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SUPPORTING INFORMATION FILE

HOLE-MEDIATED PHOTOREDOX CATALYSIS: TRIS(*p*-SUBSTITUTED)BIARYLAMINIUM RADICAL CATIONS AS TUNABLE, PRECOMPLEXING AND POTENT PHOTOOXIDANTS

Shangze Wu,† Jonas Žurauskas,†‡ Michał Domański,†‡ Patrick S. Hitzfeld,†‡ Valeria Butera,⊥ Daniel J. Scott,† Julia Rehbein,† Ajeet Kumar,§ Erling Thyrhaug,§ Jürgen Hauer,§ and Joshua P. Barham*†

† Universität Regensburg, Fakültat für Chemie und Pharmazie, 93040 Regensburg, Germany
‡ Central European Institute of Technology, CEITEC, Brno, 612 00 Czech Republic
§ Technische Universität München, Fakültat für Chemie, 85748 Garching b. München, Germany

*Corresponding Author. E-mail: Joshua-Philip.Barham@chemie.uni-regensburg.de

TABLE OF CONTENTS

1. General Experimental Information

Unless stated otherwise, reactions were carried out under an inert (N_2) atmosphere. Cryogenic conditions (-78 °C) were achieved using dry ice/acetone baths. Temperatures of 0 °C were obtained by means of an ice bath or ice/salt bath. 'Room temperature' (rt) indicates temperatures in the range of 20-25 °C. For purposes of thin layer chromatography (TLC), ALUGRAM® Xtra SIL G/UV_{254} silica plates were used, with UV light ($\lambda = 254$ nm) and potassium permanganate used for visualisation. Purification was achieved by column chromatography using Macherey-Nagel silica gel 60 (0.063-0.2 mm). Removal of solvents (in vacuo) was achieved using Heidolph rotary evaporators or Vacuubrand high vacuum pumps. All NMR data were collected using a Bruker Avance 400 Ultrashield instrument using 400 MHz, 376.5 MHz and 101 MHz for 1H, 19F and 13C NMR, respectively, except for ^{1}H NMR of **T*p*TA**, ^{1}H and ^{13}C NMR of **T*p*AA**, and ^{1}H and ^{13}C NMR of **3ab**, which a Bruker Avance 300 Ultrashield instrument was used. ^{13}C NMR was run in ^{1}H-decoupled mode. Data were manipulated using MestReNova version 12.0.0. All ^{1}H NMR experiments were measured with tetramethylsilane (0 ppm), the signal of residual $CHCl_3$ (7.26 ppm) in $CDCl_3$ or the signal of residual Acetone (2.09 ppm) in Acetone-d_6 as the internal reference, ^{13}C NMR experiments were measured in relative to the signal of $CDCl_3$ (77.0 ppm) or Acetone-d_6 (30.6 ppm). Multiplicities for coupled signals were denoted as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. = broad, apt. = apparent and dd = double doublet etc. Coupling constants (*J*) are given in Hz and are uncorrected. Where appropriate, COSY, DEPT, HSQC and HMBC experiments were carried out to aid assignment. Infra-red spectra were recorded on an Agilent Cary 630 FT-IR Spectrophotometer fitted with a Universal ATR accessory as a thin film unless otherwise stated. UV-visible absorption measurements were performed within an Ottle Cell (**Section S8** for details) using an Agilent 8453 spectrometer unless otherwise stated. All samples were prepared at 2.0 x 10^{-3} M in either DCM or MeCN containing 0.1 M *n*-tetrabutylammonium hexafluorophosphate ($^{n}Bu_4N{\cdot}PF_6$ or 'TBAP', 98%+, TCI Chemicals) in order to replicate the reaction conditions. High Resolution Mass spectral analyses were carried out in EI or ESI mode on a Finnigan MAT 95, Thermo Quest Finnigan TSQ 7000, Finnigan MATSSQ 710 A or an Agilent Q - TOF 6540 UHD instrument, masses observed are accurate to within ±5 ppm. Melting points are uncorrected and were recorded using a Stuart melting point device up to 300 °C. All solvents and reagents were purchased from Sigma-Aldrich and used as supplied. All solvents and reagents were used as supplied or purified using standard techniques.[1]

2. Material and Electrodes Preparation

Materials: Platinum wire (P/3640/88 from Alfa Aesar, 10 cm). LED details: 365 nm: CCS (Creating Customer Satisfaction) Inc. (LDL-71X12UV12-365-N); 400 nm: LED Engin (LZ440UB00-00U4); 740 nm: LED Engin (LZ4-00R308); 850 nm: LED Engin (LZ4-00R608). Eluteng (12 V, 1 A) USB cooling fan (from Amazon). Faber-Castell 2.0 mm 2B pencil lead (from Amazon). PeakTech® 6080A digital DC power supply. Glassy carbon foam, thickness: 6.35mm, porosity: 96.5% (Goodfellow, Product Code: 613-422-20).

Anode set-up: A 2B pencil lead was inserted through a septum with the help of a needle. A small square (around 7 mm x 7 mm) of carbon foam was cut from the carbon foam plate, and the pencil lead was pierced through this foam cube.

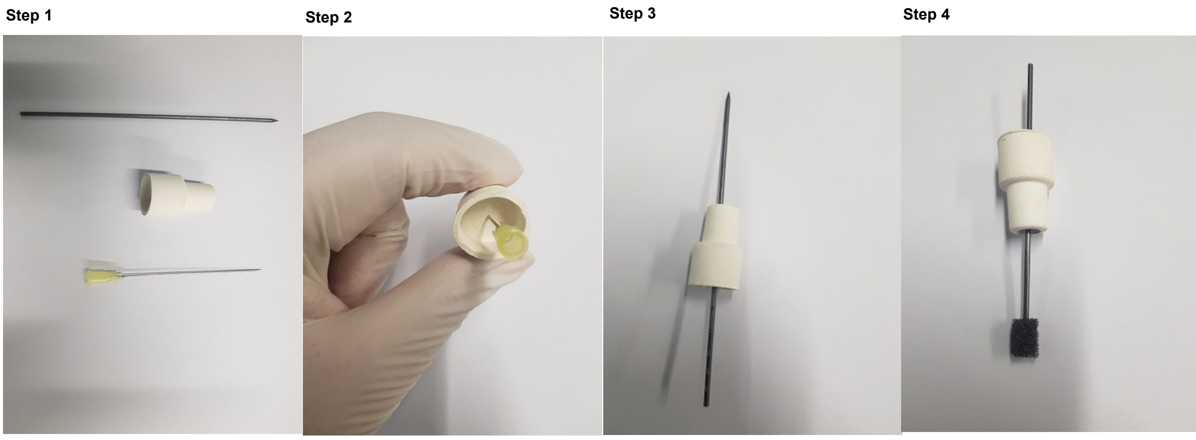


Figure S1. Anode set-up.

Cathode (Pt) set-up: A 2B pencil lead was inserted through a septum with the help of a needle. A 10 cm platinum wire was made into a spiral cathode. The spiral platinum cathode was wrapped tightly around the pencil lead.

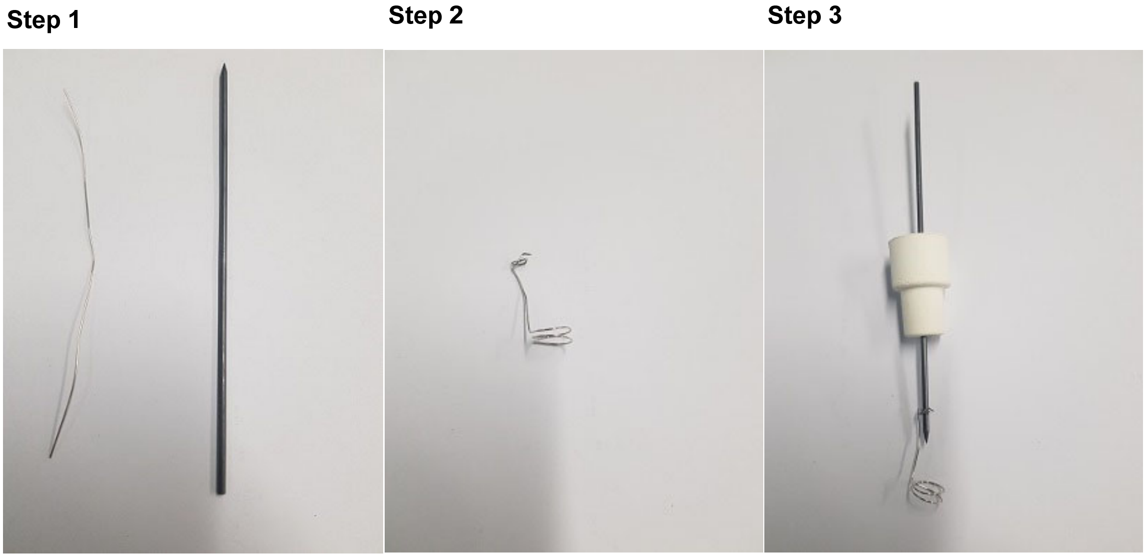


Figure S2. Cathode (Pt) set-up.

Cathode (other metal) set-up: A rectangular metal cathode (*ca.* 20 mm x 4 mm) was inserted into a conductive steel holder. With the help of a needle, the holder was inserted through a septum.

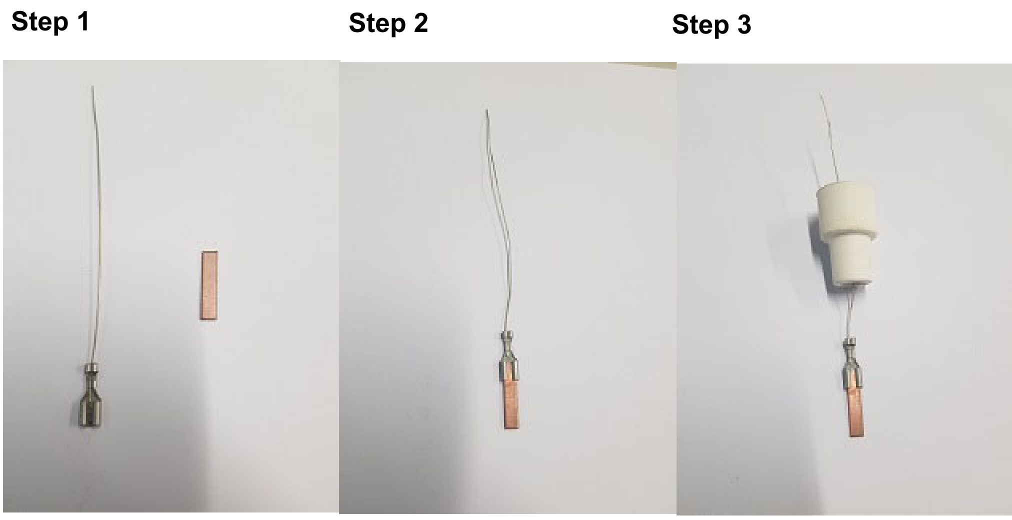


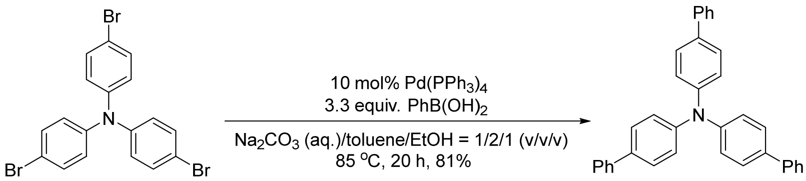
Figure S3. Cathode (other metal) set-up.

Divided H-cell: The H-type divided cell with an Ace Glass Sintered Glass Filter Disc (8 mm diameter, porosity ‘P4’) was handmade by a glassblower at the Universität Regensburg.

Figure S4. Divided H-cell.

3. Synthesis of Triarylamine Catalysts and Triarylaminium Radical Cation Salts

1). Preparation of tri([1,1'-biphenyl]-4-yl)amine (**T*p*BPA**).

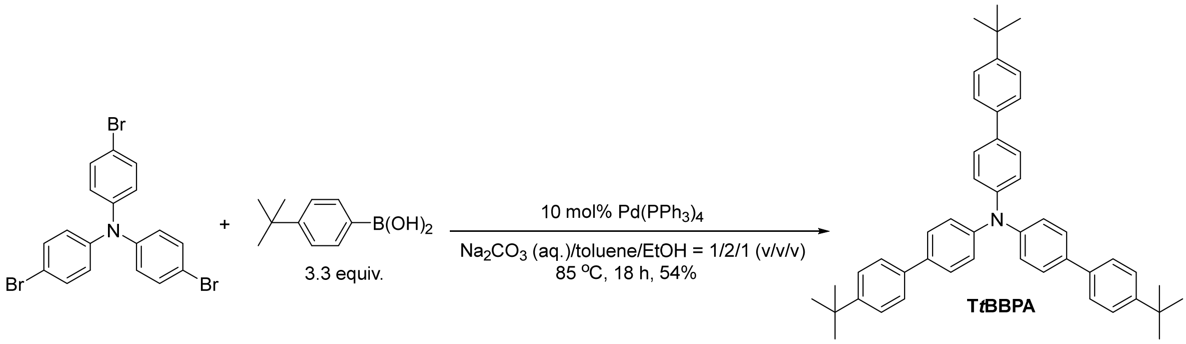


T*p*BPA

General Procedure I: To a dry 250 ml Schlenk flask equipped with a Teflon-coated magnetic stirring bar was added tris(*p*-bromophenyl)amine (4.0 g, 8.3 mmol), phenylboronic acid (3.3 g, 27.4 mmol), aqueous Na_2CO_3 (2.0 M, 57 mL), toluene (115 mL) and absolute EtOH (57 mL). The resulting mixture was degassed by bubbling nitrogen for 15 minutes via canula. Before completely sealing, $Pd(PPh_3)_4$ (1.0 g, 0.83 mmol) was added and the resulting mixture was stirred at 85 °C in complete exclusion of light. After completion as determined by TLC (20 h), the mixture was cooled to room temperature and directly extracted with $CHCl_3$ (100 mL × 3). The combined organic phase was washed with brine (50 mL × 3) and dried over anhydrous Na_2SO_4. Filtration, evaporation of the solvent and chromatography on silica gel (eluent: petroleum ether/$CHCl_3$ = 3/1) afforded **T*p*BPA** (3.7 g, 81%) as a white microcrystalline solid; m.p. 254-256 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 4.0 Hz, 6 H, Ar-H), 7.54 (d, *J* = 8.0 Hz, 6 H, Ar-H), 7.44 (t, *J* = 8.0 Hz, 6 H, Ar-H), 7.33 (t, *J* = 8.0 Hz, 3 H, Ar-H), 7.25 (d, *J* = 4.0 Hz, 6 H, Ar-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 140.6, 135.6, 128.8, 127.9, 126.9, 126.7, 124.4; IR (neat, cm^{-1}) 3056, 3034, 1599, 1517, 1484, 1323, 1293, 1193, 1115; HRMS Calcd. for $C_{36}H_{27}N$ (M^+): 473.2143; Found: 473.2137. Data are consistent with the literature.[2]

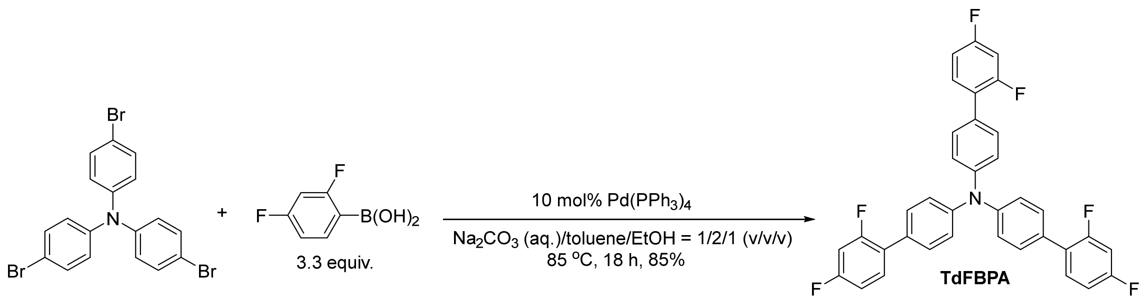
The following catalysts were prepared according to the **General Procedure I**.

2). Preparation of tris(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)amine (**T*t*BBPA**).



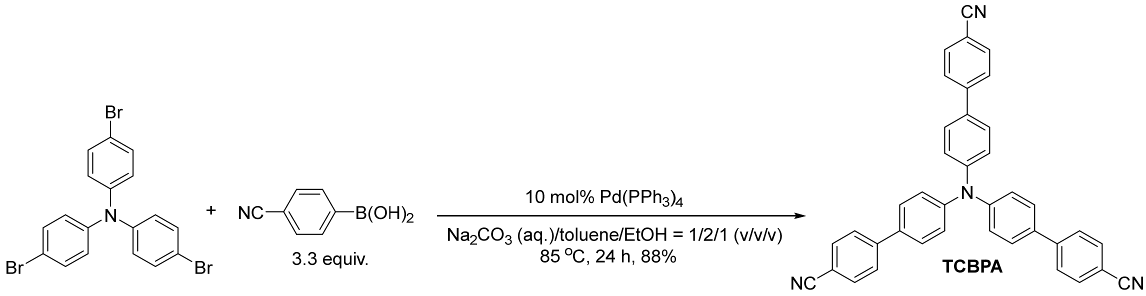
The reaction of tris(*p*-bromophenyl)amine (0.550 g, 1.15 mmol), (*p*-(*tert*-butyl)phenyl)boronic acid (0.675 g, 3.80 mmol), and $Pd(PPh_3)_4$ (0.132 g, 0.115 mmol) in aqueous Na_2CO_3 (2.0 M, 6 mL), toluene (13 mL) and absolute EtOH (6 mL) for 18 h afforded after chromatography (eluent: petroleum ether/$CHCl_3$ = 9/1) **T*t*BBPA** (0.400 g, 54%) as a white microcrystalline solid; m.p. 215-217 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (t, *J* = 10.0 Hz, 12 H, Ar-H), 7.49 (d, *J* = 8.0 Hz, 6 H, Ar-H), 7.25 (d, *J* = 8.0 Hz, 6 H, Ar-H), 1.41 (s, 27 H, 9 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 146.6, 137.7, 135.4, 127.7, 126.3, 125.7, 124.4, 34.5, 31.4; IR (neat, cm^{-1}) 3034, 2963, 2904, 2870, 1603, 1498, 1394, 1327, 1293, 1185, 1115; HRMS Calcd for $C_{48}H_{51}N$ (M^+): 641.4021; Found: 641.4017. Data are consistent with the literature.[3]

3). Preparation of tris(2',4'-difluoro-[1,1'-biphenyl]-4-yl)amine (**TdFBPA**).



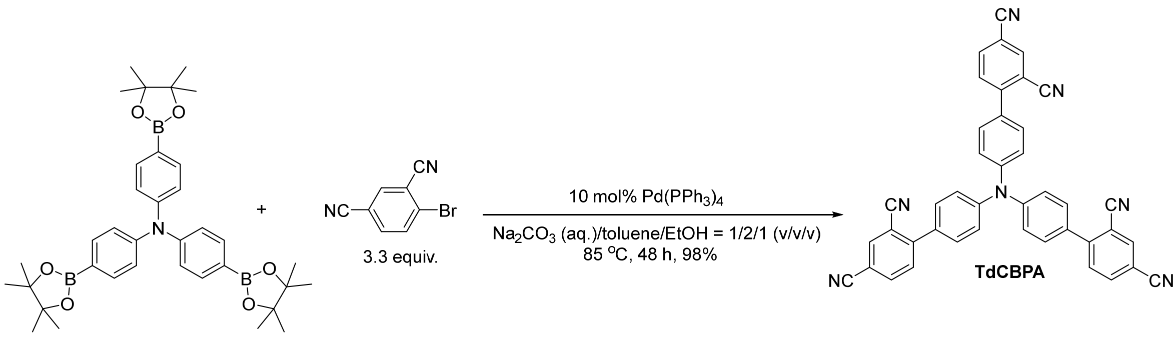
The reaction of tris(*p*-bromophenyl)amine (1.270 g, 2.63 mmol), 2,4-difluorophenylboronic acid (1.500 g, 8.7 mmol), and $Pd(PPh_3)_4$ (0.303 g, 0.263 mmol) in aqueous Na_2CO_3 (2.0 M, 19 mL), toluene (38 mL) and absolute EtOH (19 mL) after 18 h afforded after chromatography (eluent: petroleum ether/$CHCl_3$ = 9/1 to 8/2 to 7/3) **TdFBPA** (1.300 g, 85%) as a white microcrystalline solid; m.p. 177-179 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48-7.37 (m, 9 H, Ar-H), 7.26-7.21 (m, 6 H, Ar-H), 6.99-6.85 (m, 6 H, Ar-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (dd, J_1 = 233.3 Hz, J_2 = 12.1 Hz), 159.7 (dd, J_1 = 234.8 Hz, J_2 = 11.6 Hz), 146.9, 131.1 (q, *J* = 4.7 Hz), 129.8 (d, *J* = 3.0 Hz), 129.6 (d, *J* = 1.0 Hz), 124.8 (dd, J_1 = 13.1 Hz, J_2 = 4.0 Hz), 124.2, 111.6 (dd, J_1 = 20.7 Hz, J_2 = 3.5 Hz), 104.4 (dd, J_1 = 27.3 Hz, J_2 = 25.3 Hz); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -112.4 (d, *J* = 7.5 Hz), -114.0 (d, *J* = 7.5 Hz); IR (neat, cm^{-1}) 3079, 3038, 1599, 1491, 1402, 1327, 1267, 1185, 1141, 1100; HRMS Calcd for $C_{36}H_{21}F_6N$ (M^+): 581.1578; Found: 581.1571. Data are consistent with the literature.[4]

4). Preparation of 4',4''',4'''''-nitrilotris(([1,1'-biphenyl]-4-carbonitrile)) (**TCBPA**).



