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Push-pull molecules bearing a hydrazonocyclopentadiene acceptor moiety: from the synthesis to organic photovoltaic applications

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1. Experimental Section

1.1 Materials and characterization

^{1}H NMR and ^{13}C NMR spectra were recorded at 300, 75 and 282 MHz, respectively, in $CDCl_3$ or DMSO-d_6 using tetramethylsilane as the internal standard. If present, the NMR signal assignment was accomplished using DEPT, HSQC, and HMBC methods. High resolution mass spectra (HRMS) were recorded using an ESI-TOF spectrometer. Mass spectra were recorded on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct inlet probe). Column chromatography was performed on SiO_2 (230−400 mesh).

Unless otherwise noted, all of the reagents were obtained from commercial suppliers and used without additional purification. 4-Bromophenyldiazonium tetrafluoroborate,[S1] 1,2,3,4,5-penta(methoxycarbonyl)cyclopentadienyl potassium,[S2] dimethyl 2-(2-(4-bromophenyl)hydrazono)-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate[S3] and 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylamine[S4] were synthesized according to the known procedures.

Absorption profiles were recorded with a multifunctional spectrometer ALS01M. All measurements were carried out at room temperature in diluted solutions (10^{-5} M) in chloroform. Films were cast from chloroform solutions on quartz substrates.

Cyclic voltammetry (CV) measurements were performed in CH_3CN : *o*-$C_6H_4Cl_2$ = 1 : 4 solution with 0.1 M Bu_4NPF_6 added as the supporting electrolyte and using an IPC-Pro M potentiostat. The scan rate was 200 mV s^{-1}. The glassy carbon electrode was used as a work electrode. Potentials were measured relative to a saturated calomel electrode (SCE). The HOMO and LUMO energy levels were calculated using the first standard formal oxidation and reduction potentials obtained from CV experiments in films according to the following equations: LUMO = $e(\varphi_{red}+4.40)$ (eV) and HOMO = $-e(\varphi_{ox}+4.40)$ (eV).[S5,S6]

The samples of organic solar cells were prepared in the following way. Firstly, the glass substrates coated with patterned indium-tin oxide (ITO) layer were cleaned in an ultrasonic bath (in surfactant and isopropanol) and under ultraviolet lamp. Than, the 50-nm layer of poly(ethylenedioxythiophene) : polystyrene sulfonate (PEDOT : PSS) polymer complex was deposited on the ITO by spin coating at 3000 rpm and annealed at 140 °C for 15 min. The active layer was deposited on PEDOT : PSS layer by spin coating at 600 rpm from solutions of **7a :** $PC_{71}BM$ and **7b :** $PC_{71}BM$ in *o*-dichlorobenzene with concentration of 24 mg ml^{-1}. The solutions were stirred on a magnetic stirrer at 100 °C for one day before deposition**.** On the top of active layer electrodes Ca and Al layers were evaporated in a vacuum chamber. On the one substrate the eight devices were formed by using a shadow mask during top electrode evaporation (the active area (S) of each device was 3 mm^2).

Current-voltage characteristics of prepared solar cells were measured using a source-meter (Keithley SourceMeter 2400) under light of AM1.5G solar simulator (Newport) with intensity of 100 mW cm^{-2} in a glove box filled with inert atmosphere.

External quantum efficiency spectra were measured in a glove box filled with inert atmosphere on a setup composed of Laser-Driven Light Source (ENERGETIQ) and monochromator (Newport), the Thorlabs S120UV power sensor and the source-meter (Keithley SourceMeter 2400). To avoid higher diffraction orders, additional filters OG11, KG3, GG400, OG550 (Newport) were used for 300–370, 350–500, 480–620 and 600–800 spectral ranges, respectively.

1.2 Synthesis

Tetramethyl 5-(2-(4-bromophenyl)hydrazono)cyclopenta-1,3-diene-1,2,3,4-tetracarboxylate. Trifluoroacetic acid (0.46 ml, 6 mmol) was added to a mixture of penta(methoxycarbonyl)cyclopentadienyl sodium (0.79 g, 2.0 mmol) and 4-bromophenyldiazonium tetrafluoroborate (0.59 g, 2.2 mmol) in acetonitrile (20 ml), and the mixture was refluxed for 3 h. The

solvent was removed *in vacuo*, and the residue was subjected to column chromatography ($CHCl_3$–MeCN, 9 : 1) to give the desired product (0.61g, yield 64%); m.p.: 135–137 °C (decomp.); HRMS (ESI) *m*/*z* for $C_{19}H_{17}BrN_2O_8(M + H)^+$: calcd. 481.0250, 483.0229, found 481.0241, 483.0222; MS (*m*/*z* (rel intens, %)) 482 (8%, M^+), 480 (8%, M^+), 293 (100%). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.81 (s, 3H), 3.90 (s, 3H), 3.94 (s, 3H), 3.97 (s, 3H), 7.37 (d, *J* 8.3 Hz, 2H), 7.55 (d, *J* 8.3 Hz, 2H), 15.22 (s, 1H, NH); ^{13}C NMR(75.5 MHz, $CDCl_3$), δ: 52.2 (CO_2Me), 52.6 (CO_2Me), 52.7 (CO_2Me), 53.5 (CO_2Me), 109.3 (1C of C5-ring), 118.9 (2C), 121.0 (1C), 122.8 (1C of C5-ring), 132.9 (2C), 137.8, 138.7 and 140.0 (3C of C5-ring), 142.0 (1C), 142.0 (1C), 162.1 (CO), 165.0 (CO), 166.3 (CO), 166.6 (CO).

Tetramethyl 5-(2-(4′-(diphenylamino)-[1,1′-biphenyl]-4-yl)hydrazineylidene)cyclopenta-1,3-diene-1,2,3,4-tetracarboxylate(7a). A mixture of tetramethyl 5-(2-(4-bromophenyl)hydrazono)cyclopenta-1,3-diene-1,2,3,4-tetracarboxylate (**1a**) (0.48 g, 1 mmol), *N*,*N*-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**6**) (0.45 g, 1.2 mmol), acetonitrile (7 ml) and 0.4M aqueous Na_2CO_3 (7 ml) was stirred for 30 min under an argon atmosphere at room temperature. Then $Pd(PPh_3)_4$(0.05 mmol) was added and the mixture heated at reflux for 19 h. The resulted mixture was treated with water and extracted with $CHCl_3$. The organic layer was dried over anhydrous $MgSO_4$, the solvent was removed *in vacuo*, and the residue subjected to column chromatography ($CHCl_3$–MeCN, 9 : 1) to give the desired product (0.59g, yield 92%); m.p.: 152–156 °C (decomp.); HRMS (ESI) *m*/*z* for $C_{37}H_{31}N_3O_8(M + Na)^+$: calcd. 668.2001, found 668.2003; MS (*m*/*z* (rel intens, %)) 645 (67%, MH^+), 613 (100%), 293 (24%). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.80 (s, 3H), 3.90 (s, 3H), 3.94 (s, 3H), 3.99 (s, 3H), 7.05 (t, *J* 7.3 Hz, 2H), 7.16–7.09 (m, 6H), 7.31–7.24 (m, 4H), 7.47 (d, *J* 8.6 Hz, 2H), 7.55 (d, *J* 8.6 Hz, 2H), 7.61 (d, *J* 8.6 Hz, 2H), 15.40 (s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$), δ: 52.2 (CO_2Me), 52.6 (CO_2Me), 52.7 (CO_2Me), 108.5 (1C of C5-ring), 118.3 (2C), 121.9 (1C of C5-ring), 123.4 (2C), 123.5 (2C), 124.7 (4C), 127.6 (2C), 127.7 (2C), 129.4 (4C), 133.1 (1C), 137.6 and 138.3 (2C of C5-ring), 139.7 (1C), 140.4 (1C), 141.1 (1C of C5-ring), 147.5 (2C), 147.9 (1C), 162.4 (CO), 165.4 (CO), 166.7 (CO), 166.9 (CO).

