PROBHD    5 mm Dual 13C/
PULPROG                zg0dc
TD                     32768
SOLVENT                CDCl3
NS                       773
DS                         2
SWH                23980.814 Hz
FIDRES              0.731836 Hz
AQ                 0.6832628 sec
RG                   18390.4
DW                    20.850 usec
DE                      6.50 usec
TE                     299.9 K
D1                3.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P0                     13.00 usec
PL1                    -3.00 dB
PL1W             75.17808533 W
SFO1             100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  90.00 usec
PL2                    -3.00 dB
PL12                   15.50 dB
PL2W             30.07123375 W
PL12W             0.42476746 W
SFO2             400.1318764 MHz
SI                     32768
SF               100.6127690 MHz
WDW                       EM
SSB                        0
LB                      3.00 Hz
GB                         0
PC                      1.40
```

Fig. S15. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **11a** in $CDCl_3$.



```
NAME       1041130-Hsiang-All-C13
EXPNO                     1
PROCNO                    1
Date_              20151201
Time                   0.59
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                        1
DS                        0
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                2.0447731 sec
RG                    69.81
DW                   62.400 usec
DE                    16.68 usec
TE                    300.0 K
D1               2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            400.1324008 MHz
NUC1                     1H
P1                    13.30 usec
SI                    16384
SF              400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00
```

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NAME       1041130-Hsiang-All-C13
EXPNO                     2
PROCNO                    1
Date_              20151201
Time                   1.17
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG              zgpg30
TD                    32768
SOLVENT               CDCl3
NS                      320
DS                        0
SWH               24038.461 Hz
FIDRES             0.733596 Hz
AQ                0.6816244 sec
RG                   205.92
DW                   20.800 usec
DE                     6.50 usec
TE                    300.0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            100.6233329 MHz
NUC1                    13C
P1                    10.00 usec
SI                    32768
SF              100.6127685 MHz
WDW                      EM
SSB                       0
LB                     2.00 Hz
GB                        0
PC                     1.00
```

Fig. S16. ^1H NMR (upper) and ^{13}C NMR (lower) spectra of **11b** in $CDCl_3$.

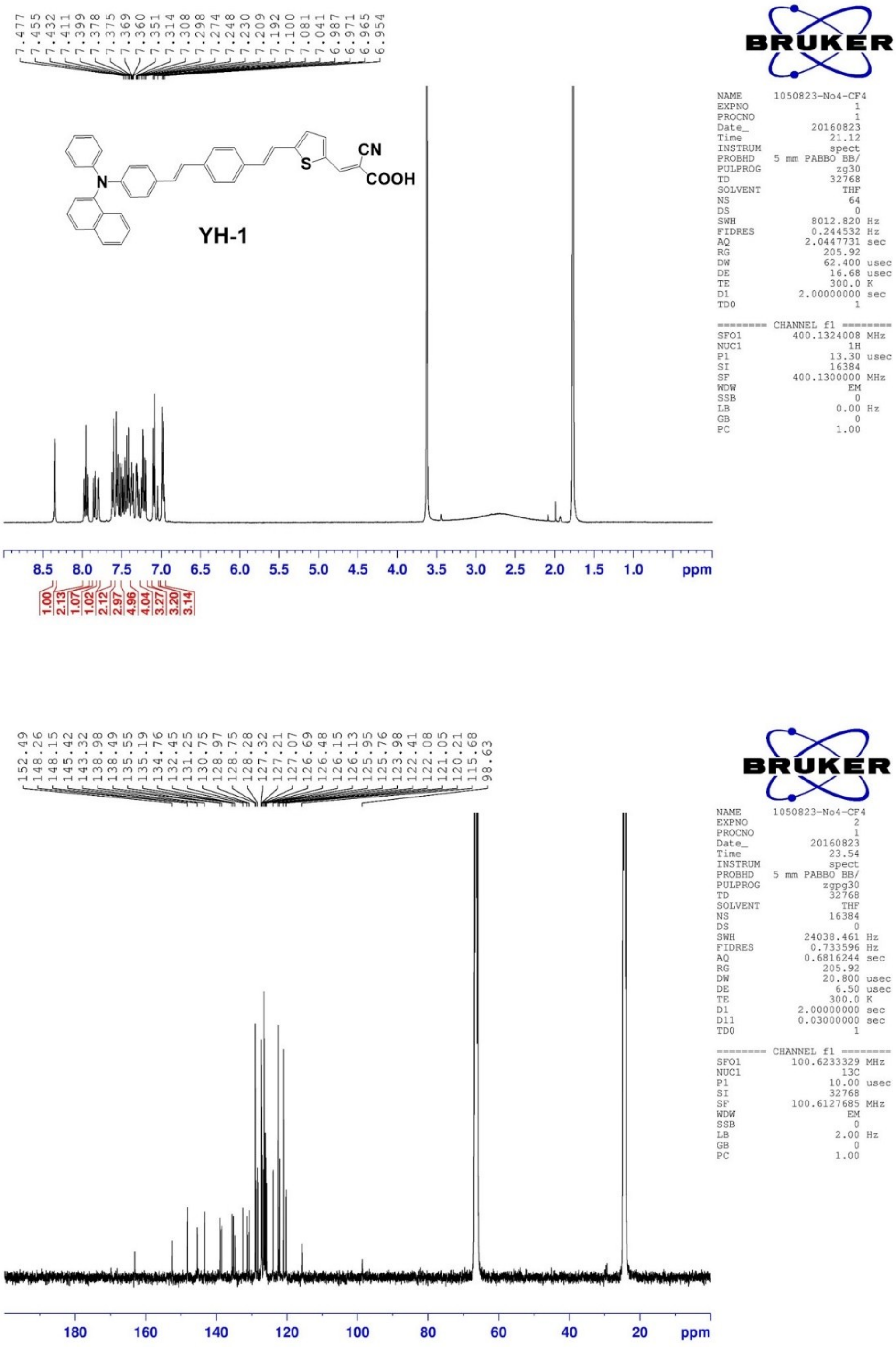


Fig. S17. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **YH-1** in THF-d_8.

