Electronic supplementary information

Synthesis

2-acetyl-5-bromothiophene, *N,N*-dimethylaminobenzaldehyde, 5-Formyl-2-thienylboronic Acid, Dichlorobis(triphenylphosphine)palladium(II), cyanoacetic acid were purchased commercially without further purification. 4-(6-methylbenzothiazol-2-yl)phenylhydrazine was synthesized by Nippon Chemical Works. Solvents and other chemicals were used as received.

General procedure 1 for the preparation of **3a–c**

To a stirred solution of 2-acetyl-5-bromothiophene (1 mmol) and respective benzaldehyde (1 mmol) in EtOH (3 ml) was added 15 % NaOH aq (0.2 ml). The solution was stirred overnight and added small amount of water. The resulting precipitate was filtered and washed with water then EtOH. The crude solid was purified by recrystallization from EtOH or column chromatography on silica gel.

General procedure 2 for the preparation of **4a–c**

To a stirred solution of **3** (1 mmol) and 4-(6-methylbenzothiazol-2-yl)phenylhydrazine (1 mmol) in EtOH (6.5 ml) were added a few drops of 37 % HCl. The solution was refluxed overnight. The reaction mixture was cooled to room temperature and extracted with water/EtOAc. The organic layer was dried over $MgSO_4$ and evaporated. The crude solid was purified by recrystallization from EtOH/THF or column chromatography on silica gel.

General procedure 3 for the preparation of **5a–c**

4 (1 mmol), 5-Formyl-2-thienylboronic Acid (1.5 mmol), Cs_2CO_3 (2.5 mmol) and $PdCl_2(PPh_3)_2$ (0.01 mmol) were dissolved in THF (6 ml)/EtOH (3 ml) and refluxed overnight. After the reaction completed, the mixture was cooled to room temperature and extracted with water/EtOAc. The organic layer was dried over $MgSO_4$ and concentrated by evaporation. The crude product was purified by recrystallization or column chromatography on silica gel.

General procedure 4 for the preparation of the pyrazoline photosensitizers (**6a–c**)

5 (1 mmol), cyanoacetic acid (3 mmol), piperidine (3.3 mmol) were dissolved in CH_3CN and refluxed for . After the reaction completed, the mixture was cooled to room temperature and diluted with EtOAc, and then washed with HCl aq and water. The organic layer was dried over $MgSO_4$ and concentrated by evaporation. The crude product was purified by recrystallization.

Synthesis of compound **3a**

Compound **3a** was synthesized according the general procedure 1 and obtained as a yellow solid.

Yield 49 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (s, 6 H), 6.68 (d, J = 8.9 Hz, 2 H), 7.11 (d, J = 15.3 Hz, 1 H), 7.12 (d, J = 4.0 Hz, 1 H), 7.53 (d, J = 8.9 Hz, 2 H), 7.55 (d, J = 4.0 Hz, 1 H), 7.81 (d, J = 15.3 Hz, 1 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 40.1, 117.8, 115.0, 121.5, 122.2, 130.6, 130.8, 131.2, 145.5, 147.9, 152.2, 180.9. Elemental analysis calcd for $C_{15}H_{14}BrNOS$ (336.25): C 53.58, H 4.20, N 4.17, S 9.54; found: C 53.20, H 4.16, N 4.41, S 9.58.

Synthesis of compound **3b**

Compound **3b** was synthesized according the general procedure 1 and obtained as a yellow solid. Yield 81 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3 H), 1.35 (m, 4 H), 1.47 (m, 2 H), 1.80 (m, 2 H), 4.00 (t, J = 6.6 Hz 3 H), 6.92 (d, J = 8.8 Hz, 2 H), 7.14 (d, J = 4.0 Hz, 1 H), 7.19 (d, J = 15.5 Hz, 1 H), 7.58 (d, J = 4.0 Hz, 1 H), 7.58 (d, J = 8.7 Hz, 1 H), 7.81 (d, J = 15.4 Hz, 1 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 14.0, 22.6, 25.7, 29.1, 31.6, 68.2, 115.0, 117.9, 122.3, 127.0, 130.4, 131.3, 131.4, 144.6, 147.4, 161.6, 180.9. Elemental analysis calcd for $C_{19}H_{21}BrO_2S$ (393.34): C 58.02, H 5.38, S 8.15; found: C 57.9, H 5.40, S 7.29.

Synthesis of compound **3c**

Compound **3c** was synthesized by 2 steps. First, carboxyl functionalized chalcone was obtained according to the general procedure 1 using terephthaldehydic acid (Yield 68 %). Then esterification using EtBr with K_2CO_3 was carried out to afford **3c** as a white solid. Yield 88 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, J = 7.1 Hz, 3 H), 4.40 (q, J = 7.1 Hz, 6 H), 7.16 (d, J = 4.0 Hz, 1 H), 7.38 (d, J = 15.6 Hz, 1 H), 7.62 (d, J = 4.1 Hz, 1 H), 7.68 (d, J = 8.2 Hz, 2 H), 7.83 (d, J = 15.6 Hz, 1 H), 8.08 (d, J = 8.3 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 14.3, 61.3, 122.4, 123.4, 128.3, 130.1, 131.5, 132.1, 138.6, 143.1, 146.8, 165.9, 180.5. Elemental analysis calcd for $C_{16}H_{13}BrO_3S$ (365.24): C 52.61, H 3.59, S 8.78; found: C 52.24, H 3.58, S 8.91.

Synthesis of compound **3d**

Compound **3d** was synthesized according the general procedure 1 and obtained as a yellow solid. Yield 39 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 4.0 Hz, 1 H), 7.33 (d, J = 15.6 Hz, 1 H), 7.43 (m, 3 H), 7.60 (d, J = 4.0 Hz, 1 H), 7.64 (m, 2 H), 7.85 (d, J = 15.6 Hz, 1 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 120.5, 122.9, 128.5, 129.0, 131.4, 131.8, 134.5, 144.7, 147.1, 180.9. Elemental analysis calcd for $C_{13}H_9BrOS$ (291.96): C 53.26, H 3.09, S 10.94; found: C 52.90, H 3.26, S 13.23.

Synthesis of compound **4a**

Compound **4a** was synthesized according the general procedure 2 and obtained as an orange solid. Yield 99 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.43 (s, 3 H), 2.84 (s, 6 H), 3.13 (dd, J = 17.4, 5.1 Hz,

1 H), 3.88 (dd, J = 17.4, 11.9 Hz, 1 H), 5.55 (dd, J = 11.9, 5.1 Hz, 1 H), 6.68 (d, J = 8.9 Hz, 2 H), 7.06 (d, J = 8.9 Hz, 2 H), 7.07 (d, J = 8.8 Hz, 2 H), 7.15 (d, J = 3.9 Hz, 1 H), 7.26 (d, J = 4.0 Hz, 1 H), 7.28 (d, J = 8.8 Hz, 1 H), 7.81 (br, 2 H), 7.84 (d, J = 8.9 Hz, 2 H). ^{13}C NMR (400 MHz, DMSO) δ 20.9, 43.1, 62.4, 112.6, 113.0, 113.2, 121.5, 121.6, 123.0, 126.4, 127.7, 128.1, 128.4, 128.6, 131.2, 134.0, 134.3, 137.0, 144.8, 145.3, 149.8, 151.8, 166.2. HRMS (ESI, m/z): $[M + H]^+$ calcd for $C_{38}H_{28}N_4O_4S_3$, 573.0777; found, 573.0760.

Synthesis of compound **4b**

Compound **4b** was synthesized according the general procedure 2 and obtained as a yellow solid. Yield 85 %. ^{1}H NMR (400 MHz, acetone-d_6) δ 0.87 (t, J = 7.0 Hz, 3 H), 1.33 (m, 4 H), 1.45 (m, 2 H), 1.73 (m, 2 H), 2.45 (s, 1 H), 3.20 (dd, J = 17.3, 5.7 Hz, 1 H), 3.96 (t, J = 6.5, 2 H), 4.00 (dd, J = 17.4, 12.1 Hz, 1 H), 5.60 (dd, J = 12.1, 5.7 Hz, 1 H), 6.92 (d, J = 8.8 Hz, 2 H), 7.08 (d, J = 3.9 Hz, 1 H), 7.14 (d, J = 8.9 Hz, 2 H), 7.17 (d, J = 3.9 Hz, 1 H), 7.26 (d, J = 8.7 Hz, 2 H), 7.28 (br, 1 H), 7.77 (br, 1 H), 7.78 (d, J = 8.3 Hz, 1 H), 7.90 (d, J = 9.0 Hz, 2 H). ^{13}C NMR (400 MHz, $(CD_3)CO$) δ 14.3, 21.4, 23.3, 26.4, 32.3, 44.2, 64.1, 68.6, 114.1, 114.3, 115.9, 122.2, 122.8, 125.1, 128.0, 128.5, 128.7, 129.1, 131.9, 134.4, 135.5, 135.6, 138.9, 145.4, 146.9, 153.5, 159.8, 167.4. Elemental analysis calcd for $C_{33}H_{32}BrN_3OS_2$ (630.66): C 62.85, H 5.11, N 6.66, S 10.17; found: C 63.21, H 5.12, N 6.90, S 9.63.

Synthesis of compound **4c**

Compound **4c** was synthesized according the general procedure 2 and obtained as a yellow solid. Yield 52 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3 H), 1.37 (t, J = 7.1 Hz, 3 H), 2.46 (s, 3 H), 3.11 (dd, J = 17.3, 5.7 Hz, 1 H), 3.85 (dd, J = 16.9, 12.4 Hz, 1 H), 4.36 (q, J = 7.1, 2 H), 5.41 (dd, J = 12.3, 6.3 Hz, 1 H), 6.78 (d, J = 3.8 Hz, 1 H), 6.98 (d, J = 3.9 Hz, 1 H), 7.01 (d, J = 8.9 Hz, 2 H), 7.24 (d, J = 8.4 Hz, 1 H), 7.35 (d, J = 8.3 Hz, 2 H), 7.62 (s, 1 H), 7.85 (d, J = 8.3 Hz, 1 H), 7.86 (d, J = 8.9 Hz, 2 H), 8.03 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 14.3, 21.5, 43.4, 61.1, 63.7, 113.3, 114.8, 121.2, 122.0, 124.9, 125.8, 126.6, 127.6, 128.5, 130.3, 130.4, 130.7, 134.6, 134.8, 137.4, 143.3, 145.4, 146.1, 152.4, 166.0, 167.1. Elemental analysis calcd for $C_{30}H_{24}BrN_3O_2S_2$ (602.56): C 59.80, H 4.01, N 6.97, S 10.64; found: C 59.51, H 4.08, N 7.29, S 10.55.

Synthesis of compound **4d**

Compound **4d** was synthesized according the general procedure 2 and obtained as a yellow solid. Yield 28 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3 H), 3.13 (dd, J = 16.9, 6.2 Hz, 1 H), 3.84 (dd, J = 16.9, 12.3 Hz, 1 H), 5.38 (dd, J = 12.3, 6.2 Hz, 1 H), 6.78 (d, J = 3.9 Hz, 1 H), 6.98 (d, J = 3.9 Hz, 1 H), 7.05 (d, J = 8.9, 2H), 7.23 (m, 6 H), 7.62 (s, 1 H), 7.84 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 8.9 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 20.9, 43.0, 62.6, 112.9, 113.4, 121.5, 121.6, 123.3, 125.6,

127.6, 128.2, 128.8, 129.1, 131.2, 134.0, 134.3, 136.7, 141.3, 144.8, 145.2, 151.8, 166.1. Elemental analysis calcd for $C_{27}H_{20}BrN_3S_2$ (529.03): C 61.13, H 3.80, N 7.92, S 12.09; found: C 61.53, H 4.22, N 7.73, S 11.59.

Synthesis of compound **5a**

Compound **5a** was synthesized according the general procedure 3 and obtained as a yellow solid. Yield 86 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.43 (s, 3 H), 2.84 (s, 6 H), 3.18 (dd, J = 17.3, 4.9 Hz, 1 H), 3.93 (dd, J = 17.3, 12.0 Hz, 1 H), 5.60 (dd, J = 11.9, 4.9 Hz, 1 H), 6.69 (d, J = 8.8 Hz, 2 H), 7.09 (d, J = 8.5 Hz, 2 H), 7.11 (d, J = 8.6 Hz, 2 H), 7.29 (d, J = 8.4 Hz, 1 H), 7.34 (d, J = 3.8 Hz, 1 H), 7.62 (d, J = 3.9 Hz, 1 H), 7.65 (d, J = 3.9 Hz, 1 H), 7.82 (d, J = 8.4 Hz, 2 H), 7.86 (d, J = 8.9 Hz, 2 H), 8.03 (d, J = 4.0 Hz, 1 H), 9.91 (s, 1 H). ^{13}C NMR (400 MHz, DMSO) δ 20.9, 43.1, 62.6, 112.6, 113.1, 121.5, 121.6, 123.2, 125.8, 126.4, 127.5, 127.7, 128.1, 128.4, 129.3, 134.0, 134.3, 135.8, 136.6, 139.2, 141.5, 144.8, 145.1, 149.8, 151.8, 166.1, 183.8. Elemental analysis calcd for $C_{34}H_{28}N_4OS_3$ (604.81): C 67.52, H 4.67, N 9.26, S 15.91; found: C 67.56, H 4.70, N 9.19, S 14.98.