Dimethyl 2-(2-(4'-(diphenylamino)-[1,1'-biphenyl]-4-yl)hydrazineylidene)-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate(7b). A mixture of dimethyl 2-(2-(4-bromophenyl)hydrazono)-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate (**1b**) (0.52 g, 1 mmol), N,N-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**6**) (0.45 g, 1.2 mmol), acetonitrile (7 ml), and 0.4M aqueous Na_2CO_3 (7 ml) was stirred for 30 min under an argon atmosphere at room temperature. Then $Pd(PPh_3)_4$(0.05 mmol) was added and the mixture was refluxed for 19 h. The resulted mixture was

treated with water and extracted with $CHCl_3$. The organic layer dried over anhydrous $MgSO_4$, the solvent was removed *in vacuo*, and the residue was subjected to column chromatography ($CHCl_3$–MeCN, 9 : 1) to give the desired product. (0.50 g, yield 73%); m.p.: 240–242 °C (decomp.) HRMS (ESI) *m*/*z* for $C_{45}H_{35}N_3O_4(M + H)^+$: calcd. 681.2605, found 681.2622; MS (*m*/*z* (rel intens, %)) 681 (56%, M^+), 613 (100%), 485 (18%); ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.54 (s, 3H), 3.77 (s, 3H), 7.07–6.95 (m, 6H), 7.17–7.10 (m, 8H), 7.31–7.22 (m, 8H), 7.49 (d, *J* 8.5 Hz, 2H), 7.53 (d, *J* 8.6 Hz, 2H), 7.61 (d, *J* 8.6 Hz, 2H), 14.65 (s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$), δ: 52.5 ($2CO_2Me$), 110.6 (1C of C5-ring), 116.7 (2C), 117.6 (1C of C5-ring), 123.1 (2C), 124.0 (2C), 124.6 (4C), 127.19 (1C), 127.25 (2C), 127.4 (1C), 127.5 (2C), 127.6 (2C), 127.7 (2C), 129.38 (4C), 129.43 (4C), 130.7 and 132.6 (2C of C5-ring), 134.3 (1C), 136.3 (1C), 137.5 (1C), 139.8 (1C of C5-ring), 141.0 (1C), 141.4 (1C), 147.3 (1C), 147.7 (2C), 154.5 (1C), 166.3 (CO), 168.5 (CO).

2. Figures

2.1 Electrochemical properties

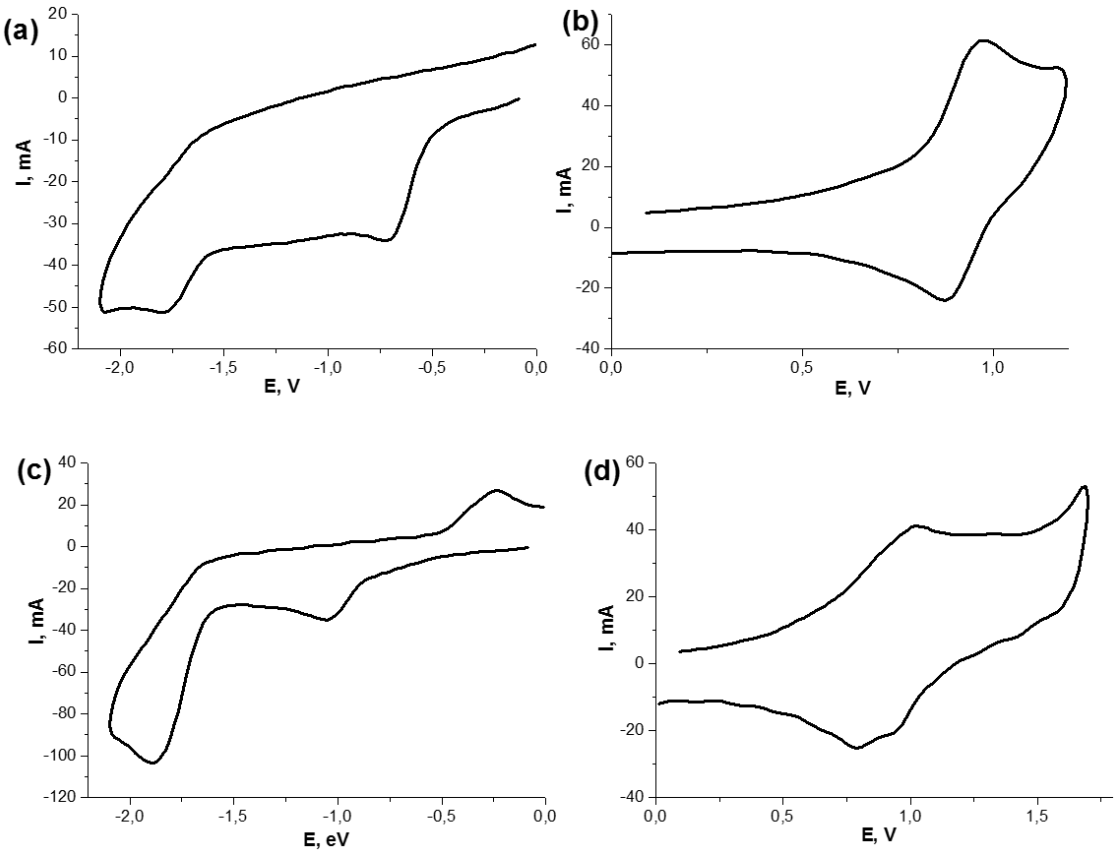


Figure S1 Cyclic voltammograms for the reduction of (*a*) **7a** and (*c*) **7b** and oxidation of (*b*) **7a** and (*d*) **7b**.