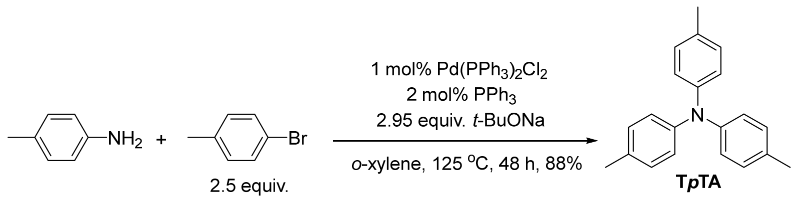
The reaction of tris(*p*-bromophenyl)amine (1.660 g, 3.4 mmol), 4-cyanophenylboronic acid pinacol ester (2.610 g, 11.4 mmol), and $Pd(PPh_3)_4$ (0.396 g, 0.34 mmol) in aqueous Na_2CO_3 (2.0 M, 24 mL), toluene (48 mL) and absolute EtOH (24 mL) after 24 h afforded after chromatography (eluent: DCM) **TCBPA** (1.660 g, 88%) as a pale yellow powder; m.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.65 (m, 12 H, Ar-H), 7.59-7.52 (m, 6 H, Ar-H), 7.31-7.23 (m, 6 H, Ar-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 144.7, 133.9, 132.6, 128.2, 127.1, 124.7, 118.9, 110.5; IR (neat, cm^{-1}) 3038, 2225, 1595, 1521, 1491, 1327, 1282, 1185, 1115, 1006; HRMS Calcd for $C_{39}H_{24}N_4$ (M^+): 548.2001; Found: 548.1990. Data are consistent with the literature.[3]

5). Preparation of 4',4''',4'''''-nitrilotris(([1,1'-biphenyl]-2,4-dicarbonitrile)) (**TdCBPA**).



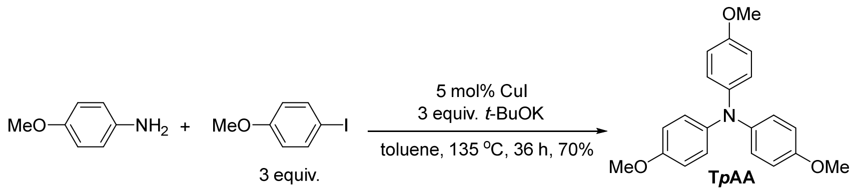
The reaction of tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine (0.611 g, 0.98 mmol), 4-bromoisophthalonitrile (0.670 g, 3.24 mmol), and $Pd(PPh_3)_4$ (0.120 g, 0.098 mmol) in aqueous Na_2CO_3 (2.0 M, 5 mL), toluene (11 mL) and absolute EtOH (5 mL) after 48 h afforded after chromatography (eluent: DCM) **TdCBPA** (0.590 g, 98%) as a yellow powder; m.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 1.6 Hz, 3 H, Ar-H), 7.92 (dd, J_1 = 8.2 Hz, J_2 = 1.7 Hz, 3 H, Ar-H), 7.69 (d, J = 8.0 Hz, 3 H, Ar-H), 7.60-7.53 (m, 6 H, Ar-H), 7.37-7.31 (m, 6 H, Ar-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 148.1, 137.3, 135.8, 131.5, 130.8, 130.1, 124.7, 116.8, 116.7, 112.3, 111.9; IR (neat, cm^{-1}) 3064, 2982, 2926, 2855, 2233, 1592, 1513, 1480, 1327, 1282, 1189; HRMS Calcd for $C_{42}H_{21}N_7$ (M^+): 623.1853; Found: 623.1834.

6). Preparation of tri-*p*-tolylamine (**T*p*TA**).



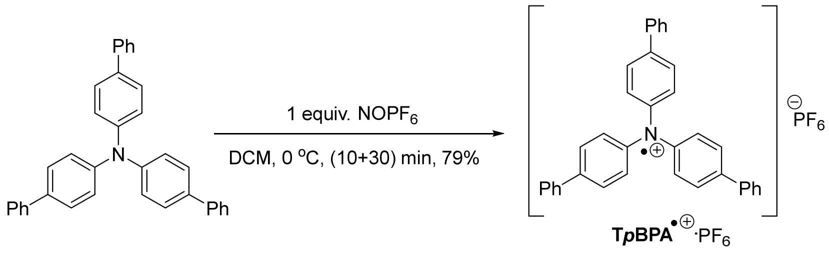
To a dry 250 ml Schlenk flask equipped with a Teflon-coated magnetic stirring bar was added *p*-toluidine (0.43 g, 4 mmol), *p*-bromotoluene (1.71 g, 10 mmol), *t*-BuONa (1.14 g, 11.8 mmol), and anhydrous *o*-xylene (25 mL). The resulting mixture was degassed by bubbling nitrogen for 15 minutes via canula. Before completely sealing, $Pd(PPh_3)_2Cl_2$ (0.03 g, 0.04 mmol) and PPh_3 (0.02 g, 0.08 mmol) was added and the resulting mixture was stirred at 125 °C in complete exclusion of light. After completion as determined by TLC (48 h), the mixture was cooled to room temperature and quenched by H_2O (100 mL) and then extracted with $CHCl_3$ (125 mL × 3). The combined organic phase was washed sequentially with H_2O (100 mL × 3), brine (50 mL × 3) and then dried over anhydrous Na_2SO_4. Filtration, evaporation of the solvent and chromatography on silica gel (eluent: petroleum ether) afforded **T*p*TA** (0.84 g, 88%) as a white microcrystalline solid; m.p. 113-115 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07-6.99 (m, 6 H, Ar-H), 6.98-6.91 (m, 6 H, Ar-H), 2.29 (s, 9 H, 3 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 131.7, 129.7, 123.8, 20.7; IR (neat, cm^{-1}) 3027, 2922, 2863, 1607, 1506, 1320, 1275, 1111; HRMS Calcd for $C_{21}H_{21}N$ (M^+): 287.1669; Found: 287.1664. Data are consistent with the literature.[2]

7). Preparation of tris(4-methoxyphenyl)amine (**T*p*AA**).



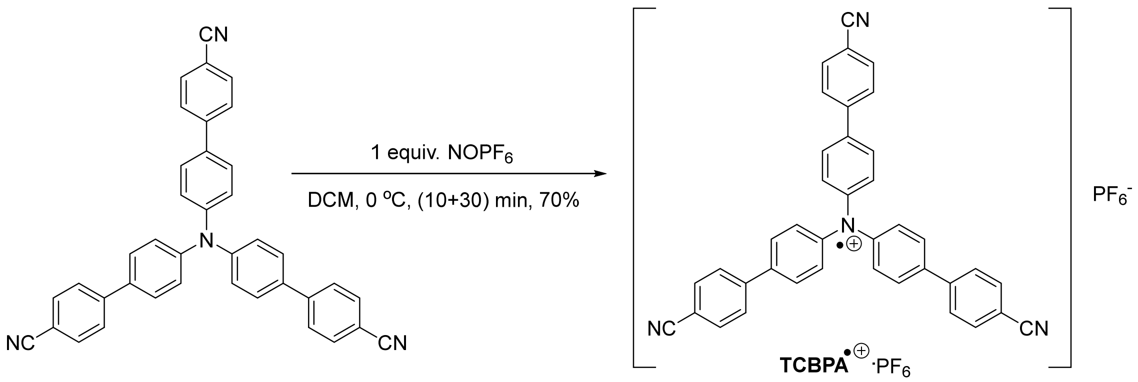
To a dried three-necked flask equipped with a Teflon-coated magnetic stirring bar were added was added 1-iodo-4-methoxybenzene (7.0205 g, 30 mmol), 4-methoxyaniline (1.2324 g, 10 mmol), CuI (0.0958 g, 0.5 mmol), *t*-BuOK (3.3665 g, 30 mmol), and anhydrous toluene (40 mL) under a nitrogen atmosphere. The resulting mixture was stirred at 135 °C. The mixture was cooled to room temperature after 36 h as monitored by TLC and quenched by H_2O (100 mL) and then extracted with ethyl acetate (50 mL × 3). The combined organic phase was washed with brine (30 mL) and dried over anhydrous Na_2SO_4. Filtration, evaporation of the solvent and chromatography on silica gel (eluent: pentane/ethyl acetate = 40/1 to 20/1) afforded **T*p*AA** (2.3412 g, 70%) as a pale orange microcrystalline solid; m.p. 94-96 °C (pentane/ethyl acetate); ^{1}H NMR (300 MHz, C_6D_6) δ 7.12-7.04 (m, 6 H, Ar-H), 6.77-6.69 (m, 6 H, Ar-H), 3.30 (s, 9 H, 3 × OCH_3); ^{13}C NMR (75 MHz, C_6D_6) δ 156.2, 143.2, 125.9, 115.6, 55.6; IR (neat, cm^{-1}) 3042, 2997, 2952, 2833, 1502, 1465, 1238, 1178, 1036; HRMS Calcd for $C_{21}H_{21}NO_3$ (M^+): 335.1516; Found: 335.1507. Data are consistent with the literature.[5]

8). Preparation of **T*p*BPA**$^{\cdot+}\cdot PF_6$.



To a dry 100 ml Schlenk flask equipped with a Teflon-coated magnetic stirring bar was added **T*p*BPA** (80.2 mg, 0.17 mmol) and anhydrous DCM (10 mL) (Flask A). To another dry 100 ml Schlenk flask was added hexafluorophosphate (29.9 mg, 0.17 mmol) and anhydrous DCM (20 mL) (Flask B). Flask A and B were connected by a canula. The resulting mixture of Flask B was slowly pushed into Flask A by N_2 at 0 °C in 10 min. Then the resulting mixture of Flask A was stirred at 0 °C for 30 min, before evaporation of most DCM by vacuum. Then ice cold Et_2O (30 mL) was added to afford a precipitate. After filtration, the precipitate was washed with ice cold Et_2O (10 mL × 2) and evaporation of the solvent afforded **T*p*BPA**$^{\cdot+}\cdot PF_6$ (83.0 mg, 79%) as a dark green microcrystalline solid.

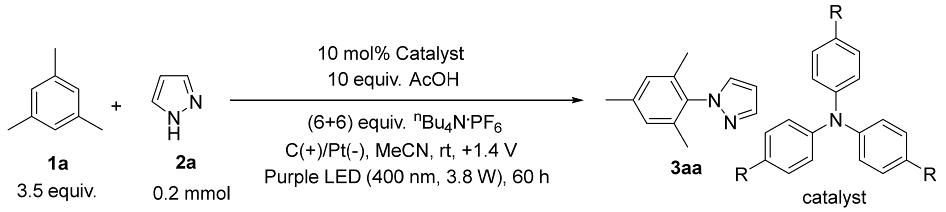
9). Preparation of **TCBPA**$^{\cdot+}\cdot PF_6$.



To a dry 100 ml Schlenk flask equipped with a Teflon-coated magnetic stirring bar was added **TCBPA** (131.8 mg, 0.24 mmol) and anhydrous DCM (10 mL) (Flask A). To another dry 100 ml Schlenk flask was added hexafluorophosphate (42.3 mg, 0.24 mmol) and anhydrous DCM (20 mL) (Flask B). Flask A and B were connected by a canula. The resulting mixture of Flask B was slowly pushed into Flask A by N_2 at 0 °C in 10 min. Then the resulting mixture of Flask A was stirred at 0 °C for 30 min, before evaporation of most DCM by vacuum. Then ice cold Et_2O (30 mL) was added to afford a precipitate. After filtration, the precipitate was washed with ice cold Et_2O (10 mL × 2) and evaporation of the solvent afforded **TCBPA**$^{\cdot+}\cdot PF_6$ (116.3 mg, 70%) as a dark green microcrystalline solid.

4. Optimization of Reaction Conditions

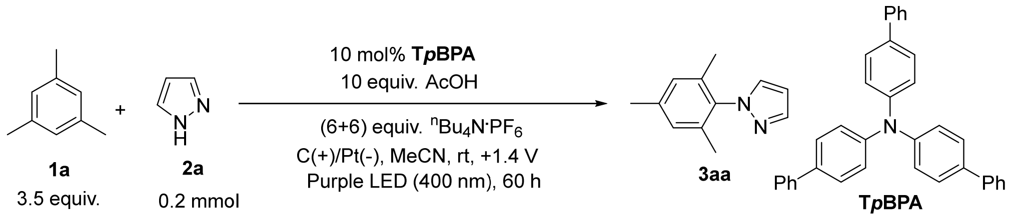
Table S1. Trial of different TPAs[a]



Entry	R	NMR yield[b]/%	
		3aa	SM
1	Br (**TBPA**)	35	-
2	Me (**T*p*TA**)	23	14
3	OMe (**T*p*AA**)	21	-
4	Ph (**T*p*BPA**)	69	15

[a] The reaction was conducted with **1a** (0.1 mL), **2a** (0.2 mmol), catalyst (0.02 mmol), AcOH (2 mmol), $^{n}Bu_4N{\cdot}PF_6$ ((1.2+1.2) mmol), MeCN (2+2 mL) and monitored by TLC. [b] Determined by ^{1}H NMR of the crude product using CH_2Br_2 as internal standard.

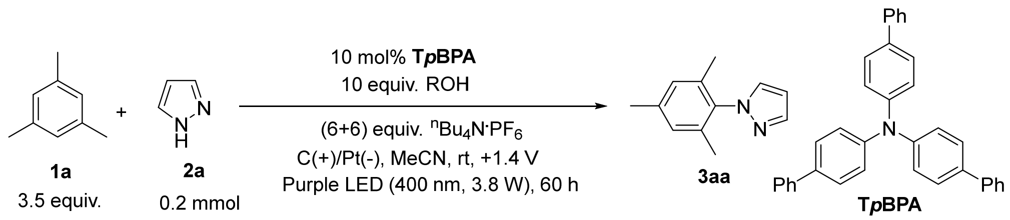
Table S2. Optimization of light intensity: [a]



Entry	Power of 400 nm LED	NMR yield[b]/%	
		3aa	SM
1	0.35 W	18	8
2	3.8 W	69	15

[a] The reaction was conducted with **1a** (0.1 mL), **2a** (0.2 mmol), **T*p*BPA** (0.02 mmol), AcOH (2 mmol), $^{n}Bu_4N{\cdot}PF_6$ ((1.2+1.2) mmol), MeCN (2+2 mL) and monitored by TLC. [b] Determined by ^{1}H NMR of the crude product using CH_2Br_2 as internal standard.

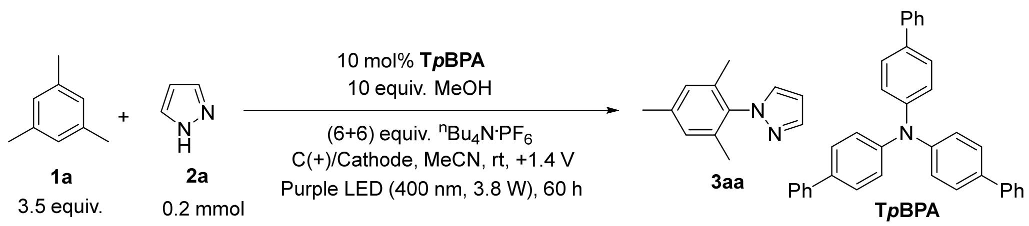
Table S3. Optimization of proton source: [a]



Entry	ROH	NMR yield[b]/%	
		3aa	SM
1	AcOH	69	15
2	MeOH	72	-
3	*i*-PrOH	64	4
4	CF_3COOH	9	21

[a] The reaction was conducted with **1a** (0.1 mL), **2a** (0.2 mmol), **T*p*BPA** (0.02 mmol), ROH (2 mmol), $^nBu_4N{\cdot}PF_6$ ((1.2+1.2) mmol), MeCN (2+2 mL) and monitored by TLC. [b] Determined by ^1H NMR of the crude product using CH_2Br_2 as internal standard.

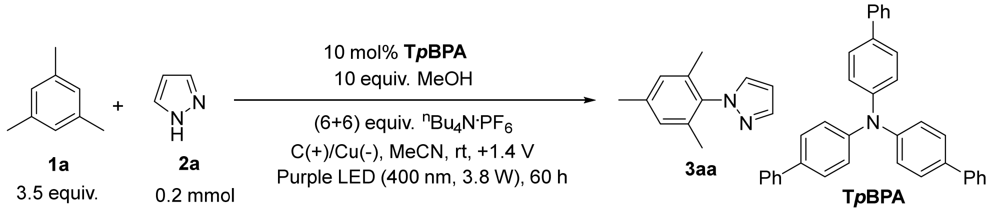
Table S4. Optimization of cathodic material: [a]



Entry	Cathode	NMR yield[b]/%	
		3aa	SM
1[c]	Pt	69	15
2	Pt	72	-
3[c]	C	31	16
4	Zn	42	-
5	Fe	70	-
6	$AlMg_3$	21	-
7	Cu	88[d]	-
8	Ni	33	-

[a] The reaction was conducted with **1a** (0.1 mL), **2a** (0.2 mmol), **T*p*BPA** (0.02 mmol), MeOH (2 mmol), $^nBu_4N{\cdot}PF_6$ ((1.2+1.2) mmol), MeCN (2+2 mL) and monitored by TLC. [b] Determined by ^1H NMR of the crude product using CH_2Br_2 as internal standard. [c] AcOH (2 mmol) was used instead of MeOH. [d] Average of two replicates.

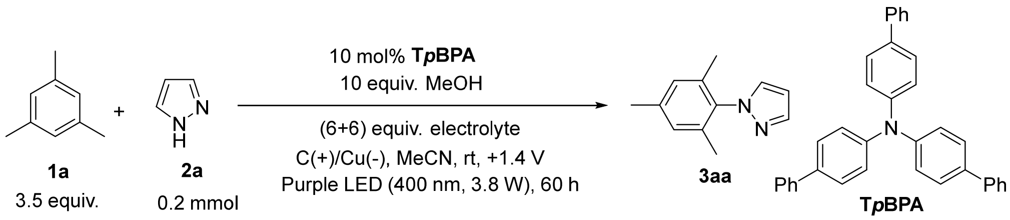
Table S5. Optimization of anodic material: [a]



Entry	Anode	NMR yield[b]/%	
		3aa	SM
1	Glassy carbon foam	88[c]	-
2	Carbon felt (amazon)	19	-
3	Carbon felt (Alfa Aesar)	53	-

[a] The reaction was conducted with **1a** (0.1 mL), **2a** (0.2 mmol), **T*p*BPA** (0.02 mmol), MeOH (2 mmol), $^{n}Bu_4N{\cdot}PF_6$ ((1.2+1.2) mmol), MeCN (2+2 mL) and monitored by TLC. [b] Determined by ^1H NMR of the crude product using CH_2Br_2 as internal standard. [c] Average of two replicates.

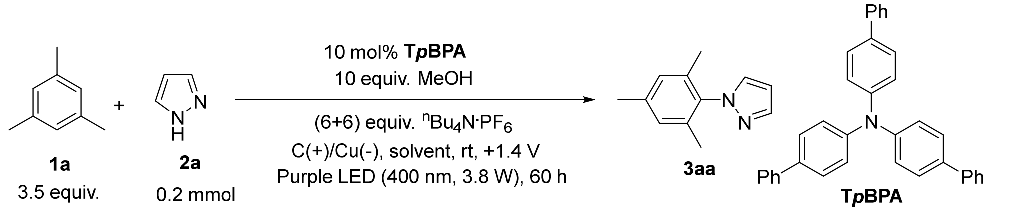
Table S6. Optimization of electrolyte: [a]



Entry	Electrolyte	NMR yield[b]/%	
		3aa	SM
1	$^{n}Bu_4N{\cdot}PF_6$	88[c]	-
2	$LiClO_4$	60	-

[a] The reaction was conducted with **1a** (0.1 mL), **2a** (0.2 mmol), **T*p*BPA** (0.02 mmol), MeOH (2 mmol), electrolyte ((1.2+1.2) mmol), MeCN (2+2 mL) and monitored by TLC. [b] Determined by ^1H NMR of the crude product using CH_2Br_2 as internal standard. [c] Average of two replicates.