Synthesis of compound **5b**

Compound **5b** was synthesized according the general procedure 3 and obtained as an orange solid. This compound was used for next step without further purification. ^{1}H NMR (400 MHz, acetone-d_6) δ 0.88 (t, J = 6.9 Hz, 3 H), 1.33 (m, 4 H), 1.45 (m, 2 H), 1.74 (m, 2 H), 2.46 (s, 3 H), 3.24 (dd, J = 17.1, 5.6 Hz, 1 H), 3.95 (t, J = 6.5, 2 H), 4.04 (dd, J = 17.1, 12.1 Hz, 1 H), 5.62 (dd, J = 12.0, 5.6 Hz, 1 H), 6.91 (d, J = 8.6 Hz, 2 H), 7.17 (d, J = 8.8 Hz, 2 H), 7.27 (m, 4 H), 7.48 (d, J = 3.8 Hz, 1 H), 7.53 (d, J = 4.0 Hz, 1 H), 7.75, (s, 1 H), 7.80 (d, J = 8.3 Hz, 1 H), 7.93 (m, 4 H), 9.94 (s, 1 H). ^{13}C NMR (400 MHz, $(CD_3)CO$) δ 14.2, 21.4, 23.2, 26.3, 32.2, 44.2, 64.2, 68.4, 114.1, 115.8, 122.1, 122.7, 125.1, 125.9, 127.6, 127.8, 128.3, 129.0, 134.1, 135.3, 135.5, 137.4, 138.2, 138.9, 143.1, 145.2, 146.3, 146.5, 153.3, 160.0, 167.3, 183.5.

Synthesis of compound **5c**

Compound **5c** was synthesized according the general procedure 3 and obtained as an orange solid. Yield 72 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.28 (t, J = 7.1 Hz, 3 H), 2.43 (s, 3 H), 3.27 (dd, J = 17.5, 5.3 Hz, 1 H), 4.05 (dd, J = 17.5, 12.3 Hz, 1 H), 4.29 (q, J = 7.1, 2 H), 5.84 (dd, J = 12.2, 5.3 Hz, 1 H), 7.07 (d, J = 8.8 Hz, 2 H), 7.29 (d, J = 8.4 Hz, 1 H), 7.35 (d, J = 3.8 Hz, 1 H), 7.45 (d, J = 8.3 Hz, 2 H), 7.62 (d, J = 4.0 Hz, 1 H), 7.66 (d, J = 3.9 Hz, 1 H), 7.82 (d, J = 8.7 Hz, 2 H), 7.88 (d, J = 8.9 Hz, 2 H), 7.97 (d, J = 8.3 Hz, 2 H), 8.04 (d, J = 4.0 Hz, 1 H), 9.91 (s, 1 H). ^{13}C NMR (400 MHz, DMSO) δ 14.1, 20.9, 42.8, 60.6, 62.5, 113.0, 121.5, 121.6, 123.6, 125.9, 126.1, 127.5, 127.7, 128.3, 129.3, 129.7, 130.0, 134.0, 134.4, 136.1, 136.2, 139.2, 141.7, 144.7, 144.8, 145.0, 146.5, 151.8, 165.2, 166.0, 183.8. Elemental analysis calcd for $C_{35}H_{27}N_3O_3S_3$ (633.80): C 66.33, H 4.29, N 6.63, S

15.18; found: C 66.00, H 4.30, N 6.75, S 14.77.

Synthesis of compound **5d**

Compound **5d** was synthesized according the general procedure 3 and obtained as an orange solid. This compound was used for next step without further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.43 (s, 3 H), 3.24 (dd, J = 17.4, 5.1 Hz, 1 H), 4.01 (dd, J = 17.4, 12.1 Hz, 1 H), 5.74 (dd, J = 12.1, 5.1 Hz, 1 H), 7.09 (d, J = 8.9 Hz, 2 H), 7.27 (m, 4 H), 7.35 (d, J = 3.9 Hz, 1 H), 7.38 (m, 2 H), 7.61 (d, J = 3.9 Hz, 1 H), 7.65, (d, J = 3.9 Hz, 1 H), 7.81 (m, 2H), 7.87 (d, J = 9.0 Hz, 2 H), 8.03 (d, J = 4.0, 1 H), 9.91 (s, 1 H). ^{13}C NMR (400 MHz, DMSO) δ 20.9, 43.1, 62.8, 113.0, 121.5, 121.6, 123.4, 125.6, 125.9, 127.5, 127.7, 128.2, 129.1, 129.5, 134.0, 134.3, 136.0, 136.3, 139.1, 141.3, 141.6, 144.8, 144.9, 145.0, 151.8, 166.1, 183.8.

Synthesis of compound **6a**

Compound **6a** was synthesized according the general procedure 4 and obtained as a dark red solid. Yield 79 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.43 (s, 3 H), 2.85 (s, 6 H), 3.19 (dd, J = 17.3, 5.0 Hz, 1 H), 3.94 (dd, J = 17.3, 12.0 Hz, 1 H), 5.61 (dd, J = 12.0, 5.0 Hz, 1 H), 6.69 (d, J = 8.9 Hz, 2 H), 7.11 (dd, J = 9.0 Hz, 4 H), 7.29 (d, J = 8.3 Hz, 1 H), 7.35 (d, J = 3.8 Hz, 1 H), 7.61 (d, J = 3.9 Hz, 1 H), 7.68 (d, J = 4.0 Hz, 1 H), 7.82 (m, 2 H), 7.86 (d, J = 9.0 Hz, 2 H), 7.98 (d, J = 4.1 Hz, 1 H), 8.48 (s, 1 H). ^{13}C NMR (400 MHz, DMSO) δ 20.9, 43.1, 62.6, 112.7, 113.2, 121.5, 121.6, 123.2, 126.4, 127.4, 127.7, 128.1, 128.4, 129.4, 131.0, 134.3, 135.7, 136.7, 144.8, 145.0, 149.8, 151.8, 163.3, 166.1. HRMS (ESI, m/z): $[M - H]^-$ calcd for $C_{37}H_{29}N_5O_2S_3$, 670.1411; found, 670.1405.

Synthesis of compound **6b**

Compound **6b** was synthesized according the general procedure 4 and obtained as a dark red solid. Yield 91 %. ^{1}H NMR (400 MHz, acetone-d_6) δ 0.84 (t, J = 6.7 Hz, 3 H), 1.27 (m, 4 H), 1.36 (m, 2 H), 1.66 (m, 2 H), 2.43 (s, 3 H), 3.20 (dd, J = 17.4, 4.7 Hz, 1 H), 3.90 (t, J = 6.5, 2 H), 3.96 (m, 1 H), 5.67 (dd, J = 11.3, 3.8 Hz, 1 H), 6.90 (d, J = 8.5 Hz, 2 H), 7.10 (d, J = 8.6 Hz, 2 H), 7.19 (d, J = 8.5 Hz, 2 H), 7.29 (d, J = 8.3 Hz, 1 H), 7.35 (br, 1 H), 7.61, (d, J = 3.7 Hz, 1 H), 7.69 (d, J = 4.0 Hz, 1 H), 7.82 (m, 2 H), 8.00 (d, J = 4.1 Hz, 1 H), 8.51 (s, 1 H). ^{13}C NMR (400 MHz, $(CD_3)CO$) δ 14.2, 21.4, 23.2, 26.3, 32.2, 44.2, 64.2, 68.4, 114.1, 115.8, 122.7, 125.1, 125.9, 127.6, 127.8, 128.3, 129.0, 129.2, 134.1, 135.3, 135.5, 137.4, 138.2, 143.1, 145.2, 146.3, 146.5, 153.3, 159.7, 167.3, 183.5. HRMS (ESI, m/z): $[M - H]^-$ calcd for $C_{41}H_{36}N_4O_3S_3$, 727.1877; found, 727.1869.

Synthesis of compound **6c**

Compound **6c** was synthesized according the general procedure 4 and obtained as a dark red solid. Yield 75 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.28 (t, J = 7.1 Hz, 3 H), 2.43 (s, 3 H), 3.27 (dd, J =

17.5, 5.3 Hz, 1 H), 4.04 (dd, *J* = 17.4, 12.3 Hz, 1 H), 4.29 (q, *J* = 7.1, 2 H), 5.84 (dd, *J* = 12.2, 5.4 Hz, 1 H), 7.08 (d, *J* = 8.9 Hz, 2 H), 7.29 (d, *J* = 8.4 Hz, 1 H), 7.36 (d, *J* = 3.8 Hz, 1 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 3.9 Hz, 1 H), 7.69 (d, *J* = 4.0 Hz, 1 H), 7.82 (m, 2 H), 7.87 (d, *J* = 9.0 Hz, 2 H), 7.97 (d, *J* = 8.5 Hz, 2 H), 8.00 (d, *J* = 4.3 Hz, 1 H), 8.49 (s, 1 H). ^{13}C NMR (400 MHz, DMSO) δ 14.1, 20.9, 60.6, 62.6, 113.1, 116.6, 121.5, 121.6, 123.6, 125.7, 126.2, 127.4, 127.7, 128.3, 129.3, 129.8, 130.0, 134.0, 134.4, 134.6, 136.0, 136.2, 144.8, 146.5, 151.8, 163.4, 165.2, 166.0. HRMS (ESI, m/z): $[M - H]^-$ calcd for $C_{38}H_{28}N_4O_4S_3$, 699.1200; found, 669.1199.

Synthesis of compound **6d**

Compound **6d** was synthesized according the general procedure 4 and obtained as a dark red solid. Yield 69 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.43 (s, 3 H), 3.24 (dd, *J* = 17.4, 5.2 Hz, 1 H), 4.00 (dd, *J* = 17.4, 12.1 Hz, 1 H), 5.74 (dd, *J* = 12.1, 5.1 Hz, 1 H), 7.10 (d, *J* = 8.9 Hz, 2 H), 7.28 (m, 4 H), 7.35 (m, 3 H), 7.61 (d, *J* = 3.9 Hz, 1 H), 7.69, (d, *J* = 4.0 Hz, 1 H), 7.81 (m, 2H), 7.87 (d, *J* = 9.0 Hz, 2 H), 8.00 (d, *J* = 4.4, 1 H), 8.51 (s, 1 H). ^{13}C NMR (400 MHz, DMSO) δ 20.9, 43.0, , 113.0, 121.5, 121.6, 125.6, 127.7, 128.2, 129.1, 129.6, 134.0, 134.3, 141.3, 145.0, 151.8, 166.1. Elemental analysis calcd for $C_{35}H_{24}N_4O_2S_3$ (628.11): C 66.85, H 3.85, N 8.91; found: C 66.97, H 4.16, N 8.60.

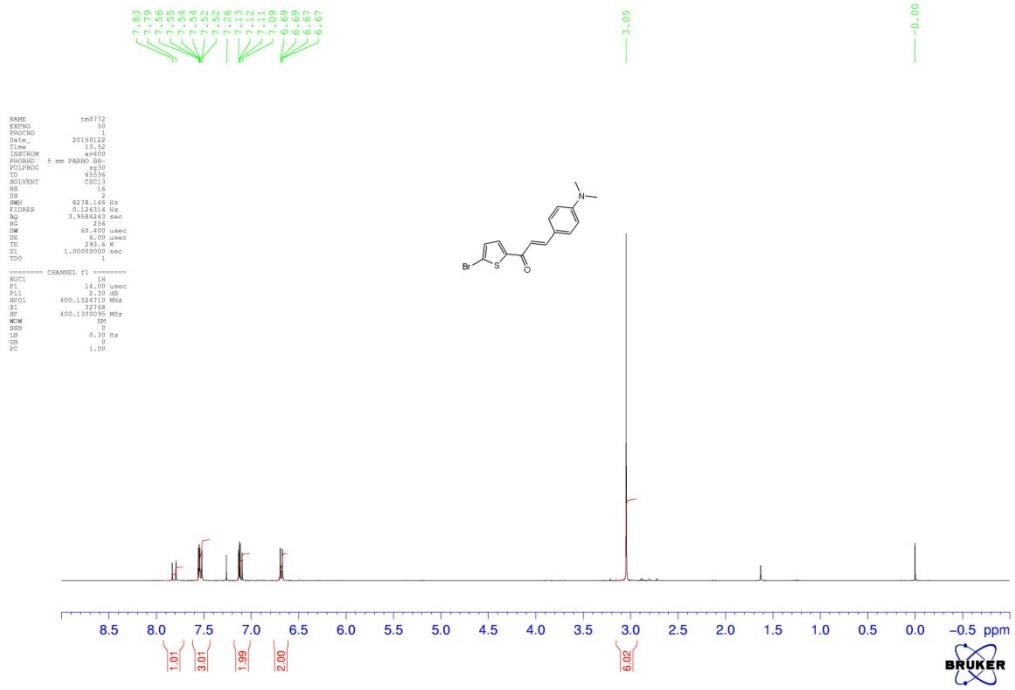

Figure S1. H^1 NMR spectra of **3a**.