2.2 Photovoltaic properties

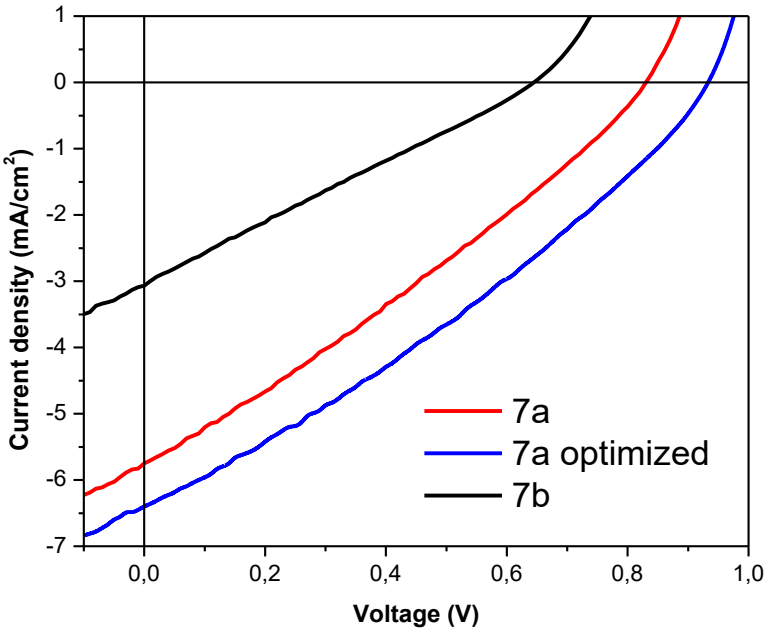


Figure S2 *J-V* curves for the best samples of solar cells.

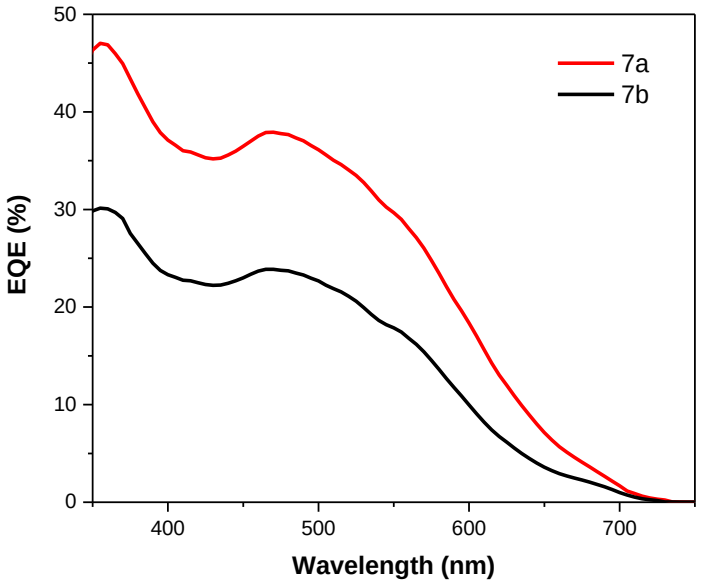


Figure S3 EQE spectra for the organic solar cells with the best mass ratio of **7**:$PC_{71}BM$.

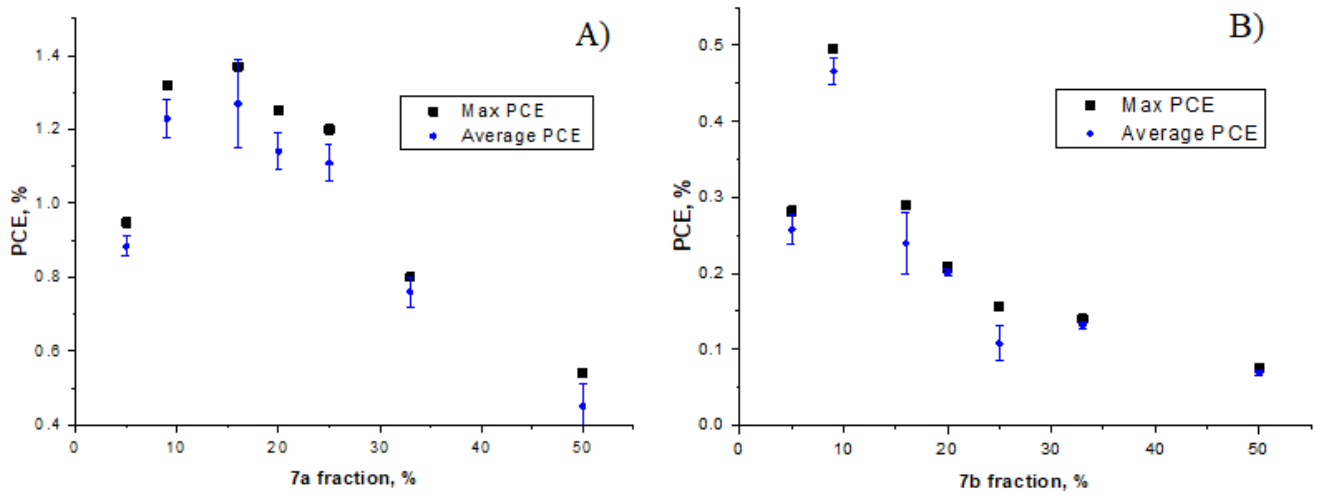
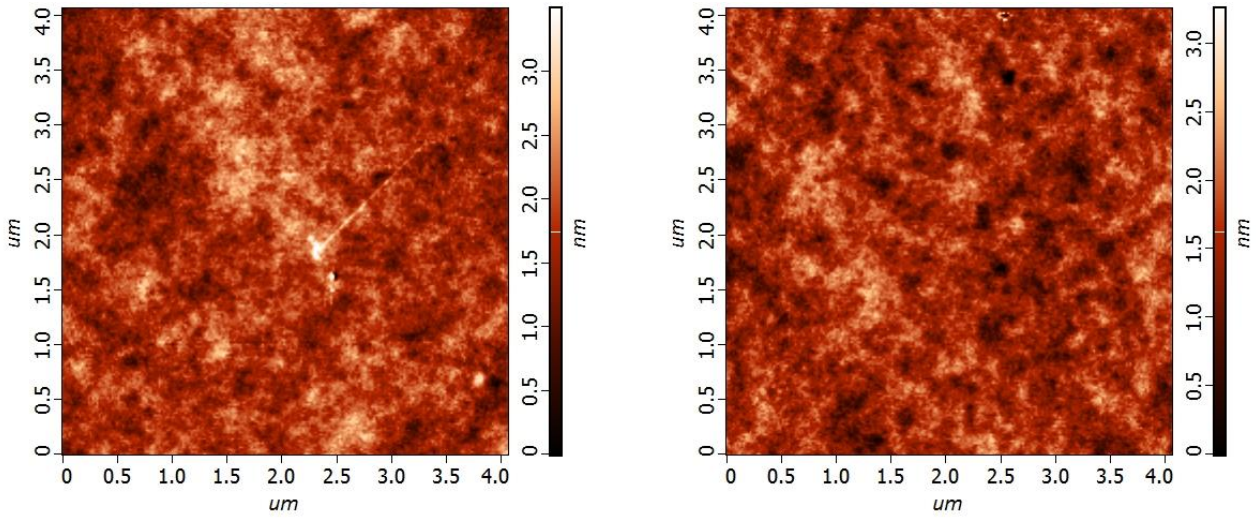


Figure S4 Dependence of PCE on the mass ratio of (*A*) **7a** : $PC_{71}BM$ and (*B*) **7b** : $PC_{71}BM$.