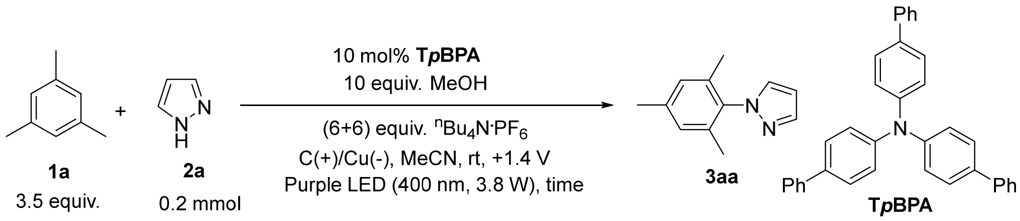
Table S7. Optimization of solvent: [a]



Entry	Solvent	NMR yield[b]/%	
		3aa	SM
1	MeCN	88[c]	-
2	DCM	82	-
3	DMF	-	-

[a] The reaction was conducted with **1a** (0.1 mL), **2a** (0.2 mmol), **T*p*BPA** (0.02 mmol), MeOH (2 mmol), $^{n}Bu_4N{\cdot}PF_6$ ((1.2+1.2) mmol), solvent (2+2 mL) and monitored by TLC. [b] Determined by ^{1}H NMR of the crude product using CH_2Br_2 as internal standard. [c] Average of two replicates.

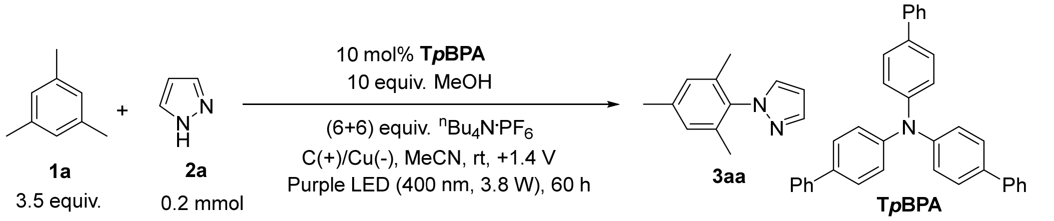
Table S8. Optimization of reaction time: [a]



Entry	Time/h	NMR yield[b]/%	
		3aa	SM
1	60	88[c]	-
2	24	53	-

[a] The reaction was conducted with **1a** (0.1 mL), **2a** (0.2 mmol), **T*p*BPA** (0.02 mmol), MeOH (2 mmol), $^{n}Bu_4N{\cdot}PF_6$ ((1.2+1.2) mmol), MeCN (2+2 mL) and monitored by TLC. [b] Determined by ^{1}H NMR of the crude product using CH_2Br_2 as internal standard. [c] Average of two replicates.

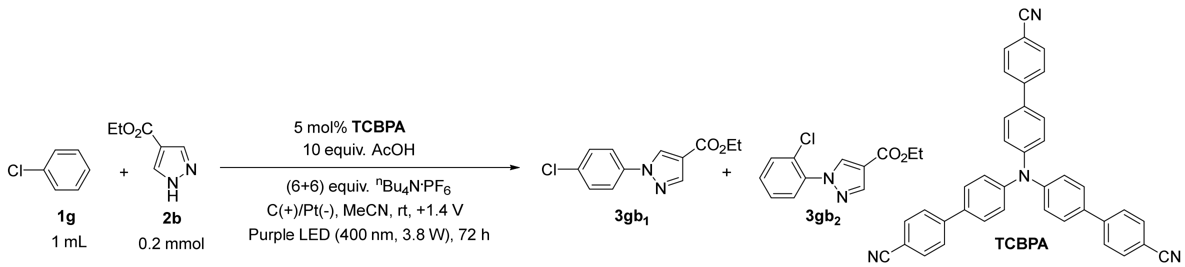
Table S9. Control experiments with **T*p*BPA**: [a]



Entry	Change of Conditions	NMR yield[b]/%	
		3aa	SM[e]
1	-	88[c]	-
2	No electricity	4	-
3	No light	-	-
4	No catalyst	2	-
5	[70mW/cm^2][d] 365 nm LED	11	-
6	2.1 W[d] 740 nm LED	1	-
7	3.8 W[d] 850 nm LED	-	-

[a] The reaction was conducted with **1a** (0.1 mL), **2a** (0.2 mmol), **T*p*BPA** (0.02 mmol), MeOH (2 mmol), $^nBu_4N{\cdot}PF_6$ ((1.2+1.2) mmol), MeCN (2+2 mL) and monitored by TLC. [b] Determined by ^1H NMR of the crude product using CH_2Br_2 as internal standard. [c] Average of two replicates. [d]Radiant power of LED specified by manufacturer, see **Section S11** for details. [e]The sublimation of pyrazole during concentration *in vacuo* meant that starting material could not be detected after reaction work up.

Table S10. Control experiments with **TCBPA**: [a]

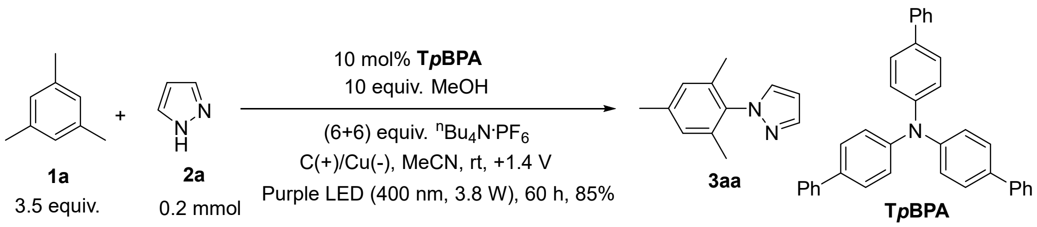


Entry	Change of Conditions	NMR yield[b]/% (**3gb$_1$** + **3gb$_2$**)	
		3aa	SM
1	-	69[c]	-
2	No electricity	9	42
3	[70mW/cm^2][d] 365 nm LED	8	30
4	2.1 W[d] 740 nm LED	0	100
5	3.8 W[d] 850 nm LED	< 5	69

[a] The reaction was conducted with **1g** (1.0 mL), **2b** (0.2 mmol), **TCBPA** (0.01 mmol), AcOH (2 mmol), $^nBu_4N{\cdot}PF_6$ ((1.2+1.2) mmol), MeCN (2+2 mL) and monitored by TLC. [b] Determined by ^1H NMR of the crude product using CH_2Br_2 as internal standard. [c] Average of two replicates. [d]Radiant power of LED specified by manufacturer, see **Section S11** for details.

5. e-PRC C-H HETEROAMINATION REACTIONS

1). Preparation of **3aa**.



General Procedure II: To a dried H-cell equipped with Teflon-coated magnetic stirring bars in each compartment were added (to the anodic chamber:) catalyst **T*p*BPA** (9.4 mg, 0.02 mmol), pyrazole **2a** (13.9 mg, 0.2 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.8 mg, 1.2 mmol), and (to the cathodic chamber:) $^{n}Bu_4N{\cdot}PF_6$ (464.2 mg, 1.2 mmol). Then, to the anodic chamber, MeCN (2 mL) and mesitylene **1a** (0.1 mL, d = 0.86 g/mL, 84.1 mg, 0.7 mmol) were added. To cathodic chamber, MeCN (2 mL) and MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) were added. Both compartments were sealed using rubber septums and parafilm then flushed with N_2 for 5 min. The resulting mixture was stirred at room temperature above a water-cooled cooling block under irradiation of 400 nm LED from beneath the anodic chamber. A constant potential of +1.4 V was applied across the cell. After being stirred for 60 h at rt, the reaction was complete as determined by TLC. The resulting mixture was poured into a flask and each compartment was washed with ethyl acetate (3 mL × 3). The carbon foam was sonicated with ethyl acetate for 5 min. After combining these organics, they were diluted with pentane to pentane/ethyl acetate = 2/1. Filtration through a short column of silica gel (eluent: pentane/ethyl acetate = 2/1, 15 mL × 3) and evaporation afforded the crude product, which was purified by flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 100/1 to 50/1) to afford **3aa** (32.3 mg, 85%) as a pale yellow solid; m.p. 55-57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.68 (m, 1 H, Ar-H), 7.43-7.38 (m, 1 H, Ar-H), 6.93 (s, 2 H, Ar-H), 6.41 (t, J = 4.0 Hz, 1 H, Ar-H), 2.31 (s, 3 H, CH_3), 1.95 (s, 6 H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 138.6, 136.8, 135.7, 130.7, 128.6, 105.6, 20.9, 17.0; IR ν (neat, cm^{-1}) 3105, 2956, 2922, 2859, 1737, 1595, 1513, 1487, 1394, 1193, 1103, 1044; HRMS Calcd for $C_{12}H_{14}N_2$ (M^+): 186.1152. Found: 186.1152. Data are consistent with the literature.[6]

Before light **With light**

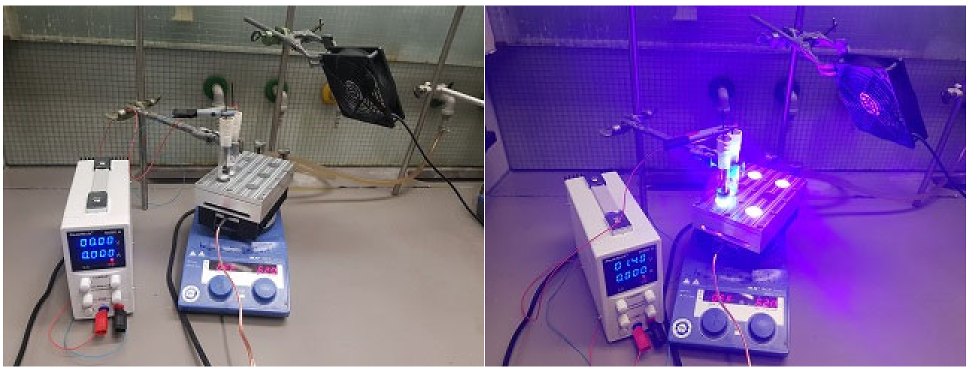
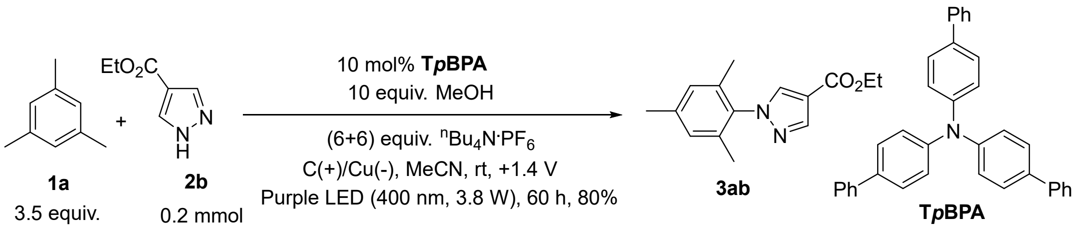


Figure S5. Reaction set-up.

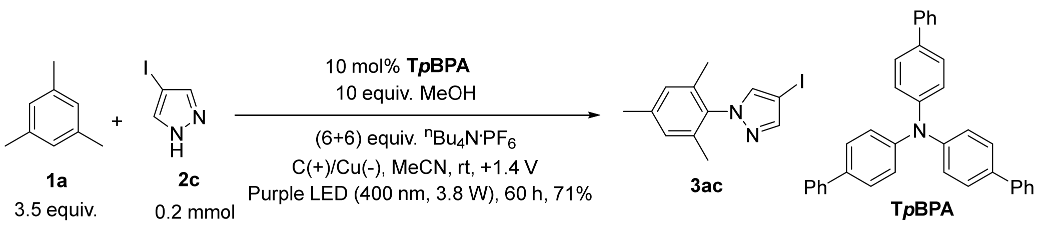
The following compounds were prepared according to the **General Procedure II**.

2). Preparation of **3ab**.



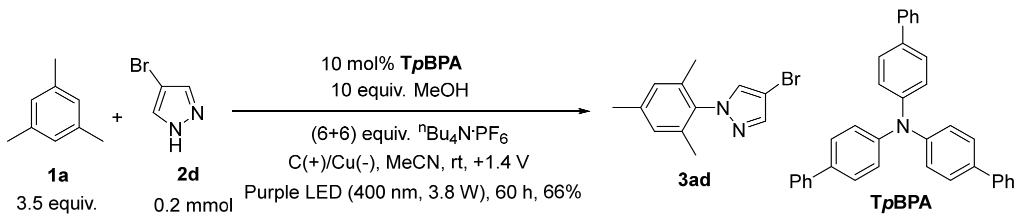
The reaction of **1a** (0.1 mL, d = 0.86 g/mL, 84.1 mg, 0.7 mmol), **2b** (28.2 mg, 0.2 mmol), **T*p*BPA** (9.6 mg, 0.02 mmol), $^{n}Bu_4N{\cdot}PF_6$ (465.4 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N.PF_6$ (464.8 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded **3ab** (41.7 mg, 80%) (eluent: pentane/ethyl acetate = 50/1 to 20/1) as a colourless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 8.14-8.10 (m, 1 H, Ar-H), 7.95-7.91 (m, 1 H, Ar-H), 6.95 (s, 2 H, Ar-H), 4.34 (q, *J* = 7.0 Hz, 2 H, CH_2), 2.34 (s, 3 H, CH_3), 1.99 (s, 6 H, 2 × CH_3), 1.38 (t, *J* = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 141.6, 139.4, 136.1, 135.4, 134.5, 128.9, 115.5, 60.3, 21.1, 17.2, 14.4; IR ν (neat, cm^{-1}) 3124, 2982, 2926, 1715, 1554, 1498, 1446, 1402, 1230, 1167, 1129; HRMS Calcd for $C_{15}H_{18}N_2O_2$ (M^+): 258.1363. Found: 258.1370. Data are consistent with the literature.[6]

3). Preparation of **3ac**.



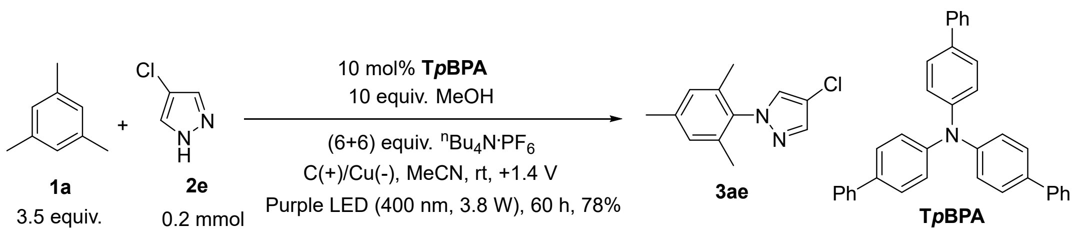
The reaction of **1a** (0.1 mL, d = 0.86 g/mL, 84.1 mg, 0.7 mmol), **2c** (38.5 mg, 0.2 mmol), **T*p*BPA** (9.6 mg, 0.02 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.2 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (465.5 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.0 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded **3ac** (43.8 mg, 71%) (eluent: pentane/ethyl acetate = 100/1 to 50/1) as a colourless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1 H, Ar-H), 7.47 (s, 1 H, Ar-H), 6.94 (s, 2 H, Ar-H), 2.33 (s, 3 H, CH_3), 1.97 (s, 6 H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 139.2, 136.3, 135.6, 135.2, 128.9, 56.5, 21.1, 17.2; IR ν (neat, cm^{-1}) 3124, 2956, 2922, 2859, 1692, 1607, 1510, 1398, 1316, 1252, 1033; HRMS Calcd for $C_{12}H_{13}IN_2$ (M^+): 312.0118. Found: 312.0110. Data are consistent with the literature.[6]

4). Preparation of **3ad**.



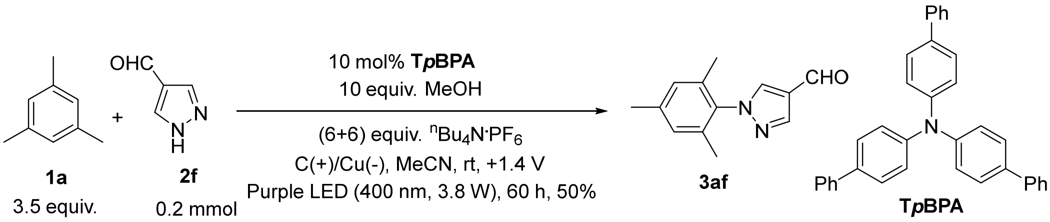
The reaction of **1a** (0.1 mL, d = 0.86 g/mL, 84.1 mg, 0.7 mmol), **2d** (29.1 mg, 0.2 mmol), **T*p*BPA** (9.5 mg, 0.02 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.2 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (465.0 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded **3ad** (34.5 mg, 66%) (eluent: pentane/ethyl acetate = 100/1 to 50/1) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1 H, Ar-H), 7.45 (s, 1 H, Ar-H), 6.94 (s, 2 H, Ar-H), 2.33 (s, 3 H, CH_3), 1.98 (s, 6 H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 139.3, 136.4, 135.7, 130.9, 128.9, 93.5, 21.1, 17.2; IR ν (neat, cm^{-1}) 3127, 3027, 2956, 2922, 2859, 1610, 1491, 1402, 1323, 1256, 1167, 1033; HRMS Calcd for $C_{12}H_{13}{}^{79}BrN_2$ (M^+): 264.0257. Found: 264.0260. Data are consistent with the literature.[6]

5). Preparation of **3ae**.



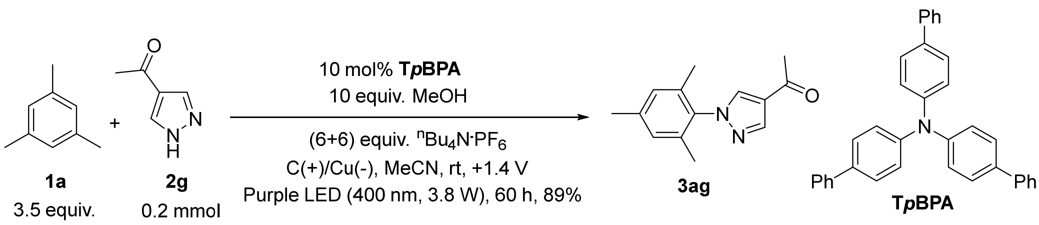
The reaction of **1a** (0.1 mL, d = 0.86 g/mL, 84.1 mg, 0.7 mmol), **2e** (20.8 mg, 0.2 mmol), **T*p*BPA** (9.7 mg, 0.02 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.2 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (465.4 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded **3ae** (34.8 mg, 78%) (eluent: pentane/ethyl acetate = 100/1 to 50/1) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1 H, Ar-H), 7.43 (s, 1 H, Ar-H), 6.94 (s, 2 H, Ar-H), 2.33 (s, 3 H, CH_3), 1.98 (s, 6 H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 138.5, 136.5, 135.7, 128.9, 128.8, 110.4, 21.1, 17.2; IR ν (neat, cm^{-1}) 3131, 3027, 2956, 2922, 2863, 1737, 1607, 1491, 1402, 1331, 1260; HRMS Calcd for $C_{12}H_{13}{}^{35}ClN_2$ (M^+): 220.0762. Found: 220.0758. Data are consistent with the literature.[6]

6). Preparation of **3af**.



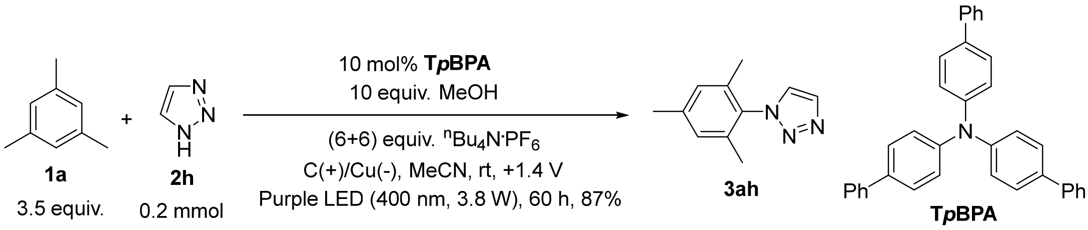
The reaction of **1a** (0.1 mL, d = 0.86 g/mL, 84.1 mg, 0.7 mmol), **2f** (19.5 mg, 0.2 mmol), **T*p*BPA** (9.5 mg, 0.02 mmol), $^nBu_4N{\cdot}PF_6$ (464.1 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^nBu_4N{\cdot}PF_6$ (464.7 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded **3af** (21.8 mg, 50%) (eluent: pentane/ethyl acetate = 40/1 to 10/1) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1 H, COH), 8.19 (s, 1 H, Ar-H), 7.97 (s, 1 H, Ar-H), 6.97 (s, 2 H, Ar-H), 2.35 (s, 3 H, CH_3), 1.99 (s, 6 H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.2, 141.2, 139.7, 135.8, 135.2, 134.6, 129.0, 124.6, 21.1, 17.2; IR ν (neat, cm^{-1}) 3116, 2922, 2855, 1681, 1543, 1495, 1361, 1200, 1156; HRMS Calcd for $C_{13}H_{14}N_2O$ (M^+): 214.1101. Found: 214.1103. Data are consistent with the literature.[6]

7). Preparation of **3ag**.