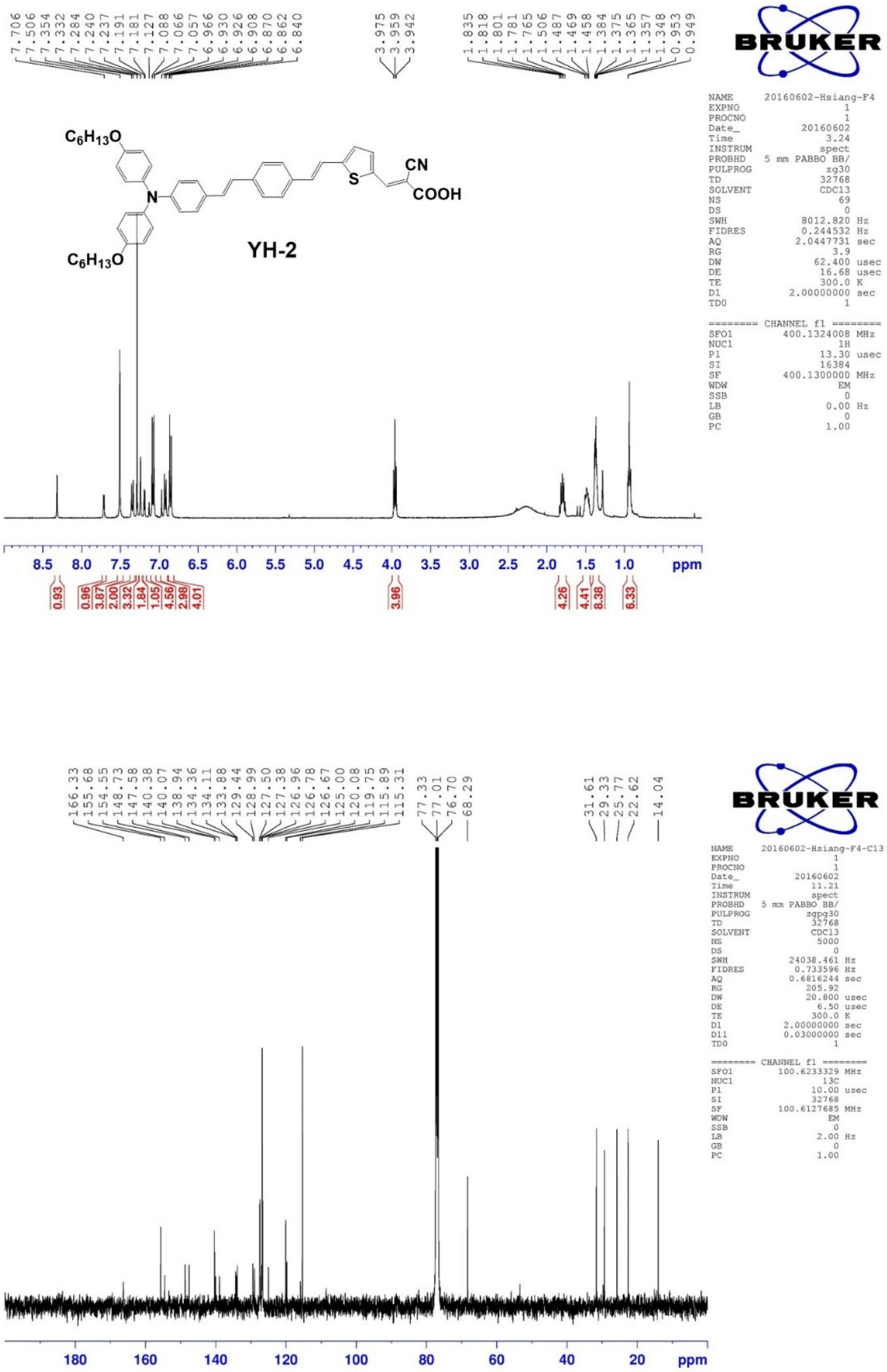


Fig. S18. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **YH-2** in CDCl$_3$.

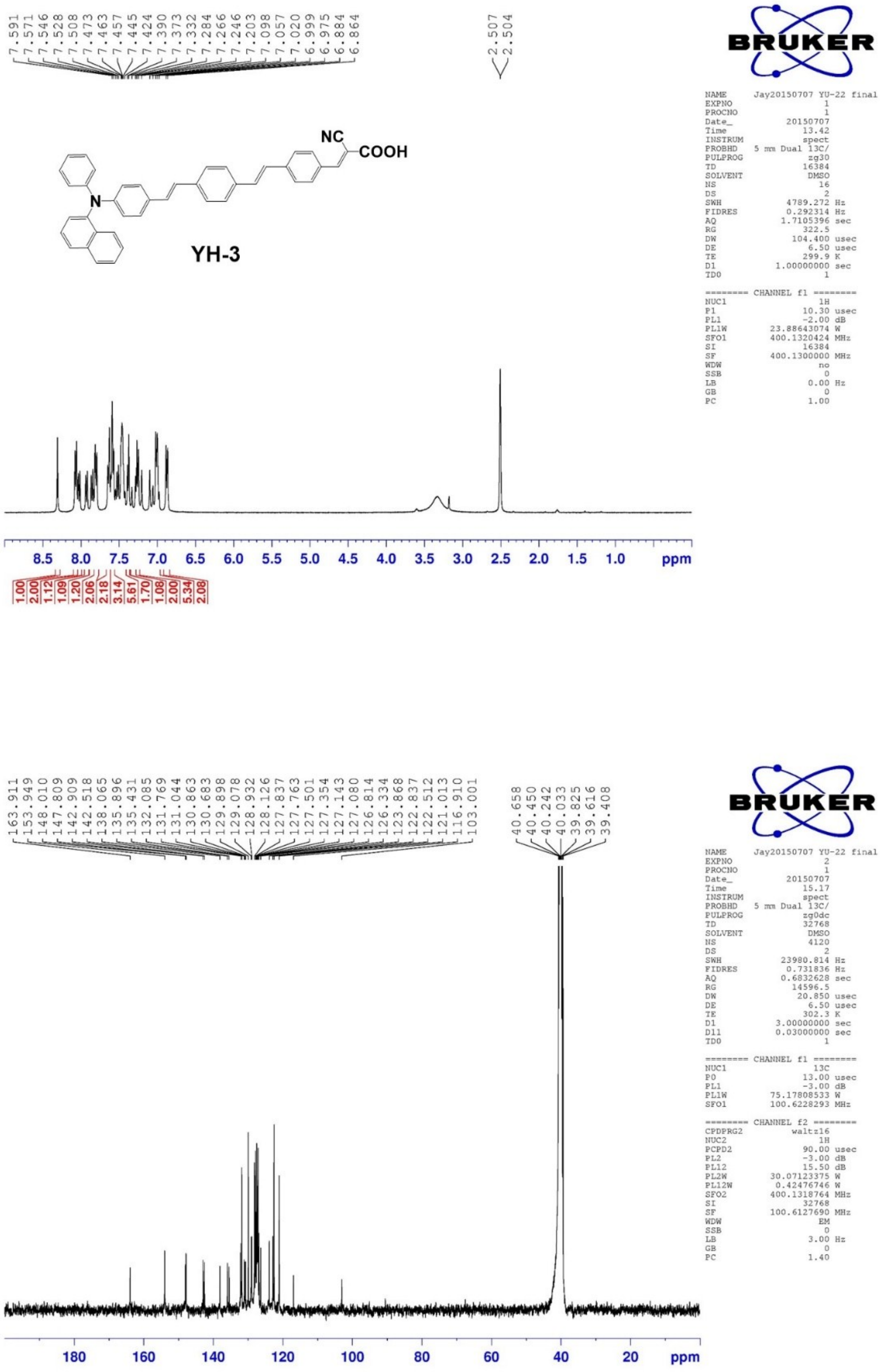
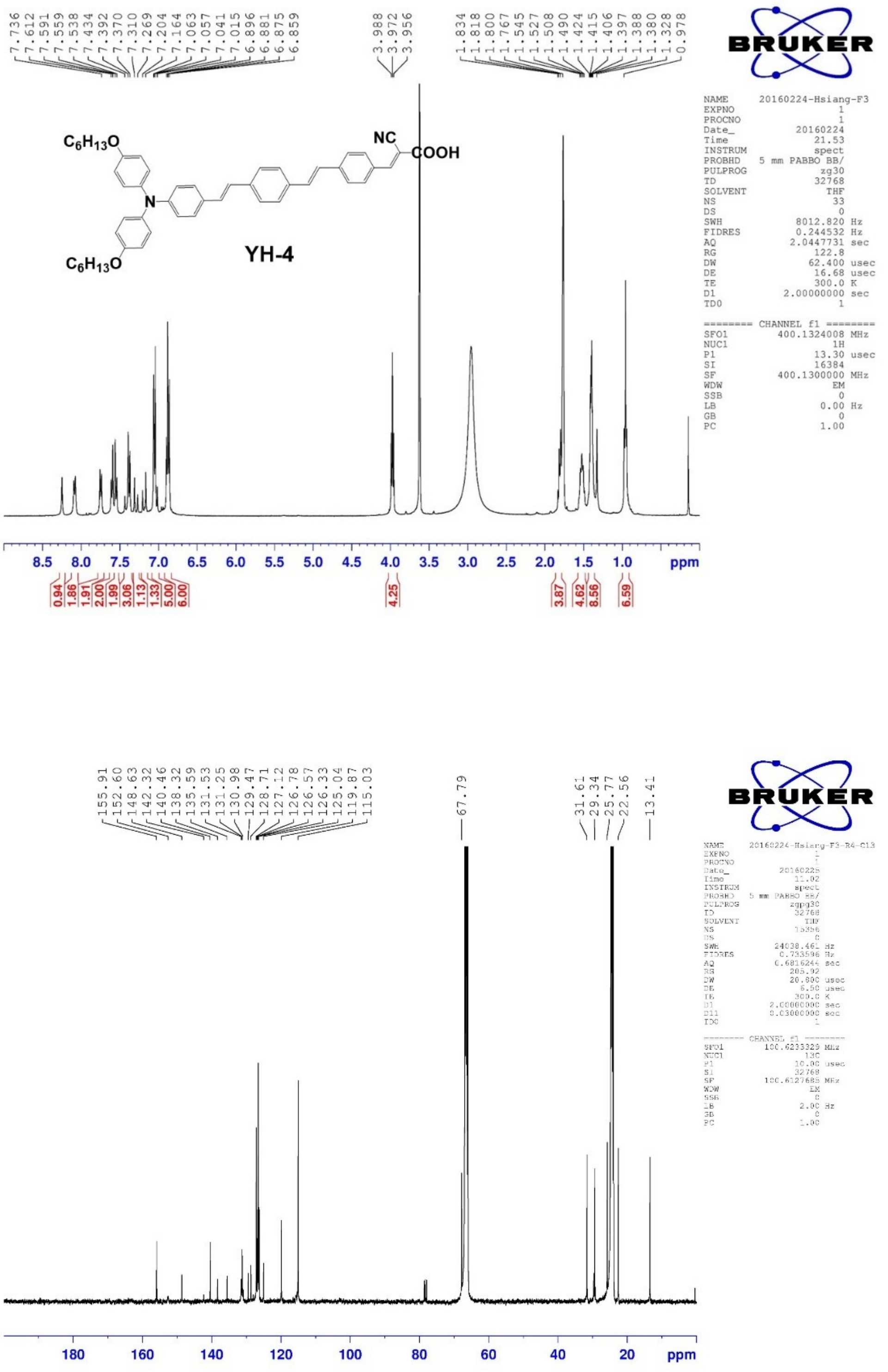