RMS = 0.40 nm RMS = 0.39 nm

Figure S5 Tapping mode AFM scans of (left) **7a**:$PC_{71}BM$(1 : 5) and (right) **7b**:$PC_{71}BM$(1 : 10) blended films.

2.3 NMR and HRMS spectra.

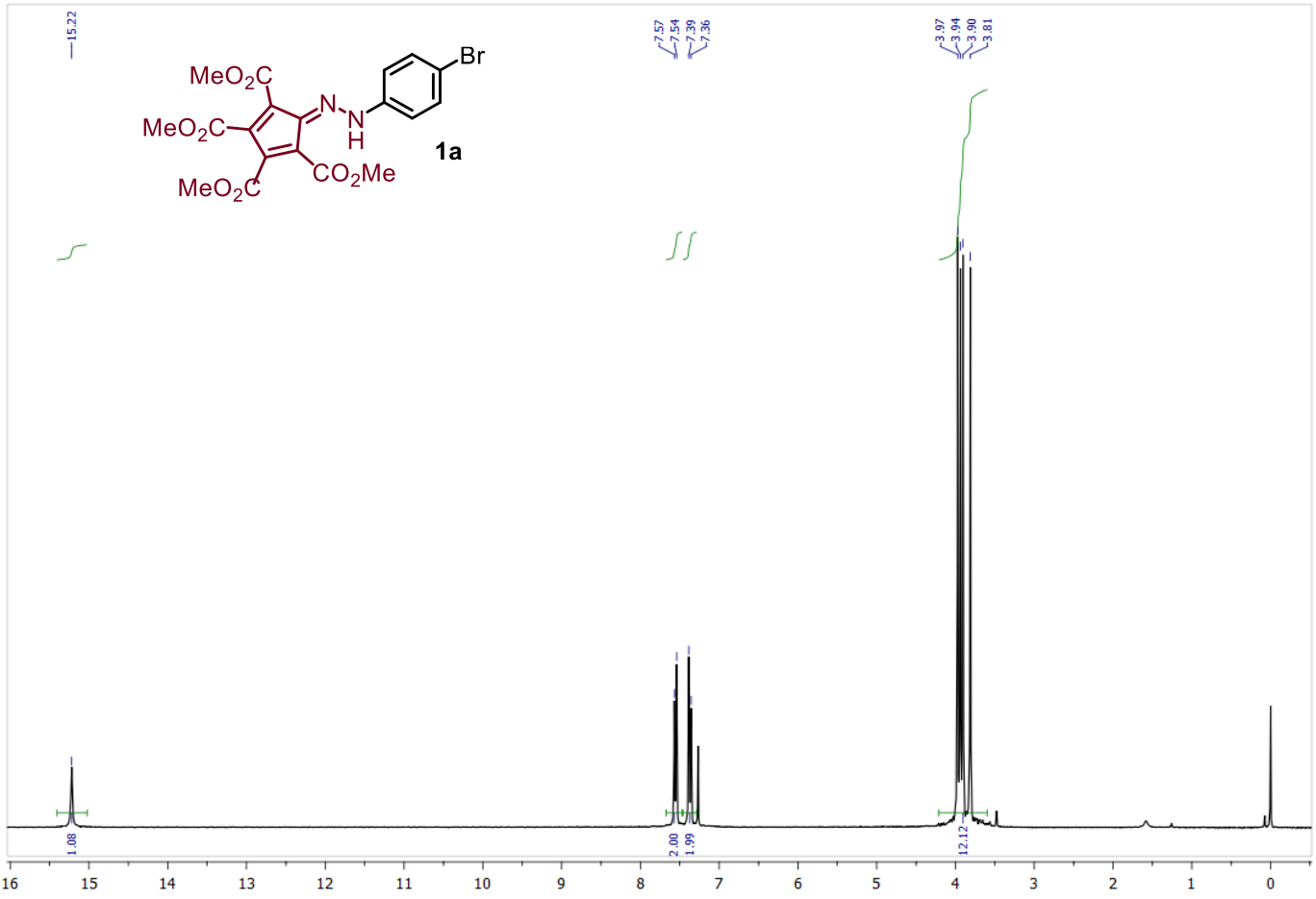


Figure S6 ^{1}H NMR spectrum of compound **1a** (300 MHz, $CDCl_3$).