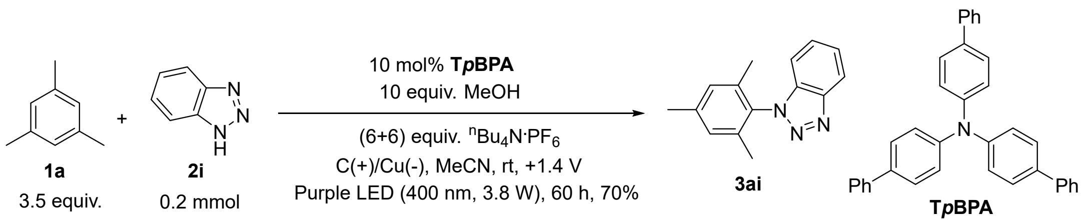
The reaction of **1a** (0.1 mL, d = 0.86 g/mL, 84.1 mg, 0.7 mmol), **2g** (22.4 mg, 0.2 mmol), **T*p*BPA** (9.2 mg, 0.02 mmol), $^nBu_4N{\cdot}PF_6$ (464.3 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^nBu_4N{\cdot}PF_6$ (464.7 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded **3ag** (41.3 mg, 89%) (eluent: pentane/ethyl acetate = 25/1 to 10/1) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1 H, Ar-H), 7.93 (s, 1 H, Ar-H), 6.96 (s, 2 H, Ar-H), 2.49 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 1.98 (s, 6 H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 140.9, 139.5, 135.9, 135.2, 133.6, 128.9, 124.5, 27.9, 21.0, 17.1; IR ν (neat, cm^{-1}) 3120, 2926, 2855, 1670, 1543, 1402, 1241; HRMS Calcd for $C_{14}H_{16}N_2O$ (M^+): 228.1257. Found: 228.1253. Data are consistent with the literature.[6]

8). Preparation of **3ah**



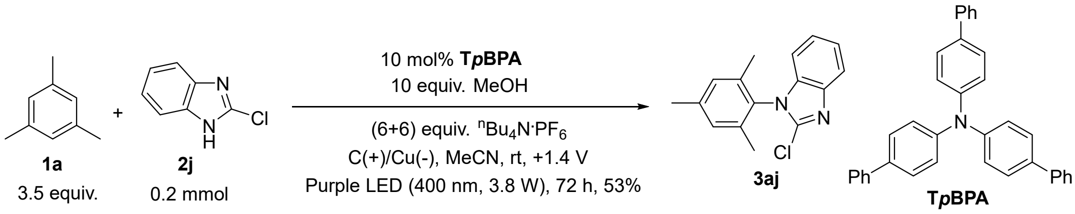
The reaction of **1a** (0.1 mL, d = 0.86 g/mL, 84.1 mg, 0.7 mmol), **2h** (13.5 mg, 0.2 mmol), **T*p*BPA** (9.3 mg, 0.02 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.8 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (465.4 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded **3ah** (31.8 mg, 87%) (eluent: pentane/ethyl acetate = 15/1 to 6/1) as a white solid; m.p. 188-189 °C (pentane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1 H, Ar-H), 7.63 (s, 1 H, Ar-H), 7.00 (s, 2 H, Ar-H), 2.36 (s, 3 H, CH_3), 1.94 (s, 6 H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 135.0, 133.5, 133.4, 129.0, 125.4, 21.0, 17.1; IR ν (neat, cm^{-1}) 3101, 2952, 2922, 2855, 1595, 1502, 1454, 1320, 1230, 1208, 1122, 1096, 1044; HRMS Calcd for $C_{11}H_{13}N_3$ (M^+): 187.1104. Found: 187.1105. Data are consistent with the literature.[6]

9). Preparation of **3ai**.



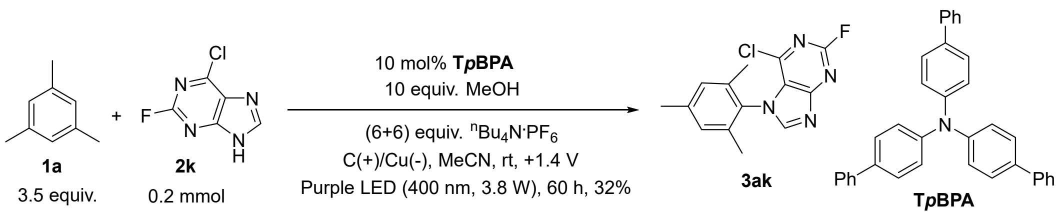
The reaction of **1a** (0.1 mL, d = 0.86 g/mL, 84.1 mg, 0.7 mmol), **2i** (23.6 mg, 0.2 mmol), **T*p*BPA** (9.7 mg, 0.02 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.4 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (465.5 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded **3ai** (33.0 mg, 70%) (eluent: pentane/ethyl acetate = 80/1 to 20/1) as a white solid; m.p. 121-122 °C (pentane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 1 H, Ar-H), 7.52-7.37 (m, 2 H, Ar-H), 7.21 (d, J = 8.0 Hz, 1 H, Ar-H), 7.07 (s, 2 H, Ar-H), 2.40 (s, 3 H, CH_3), 1.87 (s, 6 H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 140.2, 136.1, 133.8, 131.6, 129.3, 127.9, 123.9, 120.0, 109.7, 21.2, 17.3; IR ν (neat, cm^{-1}) 3027, 2952, 2922, 2863, 1610, 1498, 1454, 1379, 1275, 1193, 1070; HRMS Calcd for $C_{15}H_{15}N_3$ (M^+): 237.1261. Found: 237.1268. Data are consistent with the literature.[7]

10). Preparation of **3aj**.



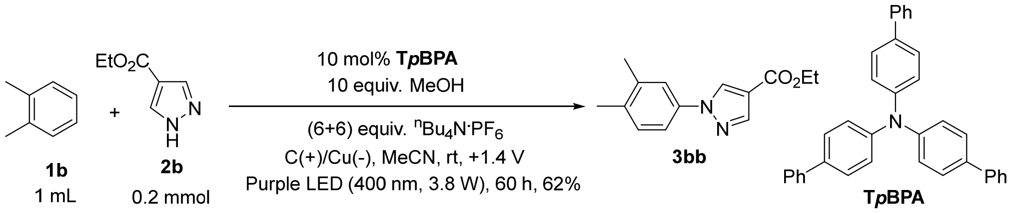
The reaction of **1a** (0.1 mL, d = 0.86 g/mL, 84.1 mg, 0.7 mmol), **2j** (30.7 mg, 0.2 mmol), **T*p*BPA** (9.6 mg, 0.02 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.3 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (465.2 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded **3aj** (28.8 mg, 53%) (eluent: pentane/ethyl acetate = 80/1 to 40/1) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.31 (t, *J* = 6.0 Hz, 1 H, Ar-H), 7.23 (t, *J* = 8.0 Hz, 1 H, Ar-H), 7.06 (s, 2 H, Ar-H), 6.90 (d, *J* = 8.0 Hz, 1 H, Ar-H), 2.40 (s, 3 H, CH_3), 1.91 (s, 6 H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 140.8, 139.9, 136.7, 135.5, 129.7, 129.4, 123.6, 122.9, 119.4, 109.9, 21.2, 17.4; IR ν (neat, cm^{-1}) 3056, 2952, 2922, 2863, 1614, 1469, 1372, 1305, 1267; HRMS Calcd for $C_{16}H_{15}{}^{35}ClN_2$ (M^+): 270.0918. Found: 270.0923.

11). Preparation of **3ak**.



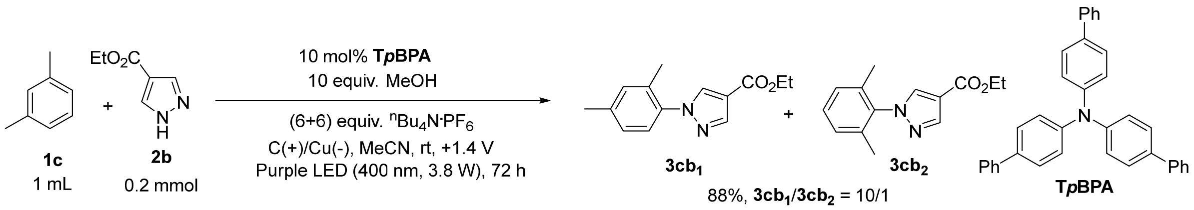
The reaction of **1a** (0.1 mL, d = 0.86 g/mL, 84.1 mg, 0.7 mmol), **2k** (34.3 mg, 0.2 mmol), **T*p*BPA** (9.4 mg, 0.02 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.7 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (464.4 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded **3ak** (18.6 mg, 32%) (eluent: pentane/ethyl acetate = 20/1 to 10/1 to 6/1) as a pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1 H, Ar-H), 7.06 (s, 2 H, Ar-H), 2.38 (s, 3 H, CH_3), 1.96 (s, 6 H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8 (d, *J* = 221.1 Hz), 153.8 (d, *J* = 16.9 Hz), 153.3 (d, *J* = 17.5 Hz), 146.4 (d, *J* = 3.2 Hz), 140.7, 135.5, 130.0 (d, *J* = 4.8 Hz), 129.7, 128.4, 21.1, 17.7; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -49.0; IR ν (neat, cm^{-1}) 3101, 2960, 2926, 2859, 1573, 1506, 1424, 1394, 1338, 1297, 1260, 1238, 1200, 1044; HRMS Calcd for $C_{14}H_{12}{}^{35}ClFN_4$ (M^+): 290.0729. Found: 290.0730. Data are consistent with the literature.[6]

12). Preparation of **3bb**.



The reaction of **1b** (1 mL), **2b** (28.2 mg, 0.2 mmol), **T*p*BPA** (9.4 mg, 0.02 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.3 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (465.2 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded **3bb** (30.4 mg, 62%) (eluent: pentane/ethyl acetate = 50/1 to 20/1) as a white solid; m.p. 93-94 °C (pentane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1 H, Ar-H), 8.09 (s, 1 H, Ar-H), 7.50 (d, *J* = 4.0 Hz, 1 H, Ar-H), 7.39 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1 H, Ar-H), 7.21 (d, *J* = 8.0 Hz, 1 H, Ar-H), 4.34 (q, *J* = 6.7 Hz, 2 H, CH_2), 2.33 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 1.38 (t, *J* = 6.0 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 141.9, 138.1, 137.3, 130.5, 129.9, 120.8, 116.8, 116.5, 60.3, 19.9, 19.3, 14.4; IR *ν* (neat, cm^{-1}) 3120, 2989, 2922, 2855, 1711, 1554, 1506, 1409, 1293, 1238, 1141, 1025; HRMS Calcd for $C_{14}H_{16}N_2O_2$ (M^+): 244.1206. Found: 244.1201. Data are consistent with the literature.[8]

13). Preparation of **$3cb_1$** and **$3cb_2$**.



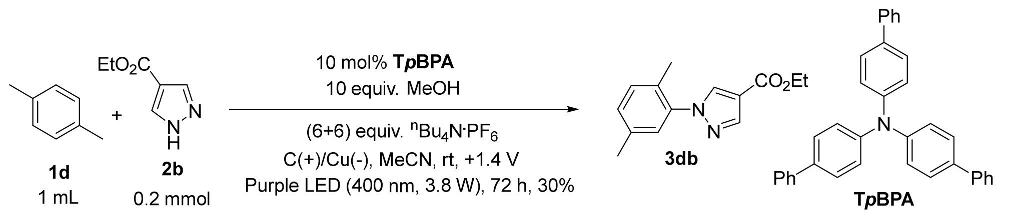
The reaction of **1c** (1 mL), **2b** (27.8 mg, 0.2 mmol), **T*p*BPA** (9.5 mg, 0.02 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.3 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (465.0 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded a mixture of **$3cb_1$ and $3cb_2$** (42.8 mg, 88%, **$3cb_1$/$3cb_2$** = 10/1) (eluent: pentane/ethyl acetate = 40/1 to 20/1) as a pale yellow oil.

$3cb_1$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1 H, Ar-H), 8.05 (s, 1 H, Ar-H), 7.19 (d, *J* = 7.9 Hz, 1 H, Ar-H), 7.13 (s, 1 H, Ar-H), 7.08 (d, *J* = 8.0 Hz, 1 H, Ar-H), 4.33 (q, *J* = 7.1 Hz, 2 H, CH_2), 2.37 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 1.37 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 141.4, 139.1, 136.7, 133.9, 133.3, 131.9, 127.2, 125.8, 115.7, 60.2, 21.0, 17.7, 14.3.

$3cb_2$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1 H, Ar-H), 7.96 (s, 1 H, Ar-H), 7.27 (t, *J* = 8.0 Hz, 1 H, Ar-H), 7.14 (d, *J* = 8.0 Hz, 2 H, Ar-H), 4.34 (q, *J* = 8.0 Hz, 2 H, CH_2), 2.03 (s, 6 H, 2 × CH_3), 1.38 (t, *J* = 6.0 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 141.6, 138.4, 135.4, 134.3, 129.5, 128.2, 115.6, 60.3, 17.2, 14.3.

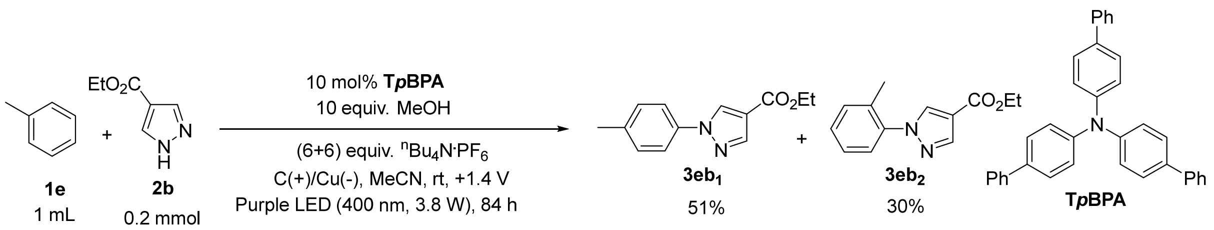
$3cb_1$ and **$3cb_2$**: IR *ν* (neat, cm^{-1}) 3124, 2982, 2930, 1715, 1554, 1510, 1446, 1405, 1226, 1141, 1029; HRMS Calcd for $C_{14}H_{16}N_2O_2$ (M^+): 244.1206. Found: 244.1206. Data of **$3cb_1$** are consistent with the literature.[8]

14). Preparation of **3db**.



The reaction of **1d** (1 mL), **2b** (28.3 mg, 0.2 mmol), **T*p*BPA** (9.5 mg, 0.02 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.3 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (464.9 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded **3db** (14.7 mg, 30%) (eluent: pentane/ethyl acetate = 50/1 to 10/1 to 6/1) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1 H, Ar-H), 8.07 (s, 1 H, Ar-H), 7.21 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.16 (d, *J* = 8.0 Hz, 2 H, Ar-H), 4.34 (q, *J* = 6.7 Hz, 2 H, CH_2), 2.36 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 1.37 (t, *J* = 8.0 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 141.5, 138.9, 136.7, 133.8, 131.2, 130.2, 129.8, 126.5, 115.8, 60.3, 20.7, 17.5, 14.4; IR ν (neat, cm^{-1}) 3124, 2982, 2930, 1715, 1554, 1513, 1461, 1405, 1241, 1193, 1148, 1025; HRMS Calcd for $C_{14}H_{16}N_2O_2$ (M^+): 244.1206. Found: 244.1203.

15). Preparation of **3eb₁** and **3eb₂**.

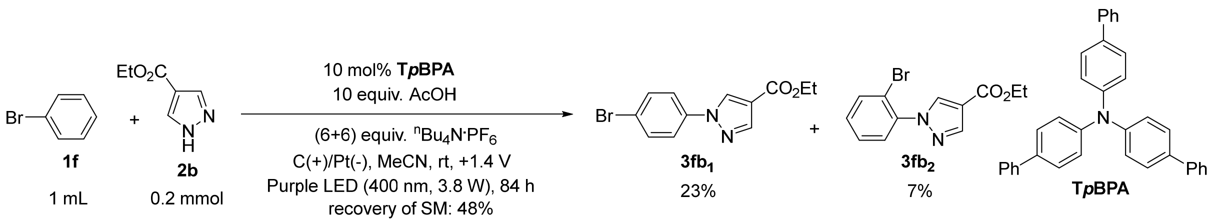


The reaction of **1e** (1 mL), **2b** (28.2 mg, 0.2 mmol), **T*p*BPA** (9.3 mg, 0.02 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.2 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (464.9 mg, 1.2 mmol), MeCN (2 mL), MeOH (0.08 mL, d = 0.79 g/mL, 64.0 mg, 2 mmol) (cathodic chamber) afforded **$3eb_1$** (23.7 mg, 51%) and **$3eb_2$** (13.9 mg, 30%) (eluent: pentane/ethyl acetate = 40/1 to 25/1 to 10/1).

$3eb_1$ as a white solid; m.p. 102-103 °C (pentane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1 H, Ar-H), 8.09 (s, 1 H, Ar-H), 7.58 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.27 (d, *J* = 8.8 Hz, 2 H, Ar-H), 4.34 (q, *J* = 7.1 Hz, 2 H, CH_2), 2.40 (s, 3 H, CH_3), 1.38 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 142.0, 137.5, 137.2, 130.1, 129.9, 119.5, 116.7, 60.4, 21.0, 14.4; IR ν (neat, cm^{-1}) 3112, 3049, 2989, 2870, 1707, 1558, 1413, 1264, 1156, 1025; HRMS Calcd for $C_{13}H_{14}N_2O_2$ (M^+): 230.1050. Found: 230.1051. Data are consistent with the literature.[8]

$3eb_2$ as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1 H, Ar-H), 8.09 (s, 1 H, Ar-H), 7.40-7.27 (m, 4 H, Ar-H), 4.34 (q, *J* = 7.1 Hz, 2 H, CH_2), 2.25 (s, 3 H, CH_3), 1.37 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 141.6, 139.1, 133.9, 133.7, 131.4, 129.1, 126.7, 126.0, 115.9, 60.3, 17.9, 14.4; IR ν (neat, cm^{-1}) 3124, 2982, 2930, 1715, 1554, 1506, 1461, 1405, 1234, 1137, 1029; HRMS Calcd for $C_{13}H_{14}N_2O_2$ (M^+): 230.1050. Found: 230.1050. Data are consistent with the literature.[8]

16). Preparation of **3fb₁** and **3fb₂**.

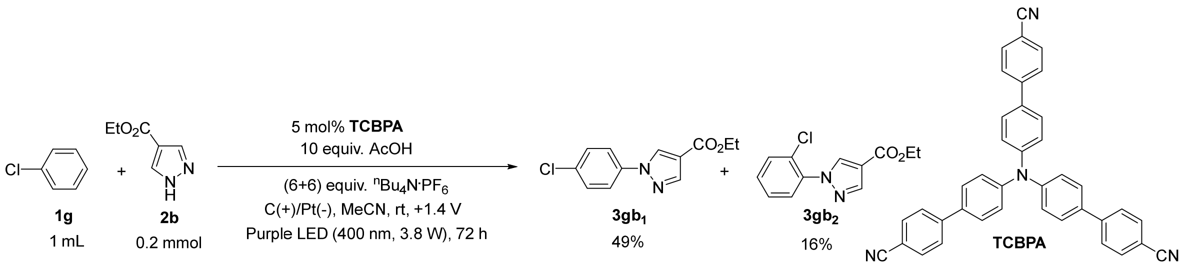


The reaction of **1f** (1 mL), **2b** (27.8 mg, 0.2 mmol), **T*p*BPA** (9.5 mg, 0.02 mmol), $^nBu_4N{\cdot}PF_6$ (465.2 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^nBu_4N{\cdot}PF_6$ (465.3 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **$3fb_1$** (13.4 mg, 23%) and **$3fb_2$** (4.2 mg, 7%) (eluent: pentane/ethyl acetate = 30/1 to 15/1 to 5/1):

$3fb_1$ as a white solid; m.p. 134-135 °C (pentane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1 H, Ar-H), 8.09 (s, 1 H, Ar-H), 7.60 (s, 4 H, Ar-H), 4.35 (q, *J* = 6.7 Hz, 2 H, CH_2), 1.38 (t, *J* = 8.0 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 142.4, 138.4, 132.7, 129.9, 121.0, 120.9, 117.3, 60.5, 14.4; IR ν (neat, cm^{-1}) 3124, 2978, 1707, 1558, 1498, 1416, 1260, 1141, 1025; HRMS Calcd for $C_{12}H_{11}{}^{79}BrN_2O_2$ (M^+): 293.9998. Found: 293.9993. Data are consistent with the literature.[8]

$3fb_2$ as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1 H, Ar-H), 8.13 (s, 1 H, Ar-H), 7.73 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 1 H, Ar-H), 7.52 (dd, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1 H, Ar-H), 7.45 (td, J_1 = 7.7 Hz, J_2 = 1.4 Hz, 1 H, Ar-H), 7.33 (td, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1 H, Ar-H), 4.34 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.38 (t, *J* = 6.0 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 142.0, 139.0, 134.7, 133.9, 130.4, 128.4, 128.2, 118.6, 116.2, 60.4, 14.4; IR ν (neat, cm^{-1}) 3124, 2982, 2930, 1718, 1558, 1491, 1409, 1241, 1141, 1029; HRMS Calcd for $C_{12}H_{11}{}^{79}BrN_2O_2$ (M^+): 293.9998. Found: 293.9990. Data are consistent with the literature.[9]

17). Preparation of **3gb₁** and **3gb₂**.