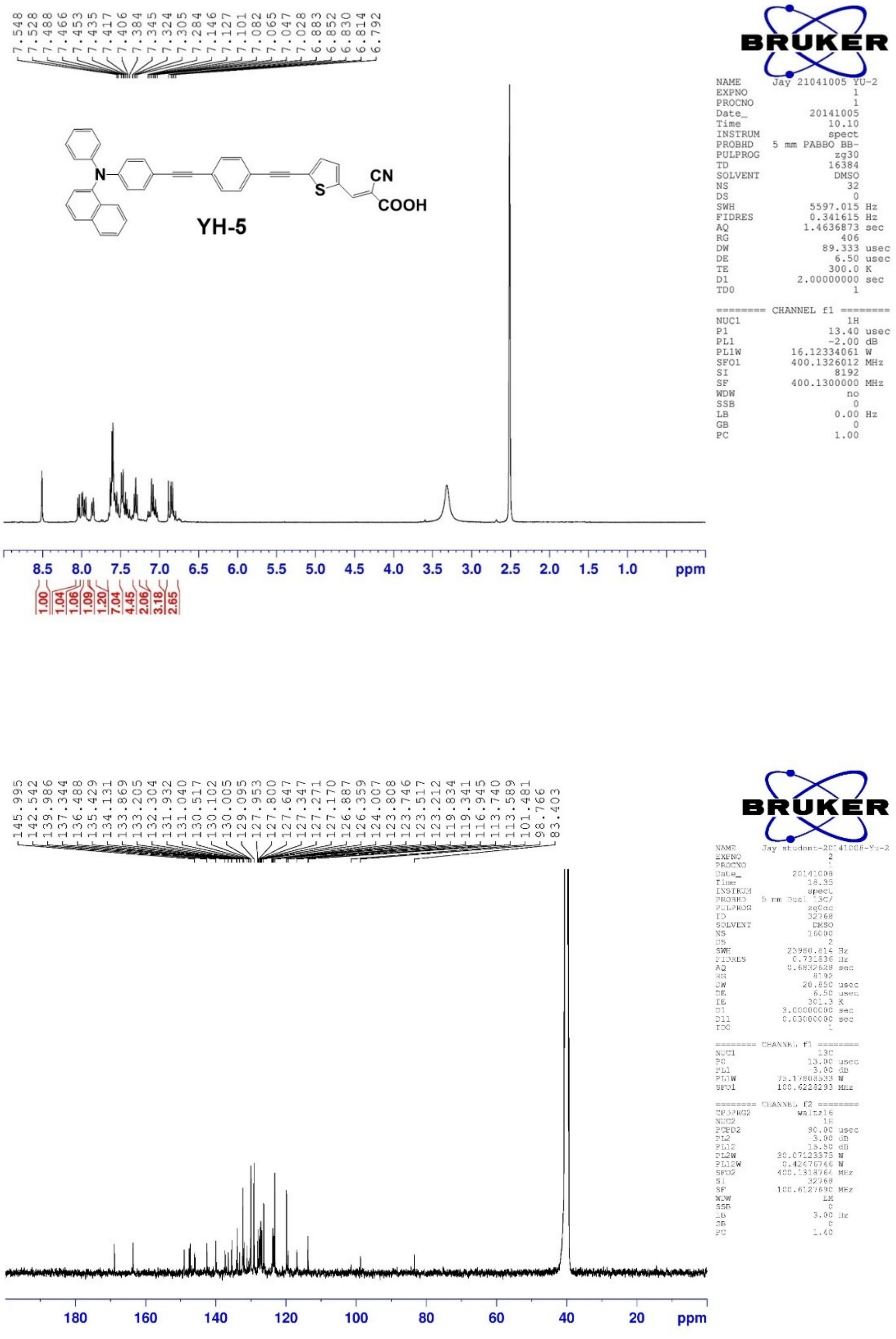
Fig. S19. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **YH-3** in DMSO-d_6.



```
NAME       20160224-Hsiang-F3
EXPNO                     1
PROCNO                    1
Date_              20160224
Time                  21.53
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    32768
SOLVENT                 THF
NS                       33
DS                        0
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                2.0447731 sec
RG                    122.8
DW                   62.400 usec
DE                    16.68 usec
TE                    300.0 K
D1               2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            400.1324008 MHz
NUC1                     1H
P1                    13.30 usec
SI                    16384
SF              400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00
```

```
NAME       20160224-Hsiang-F3-R4-C13
EXPNO                     1
PROCNO                    1
Date_              20160225
Time                  11.02
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG              zgpg30
TD                    32768
SOLVENT                 THF
NS                    15356
DS                        0
SWH               24038.461 Hz
FIDRES             0.733596 Hz
AQ                0.6816244 sec
RG                   205.92
DW                   20.800 usec
DE                     6.50 usec
TE                    300.0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            100.6233329 MHz
NUC1                    13C
P1                    10.00 usec
SI                    32768
SF              100.6127685 MHz
WDW                      EM
SSB                       0
LB                     2.00 Hz
GB                        0
PC                     1.00
```