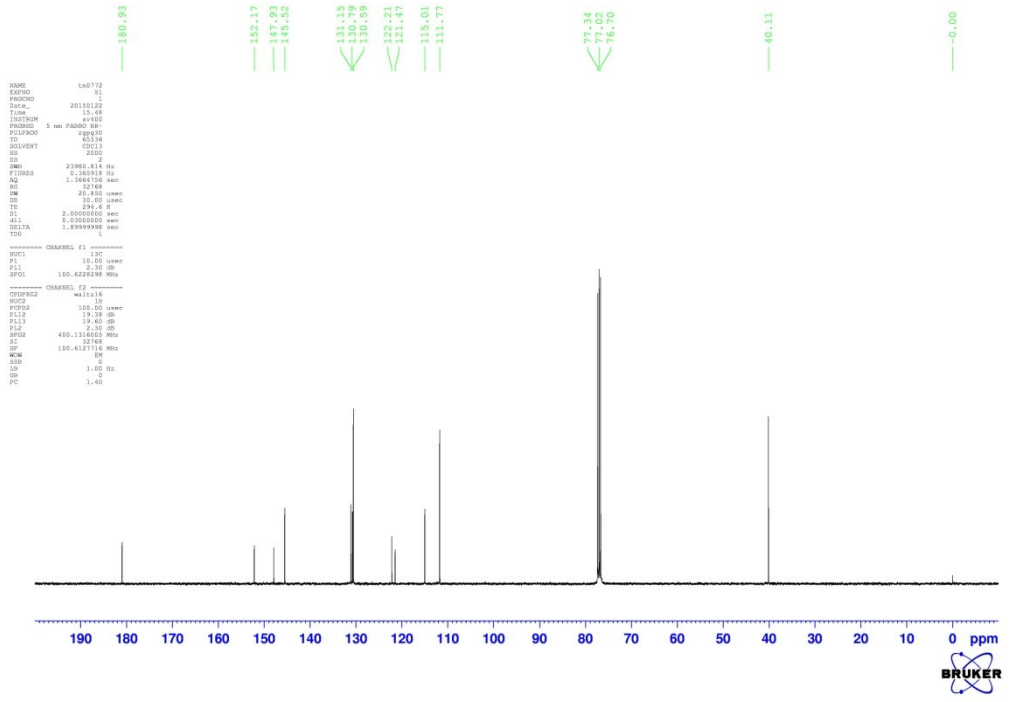

Figure S2. C^{13} NMR spectra of **3a**.

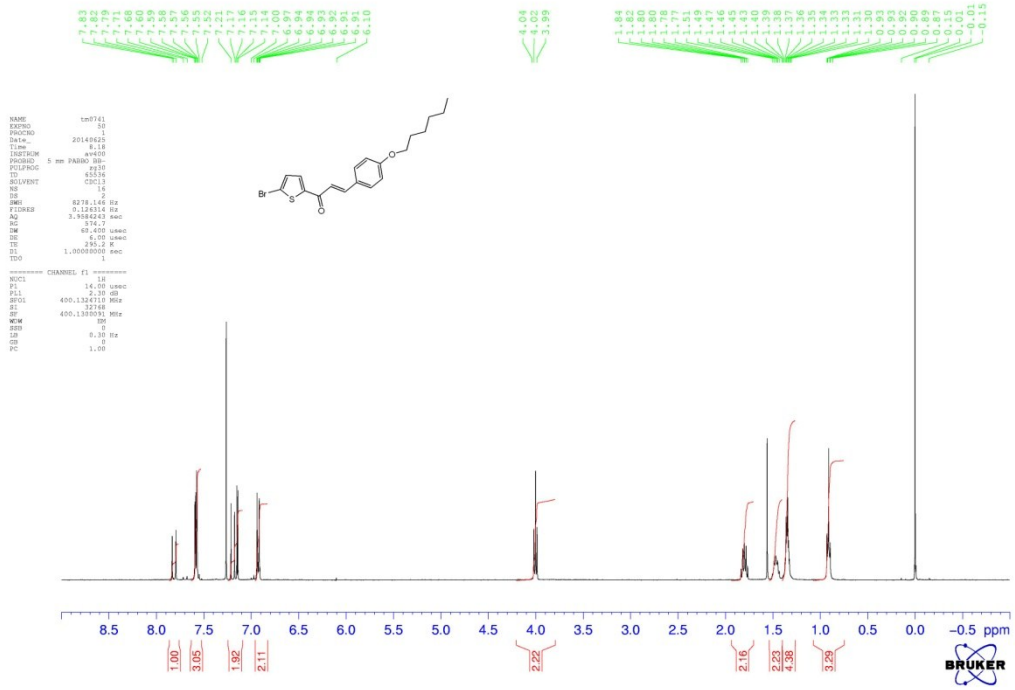

Figure S3. H^1 NMR spectra of **3b**.

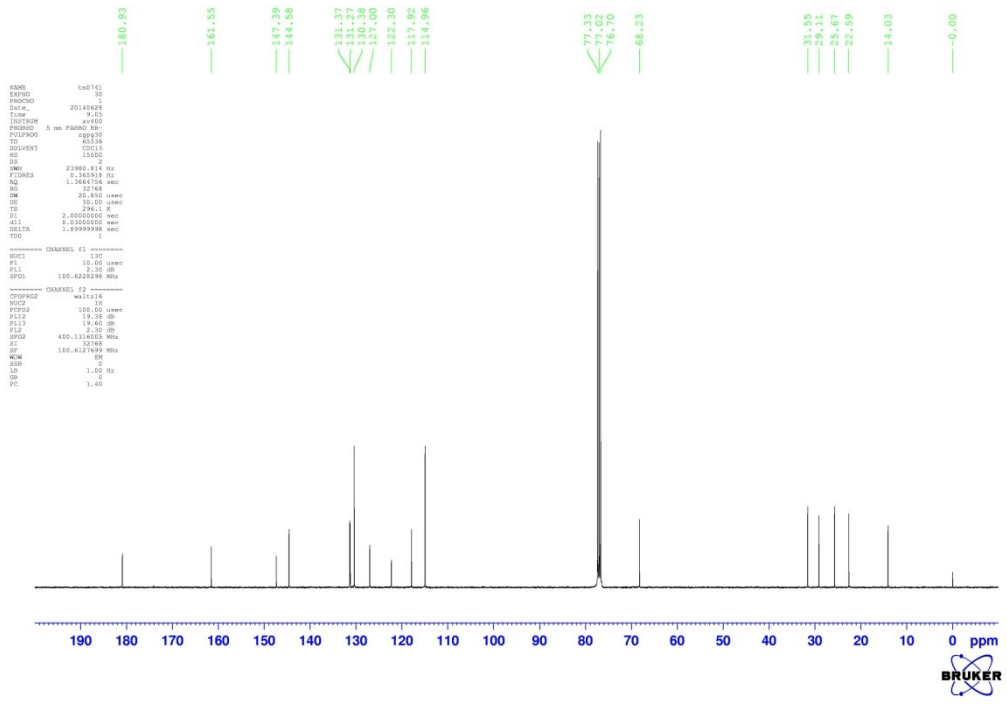

Figure S4. C^{13} NMR spectra of **3b**.

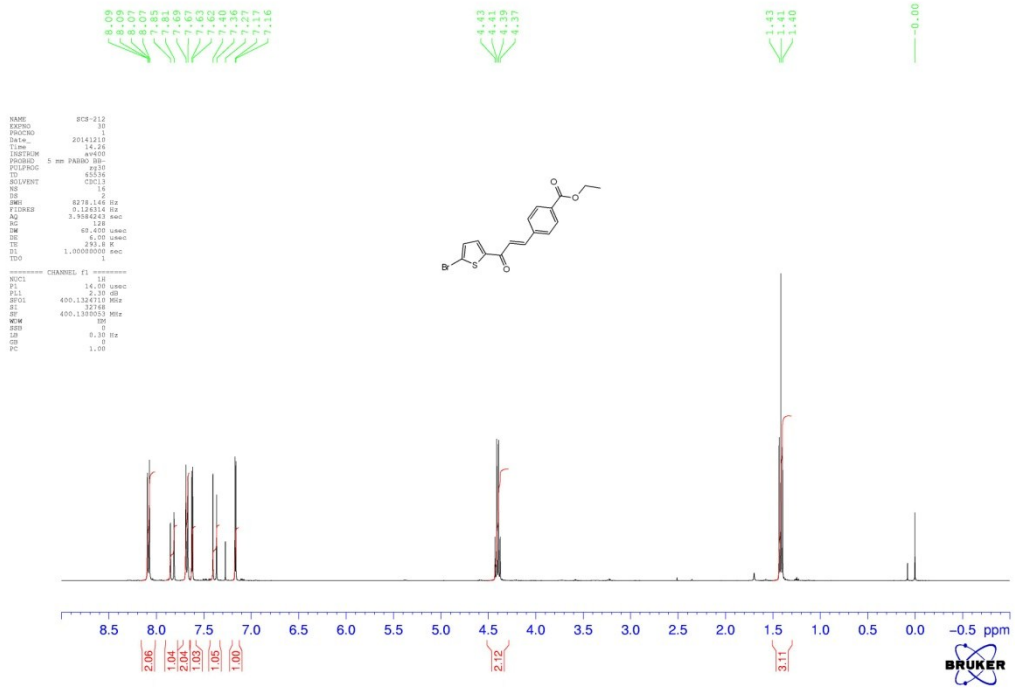

Figure S5. H^1 NMR spectra of **3c**.

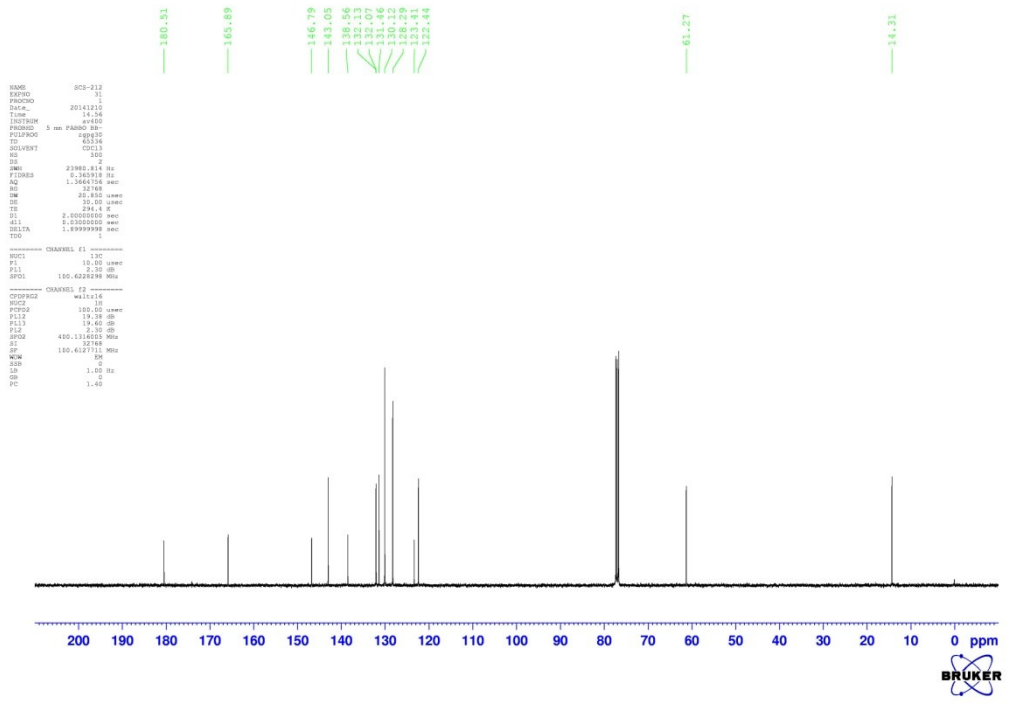

Figure S6. C^{13} NMR spectra of **3c**.