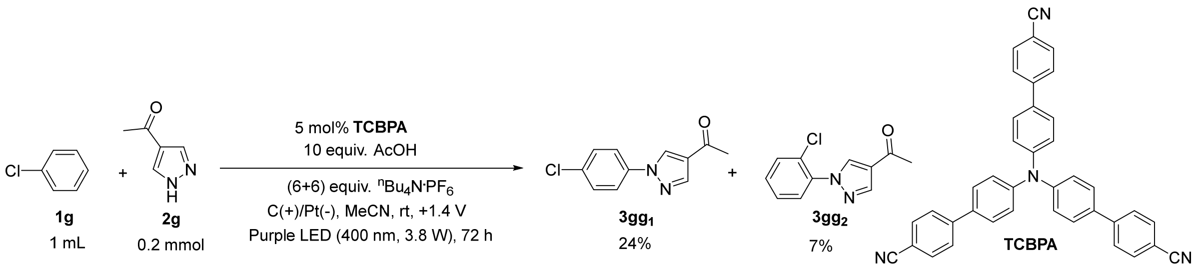


The reaction of **1g** (1 mL), **2b** (28.1 mg, 0.2 mmol), **TCBPA** (5.6 mg, 0.01 mmol), $^nBu_4N{\cdot}PF_6$ (465.2 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^nBu_4N{\cdot}PF_6$ (465.7 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **$3gb_1$** (24.5 mg, 49%) and **$3gb_2$** (8.2 mg, 16%) (eluent: pentane/ethyl acetate = 30/1 to pentane/ethyl acetate/DCM = 100/10/1):

3gb₁ as a white solid; m.p. 127-129 °C (pentane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1 H, Ar-H), 8.09 (s, 1 H, Ar-H), 7.69-7.63 (m, 2 H, Ar-H), 7.48-7.40 (m, 2 H, Ar-H), 4.34 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.38 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 142.3, 137.9, 133.1, 129.9, 129.6, 120.6, 117.2, 60.5, 14.3; IR ν (neat, cm^{-1}) 3116, 2982, 2930, 1707, 1562, 1502, 1413, 1264, 1156, 1092, 1025; HRMS Calcd for $C_{12}H_{11}{}^{35}ClN_2O_2$ (M^+): 250.0504. Found: 250.0501. Data are consistent with the literature.[8]

3gb₂ as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1 H, Ar-H), 8.13 (s, 1 H, Ar-H), 7.63-7.49 (m, 2 H, Ar-H), 7.44-7.34 (m, 2 H, Ar-H), 4.34 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.37 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 142.0, 137.3, 134.6, 130.7, 129.8, 128.4, 127.74, 127.66, 116.3, 60.4, 14.3; IR ν (neat, cm^{-1}) 3124, 2982, 1715, 1558, 1495, 1409, 1230, 1137, 1029; HRMS Calcd for $C_{12}H_{11}{}^{35}ClN_2O_2$ (M^+): 250.0504. Found: 250.0510. Data are consistent with the literature.[6]

18). Preparation of **3gg₁** and **3gg₂**.

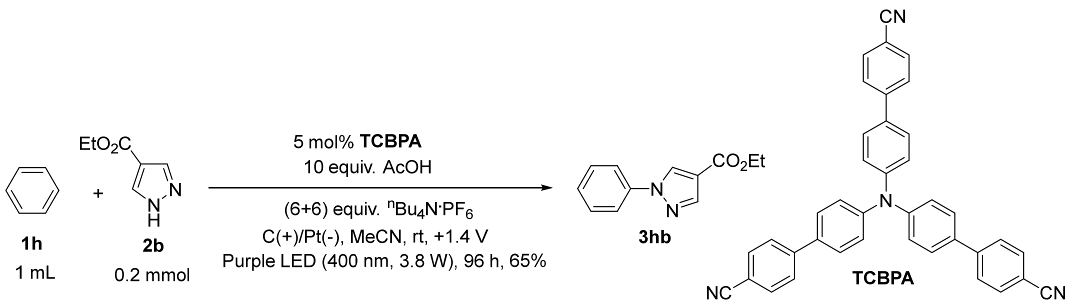


The reaction of **1g** (1 mL), **2g** (22.2 mg, 0.2 mmol), **TCBPA** (5.3 mg, 0.01 mmol), $^nBu_4N{\cdot}PF_6$ (464.6 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^nBu_4N{\cdot}PF_6$ (465.2 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **3gg₁** (10.7 mg, 24%) and **3gg₂** (3.0 mg, 7%) (eluent: pentane/ethyl acetate = 30/1 to 10/1 to 6/1):

3gg₁ as white solid; m.p. 144-146 °C (pentane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1 H, Ar-H), 8.09 (s, 1 H, Ar-H), 7.69-7.64 (m, 2 H, Ar-H), 7.49-7.44 (m, 2 H, Ar-H), 2.51 (s, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 141.7, 137.8, 133.4, 129.8, 128.9, 125.9, 120.8, 28.1; IR ν (neat, cm^{-1}) 3135, 3105, 1666, 1554, 1510, 1413, 1357, 1264, 1100, 1025; HRMS Calcd for $C_{19}H_9{}^{35}ClN_2O$ (M^+): 220.0398. Found: 220.0393. Data are consistent with the literature.[10]

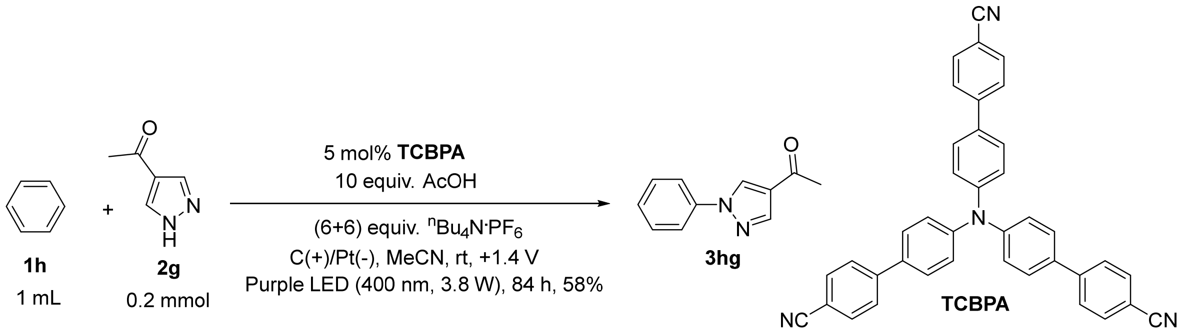
3gg₂ as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1 H, Ar-H), 8.13 (s, 1 H, Ar-H), 7.63-7.53 (m, 2 H, Ar-H), 7.46-7.37 (m, 2 H, Ar-H), 2.51 (s, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 141.3, 137.3, 133.8, 130.8, 130.0, 128.4, 127.9, 127.7, 125.1, 28.1; IR ν (neat, cm^{-1}) 3116, 3071, 2926, 2855, 1677, 1547, 1495, 1405, 1238, 1074; HRMS Calcd for $C_{19}H_9{}^{35}ClN_2O$ (M^+): 220.0398. Found: 220.0393.

19). Preparation of **3hb**.



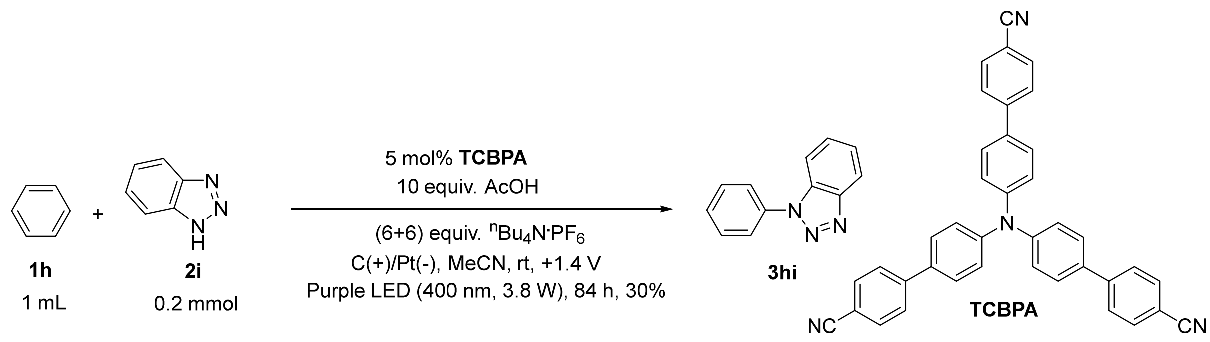
The reaction of **1h** (1 mL), **2b** (27.8 mg, 0.2 mmol), **TCBPA** (5.7 mg, 0.01 mmol), $^{n}Bu_4N{\cdot}PF_6$ (465.2 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (464.4 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **3hb** (28.1 mg, 65%) (eluent: pentane/ethyl acetate = 40/1 to 20/1) as a white solid; m.p. 96-98 ^{o}C (pentane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1 H, Ar-H), 8.10 (s, 1 H, Ar-H), 7.74-7.67 (m, 2 H, Ar-H), 7.51-7.43 (m, 2 H, Ar-H), 7.38-7.31 (m, 1 H, Ar-H), 4.34 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.38 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 142.1, 139.3, 129.9, 129.5, 127.5, 119.5, 116.9, 60.4, 14.3; IR ν (neat, cm^{-1}) 3127, 2986, 2904, 1711, 1599, 1562, 1506, 1416, 1256, 1152, 1029; HRMS Calcd for $C_{12}H_{12}N_2O_2$ (M^+): 216.0893. Found: 216.0896. Data are consistent with the literature.[6]

20). Preparation of **3hg**.



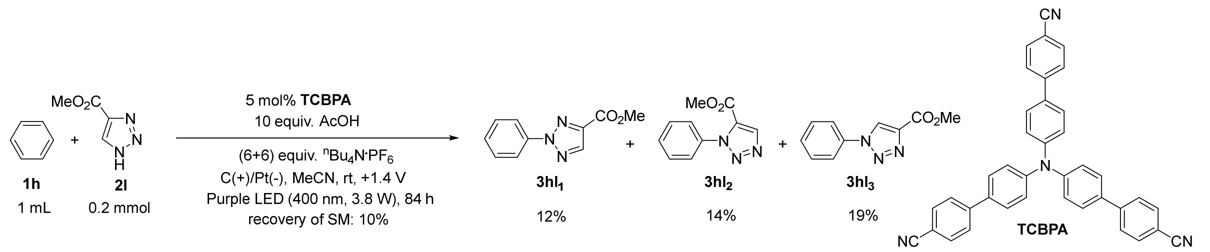
The reaction of **1h** (1 mL), **2g** (22.3 mg, 0.2 mmol), **TCBPA** (5.4 mg, 0.01 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.8 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (464.3 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **3hg** (21.9 mg, 58%) (eluent: pentane/ethyl acetate = 15/1 to 5/1) as a white solid; m.p. 126-127 ^{o}C (pentane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1 H, Ar-H), 8.10 (s, 1 H, Ar-H), 7.71 (d, *J* = 7.9 Hz, 2 H, Ar-H), 7.49 (t, *J* = 7.9 Hz, 2 H, Ar-H), 7.37 (t, *J* = 7.4 Hz, 1 H, Ar-H), 2.51 (s, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 141.5, 139.3, 129.6, 129.0, 127.7, 125.6, 119.7, 28.0; IR ν (neat, cm^{-1}) 3105, 2922, 1659, 1599, 1551, 1502, 1413, 1353, 1260, 1219, 1122, 1033; HRMS Calcd for $C_{11}H_{10}N_2O$ (M^+): 186.0788. Found: 186.0789. Data are consistent with the literature.[6]

21). Preparation of **3hi**.



The reaction of **1h** (1 mL), **2i** (23.5 mg, 0.2 mmol), **TCBPA** (5.6 mg, 0.01 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.7 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (464.9 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **3hi** (11.5 mg, 30%) (eluent: pentane/ethyl acetate = 25/1 to 20/1) as a white solid; m.p. 87-89 °C (pentane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.80 (d, *J* = 7.5 Hz, 2 H, Ar-H), 7.76 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.63 (t, *J* = 7.9 Hz, 1 H, Ar-H), 7.59-7.48 (m, 2 H, Ar-H), 7.45 (t, *J* = 7.7 Hz, 2 H, Ar-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 137.0, 132.3, 129.9, 128.7, 128.2, 124.4, 122.9, 120.3, 110.3; IR ν (neat, cm^{-1}) 3064, 2926, 2855, 1595, 1498, 1457, 1390, 1279, 1245, 1189, 1085, 1055, 1010; HRMS Calcd for $C_{12}H_9N_3$ (M^+): 195.0791. Found: 195.0789. Data are consistent with the literature.[11]

22). Preparation of **3hl₁**, **3hl₂** and **3hl₃**.



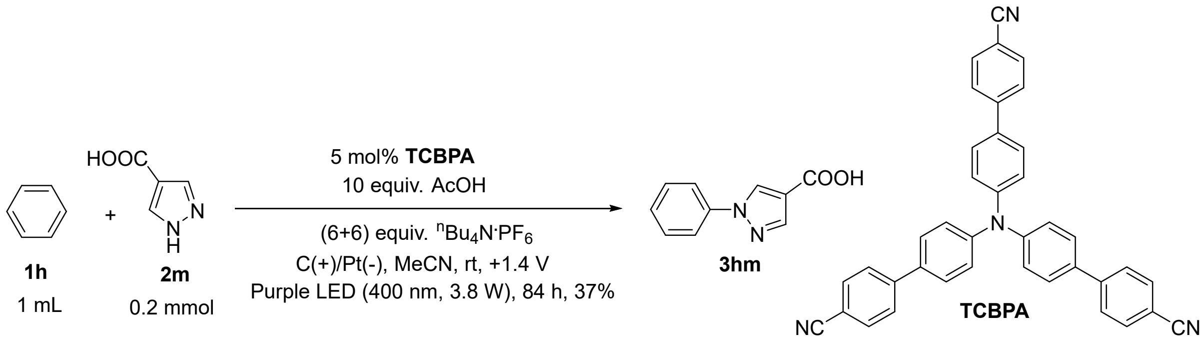
The reaction of **1h** (1 mL), **2l** (25.6 mg, 0.2 mmol), **TCBPA** (5.4 mg, 0.01 mmol), $^{n}Bu_4N{\cdot}PF_6$ (465.2 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (464.8 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **3hl$_1$** (5.0 mg, 12%), **3hl$_2$** (5.7 mg, 14%) and **3hl$_3$** (7.7 mg, 19%) (eluent: pentane/ethyl acetate = 30/1 to 15/1 to pentane/ethyl acetate/DCM = 50/10/1):

3hl$_1$ as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1 H, Ar-H), 8.15 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.51 (t, *J* = 7.6 Hz, 2 H, Ar-H), 7.42 (t, *J* = 7.3 Hz, 1 H, Ar-H), 4.01 (s, 3 H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 140.8, 139.3, 137.9, 129.4, 128.7, 119.6, 52.5; IR ν (neat, cm^{-1}) 3138, 2956, 2855, 1730, 1599, 1495, 1334, 1238, 1137, 1029; HRMS Calcd for $C_{10}H_9N_3O_2$ (M^+): 203.0689. Found: 203.0690. Data are consistent with the literature.[12]

3hl₂ as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1 H, Ar-H), 7.59-7.52 (m, 3 H, Ar-H), 7.51-7.45 (m, 2 H, Ar-H), 3.85 (s, 3 H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 138.2, 136.4, 130.1, 128.9, 128.8, 125.8, 52.5; IR ν (neat, cm^{-1}) 3138, 2926, 2855, 1741, 1525, 1439, 1312, 1204, 1170, 1126, 1088, 1018; HRMS Calcd for $C_{10}H_9N_3O_2$ (M^+): 203.0689. Found: 203.0692. Data are consistent with the literature.[13]

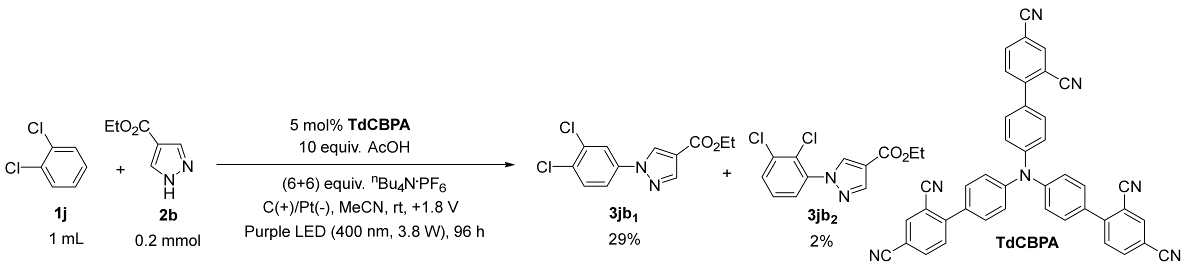
3hl₃ as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1 H, Ar-H), 7.77 (d, *J* = 7.9 Hz, 2 H, Ar-H), 7.57 (t, *J* = 7.6 Hz, 2 H, Ar-H), 7.51 (t, *J* = 6.9 Hz, 1 H, Ar-H), 4.01 (s, 3 H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 140.6, 136.4, 130.0, 129.6, 125.6, 120.8, 52.4; IR ν (neat, cm^{-1}) 3138, 2952, 2926, 2855, 1718, 1599, 1543, 1506, 1439, 1372, 1260, 1148, 1036; HRMS Calcd for $C_{10}H_9N_3O_2$ (M^+): 203.0689. Found: 203.0692. Data are consistent with the literature.[14]

23). Preparation of **3hm**.



The reaction of **1h** (1 mL), **2m** (22.3 mg, 0.2 mmol), **TCBPA** (5.5 mg, 0.01 mmol), $^nBu_4N{\cdot}PF_6$ (465.1 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^nBu_4N{\cdot}PF_6$ (464.6 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **3hm** (13.9 mg, 37%) (eluent: DCM/ethyl acetate = 40/1 to DCM/ethyl acetate/MeOH = 5/5/1) as a white solid; m.p. 207-209 ^{o}C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.83 (s, 1 H, Ar-H), 8.10 (s, 1 H, Ar-H), 7.98 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.59 (t, *J* = 8.0 Hz, 2 H, Ar-H), 7.44 (t, *J* = 7.4 Hz, 1 H, Ar-H); ^{13}C NMR (101 MHz, Acetone-d_6) δ 164.5, 143.6, 132.2, 131.2, 130.4, 128.9, 120.9, 118.6; IR ν (neat, cm^{-1}) 3116, 2922, 2855, 1662, 1569, 1510, 1450, 1275, 1170; HRMS Calcd for $C_{10}H_9N_2O_2$ (ESI, $M+H^+$): 189.0664. Found: 189.0659.

24). Preparation of **3jb₁** and **3jb₂**.