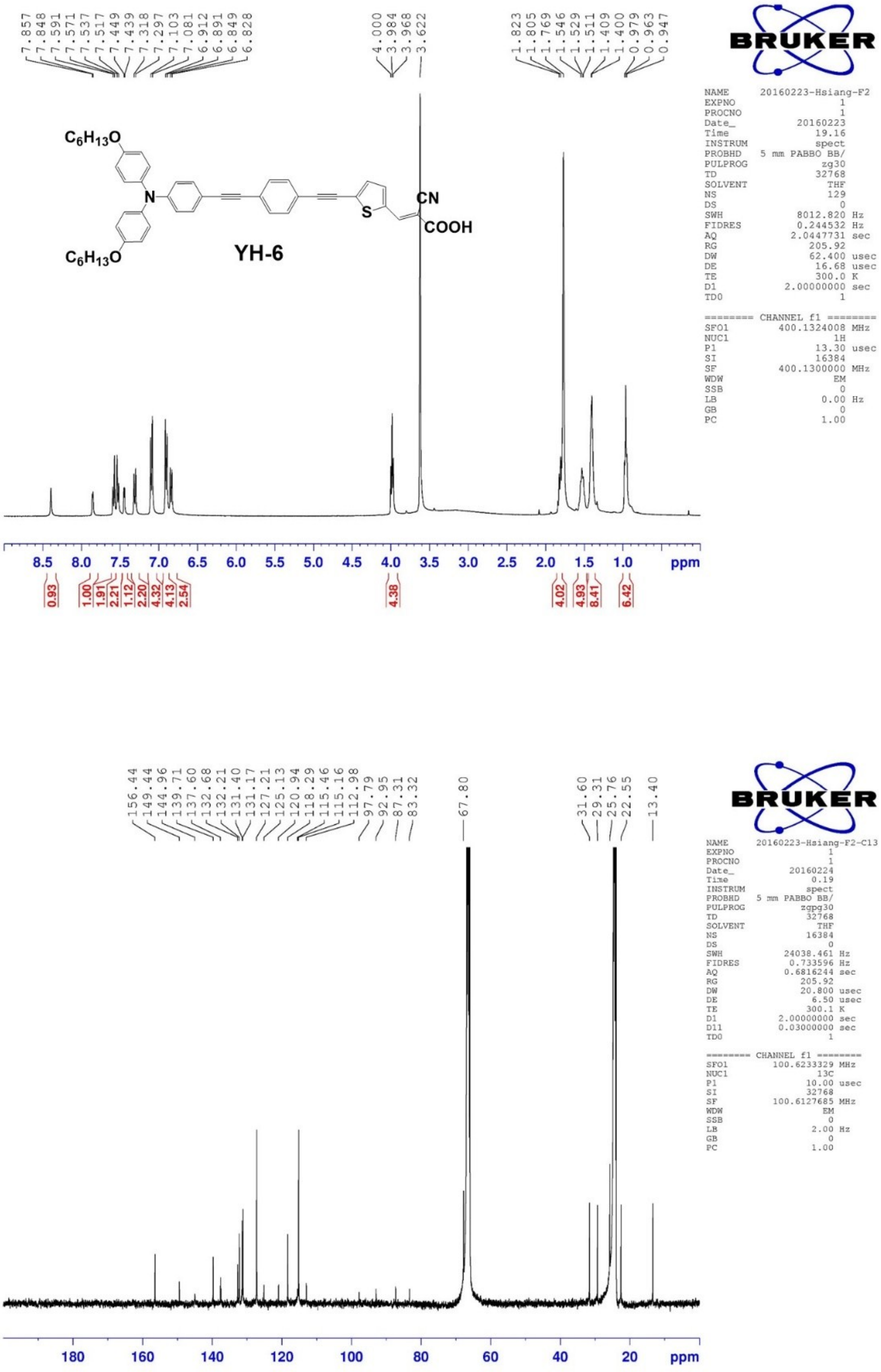
Fig. S20. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **YH-4** in THF-d_8.



```
NAME       Jay 21041005 YU-2
EXPNO                      1
PROCNO                     1
Date_               20141005
Time                   10.10
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     16384
SOLVENT                 DMSO
NS                        32
DS                         0
SWH                 5597.015 Hz
FIDRES              0.341615 Hz
AQ                 1.4636873 sec
RG                       406
DW                    89.333 usec
DE                      6.50 usec
TE                     300.0 K
D1                2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.40 usec
PL1                    -2.00 dB
PL1W             16.12334061 W
SFO1             400.1326012 MHz
SI                      8192
SF               400.1300000 MHz
WDW                       no
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.00
```

```
NAME       Jay student-20141008-Yu-2
EXPNO                      2
PROCNO                     1
Date_               20141008
Time                   18.35
INSTRUM                spect
PROBHD   5 mm Dual 13C/
PULPROG                zg0dc
TD                     32768
SOLVENT                 DMSO
NS                     16000
DS                         2
SWH                23980.814 Hz
FIDRES              0.731836 Hz
AQ                 0.6832628 sec
RG                      8192
DW                    20.850 usec
DE                      6.50 usec
TE                     301.3 K
D1                3.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P0                     13.00 usec
PL1                    -3.00 dB
PL1W             75.17808533 W
SFO1             100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  90.00 usec
PL2                    -3.00 dB
PL12                   15.50 dB
PL2W             30.07123375 W
PL12W             0.42476746 W
SFO2             400.1318764 MHz
SI                     32768
SF               100.6127690 MHz
WDW                       EM
SSB                        0
LB                      3.00 Hz
GB                         0
PC                      1.40
```

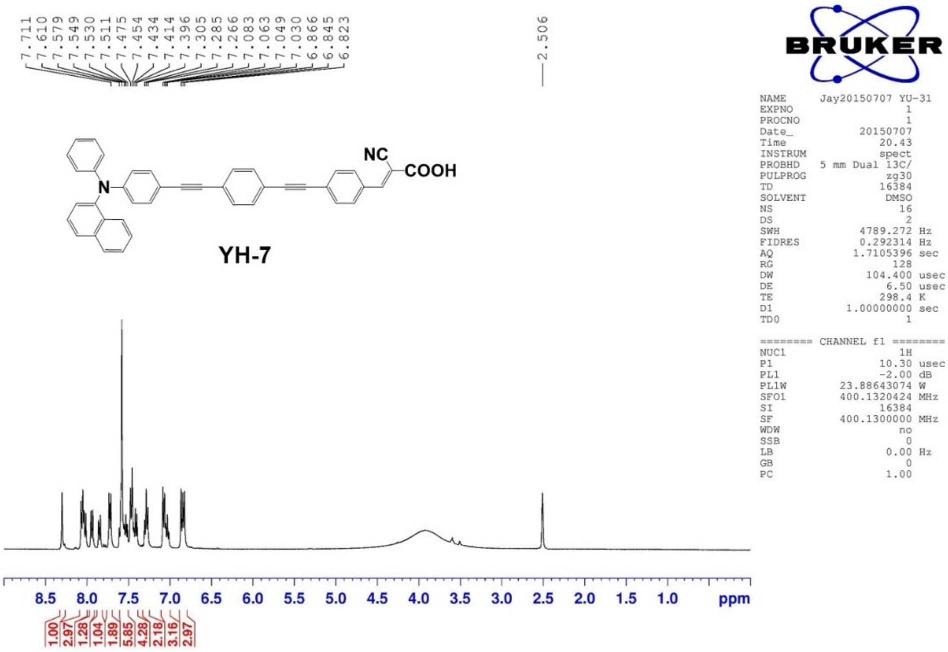
Fig. S21. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **YH-5** in DMSO-d_6.