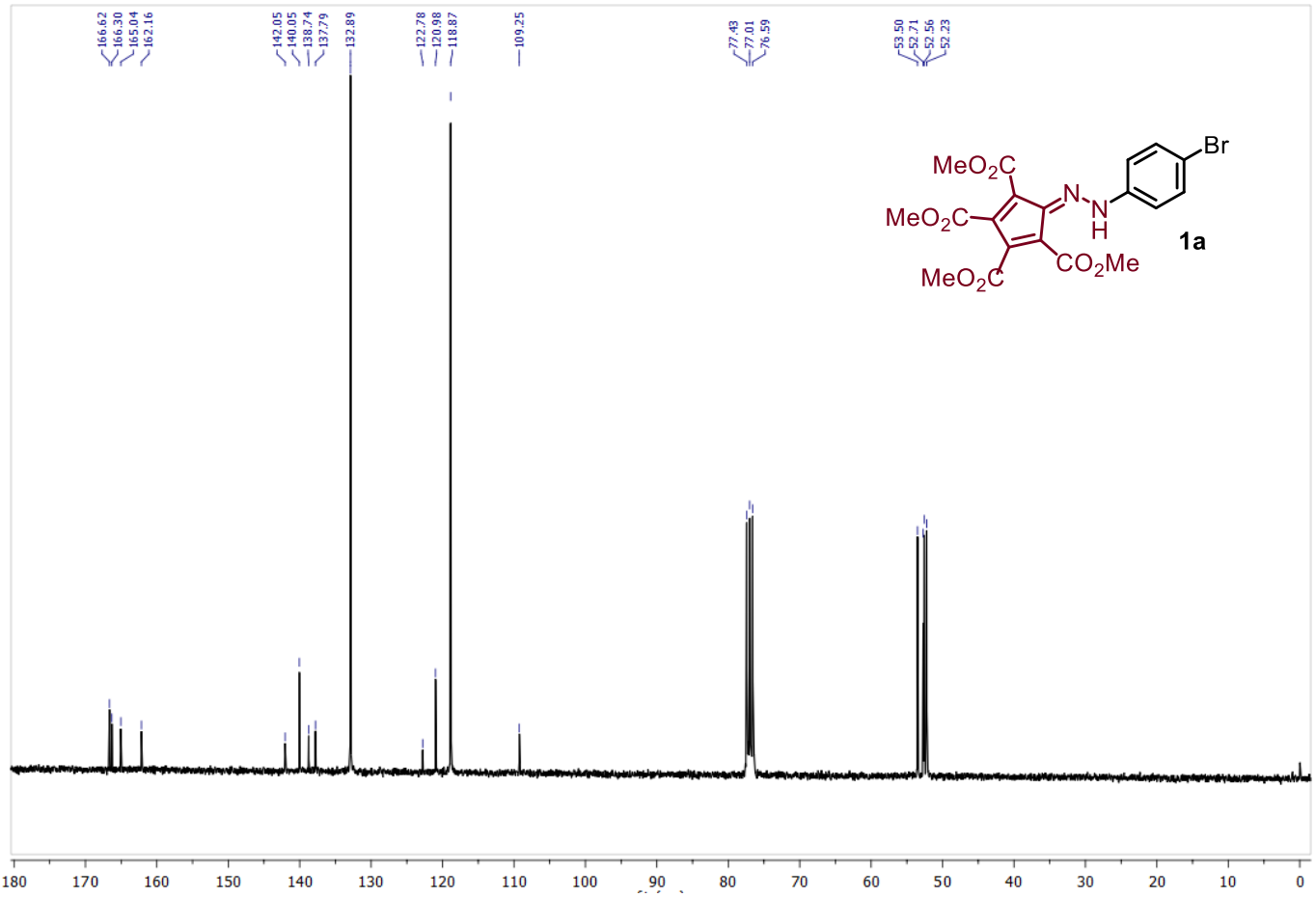


Figure S7 ^{13}C NMR spectrum of compound **1a** (75.5 MHz, $CDCl_3$).

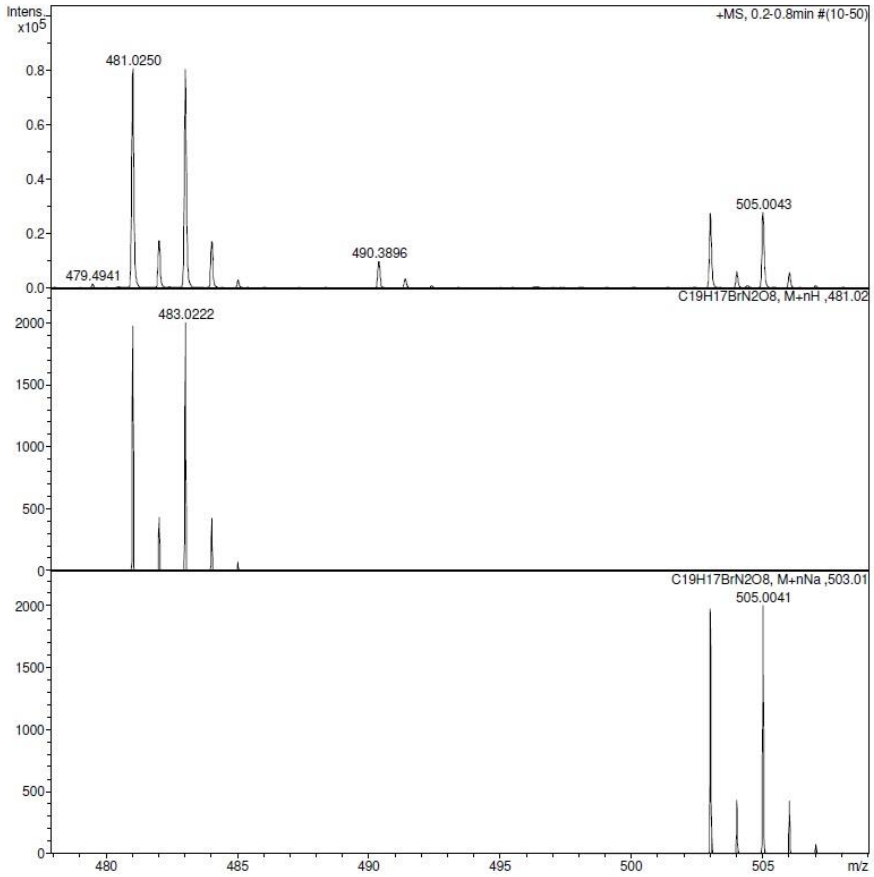


Figure S8 HRMS spectrum of compound **1a**.