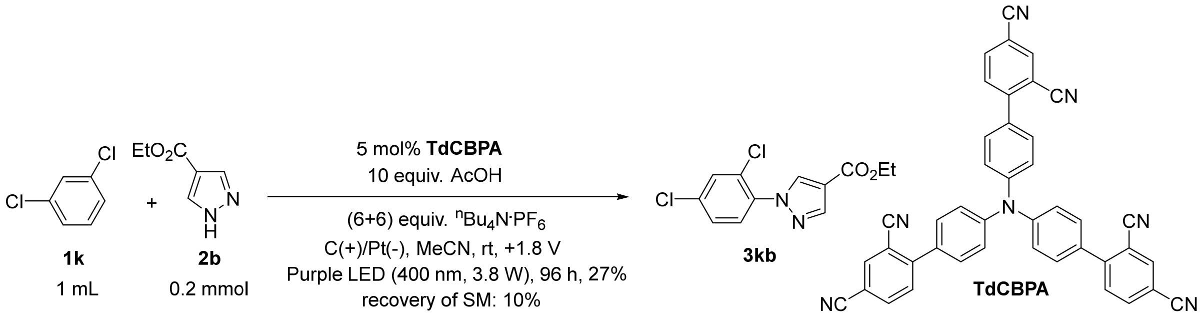


The reaction of **1j** (1 mL), **2b** (28.2 mg, 0.2 mmol), **TdCBPA** (6.4 mg, 0.01 mmol), $^nBu_4N{\cdot}PF_6$ (464.7 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^nBu_4N{\cdot}PF_6$ (464.5 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **3jb₁** (16.7 mg, 49%) and **3jb₂** (1.2 mg, 2%) (eluent: pentane/ethyl acetate = 50/1 to 20/1 to 10/1):

3jb₁ as a white solid; m.p. 143-144 °C (pentane/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1 H, Ar-H), 8.10 (s, 1 H, Ar-H), 7.88 (d, *J* = 2.1 Hz, 1 H, Ar-H), 7.60-7.52 (m, 2 H, Ar-H), 4.35 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.38 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 142.6, 138.5, 133.8, 131.4, 131.2, 129.9, 121.4, 118.3, 117.7, 60.6, 14.3; IR ν (neat, cm^{-1}) 3120, 2982, 1700, 1584, 1491, 1416, 1282, 1148, 1025; HRMS Calcd for $C_{12}H_{10}{}^{35}Cl_2N_2O_2$ (M^+): 284.0114. Found: 284.0113.

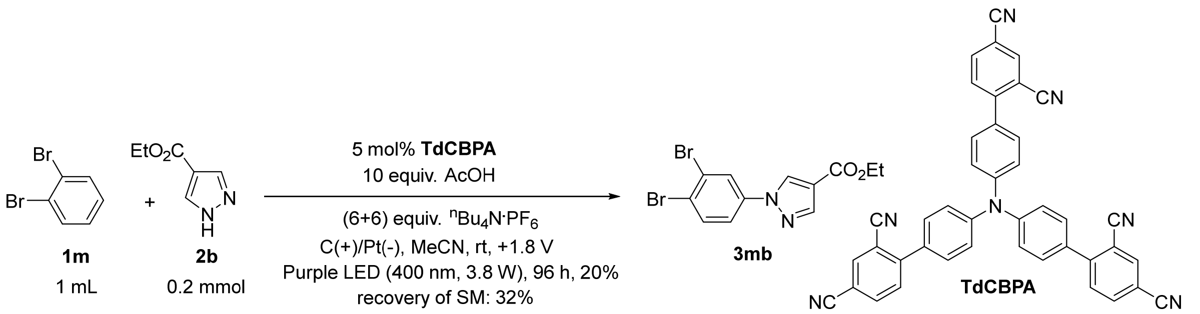
3jb₂ as a colourless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1 H, Ar-H), 8.13 (s, 1 H, Ar-H), 7.58 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1 H, Ar-H), 7.50 (dd, J_1 = 8.1 Hz, J_2 = 1.6 Hz, 1 H, Ar-H), 7.35 (t, *J* = 8.1 Hz, 1 H, Ar-H), 4.35 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.38 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 142.2, 139.0, 134.7, 134.5, 130.8, 128.1, 127.7, 126.1, 116.6, 60.5, 14.4; IR ν (neat, cm^{-1}) 3124, 3086, 2982, 2930, 2855, 1715, 1558, 1476, 1431, 1245, 1141, 1025; HRMS Calcd for $C_{12}H_{10}{}^{35}Cl_2N_2O_2$ (M^+): 284.0114. Found: 284.0114. Data are consistent with the literature.[15]

25). Preparation of **3kb**.



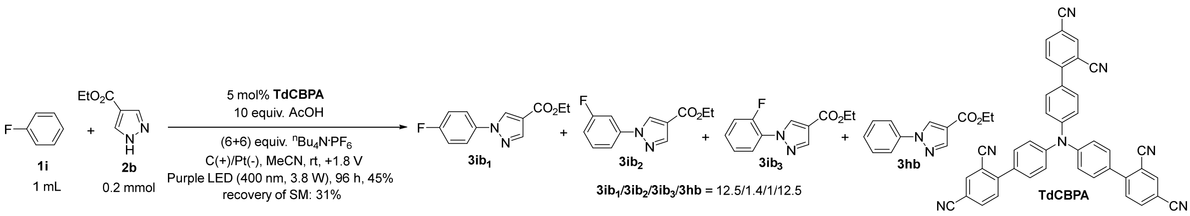
The reaction of **1k** (1 mL), **2b** (28.2 mg, 0.2 mmol), **TdCBPA** (6.3 mg, 0.01 mmol), $^nBu_4N{\cdot}PF_6$ (464.5 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^nBu_4N{\cdot}PF_6$ (464.8 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **3kb** (15..4 mg, 27%) (eluent: pentane/ethyl acetate = 50/1 to 20/1) as a pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1 H, Ar-H), 8.12 (s, 1 H, Ar-H), 7.57 (d, *J* = 1.9 Hz, 1 H, Ar-H), 7.55 (d, *J* = 8.7 Hz, 1 H, Ar-H), 7.39 (dd, J_1 = 8.6 Hz, J_2 = 1.9 Hz, 1 H, Ar-H), 4.34 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.37 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 142.3, 136.1, 135.1, 134.6, 130.5, 129.1, 128.5, 128.2, 116.7, 60.5, 14.4; IR ν (neat, cm^{-1}) 3090, 2982, 1715, 1558, 1495, 1409, 1260, 1234, 1137, 1103, 1029; HRMS Calcd for $C_{12}H_{10}{}^{35}Cl_2N_2O_2$ (M^+): 284.0114. Found: 284.0107.

26). Preparation of **3mb**.



The reaction of **1m** (1 mL), **2b** (27.9 mg, 0.2 mmol), **TdCBPA** (6.1 mg, 0.01 mmol), $^nBu_4N{\cdot}PF_6$ (464.8 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^nBu_4N{\cdot}PF_6$ (465.3 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **3mb** (14.8 mg, 20%) (eluent: pentane/ethyl acetate = 50/1 to 25/1) as a white solid; m.p. 150-151 ^{o}C (pentane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1 H, Ar-H), 8.10 (s, 1 H, Ar-H), 8.05 (d, *J* = 2.6 Hz, 1 H, Ar-H), 7.72 (d, *J* = 8.7 Hz, 1 H, Ar-H), 7.53 (dd, J_1 = 8.7 Hz, J_2 = 2.6 Hz, 1 H, Ar-H), 4.34 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.38 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 142.7, 139.0, 134.4, 129.9, 125.9, 124.4, 123.4, 119.2, 117.7, 60.6, 14.4; IR ν (neat, cm^{-1}) 3124, 2978, 1703, 1588, 1484, 1416, 1282, 1144, 1029; HRMS Calcd for $C_{12}H_{10}{}^{79}Br_2N_2O_2$ (M^+): 371.9104. Found: 371.9096.

27). Preparation of **3ib₁**, **3ib₂**, **3ib₃**, and **3hb**.



The reaction of **1i** (1 mL), **2b** (28.1 mg, 0.2 mmol), **TdCBPA** (6.1 mg, 0.01 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.6 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (465.1 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded a mixture of **3ib$_1$**, **3ib$_2$**, **3ib$_3$** and **3hb** (20.5 mg, 45%) (eluent: pentane/ethyl acetate = 30/1 to 10/1):

3ib$_1$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1 H, Ar-H), 8.09 (s, 1 H, Ar-H), 7.69-7.63 (m, 2 H, Ar-H), 7.17 (t, *J* = 8.4 Hz, 2 H, Ar-H), 4.34 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.38 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -114.7 (d, *J* = 7.0 Hz).

3ib$_2$: ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -110.7.

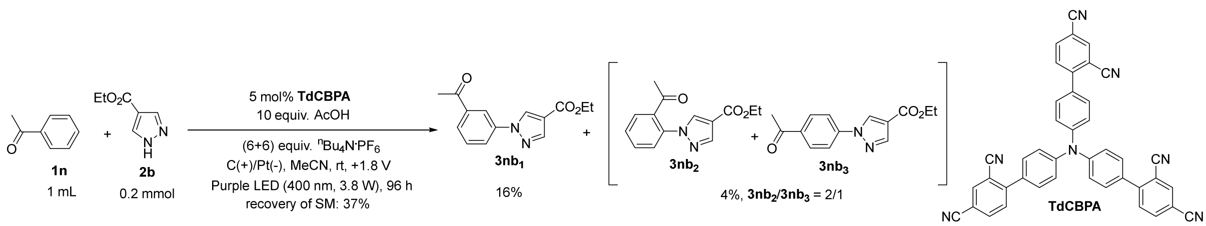
3ib$_3$: ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -125.3.

3hb: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1 H, Ar-H), 8.10 (s, 1 H, Ar-H), 7.71 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.48 (t, *J* = 7.6 Hz, 2 H, Ar-H), 7.36 (t, *J* = 7.4 Hz, 1 H, Ar-H), 4.34 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.38 (t, *J* = 7.1 Hz, 3 H, CH_3).

^{1}H NMR (400 MHz, $CDCl_3$) of **3ib$_2$** and **3ib$_3$**, and ^{13}C NMR (101 MHz, $CDCl_3$) of the mixture of **3ib$_1$**, **3ib$_2$**, **3ib$_3$** and **3hb** are shown as they are.

3ib$_1$, **3ib$_2$**, **3ib$_3$** and **3hb** as a white solid; IR ν (neat, cm^{-1}) 3124, 3101, 3068, 2989, 2904, 1707, 1558, 1517, 1413, 1256, 1148, 1025; HRMS Calcd for $C_{12}H_{11}FN_2O_2$ (M^+): 234.0799. Found: 234.0797. Data of **3ib$_1$**[8] and **3hb**[6] are consistent with the literature.

28). Preparation of **3nb$_1$**, **3nb$_2$** and **3nb$_3$**.



The reaction of **1n** (1 mL), **2b** (28.1 mg, 0.2 mmol), **TdCBPA** (6.2 mg, 0.01 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.7 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (465.5 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **3nb$_1$** (8.4 mg, 16%) and a mixture of **3nb$_2$** and **3nb$_3$** (2.1 mg, 4%, **3nb$_2$**/**3nb$_3$** = 2/1) (eluent: pentane/ethyl acetate = 15/1 to 8/1 to 4/1):

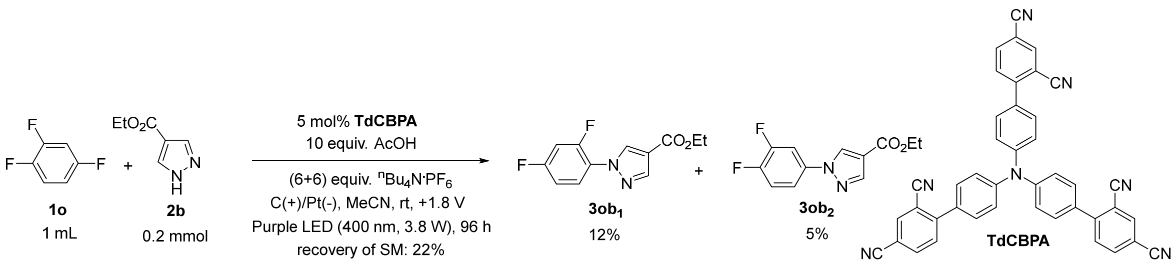
3nb₁ as an amorphous white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1 H, Ar-H), 8.28 (s, 1 H, Ar-H), 8.13 (s, 1 H, Ar-H), 8.00-7.90 (m, 2 H, Ar-H), 7.61 (t, *J* = 7.9 Hz, 1 H, Ar-H), 4.36 (q, *J* = 7.1 Hz, 2 H, CH_2), 2.68 (s, 3 H, CH_3), 1.39 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 162.6, 142.5, 139.8, 138.4, 130.1, 130.0, 127.2, 123.8, 118.8, 117.4, 60.6, 26.8, 14.4; IR ν (neat, cm^{-1}) 3124, 2982, 2930, 1718, 1689, 1595, 1558, 1409, 1357, 1271, 1141, 1025; HRMS Calcd for $C_{14}H_{14}N_2O_3$ (M^+): 258.0999. Found: 258.1004.

3nb₂: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1 H, Ar-H), 8.14 (s, 1 H, Ar-H), 7.62 (dd, J_1 = 7.7 Hz, J_2 = 1.6 Hz, 1 H, Ar-H), 7.59 (td, J_1 = 7.7 Hz, J_2 = 1.7 Hz, 1 H, Ar-H), 7.51 (td, J_1 = 7.6 Hz, J_2 = 1.3 Hz, 1 H, Ar-H), 7.46 (dd, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 1 H, Ar-H), 4.35 (q, *J* = 6.7 Hz, 2 H, CH_2), 2.14 (s, 3 H, CH_3), 1.38 (t, *J* = 6.0 Hz, 3 H, CH_3).

3nb₃: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1 H, Ar-H), 8.14 (s, 1 H, Ar-H), 8.11-8.06 (m, 2 H, Ar-H), 7.86-7.81 (m, 2 H, Ar-H), 4.36 (q, *J* = 6.7 Hz, 2 H, CH_2), 2.64 (s, 3 H, CH_3), 1.39 (t, *J* = 8.0 Hz, 3 H, CH_3).

3nb₂ and **3nb₃** as a colourless oil; ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 196.6, 162.6, 162.5, 142.8, 142.5, 137.3, 136.4, 135.8, 133.0, 131.6, 130.1, 130.0, 128.9, 128.8, 124.4, 119.0, 117.8, 117.4, 60.64, 60.56, 29.4, 26.6, 14.4; IR ν (neat, cm^{-1}) 3131, 2982, 2930, 2855, 1718, 1603, 1558, 1502, 1409, 1357, 1252, 1141, 1021; HRMS Calcd for $C_{14}H_{14}N_2O_3$ (M^+): 258.0999. Found: 258.0992.

29). Preparation of **3ob₁** and **3ob₂**.

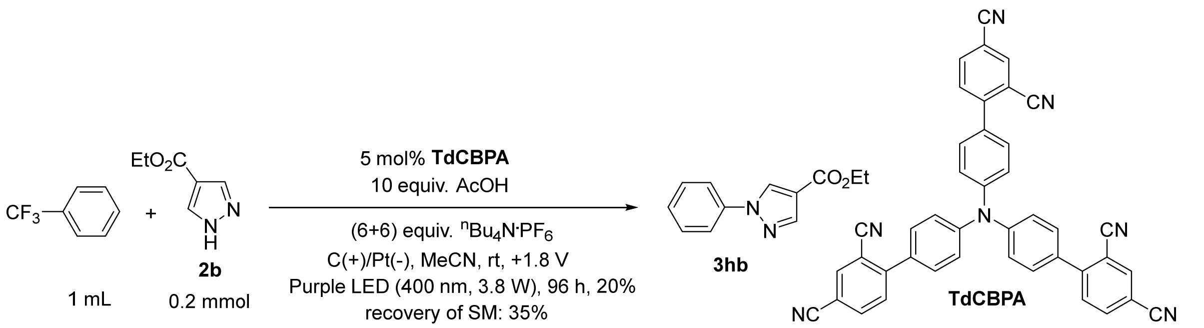


The reaction of **1o** (1 mL), **2b** (27.8 mg, 0.2 mmol), **TdCBPA** (6.2 mg, 0.01 mmol), ^{n}Bu$_4$N·PF$_6$ (464.4 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and ^{n}Bu$_4$N·PF$_6$ (465.0 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **3ob₁** (6.1 mg, 12%) and **3ob₂** (2.5 mg, 5%) (eluent: pentane/ethyl acetate = 30/1 to 10/1):

3ob₁ as an amorphous white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 2.6 Hz, 1 H, Ar-H), 8.11 (s, 1 H, Ar-H), 7.91-7.82 (m, 1 H, Ar-H), 7.07-6.99 (m, 1 H, Ar-H), 4.34 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.38 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 142.1, 133.9 (d, *J* = 9.2 Hz), 125.9 (dd, J_1 = 9.6 Hz, J_2 = 1.2 Hz), 124.3 (d, *J* = 9.1 Hz), 117.8 (d, *J* = 1.0 Hz), 112.3 (dd, J_1 = 22.5 Hz, J_2 = 3.7 Hz), 105.4 (d, *J* = 24.2 Hz), 105.1 (d, *J* = 24.0 Hz), 60.5, 14.4; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -110.1 (d, *J* = 7.0 Hz), -120.7 (d, *J* = 6.8 Hz); IR ν (neat, cm^{-1}) 3165, 3124, 3075, 2986, 2930, 2855, 1711, 1610, 1566, 1521, 1416, 1260, 1234, 1148, 1107, 1033; HRMS Calcd for $C_{12}H_{10}F_2N_2O_2$ (M^+): 252.0705. Found: 252.0698.

3ob₂ as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1 H, Ar-H), 8.09 (s, 1 H, Ar-H), 7.66-7.58 (m, 1 H, Ar-H), 7.46-7.39 (m, 1 H, Ar-H), 7.33-7.23 (m, 1 H, Ar-H), 4.34 (q, J = 7.1 Hz, 2 H, CH_2), 1.38 (t, J = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 142.5, 130.0, 118.1 (d, J = 18.7 Hz), 117.6, 115.1 (dd, J_1 = 6.4 Hz, J_2 = 3.9 Hz), 109.7 (d, J = 21.9 Hz), 60.6, 14.4; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -134.5 (d, J = 21.3 Hz), -138.9 (d, J = 21.1 Hz); IR ν (neat, cm^{-1}) 3116, 2922, 2855, 1700, 1618, 1562, 1525, 1446, 1416, 1249, 1189, 1148, 1025; HRMS Calcd for $C_{12}H_{10}F_2N_2O_2$ (M^+): 252.0705. Found: 252.0698.

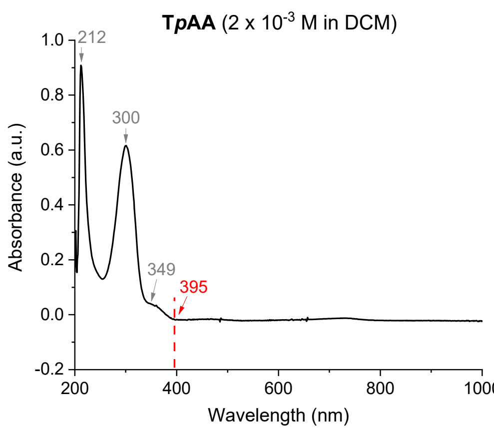
30). Preparation of **3hb** (using trifluorotoluene as strating material).