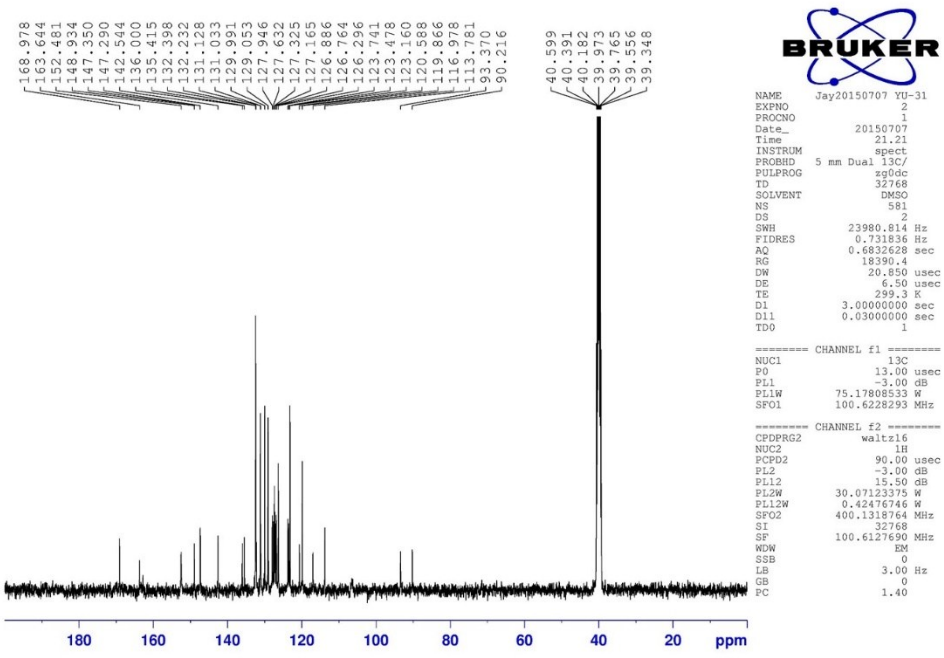
```
NAME       20160223-Hsiang-F2
EXPNO                       1
PROCNO                      1
Date_                20160223
Time                    19.16
INSTRUM                 spect
PROBHD     5 mm PABBO BB/
PULPROG                  zg30
TD                      32768
SOLVENT                   THF
NS                        129
DS                          0
SWH                  8012.820 Hz
FIDRES               0.244532 Hz
AQ                  2.0447731 sec
RG                     205.92
DW                     62.400 usec
DE                      16.68 usec
TE                      300.0 K
D1                 2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              400.1324008 MHz
NUC1                       1H
P1                      13.30 usec
SI                      16384
SF                400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.00
```

```
NAME       20160223-Hsiang-F2-C13
EXPNO                       1
PROCNO                      1
Date_                20160224
Time                     0.19
INSTRUM                 spect
PROBHD     5 mm PABBO BB/
PULPROG                zgpg30
TD                      32768
SOLVENT                   THF
NS                      16384
DS                          0
SWH                 24038.461 Hz
FIDRES               0.733596 Hz
AQ                  0.6816244 sec
RG                     205.92
DW                     20.800 usec
DE                       6.50 usec
TE                      300.1 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              100.6233329 MHz
NUC1                      13C
P1                      10.00 usec
SI                      32768
SF                100.6127685 MHz
WDW                        EM
SSB                         0
LB                       2.00 Hz
GB                          0
PC                       1.00
```

Fig. S22. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **YH-6** in THF-d_8.



```
NAME       Jay20150707 YU-31
EXPNO                      1
PROCNO                     1
Date_               20150707
Time                   20.43
INSTRUM                spect
PROBHD     5 mm Dual 13C/
PULPROG                 zg30
TD                     16384
SOLVENT                 DMSO
NS                        16
DS                         2
SWH                 4789.272 Hz
FIDRES              0.292314 Hz
AQ                 1.7105396 sec
RG                       128
DW                   104.400 usec
DE                      6.50 usec
TE                     298.4 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     10.30 usec
PL1                    -2.00 dB
PL1W             23.88643074 W
SFO1             400.1320424 MHz
SI                     16384
SF               400.1300000 MHz
WDW                       no
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.00
```



```
NAME       Jay20150707 YU-31
EXPNO                      2
PROCNO                     1
Date_               20150707
Time                   21.21
INSTRUM                spect
PROBHD     5 mm Dual 13C/
PULPROG                 zg0dc
TD                     32768
SOLVENT                 DMSO
NS                       581
DS                         2
SWH                23980.814 Hz
FIDRES              0.731836 Hz
AQ                 0.6832628 sec
RG                   18390.4
DW                    20.850 usec
DE                      6.50 usec
TE                     299.3 K
D1                3.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P0                     13.00 usec
PL1                    -3.00 dB
PL1W             75.17808533 W
SFO1             100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  90.00 usec
PL2                    -3.00 dB
PL12                   15.50 dB
PL2W             30.07123375 W
PL12W             0.42476746 W
SFO2             400.1318764 MHz
SI                     32768
SF               100.6127690 MHz
WDW                       EM
SSB                        0
LB                      3.00 Hz
GB                         0
PC                      1.40
```

Fig. S23. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **YH-7** in DMSO-d_6.