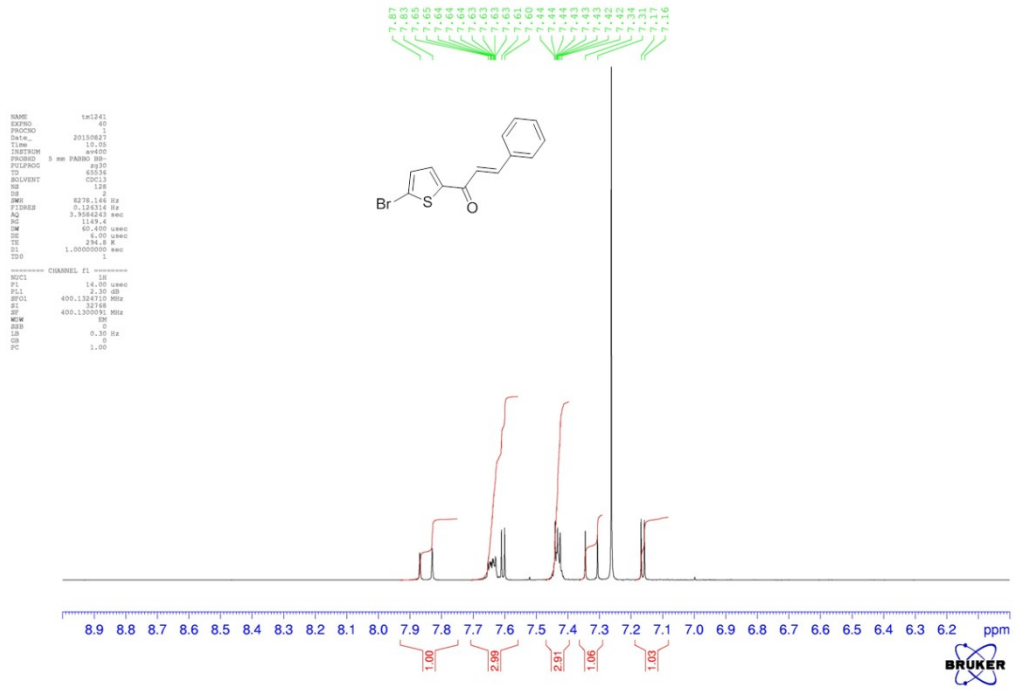

Figure S7. H^1 NMR spectra of **3d**.

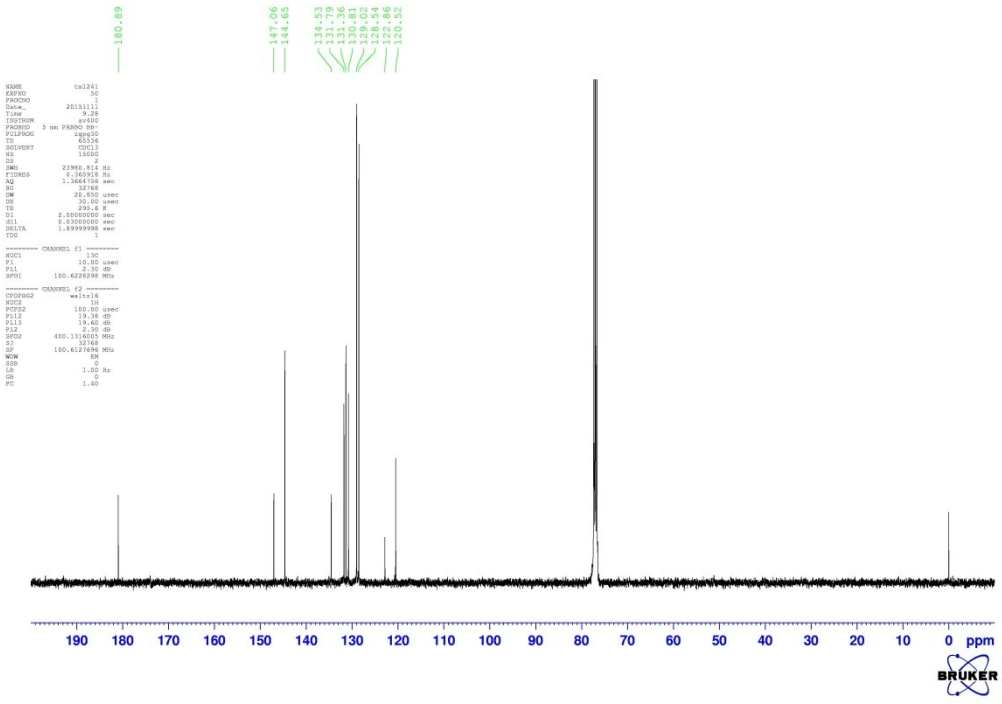

Figure S8. C^{13} NMR spectra of **3d**.

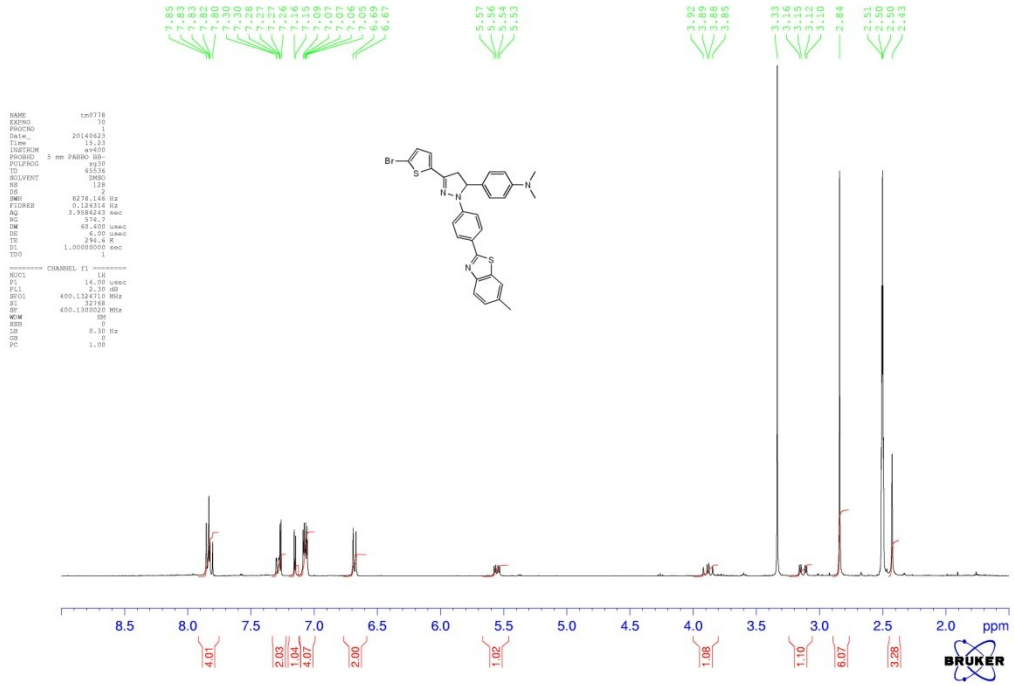

Figure S9 H^1 NMR spectra of **4a**.

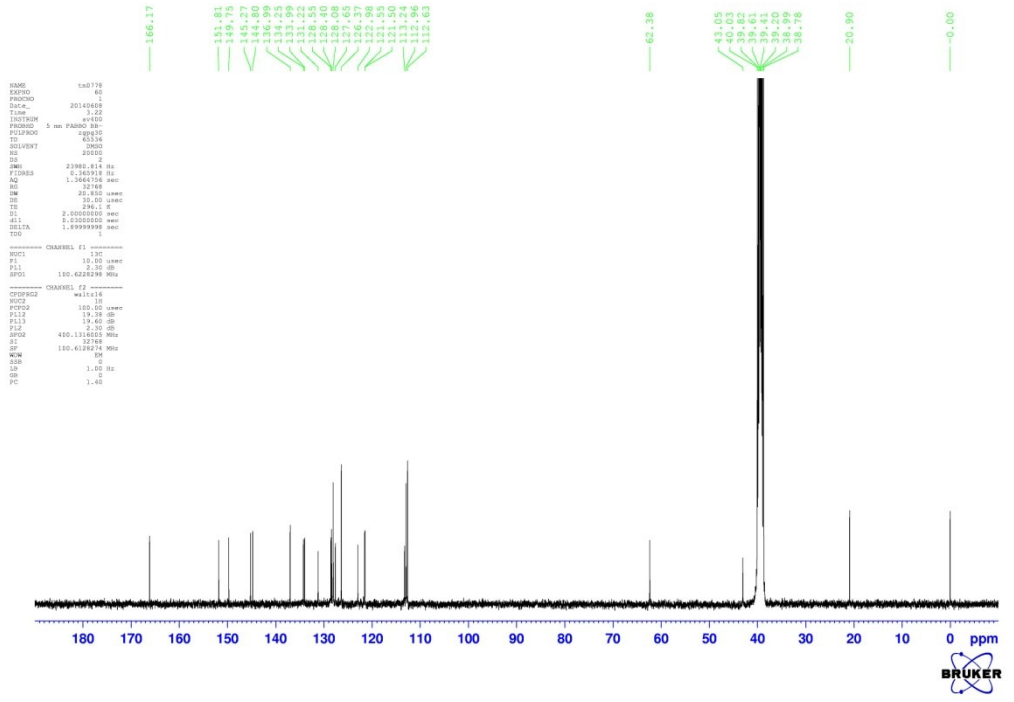

Figure S10. C^{13} NMR spectra of **4a**.

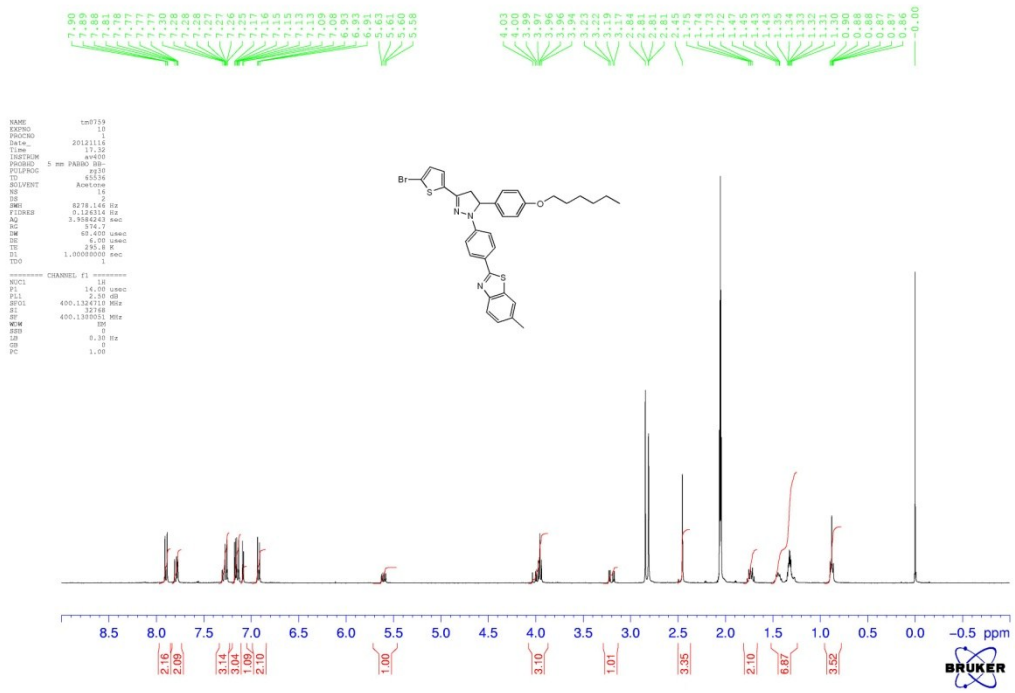

Figure S11. H^1 NMR spectra of **4b**.