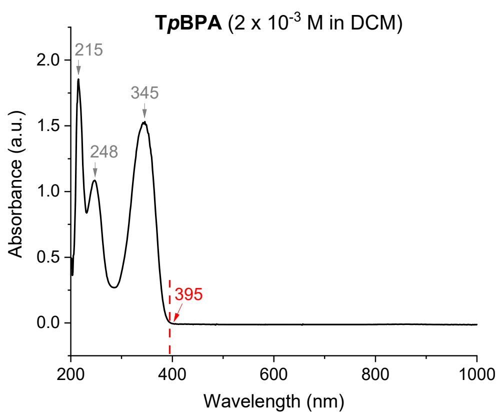


The reaction of trifluorotoluene (1 mL), **2b** (28.1 mg, 0.2 mmol), **TdCBPA** (6.3 mg, 0.01 mmol), $^{n}Bu_4N{\cdot}PF_6$ (464.2 mg, 1.2 mmol), MeCN (2 mL) (anodic chamber), and $^{n}Bu_4N{\cdot}PF_6$ (464.9 mg, 1.2 mmol), MeCN (2 mL), AcOH (0.11 mL, d = 1.05 g/mL, 120.2 mg, 2 mmol) (cathodic chamber) afforded **3hb** (8.7 mg, 20%) (eluent: pentane/ethyl acetate = 20/1 to 10/1) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1 H, Ar-H), 8.10 (s, 1 H, Ar-H), 7.71 (d, J = 8.4 Hz, 2 H, Ar-H), 7.49 (t, J = 7.7 Hz, 2 H, Ar-H), 7.36 (t, J = 7.7 Hz, 1 H, Ar-H), 4.35 (q, J = 7.1 Hz, 2 H, CH_2), 1.38 (t, J = 7.1 Hz, 3 H, CH_3). Data are consistent with the literature.[6]

6. UV-VIS SPECTRA

6.1. UV-vis Spectra of neutral TPAs





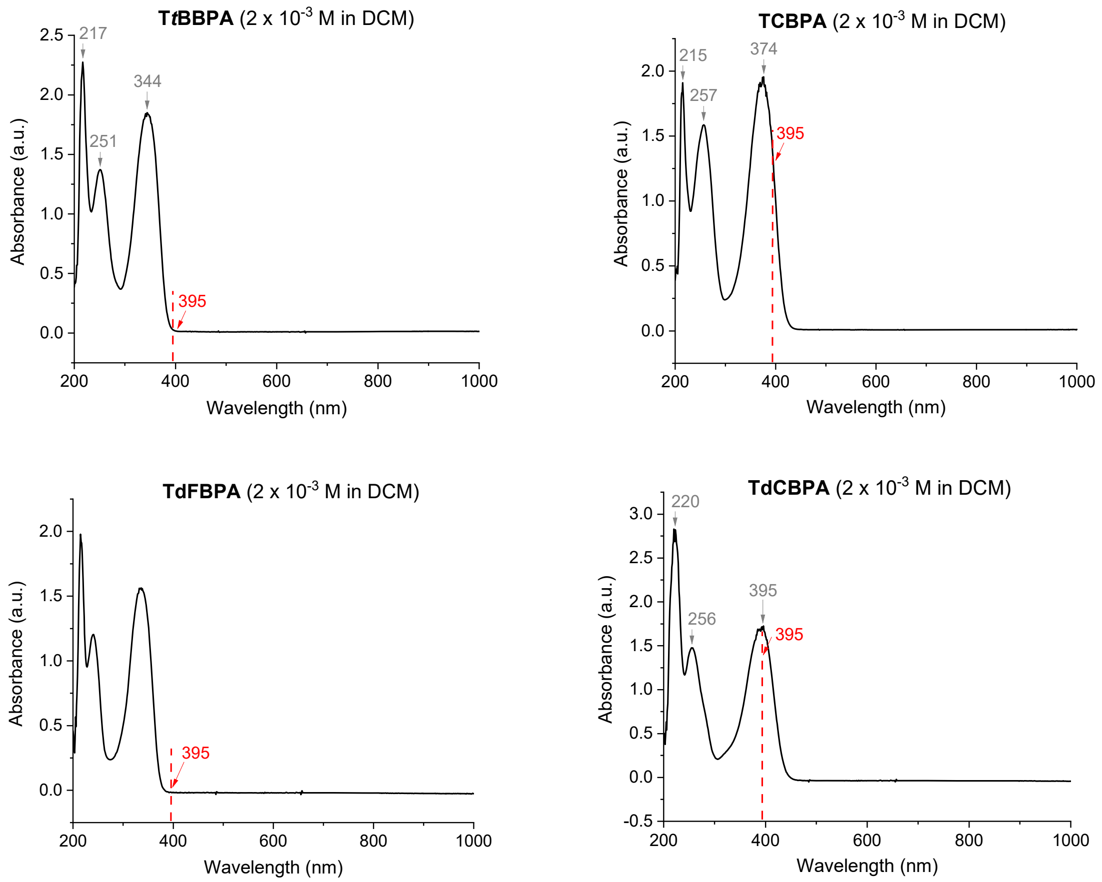
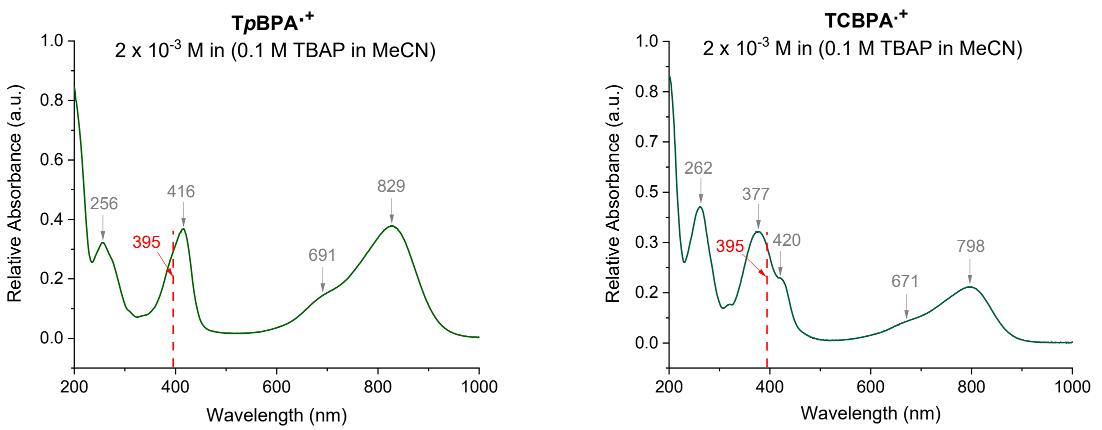


Figure S6. UV-vis spectra for neutral TPAs in DCM solvent.

6.2. UV-vis Spectra of TPA·+s (PF$_6$ salts)



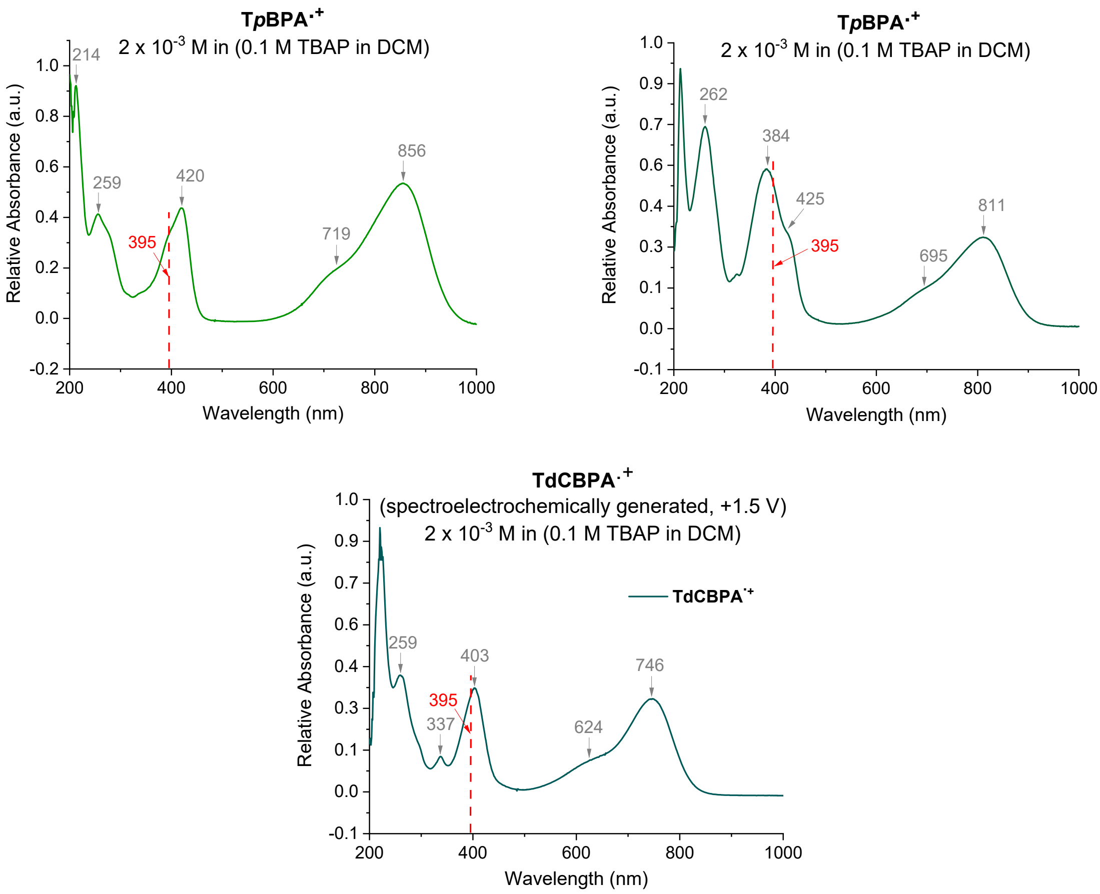


Figure S7. UV-vis spectra for isolated **T*p*BPA$^{\cdot+}$** (left) and **TCBPA$^{\cdot+}$** (right) in MeCN (top) and DCM (middle) containing 0.1 M $^{n}Bu_4N{\cdot}PF_6$. UV-vis spectra for spectroelectrochemically-generated **TdCBPA$^{\cdot+}$** (bottom) in DCM containing 0.1 M $^{n}Bu_4N{\cdot}PF_6$ (see **Section S8** for details).

6.3. UV-vis Spectra of TPA$^{\cdot+}$ precomplexes (PF_6 salts)

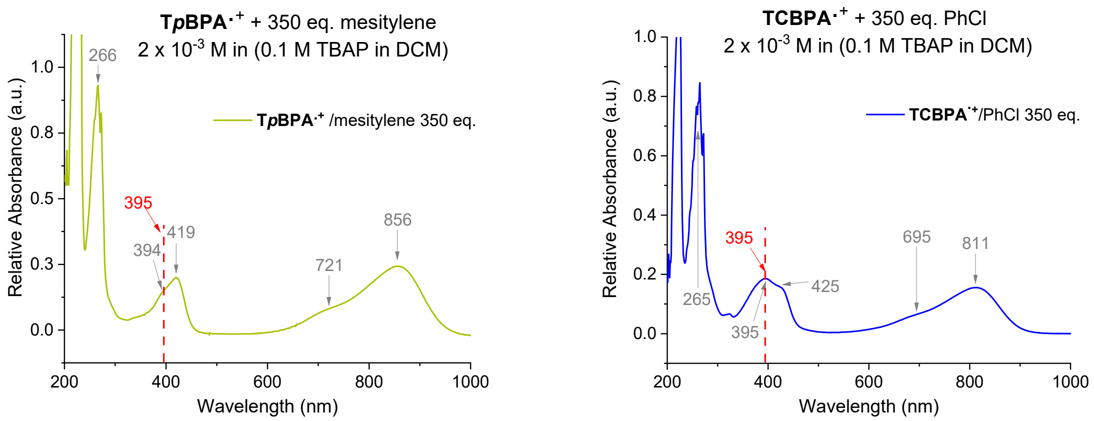


Figure S8. UV-vis spectra for **T*p*BPA$^{\cdot+}$** in the presence of 350 eq. mesitylene (left, 'precomplex' not observed) and **TCBPA$^{\cdot+}$** in the presence of 350 eq. PhCl (right, 'precomplex' observed), recorded after aging the sample for 1 min in the dark. In DCM solvent containing 0.1 M $^{n}Bu_4N{\cdot}PF_6$.

It was observed that the 'precomplex' is destroyed by irradiation of the sample cell that occurs during the UV-vis measurement inside the spectrometer (**Figure S9**, red line vs. green line). This was confirmed when a 'fresh sample' from the bulk (aged for 15 min in the dark) was charged to the cell and gave an identical spectrum as the first measurement (**Figure S9**, red line vs. blue line).

6.4. UV-vis Spectra of TPA$^{\cdot+}$s in the presence of reaction components and during irradiation

After filling an Ottle cell (Section S8) with a sample of TPA$^{\cdot+}$ containing the reaction component, the thin film was irradiated using the 3.8 W 395 nm LED (Section 11) at a distance of *ca.* 3.0 cm for the time specified and the UV-vis spectrum immediately recorded.

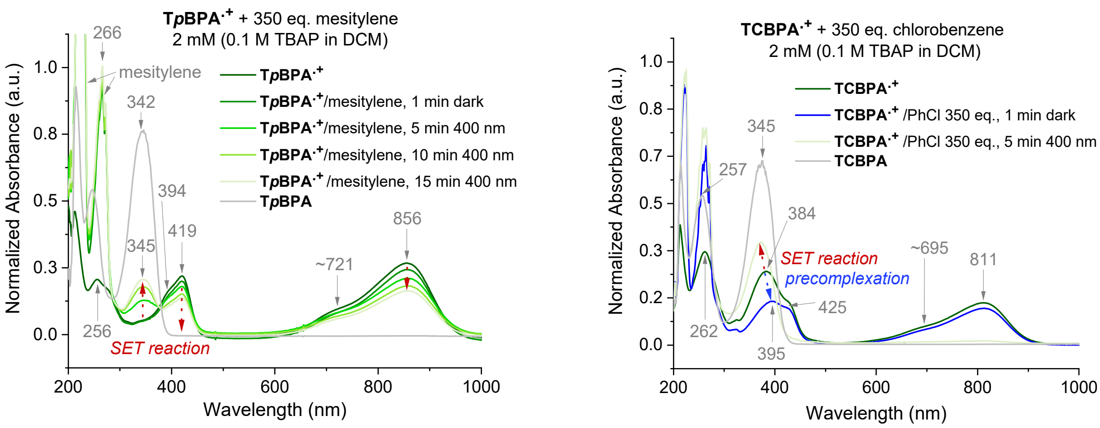


Figure S9. UV-vis spectra for **T*p*BPA$^{\cdot+}$** (left) and **TCBPA$^{\cdot+}$** (right) in the presence of 350 eq. mesitylene or PhCl (respectively) over time and with light irradiation.

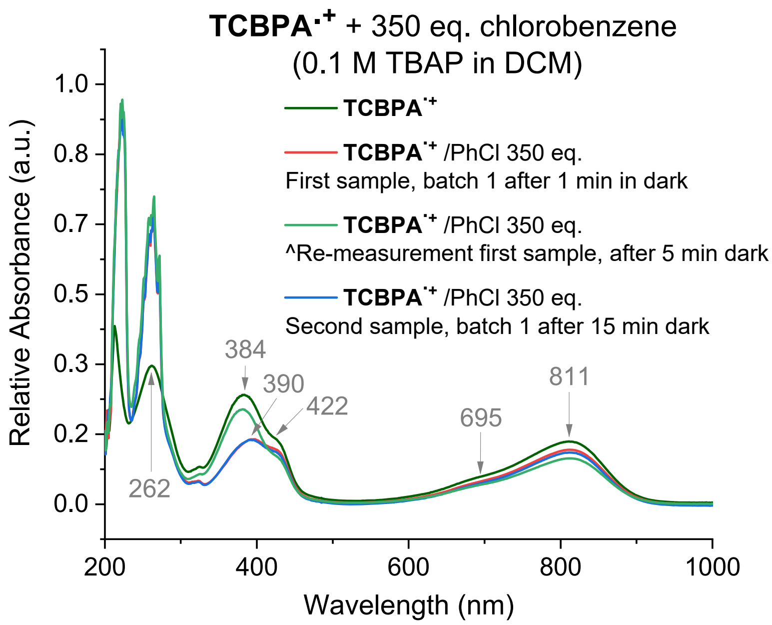


Figure S10. UV-vis spectra for **TCBPA$^{\cdot+}$** in the presence of 350 eq. PhCl after repeat measurements of the UV-vis and after preparing a fresh sample.

Moreover, it was observed that pyrazole and ethyl 3-pyrazolecarboxylate ("esterpyrazole") reacted with **T*p*BPA$^{\cdot+}$** and **TCBPA$^{\cdot+}$** (respectively) *in the dark* to regenerate their corresponding TPAs (**Figure S10**-**S11**). While we cannot rule out the involvement of pyrazole in the reaction mechanism or in a precomplex with TPA$^{\cdot+}$s at this stage due to such reactivity, we note the following:

- Control reactions confirm both light and applied potential are necessary for successful reaction.
- The TPA$^{\cdot+}$ is continuously regenerated under the electrochemical reaction conditions even if it is quenched by pyrazole.
- Product yields show a strong dependence on the *electronics of the arene substrate* employed, suggesting against a mechanism involving SET oxidation of pyrazoles and S_NAr on the pyrazole radical cations by the arenes as nucleophiles.

Therefore, we conclude that although the *dark* reaction of pyrazole is a fast reaction, it is *not* the reactive pathway of the reaction, and merely serves to hinder the overall reaction rate. This may be one factor behind long required reaction times.

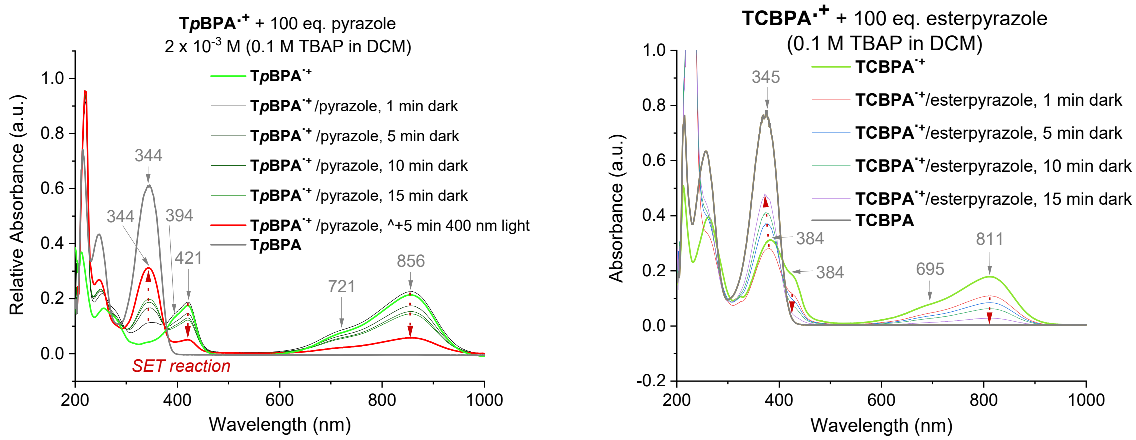


Figure S11. UV-vis spectra for **T*p*BPA$^{\cdot+}$** (left) or **TCBPA$^{\cdot+}$** (right) in the presence of 100 eq. pyrazole or 100 eq. ethyl 3-pyrazolecarboxylate ('esterpyrazole') over time and with light irradiation.

7. CYCLIC VOLTAMMETRY

Cyclic voltammetry was conducted using a three-electrode setup consisting of an IKA glassy carbon disc working electrode 'WE' (d = 3.0 mm), an IKA Ag/AgCl wire reference electrode 'RE' (containing sat. aq. KCl) and an IKA platinum sheet counter-electrode 'CE'. Electrochemical measurements were carried out under N_2 using an IKA ElectraSyn2.0 potentiostat at room temperature (298 K). According to its technical datasheet specification, the ElectraSyn2.0 has a current measuring accuracy of ±0.1 mA, a voltage measuring accuracy of ±0.01 mV, a current measuring resolution of 0.1 mA and a voltage measuring resolution of 0.01 V. For further details of the potentiostat and electrodes, see: https://www.ika.com/en/Products-Lab-Eq/Electrochemistry-Kit-csp-516/ElectraSyn-20-pro-Package-cpdt-40003261/

Before use and between measurements, the WE was mechanically cleaned with an alumina suspension (BASi) and rinsed with distilled water repeatedly until its surface was reflective by eye, then allowed to air dry. The RE was washed with electrolyte solution and distilled water and stored in 3.0 M aq. KCl when not in use/between measurements. The CE was cleaned by soaking in 2.0 M HCl for 1-2 h, then rinsed with distilled water and allowed to air dry.

Ferrocene was recrystallized twice from *n*-hexane prior to use. $^{n}Bu_4N{\cdot}PF_6$ ('TBAP') was used as supplied commercially from TCI (98%+). Unless otherwise stated, all solutions were prepared at 5.0 mM concentration (in 0.1 M TBAP/DCM) or at 10 mM (0.1 M TBAP/MeCN as solvent) using anhydrous DCM or MeCN (dried over 4 Å activated molecular sieves and filtered prior to use).

The anodic-cathodic peak separation for ferrocene at a concentration of 10 mM in MeCN (ΔE^p = 194 mV) was typical of that experimentally observed (compared to 59 mV/n for an 'ideal' one-electron transfer), indicating a reasonable degree of reversibility (and so rapid kinetics) for the electron transfer process. However, **TPAs** were generally insoluble in MeCN at 10 mM (or 5 mM) concentrations. For ferrocene at 5 mM in the less polar solvent DCM, the larger anodic-cathodic peak separation was observed ΔE^p = 237 mV, consistent with that observed in the literature (ΔE^p = 213 mV was reported for a 2.0 mM ferrocene in 0.1 M *n*-Bu_4NCl/DCM).[16]

A scan rate of 200 mV s^{-1} (**Figure S14**) was found to be optimal for measurements of **TPAs** (ΔE^p = 351 mV). The half potentials $E_{1/2}$ for ferrocene in 0.1 M TBAP/DCM vs. Ag/AgCl were +0.545 V (at 100 mV s^{-1}) and +0.582 V (at 200 mV s^{-1}). These $E_{1/2}$ corresponded very well to the previously reported $E_{1/2}$ for ferrocene (+0.56 V) measured under identical sample conditions (5 mM in 0.1 M TBAP/DCM, 200 mV s^{-1} scan rate).[17] Literature $E_{1/2}$ values for ferrocene in 0.1 M TBAP/DCM vs. SCE were +0.470 vs. SCE in DCM (at 250 mV s^{-1}) and +0.462 vs. SCE in DCM (at 50 mV s^{-1}). Therefore, all measured potentials were calibrated to their values vs. SCE in DCM (+0.470 V) by subtracting 0.075 V.