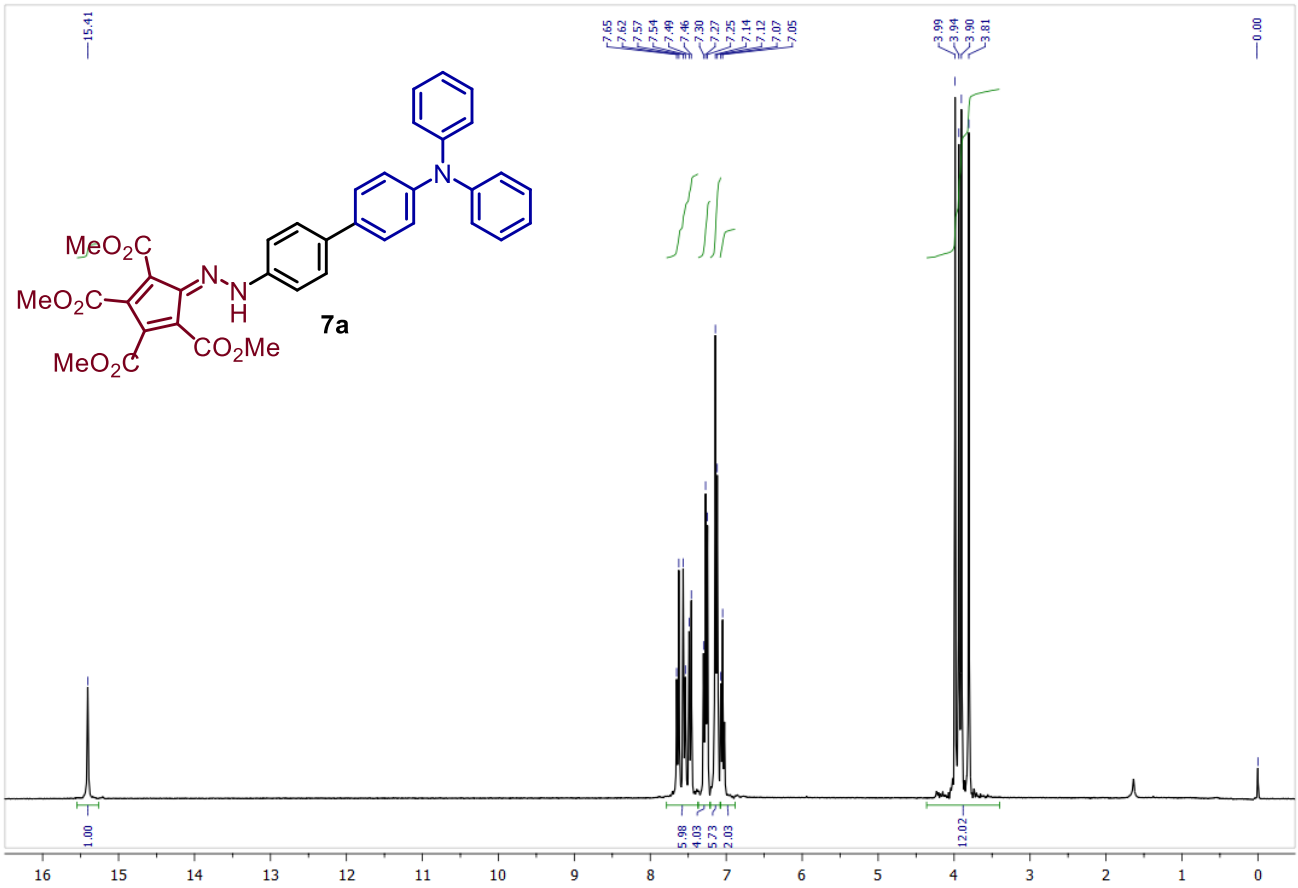


Figure S9 ^{1}H NMR spectrum of compound **7a** (300 MHz, $CDCl_3$).

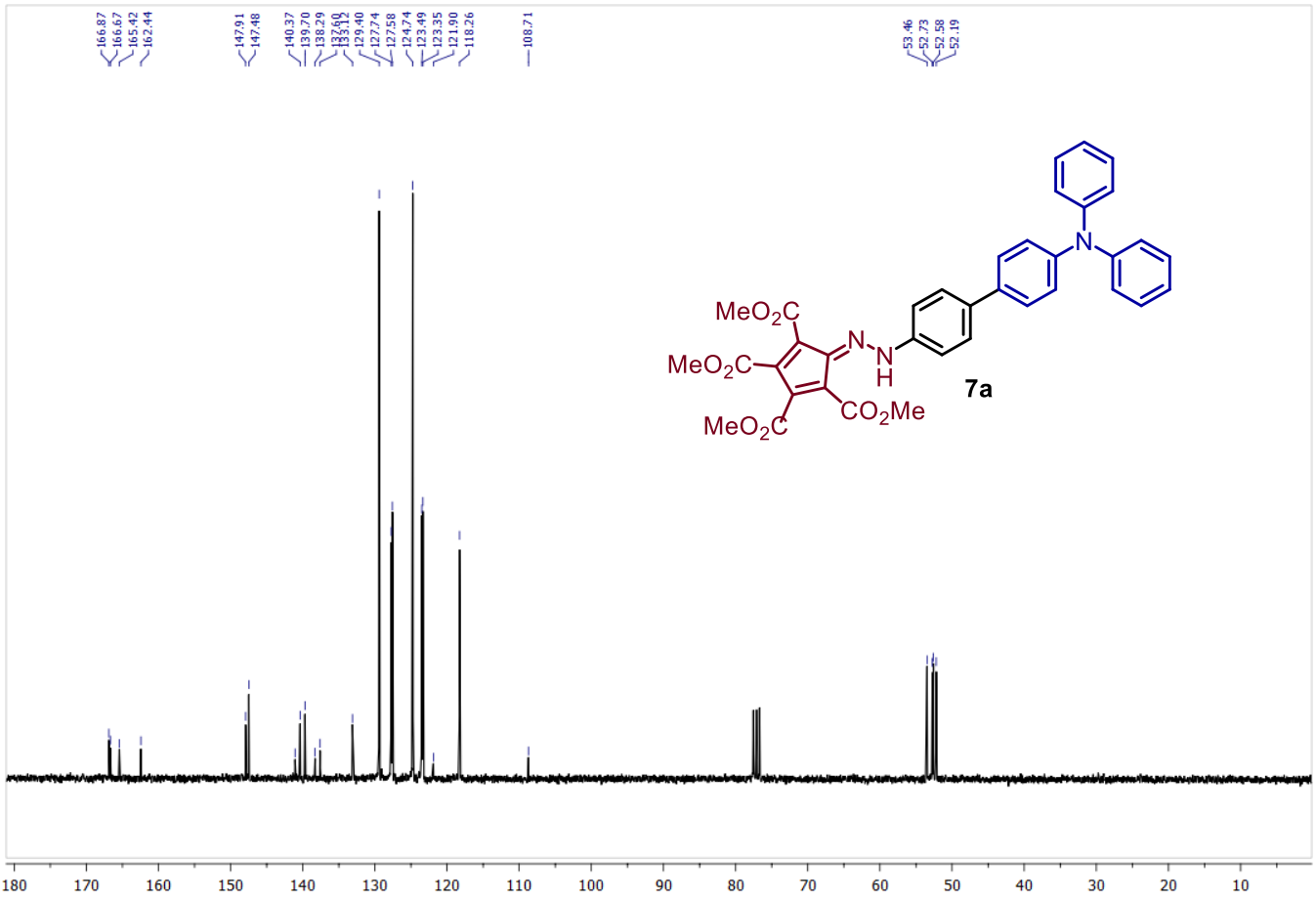


Figure S10 ^{13}C NMR spectrum of compound **7a** (75.5 MHz, $CDCl_3$).