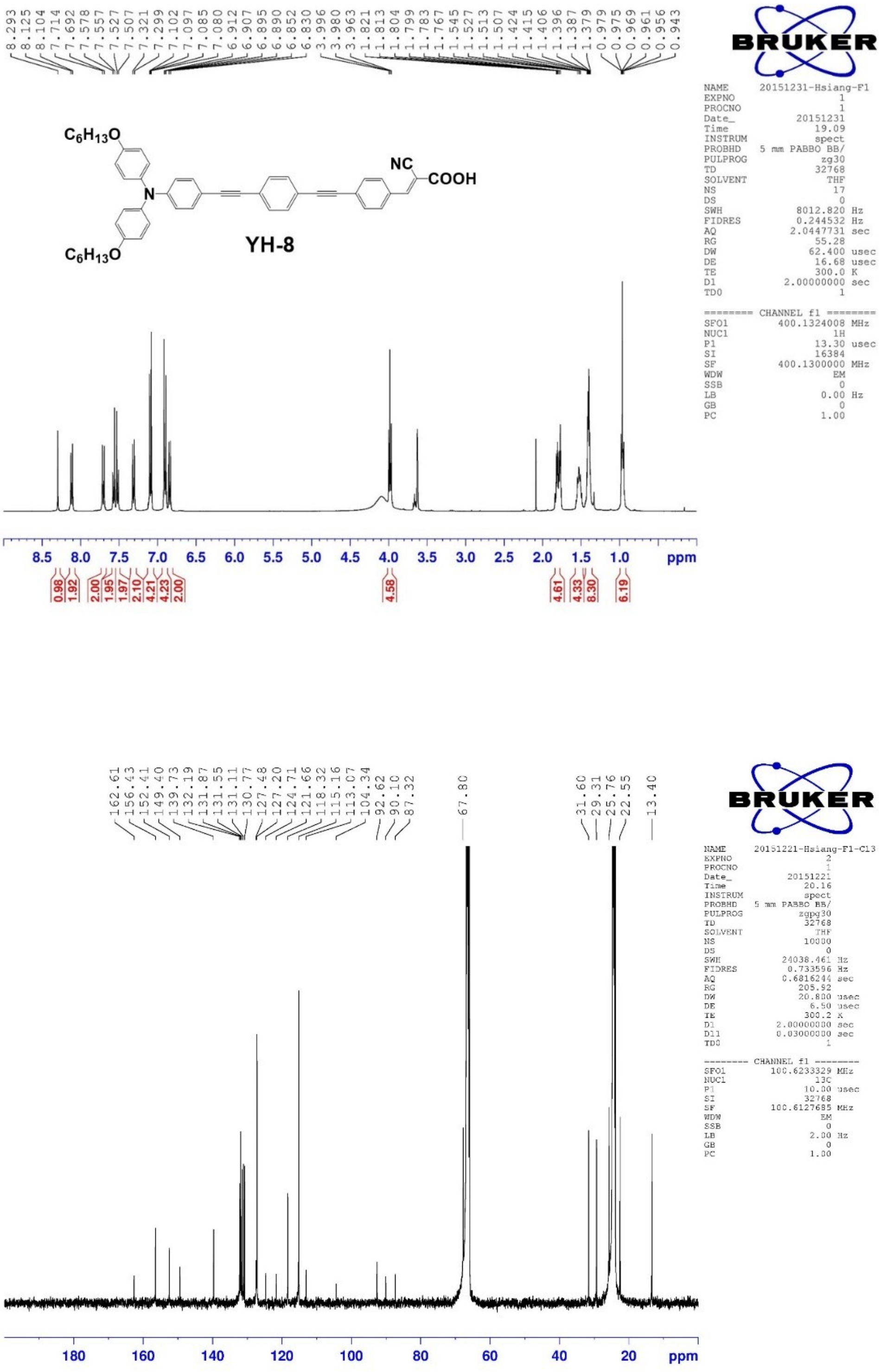
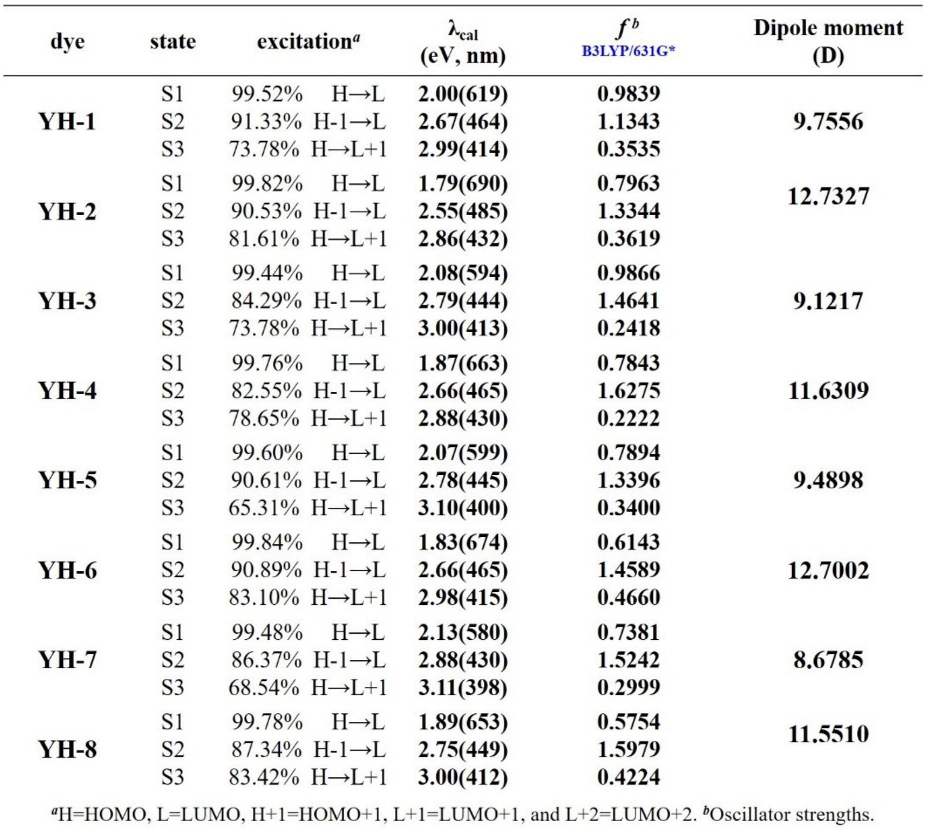


Fig. S24. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **YH-8** in THF-d_8.

3． Theoretical calculation

Table S1. Calculated Low-Lying Transition for **YH**-series dyes.



dye	state	excitation^a	λ_{cal} (eV, nm)	f^b B3LYP/631G*	Dipole moment (D)
YH-1	S1	99.52% H→L	**2.00(619)**	**0.9839**	**9.7556**
	S2	91.33% H-1→L	**2.67(464)**	**1.1343**	
	S3	73.78% H→L+1	**2.99(414)**	**0.3535**	
YH-2	S1	99.82% H→L	**1.79(690)**	**0.7963**	**12.7327**
	S2	90.53% H-1→L	**2.55(485)**	**1.3344**	
	S3	81.61% H→L+1	**2.86(432)**	**0.3619**	
YH-3	S1	99.44% H→L	**2.08(594)**	**0.9866**	**9.1217**
	S2	84.29% H-1→L	**2.79(444)**	**1.4641**	
	S3	73.78% H→L+1	**3.00(413)**	**0.2418**	
YH-4	S1	99.76% H→L	**1.87(663)**	**0.7843**	**11.6309**
	S2	82.55% H-1→L	**2.66(465)**	**1.6275**	
	S3	78.65% H→L+1	**2.88(430)**	**0.2222**	
YH-5	S1	99.60% H→L	**2.07(599)**	**0.7894**	**9.4898**
	S2	90.61% H-1→L	**2.78(445)**	**1.3396**	
	S3	65.31% H→L+1	**3.10(400)**	**0.3400**	
YH-6	S1	99.84% H→L	**1.83(674)**	**0.6143**	**12.7002**
	S2	90.89% H-1→L	**2.66(465)**	**1.4589**	
	S3	83.10% H→L+1	**2.98(415)**	**0.4660**	
YH-7	S1	99.48% H→L	**2.13(580)**	**0.7381**	**8.6785**
	S2	86.37% H-1→L	**2.88(430)**	**1.5242**	
	S3	68.54% H→L+1	**3.11(398)**	**0.2999**	
YH-8	S1	99.78% H→L	**1.89(653)**	**0.5754**	**11.5510**
	S2	87.34% H-1→L	**2.75(449)**	**1.5979**	
	S3	83.42% H→L+1	**3.00(412)**	**0.4224**	

^{a}H=HOMO, L=LUMO, H+1=HOMO+1, L+1=LUMO+1, and L+2=LUMO+2. ^{b}Oscillator strengths.