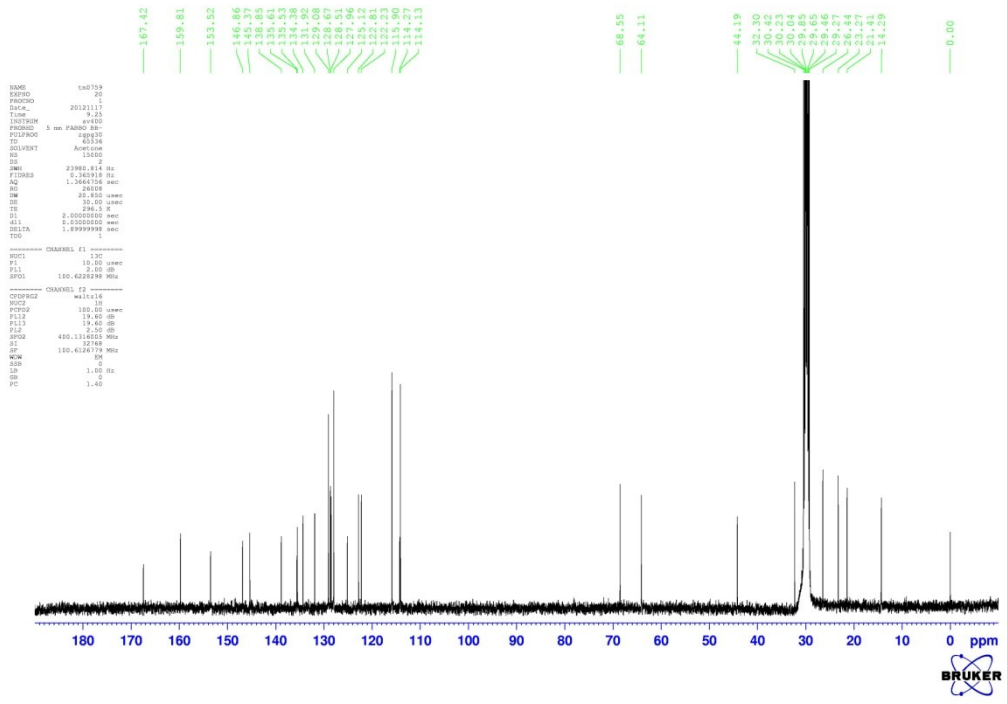

Figure S12. C^{13} NMR spectra of **4b**.

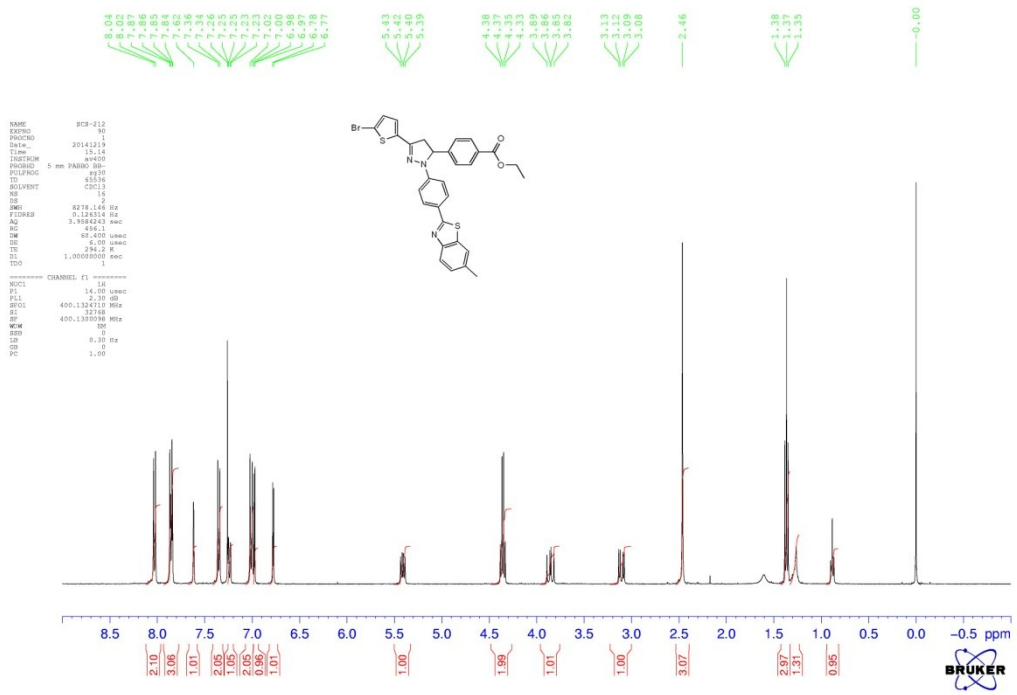

Figure S13. H^1 NMR spectra of **4c**.

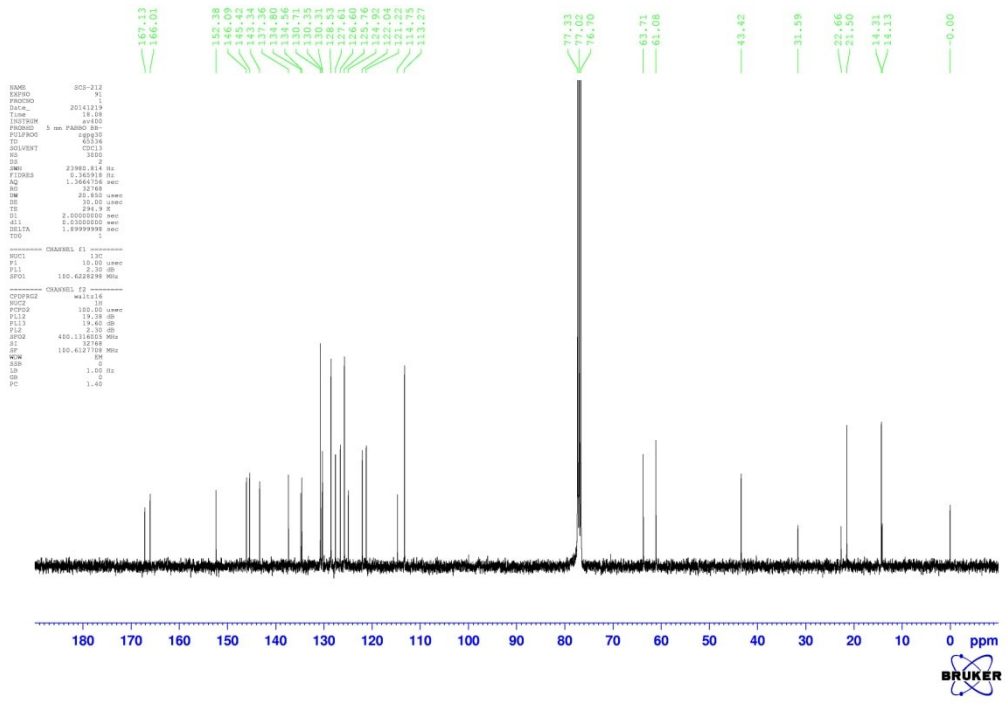

Figure S14. C^{13} NMR spectra of **4c**.

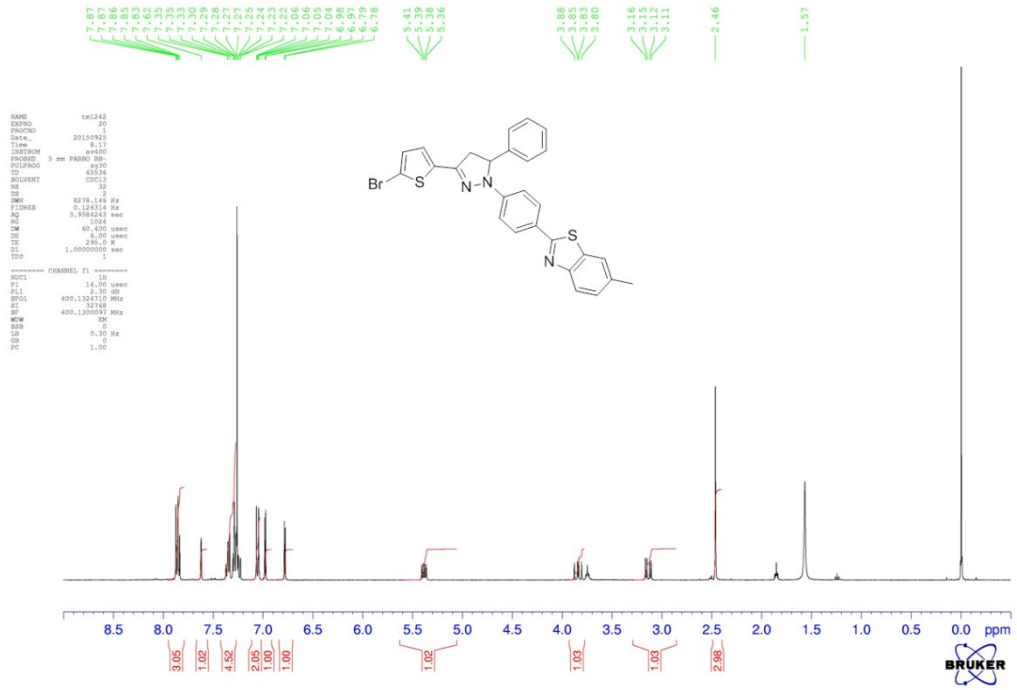

Figure S15. H^1 NMR spectra of **4d**.

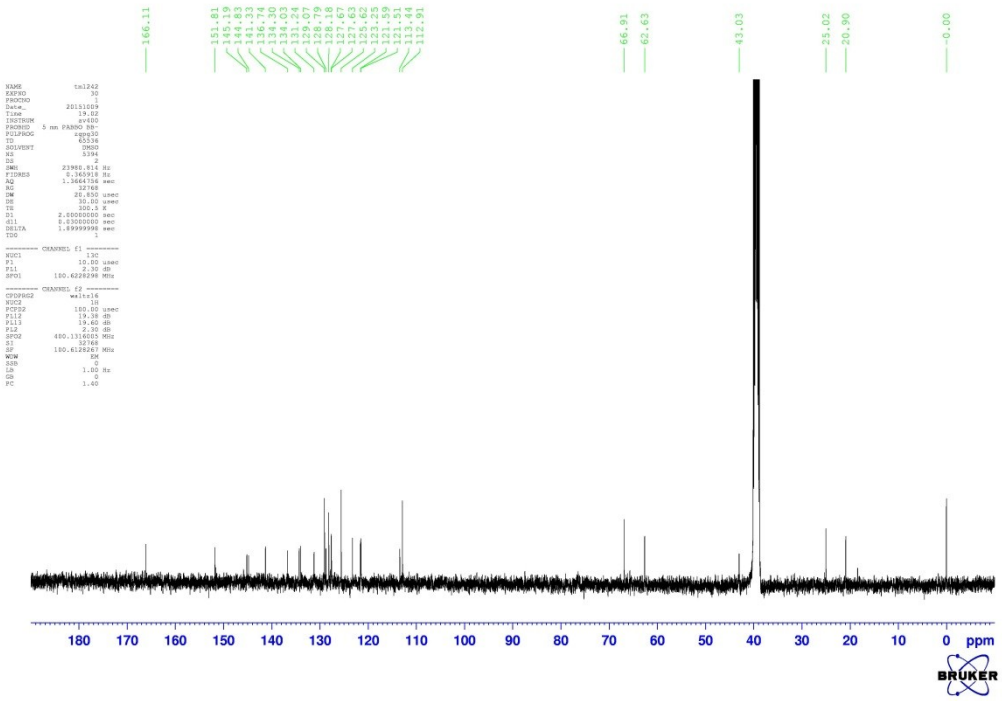

Figure S16. C^{13} NMR spectra of **4d**.

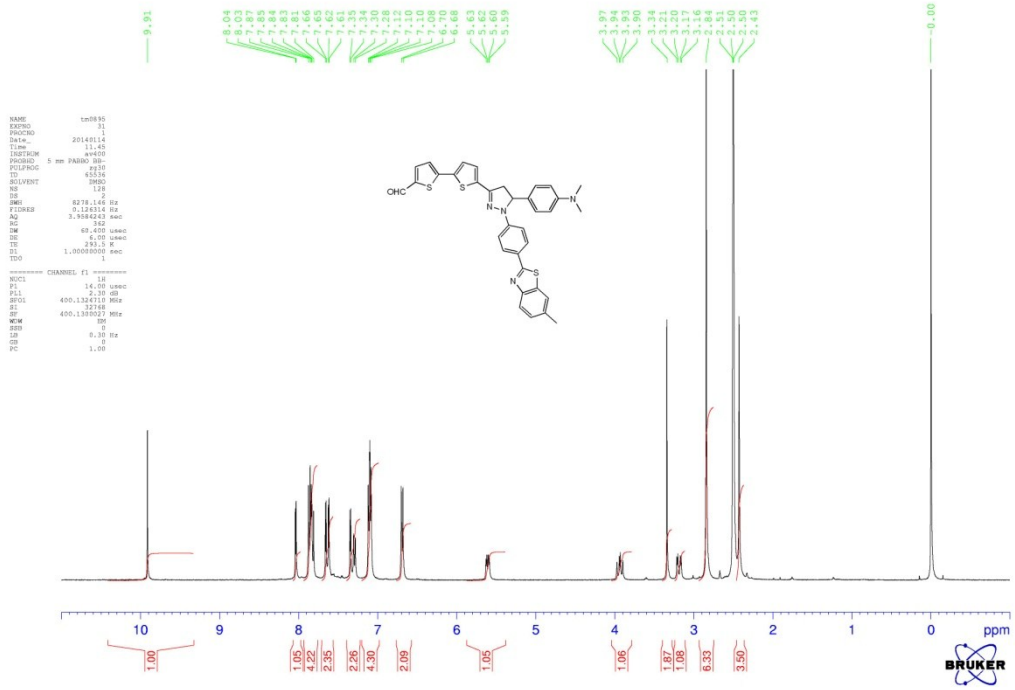

Figure S17. H^1 NMR spectra of **5a**.