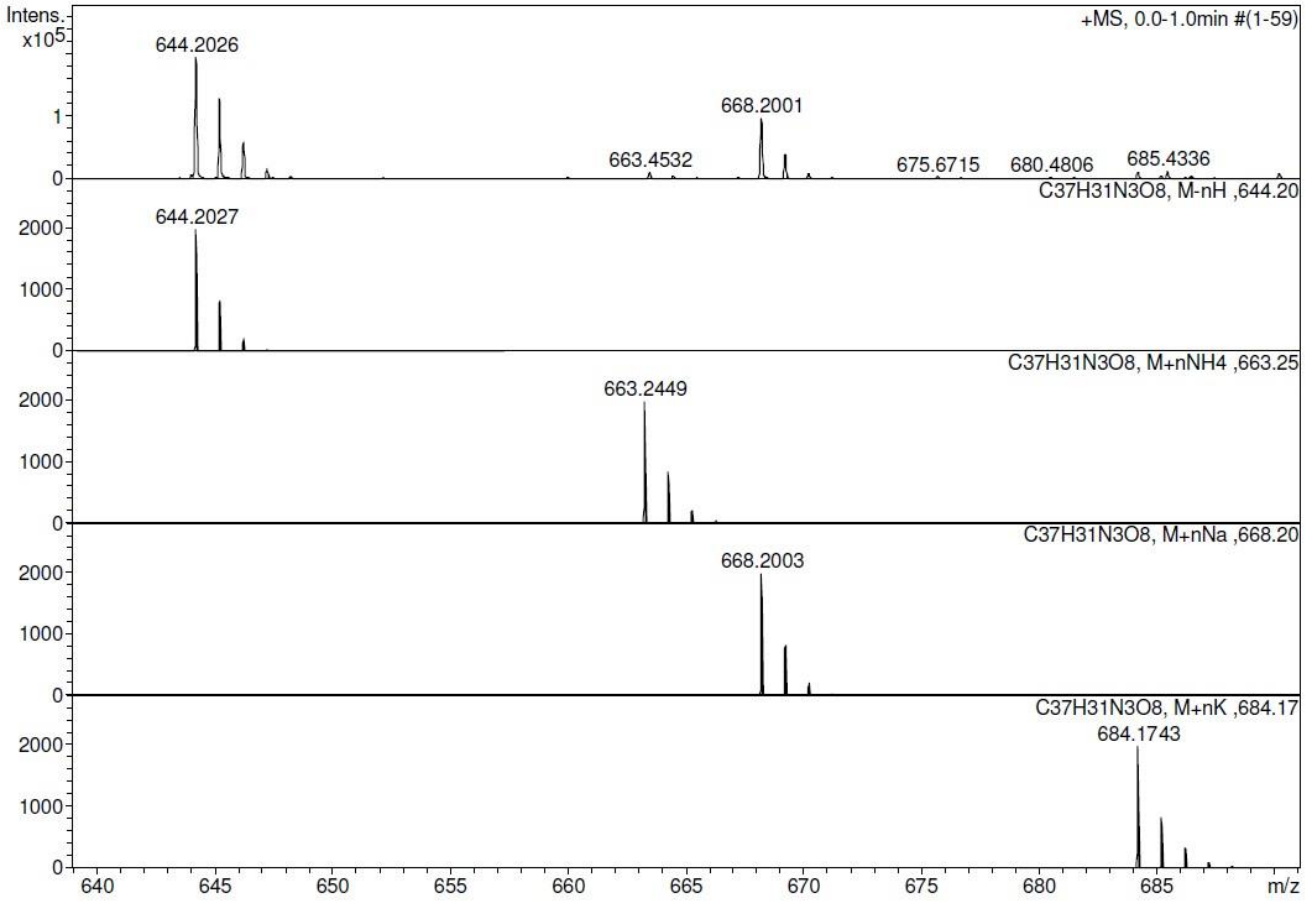


Figure S11 HRMS spectrum of compound **7a**.

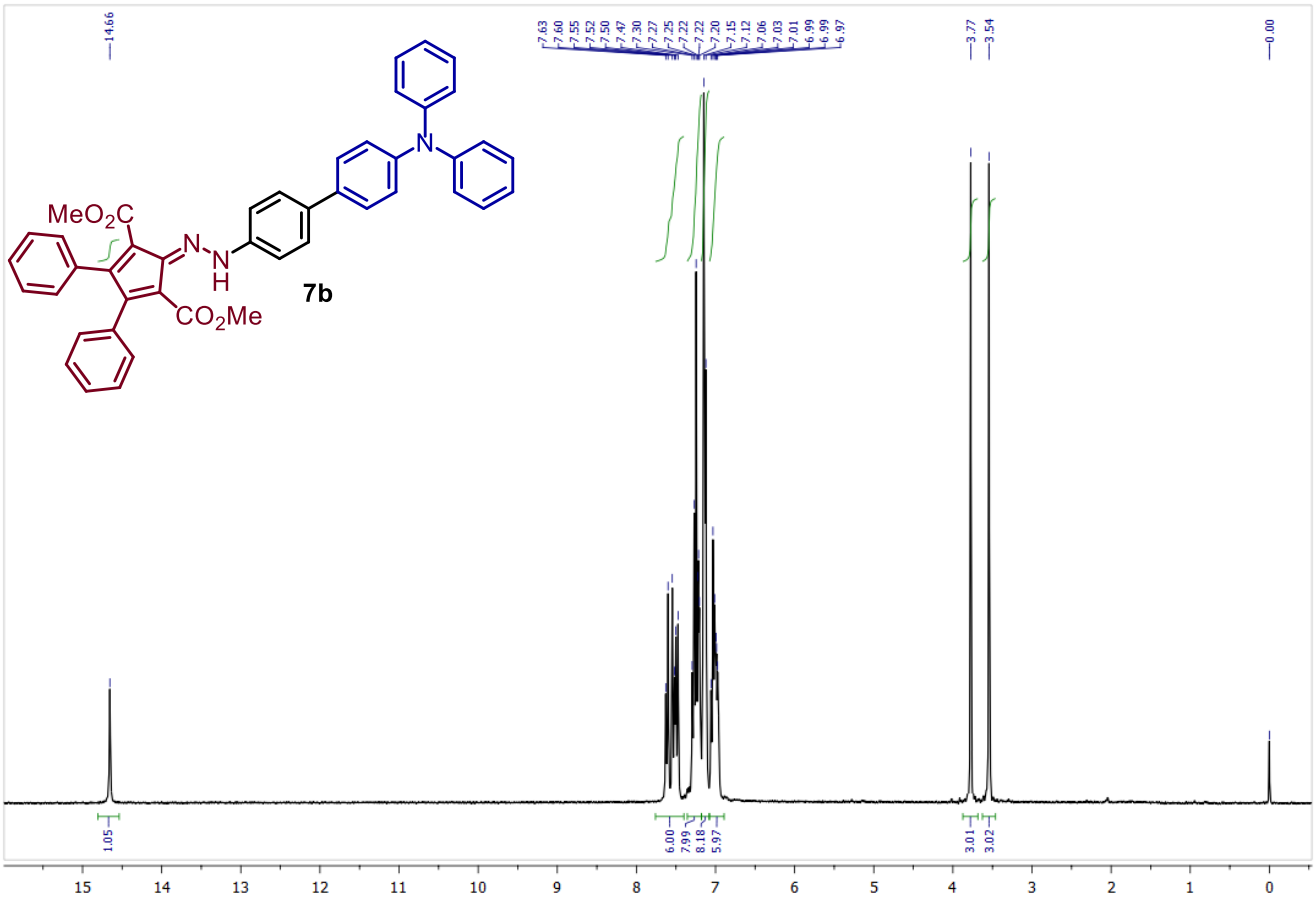


Figure S12 ^{1}H NMR spectrum of compound **7b** (300 MHz, $CDCl_3$).