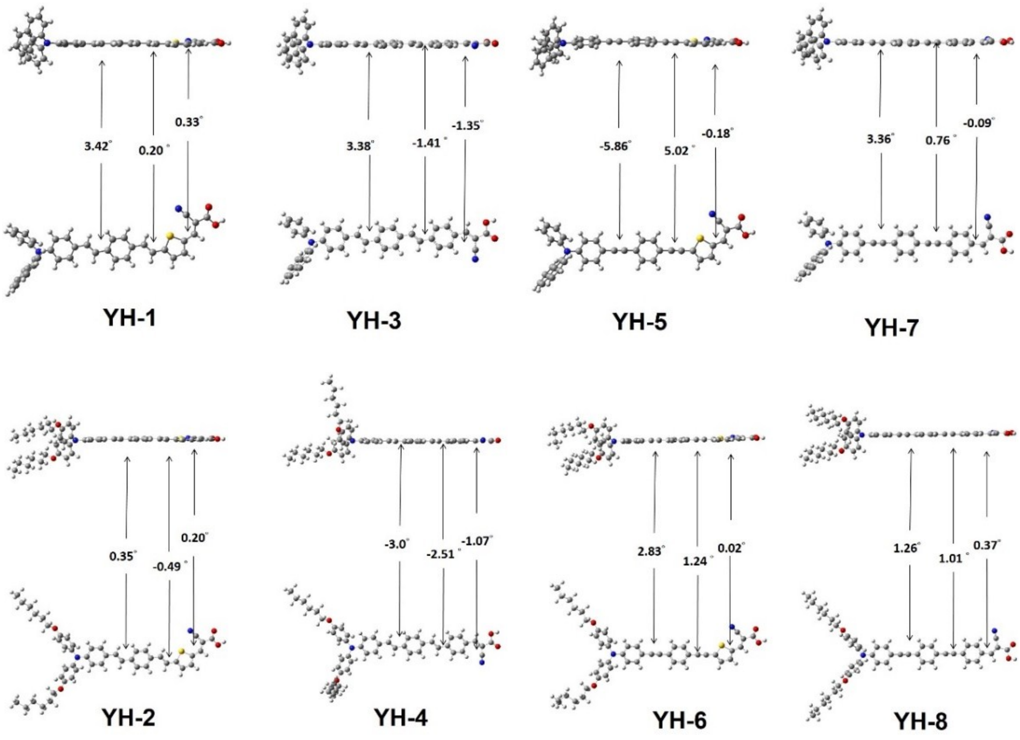


Fig. S25. Computed dihedral angles of **YH**-series dyes.

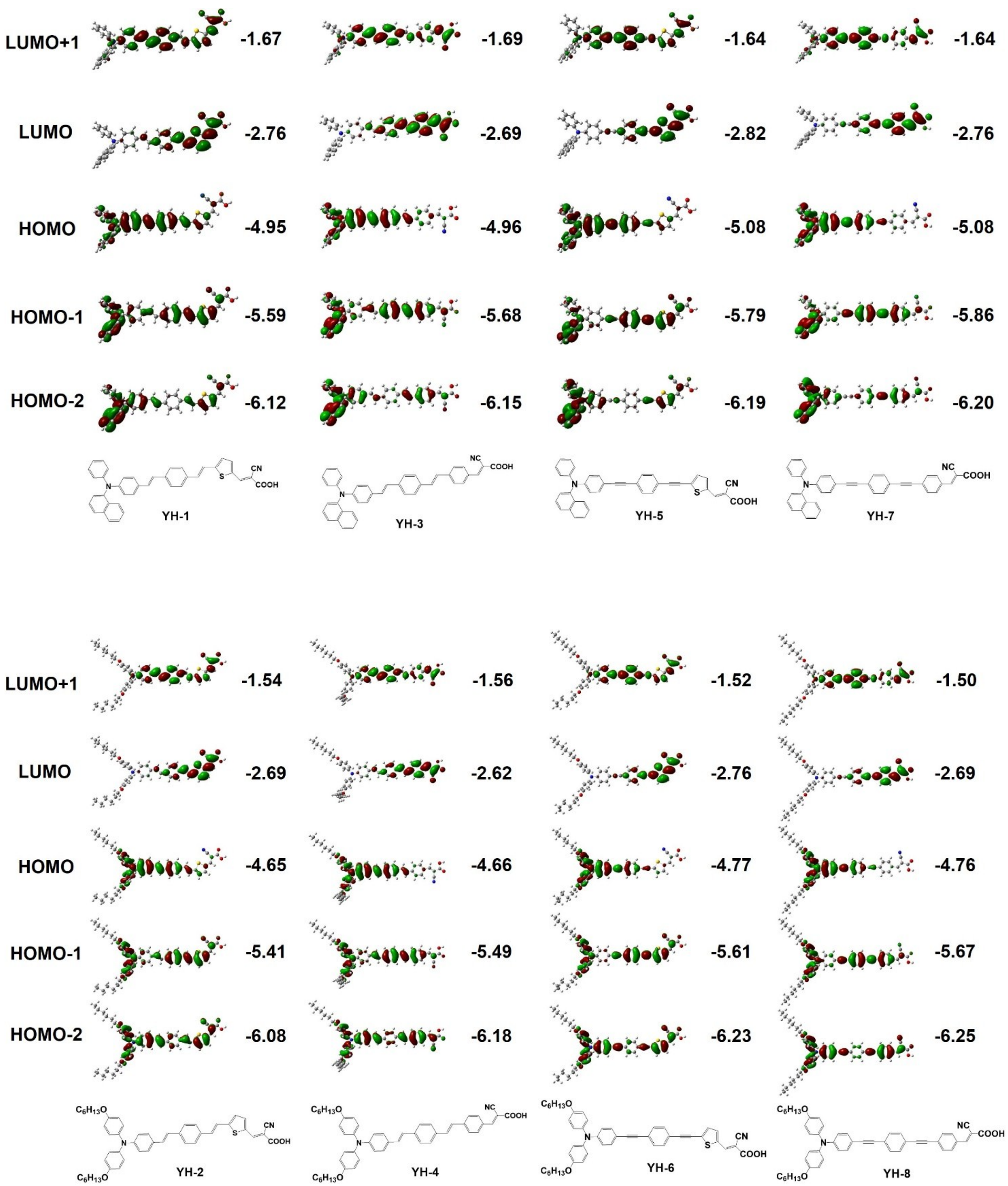


Fig. S26. Computed HOMO and LUMO energy levels and molecule orbitals of **YH**-series dyes.

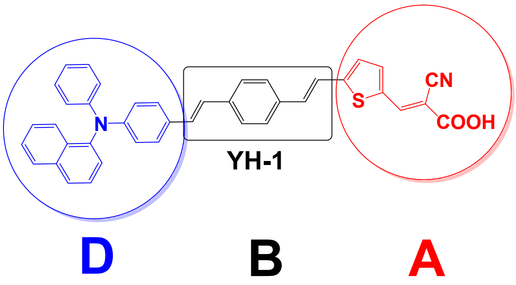


Table S2. Difference of Mulliken charges between ground state (S_0) and excited state (S_1), estimated by time dependent DFT/B3LYP model.

dye	state	D	B	A
YH-1	S_1	0.63989	-0.01959	-0.62030
	S_2	0.300726	0.090514	-0.39124
YH-2	S_1	0.7468	-0.09424	-0.65256
	S_2	0.286464	0.146166	-0.43263
YH-3	S_1	0.65280	0.00761	-0.66041
	S_2	0.339736	0.141904	-0.48164
YH-4	S_1	0.74532	-0.0513	-0.69402
	S_2	0.34298	0.16679	-0.50977
YH-5	S_1	0.657632	0.009228	-0.66686
	S_2	0.17948	0.17254	-0.35202
YH-6	S_1	0.799354	-0.056344	-0.74301
	S_2	0.284356	0.220314	-0.50467
YH-7	S_1	0.71855	0.03329	-0.75184
	S_2	0.322709	0.226131	-0.54884
YH-8	S_1	0.75998	-0.01996	-0.77994
	S_2	0.329854	0.259556	-0.58941

Difference of Mulliken charge between ground state and excited state.