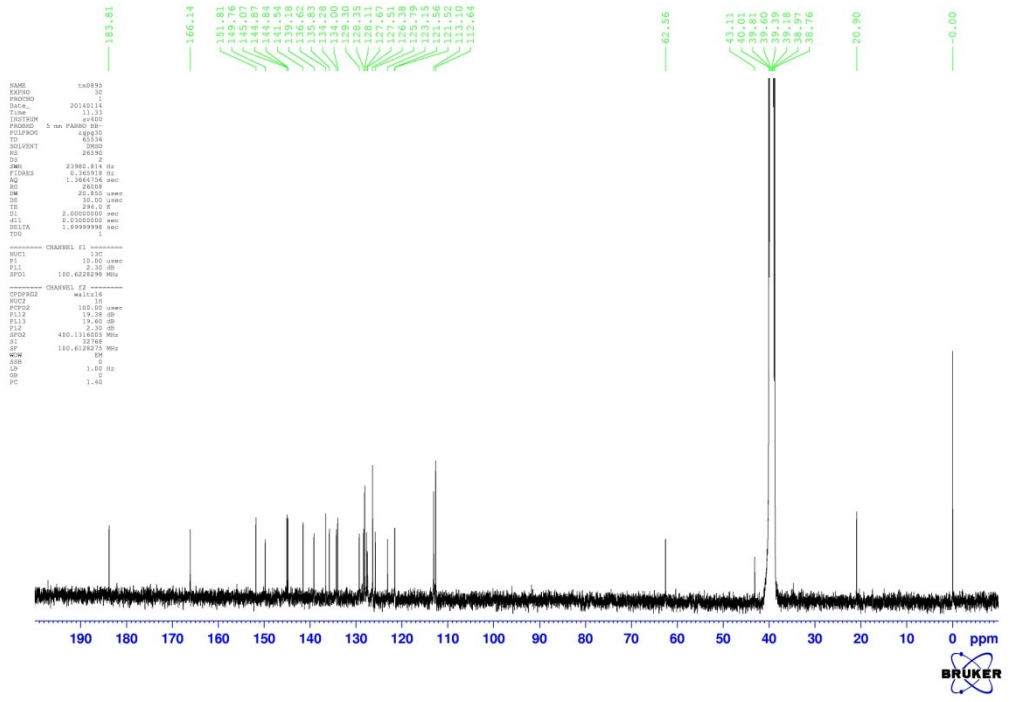

Figure S18. C^{13} NMR spectra of **5a**.

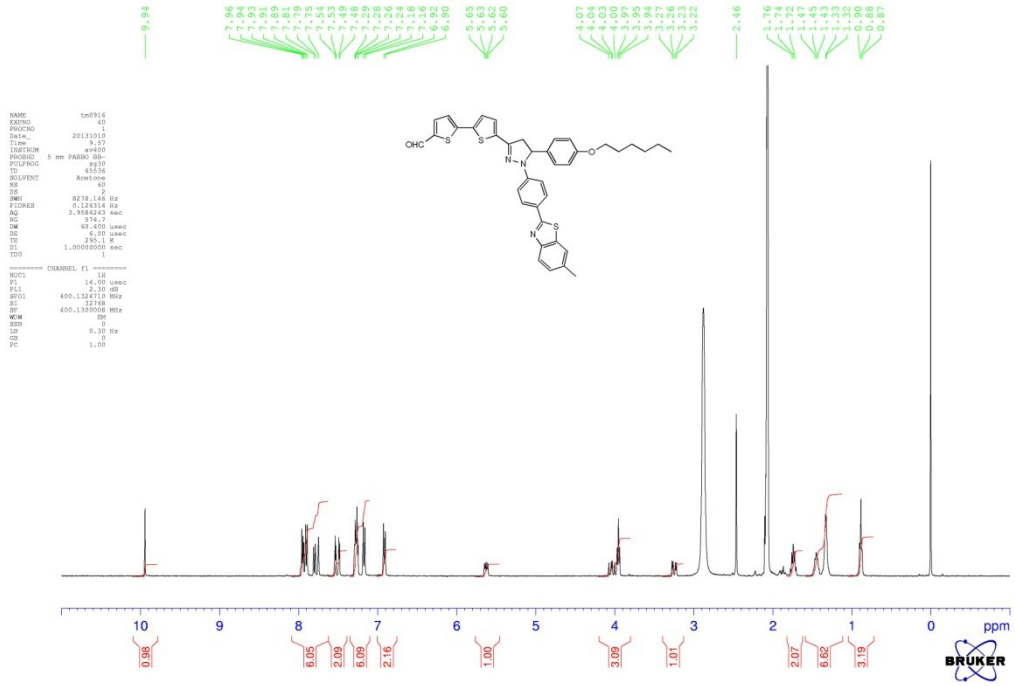

Figure S19. H^1 NMR spectra of **5b**.

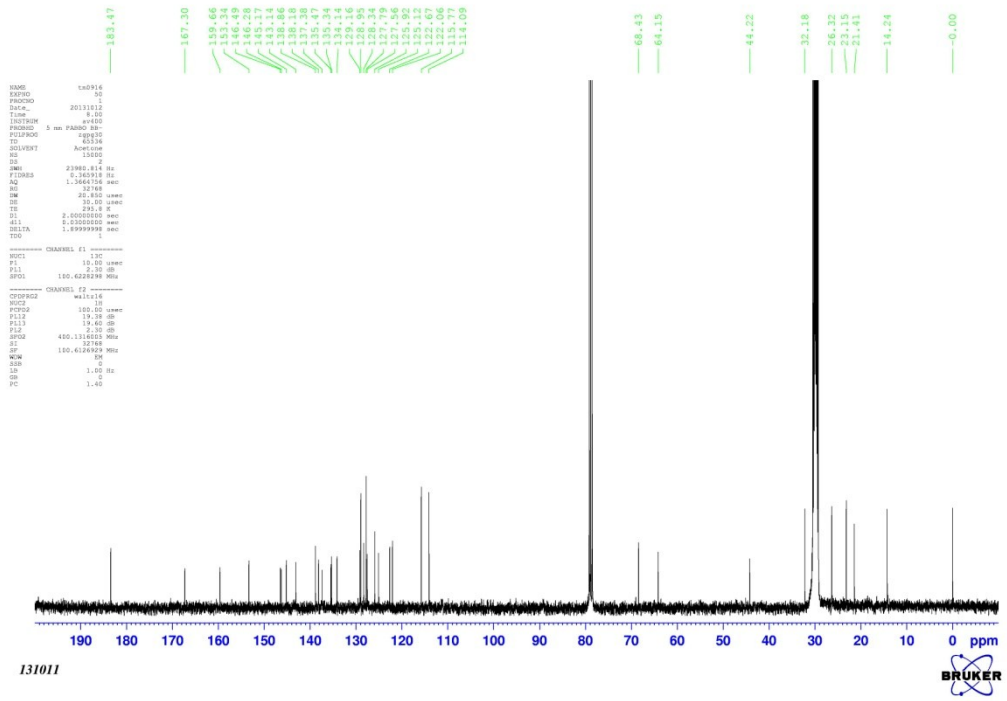

Figure S20. C^{13} NMR spectra of **5b**.

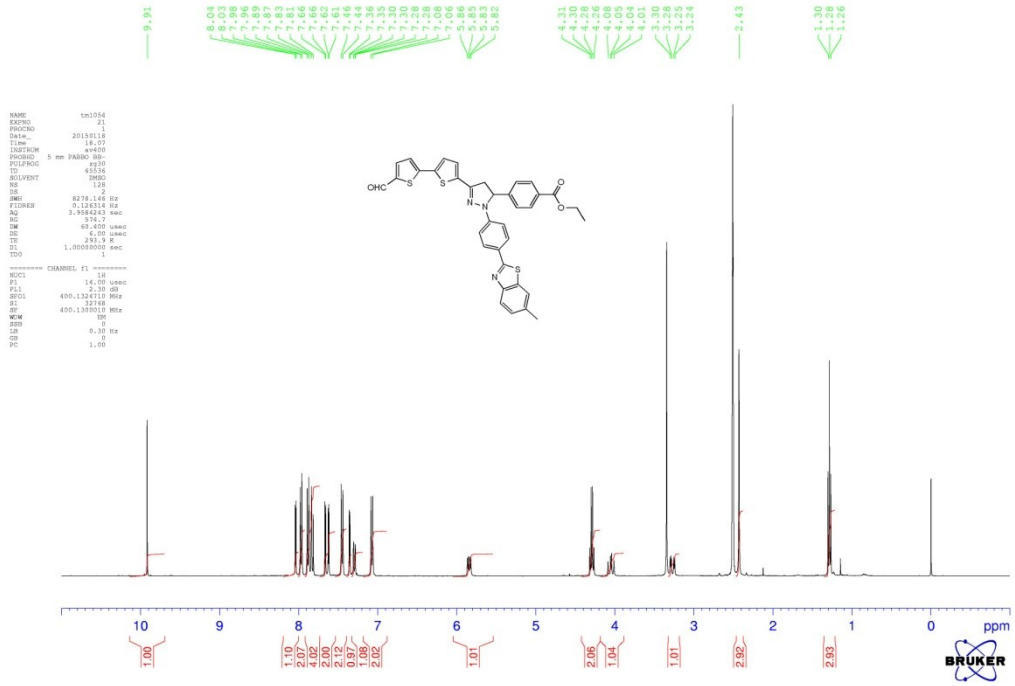

Figure S21. H^1 NMR spectra of **5c**.

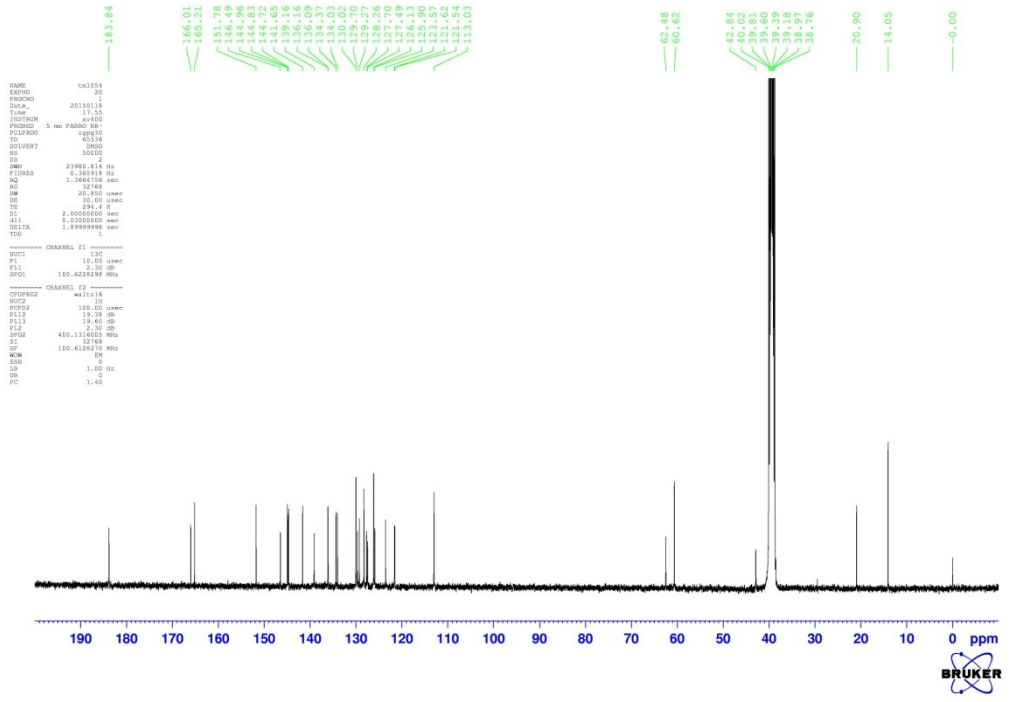

Figure S22. C^{13} NMR spectra of **5c**.