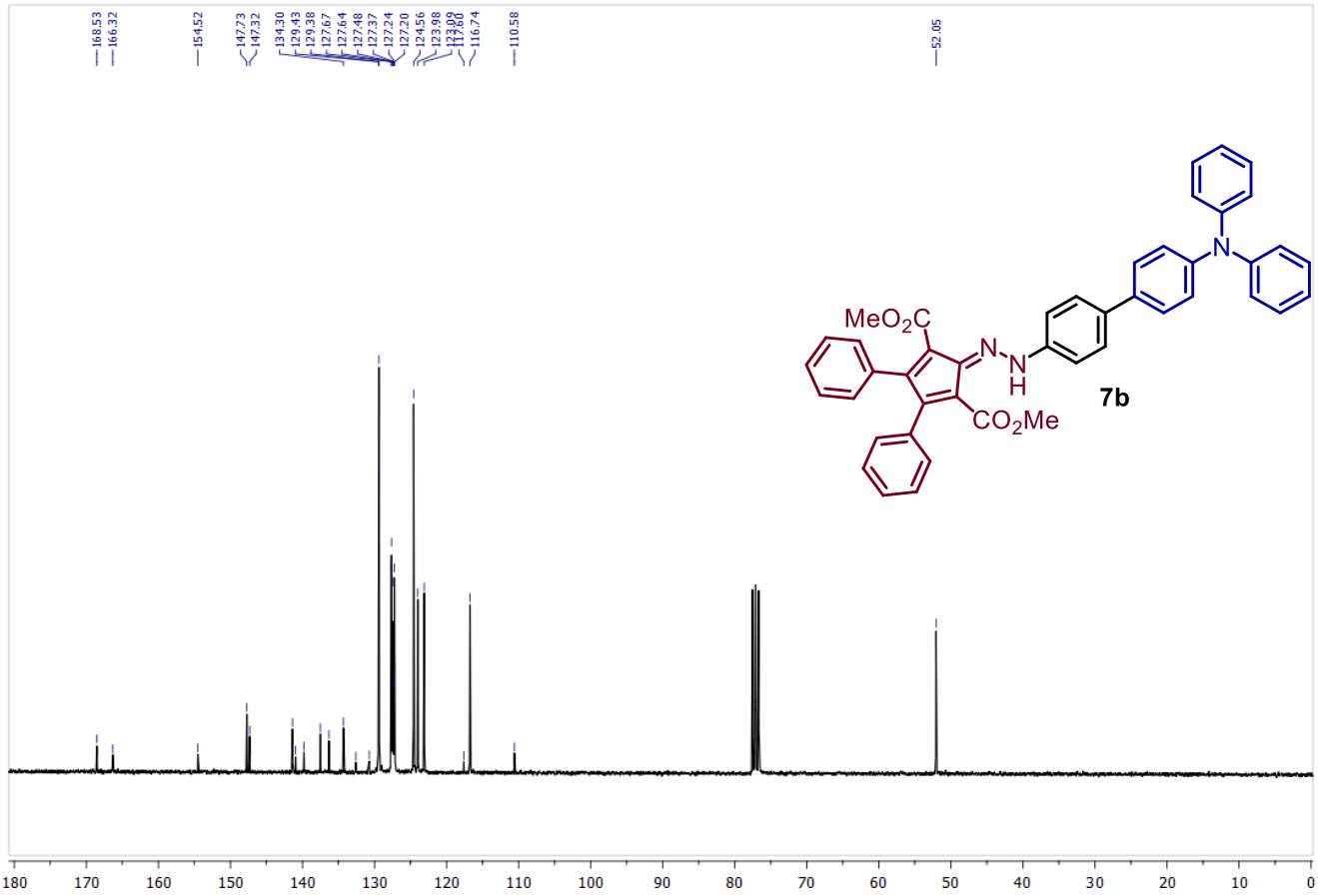


Figure S13 ^{13}C NMR spectrum of compound **7b** (75.5 MHz, $CDCl_3$).

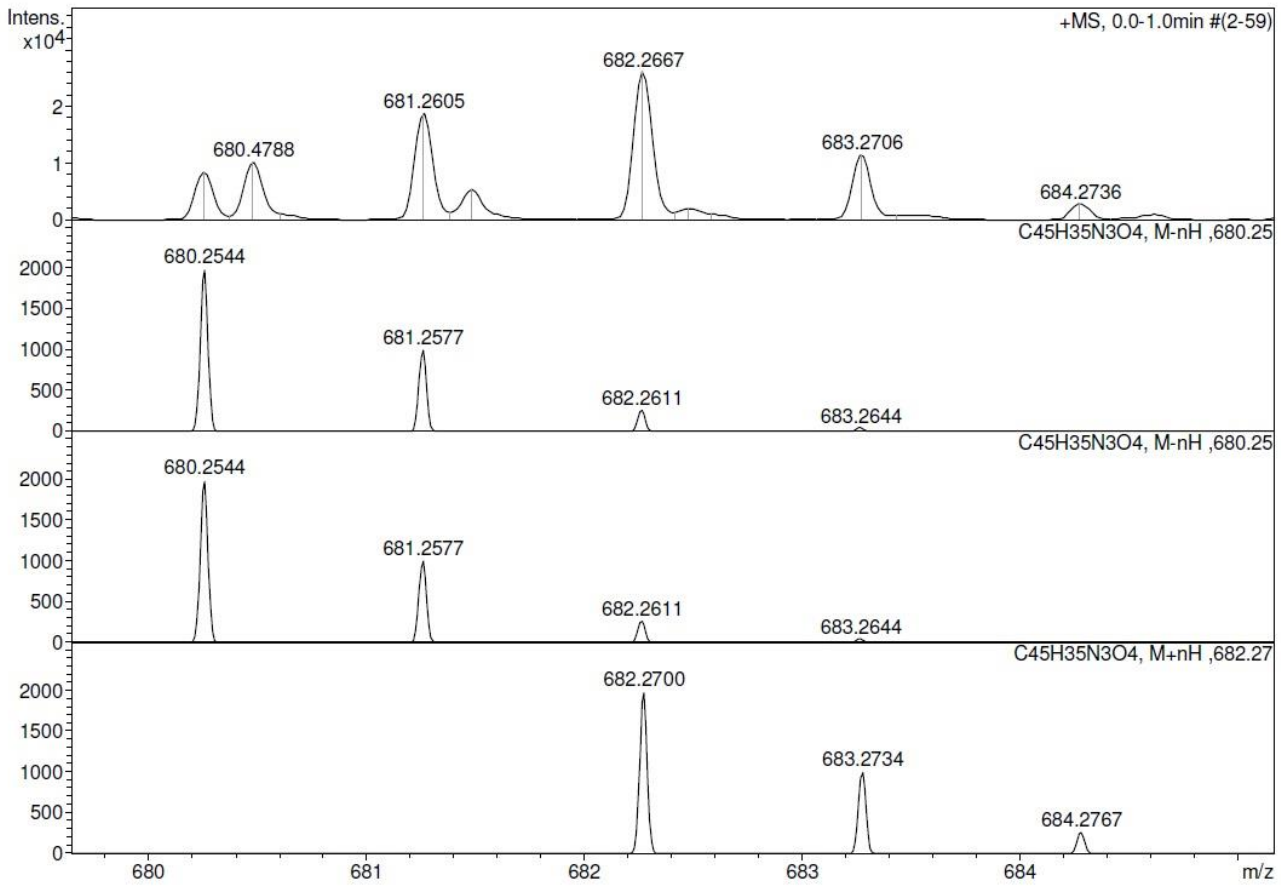


Figure S14 HRMS spectrum of compound **7b**.

3. References

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