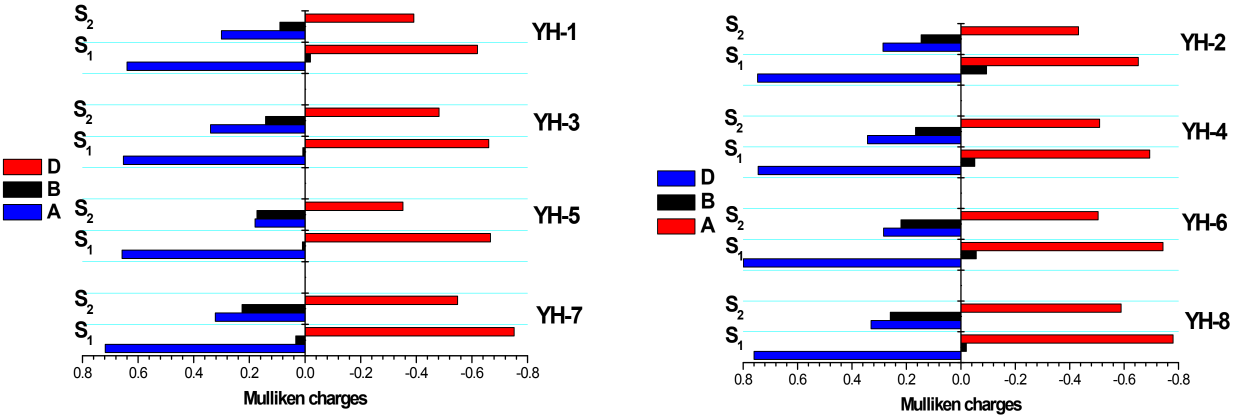


Fig. S27. Bar-chart plots foe the difference of Mulliken charge listed in Table S2.

4. CV spectra and HOMO-LUMO level

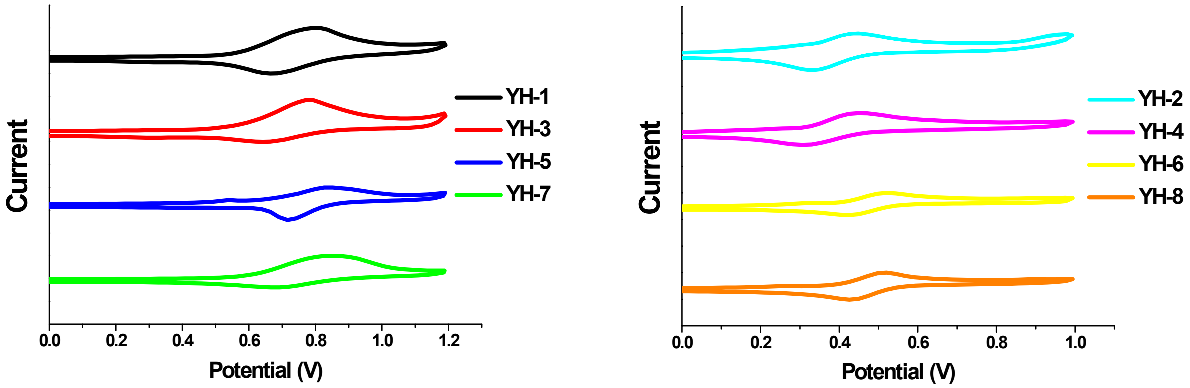


Fig. S28. Oxidative voltammograms of **YH**-series dyes.

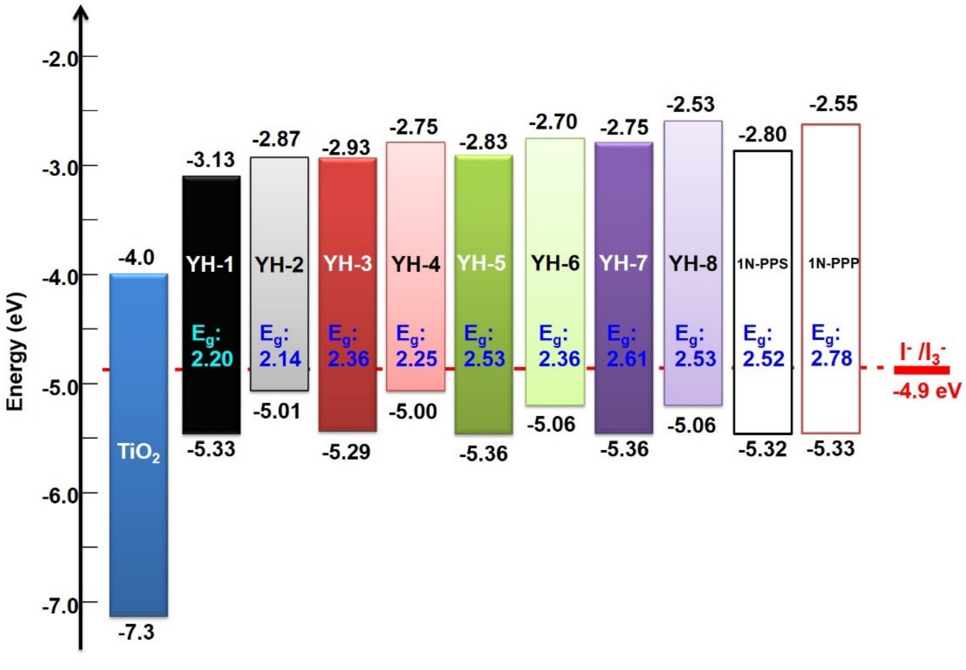


Fig. S29. HOMO - LUMO energy levels of **YH**-series dyes.

5. Improving efficiency of Photovoltaic parameters fabricated with /without DCA of YH-series dyes in DSSCs.

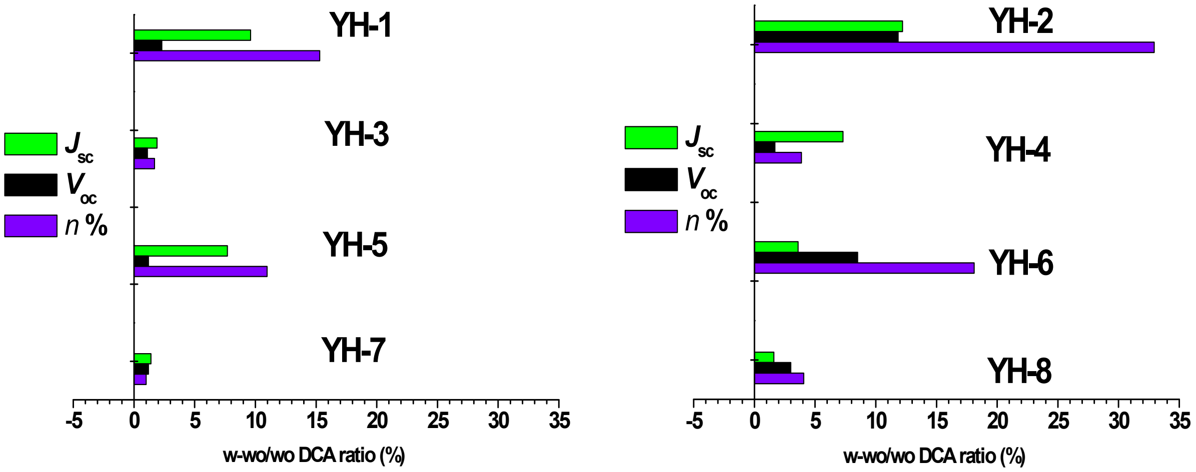


Fig. S30. Improving efficiency of Photovoltaic parameters fabricated with /without DCA of **YH**-series dyes in DSSCs.