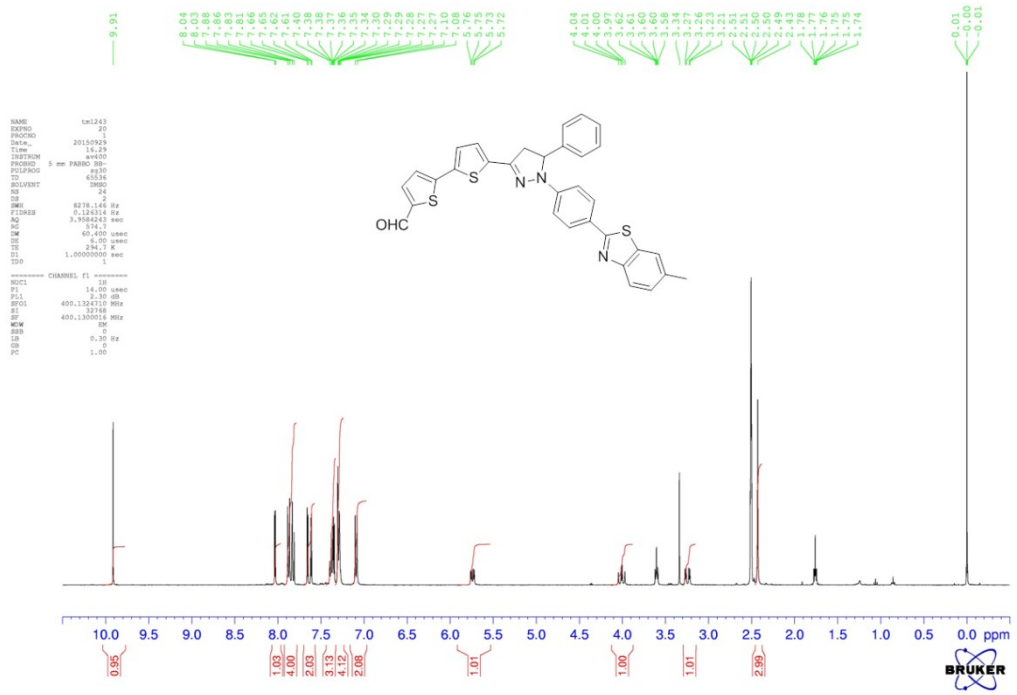

Figure S23. H^1 NMR spectra of **5d**.

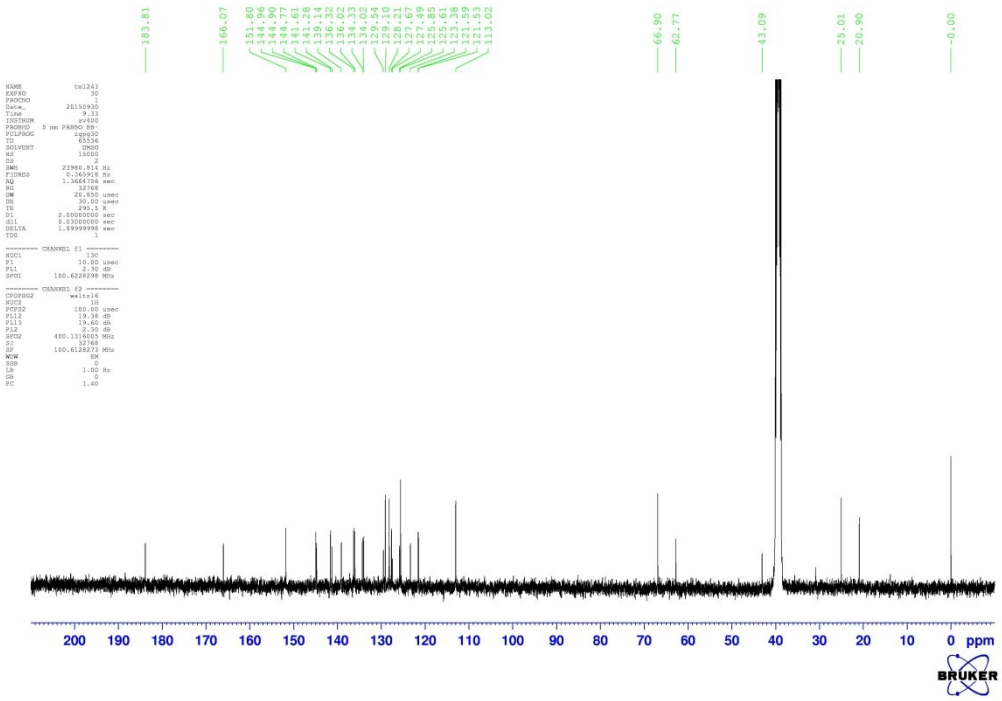

Figure S24. C^{13} NMR spectra of **5d**.

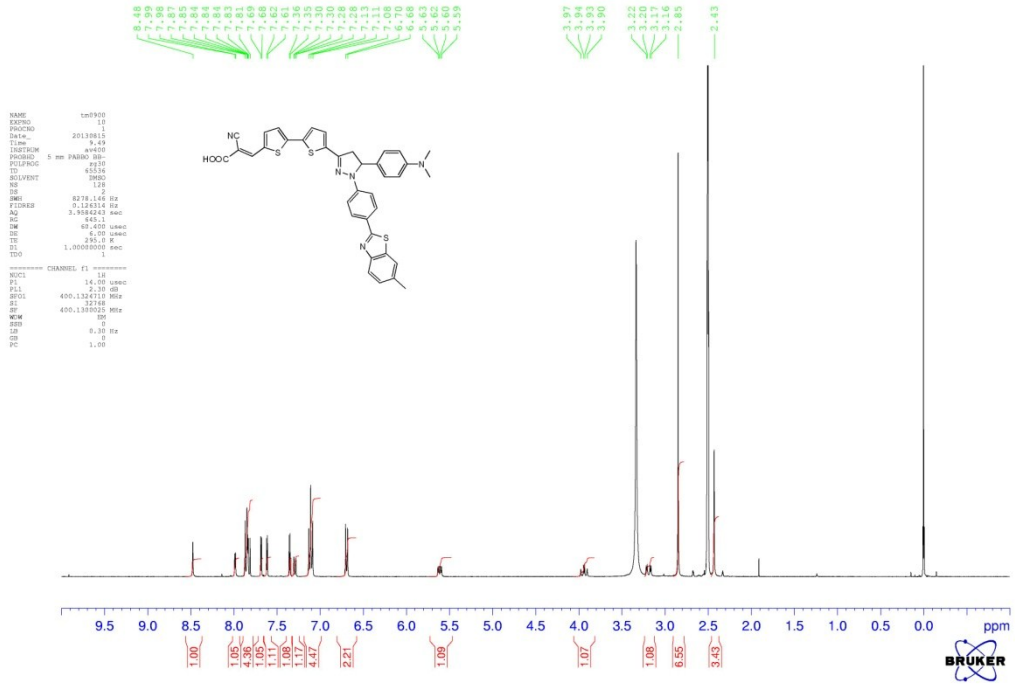

Figure S25. H^1 NMR spectra of **6a**.

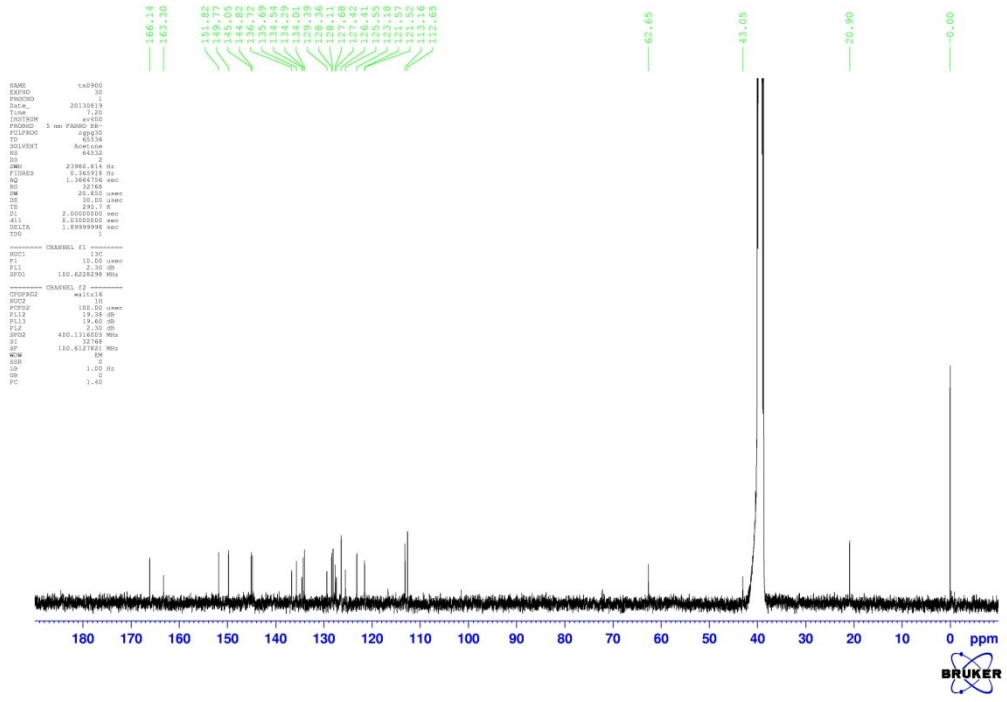

Figure S26. C^{13} NMR spectra of **6a**.

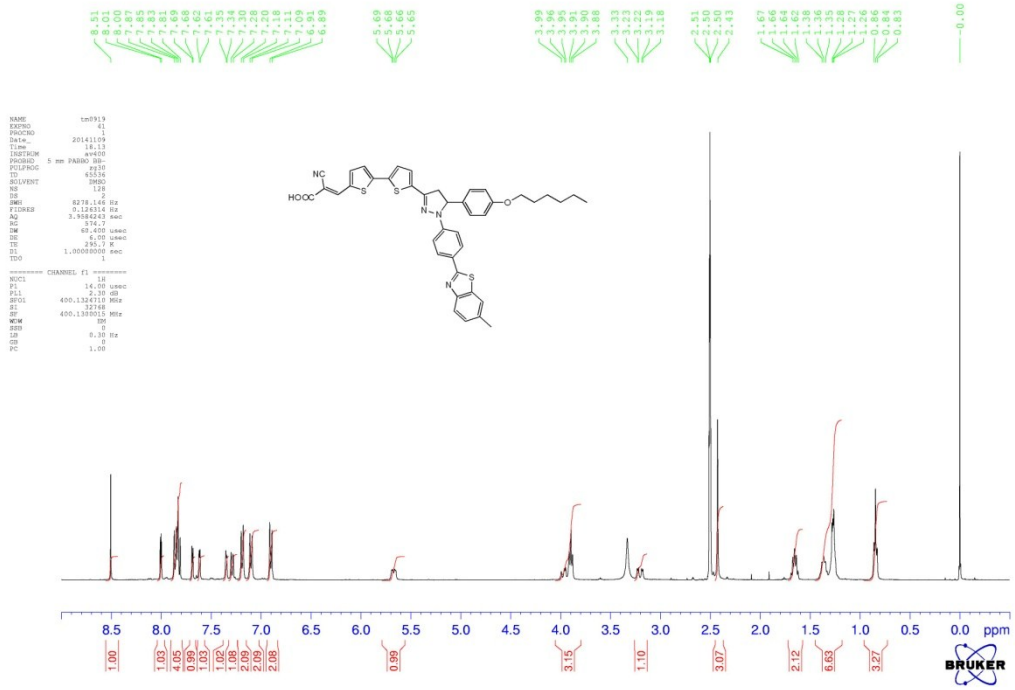

Figure S27. H^1 NMR spectra of **6b**.

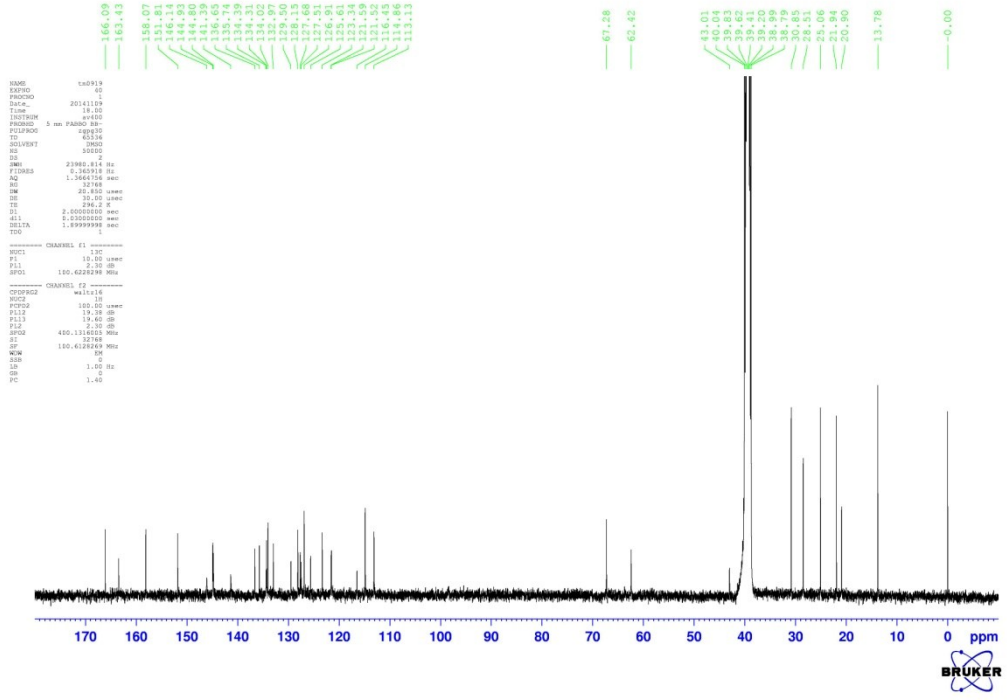

Figure S28. C^{13} NMR spectra of **6b**.

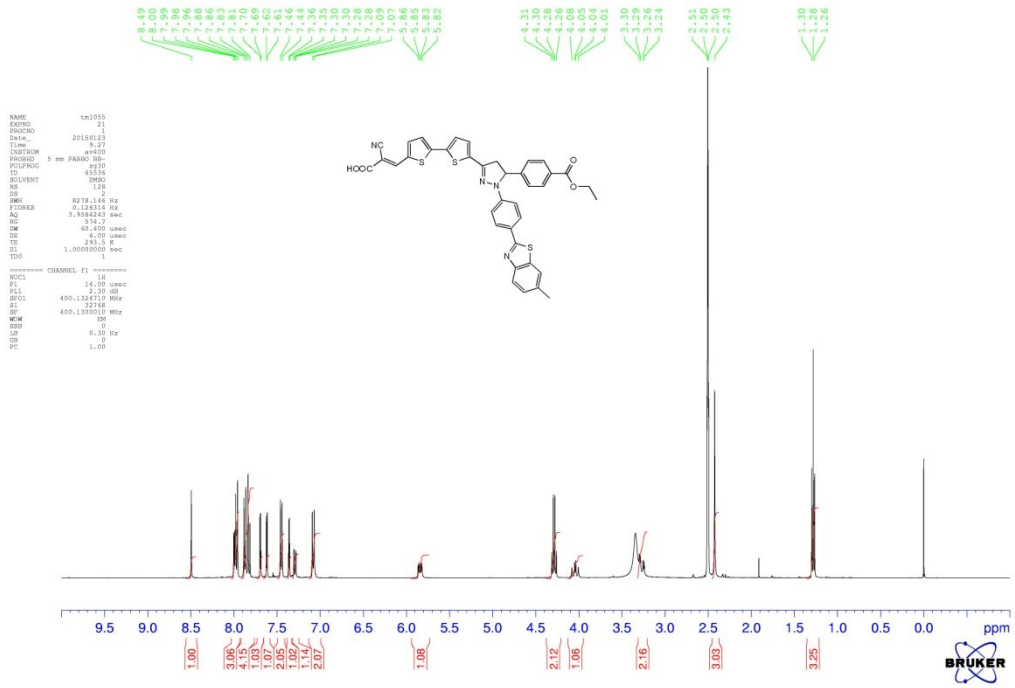

Figure S29. H^1 NMR spectra of **6c**.

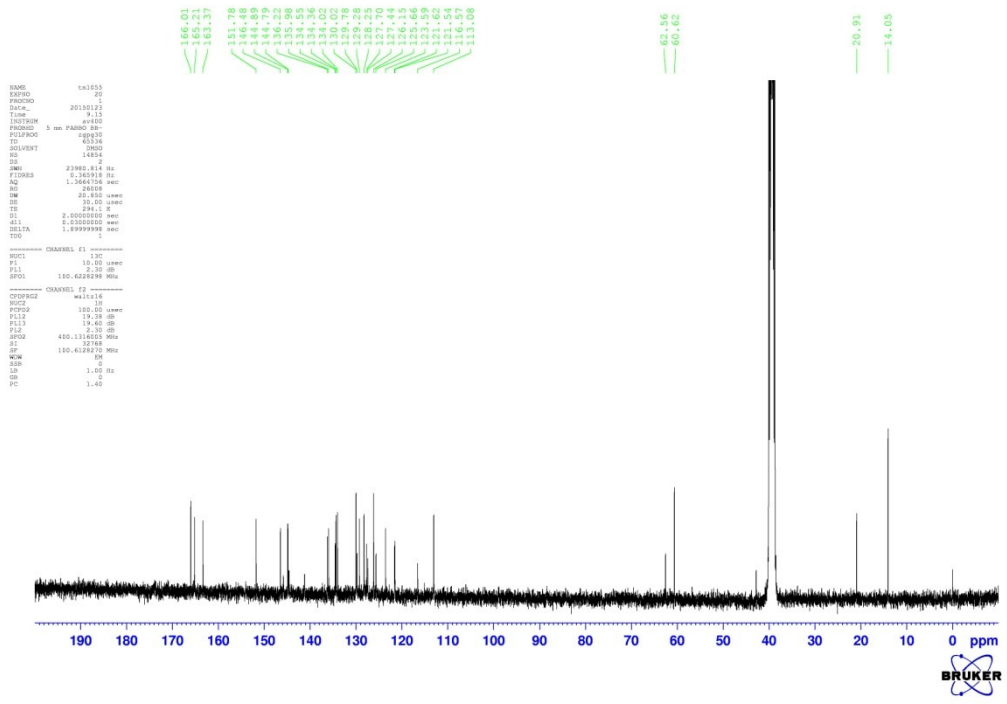

Figure S30. C^{13} NMR spectra of **6c**.

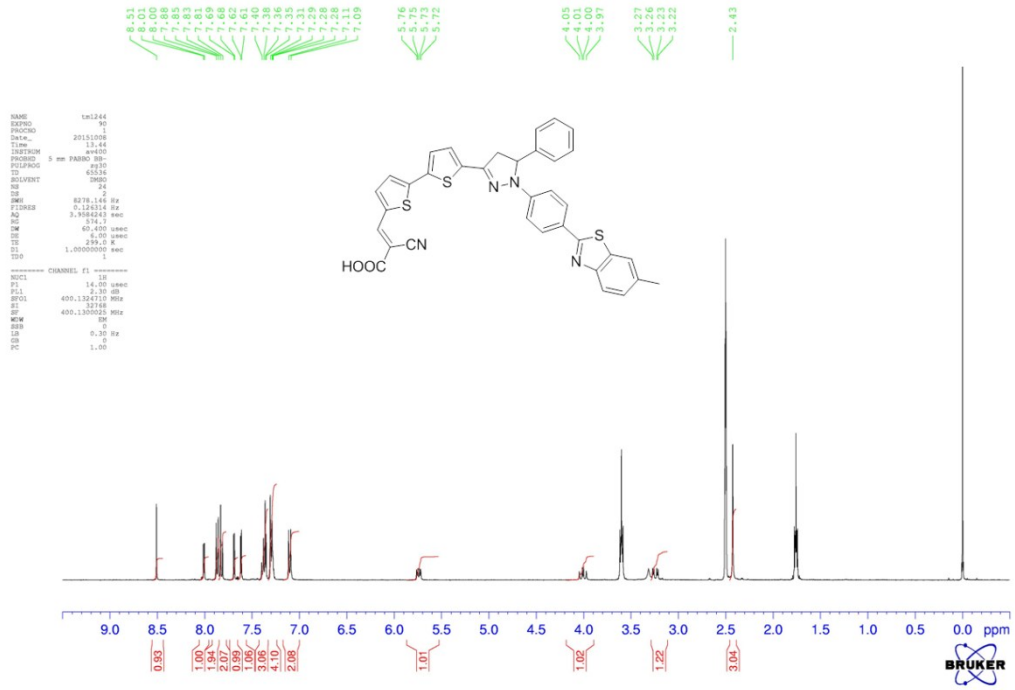

Figure S31. H[1] NMR spectra of **6d**.

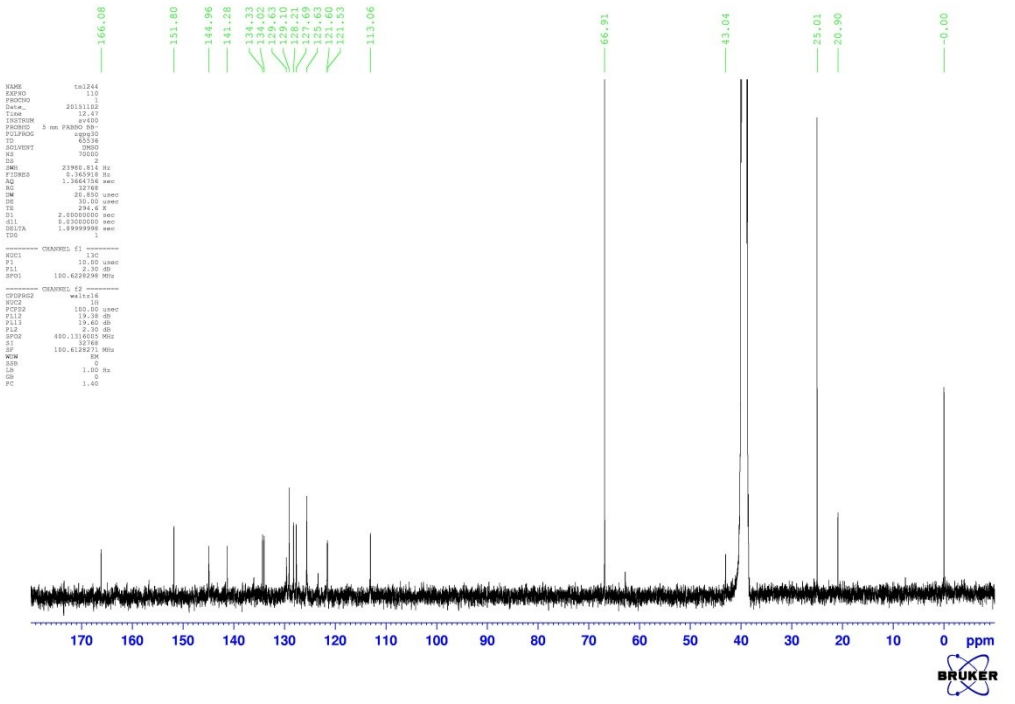

Figure S32. C[13] NMR spectra of **6d**.

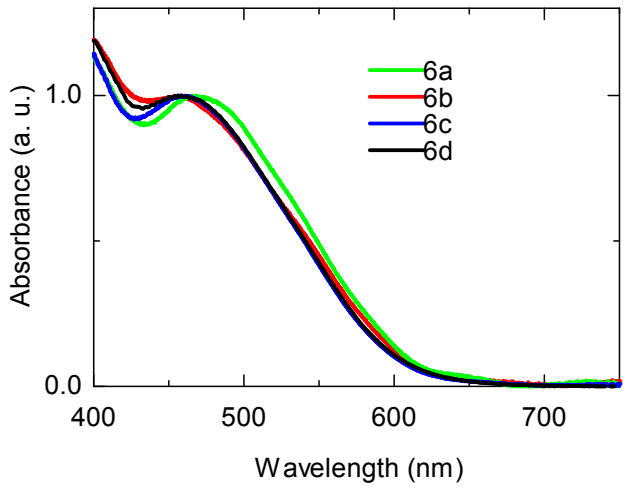

Figure S33. Absorption spectra of **6a –6d** adsorbed on TiO_2.

Table S1. Photovoltaic parameters of all obtained data measured under AM 1.5G (100 mW/cm^2).

Dye	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	η (%)
6a	10.4 ± 0.1	656 ± 3	0.74 ± 0.00	5.1 ± 0.1
6b	9.53 ± 0.11	641 ± 0	0.74 ± 0.00	4.5 ± 0.0
6c	8.80 ± 0.07	624 ± 2	0.73 ± 0.01	4.0 ± 0.0
6d	9.04 ± 0.06	620 ± 1	0.73 ± 0.00	4.1 ± 0.0

The tendency between dye structure and solar cell performance was reproducible.

Table S2. Photovoltaic parameters of DSSCs with a double-layer TiO_2 film employing **6a–d** measured under AM 1.5G (100 mW/cm^2).

Dye	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	η (%)
6a	12.3	636	0.73	5.7
6b	11.4	622	0.73	5.1
6c	10.5	608	0.73	4.6
6d	10.0	579	0.70	4.1