Ferrocene was used as an external standard, measured both before and after running any series of analytes, to ensure consistency and whose peak height (*ca.* 1.8 x 10^{-4} A at 200 mV s^{-1}) corresponds to a 1-electron oxidation.

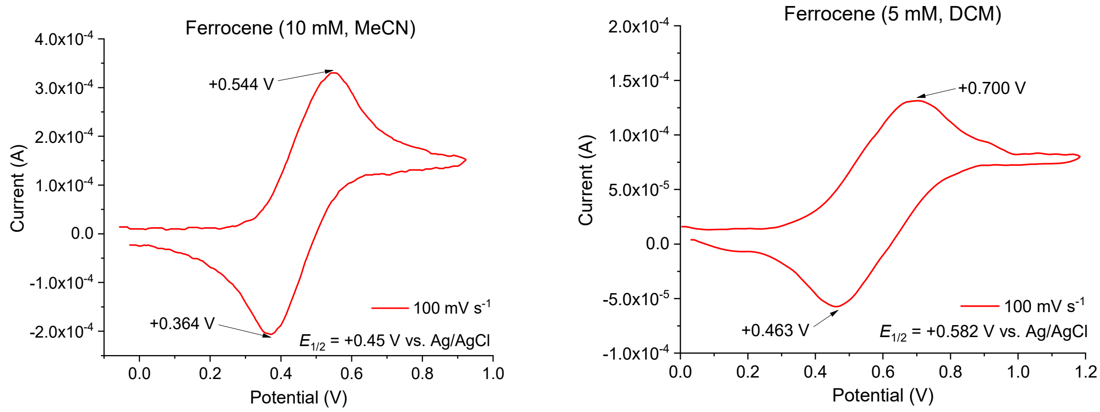


Figure S12. Cyclic voltammetry of ferrocene in MeCN (left) and in DCM (right). Uncalibrated.

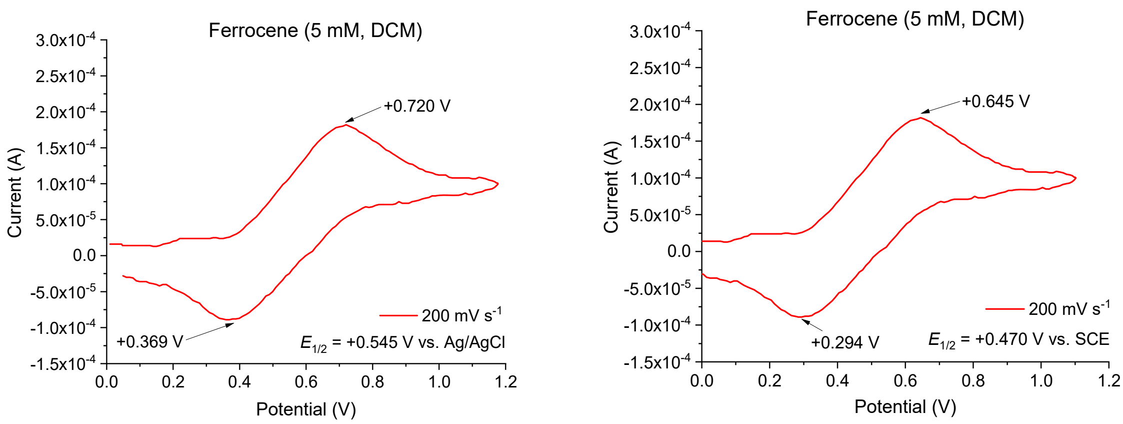
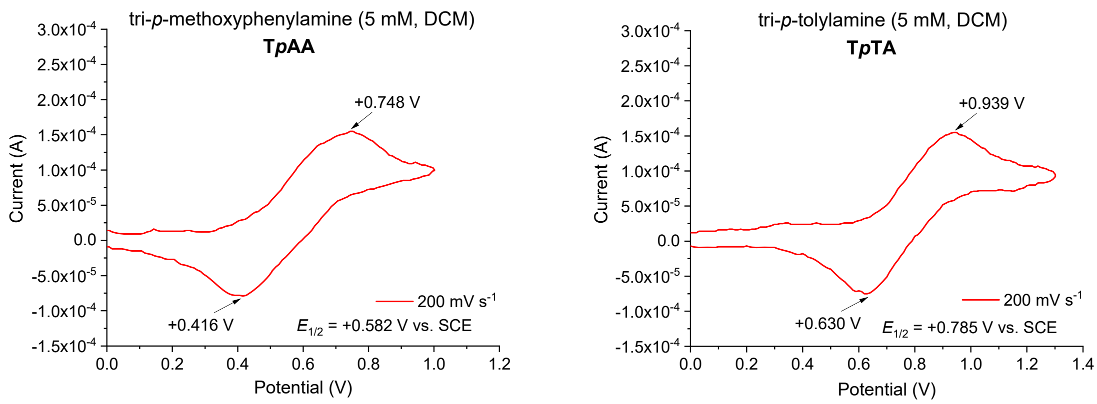


Figure S13. Cyclic voltammetry of ferrocene under the identified optimal conditions for triarylamines. Uncalibrated (left). Calibrated (right).

7.1. Cyclic Voltammetry of TPAs



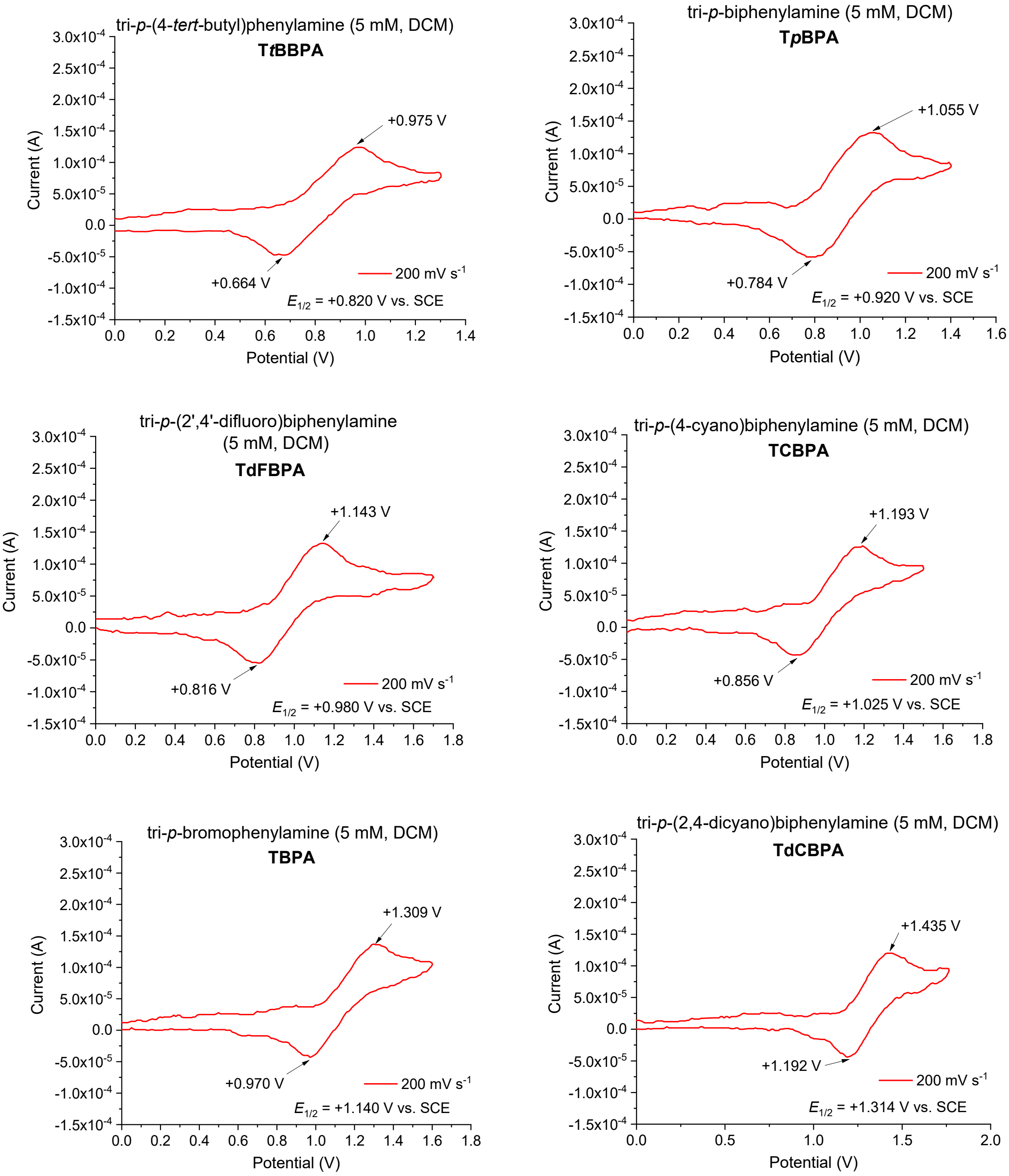
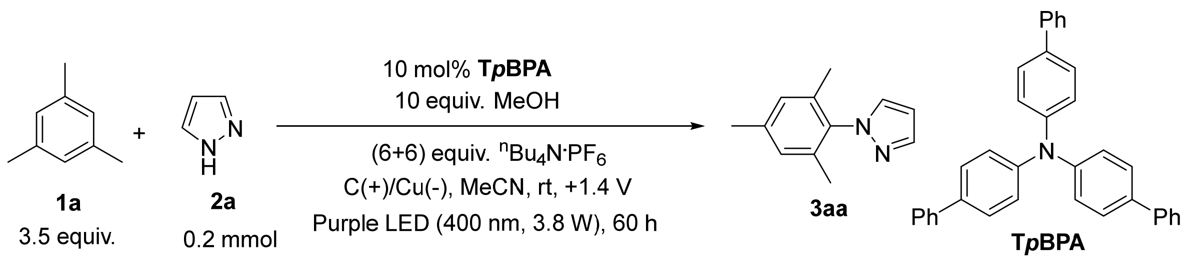


Figure S14. Cyclic voltammetry of tri(*p*-substituted)arylamines (**TPAs**).

7.2. Applied Constant Potential Dependence on Reaction Yield



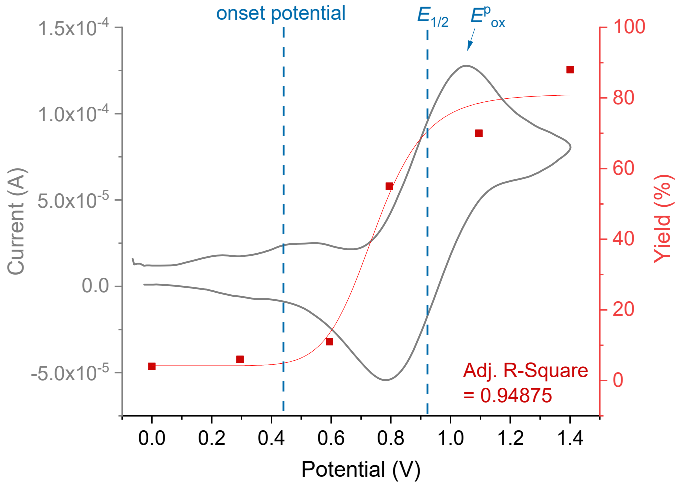


Figure S15. Yield of **3aa** under conditions depicted in **Table 2** of the main manuscript, as a function of increasing constant potential.

Figure S16. Intensification of colour in the anodic chamber as a function of increasing constant potential.

8. Spectroelectrochemistry

Measurements were performed in an Ottle Cell (Optically transparent thin-layer electro-chemical cell), pathlength = 0.02 cm, working electrode: Pt minigrid, counter electrode: Pt minigrid, pseudo reference electrode: Ag wire. A constant potential of 0 to +1.75 V was applied to the cell, and UV/Vis absorption spectra were recorded every 5 s (using an Agilent 8453 spectrometer).

For further details of Ottle Cell, see: https://research.reading.ac.uk/spectroelectrochemistry/optically-transparent-thin-layer-electrochemical-cells/room-temperature-ottle-cell/

8.1. Spectroelectrochemistry of TPAs

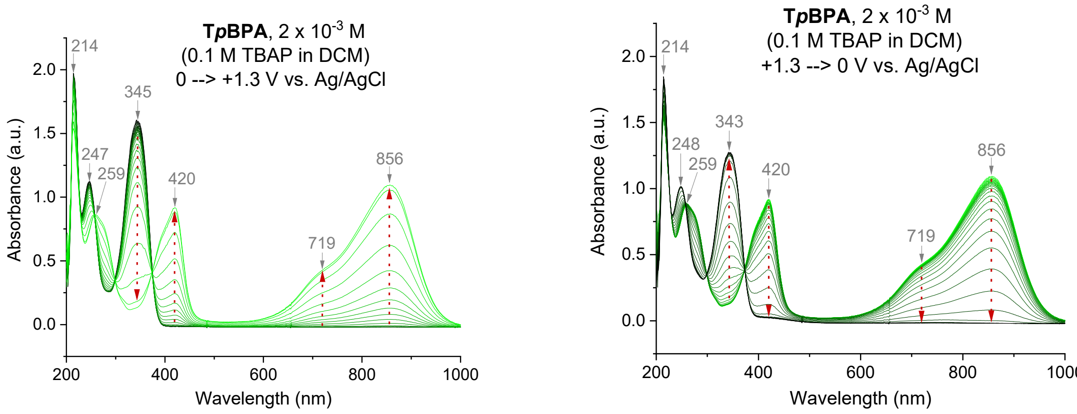


Figure S17. Spectroelectrochemistry of **T*p*BPA** from 0 to +1.3 V (left) and from +1.3 to 0 V (right).

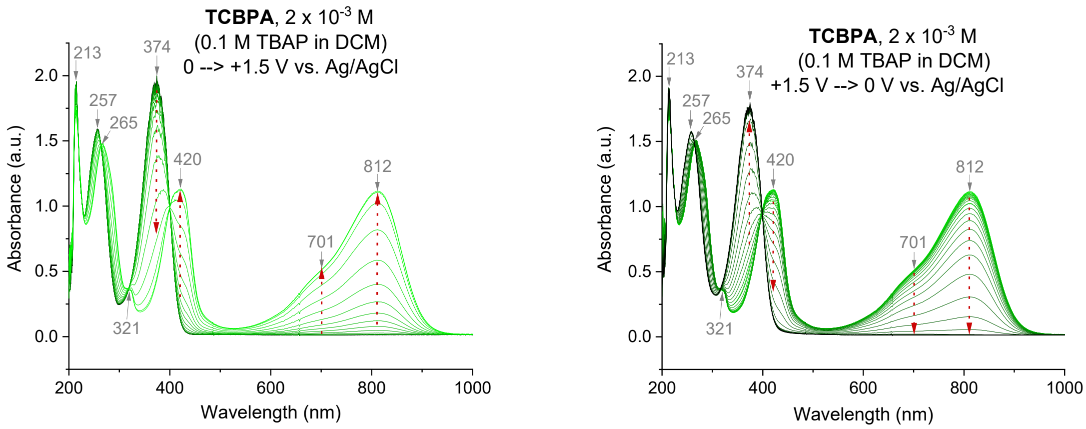


Figure S18. Spectroelectrochemistry of **TCBPA** from 0 to +1.5 V (left) and from +1.5 to 0 V (right).

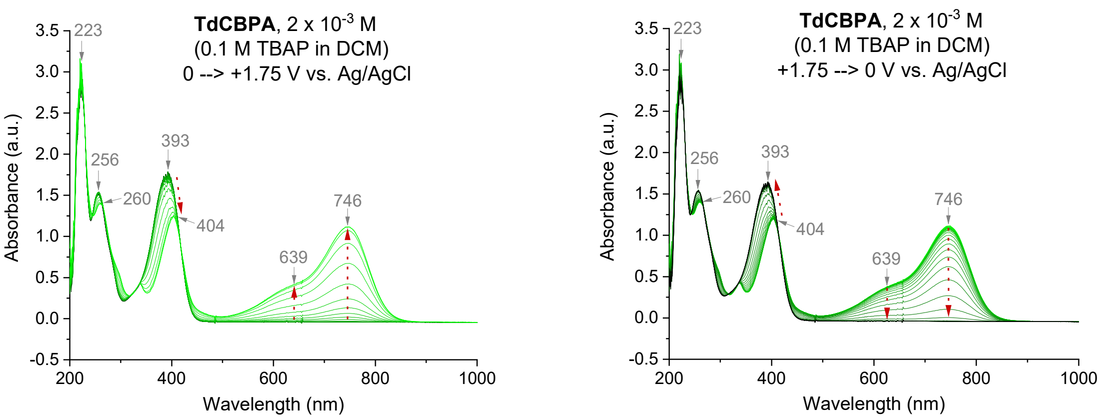


Figure S19. Spectroelectrochemistry of **TdCBPA** in the presence of 350 eq. PhCl from 0 to +1.75 V (left) and from +1.75 to 0 V (right). Potentials vs. Ag/AgCl.

8.2. Spectroelectrochemistry of TPAs in presence of substrates.

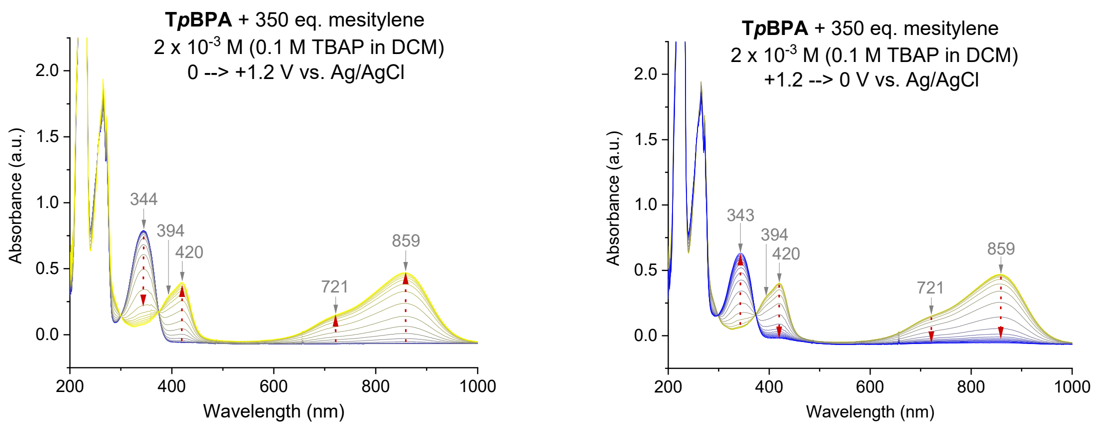


Figure S20. Spectroelectrochemistry of **T*p*BPA** in the presence of 350 eq. mesitylene from 0 to +1.2 V (left) and from +1.2 to 0 V (right).

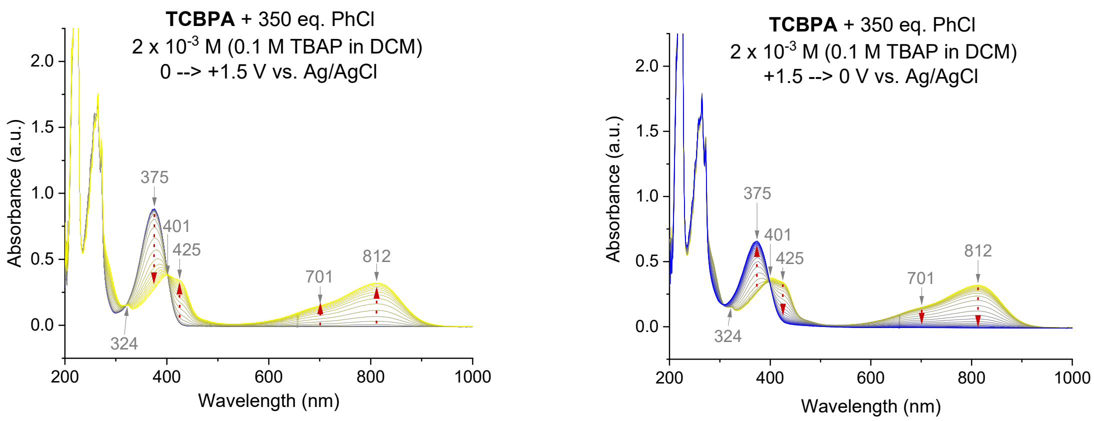


Figure S21. Spectroelectrochemistry of **TCBPA** in the presence of 350 eq. PhCl from 0 to +1.5 V (left) and from +1.5 to 0 V (right). Potentials vs. Ag/AgCl.

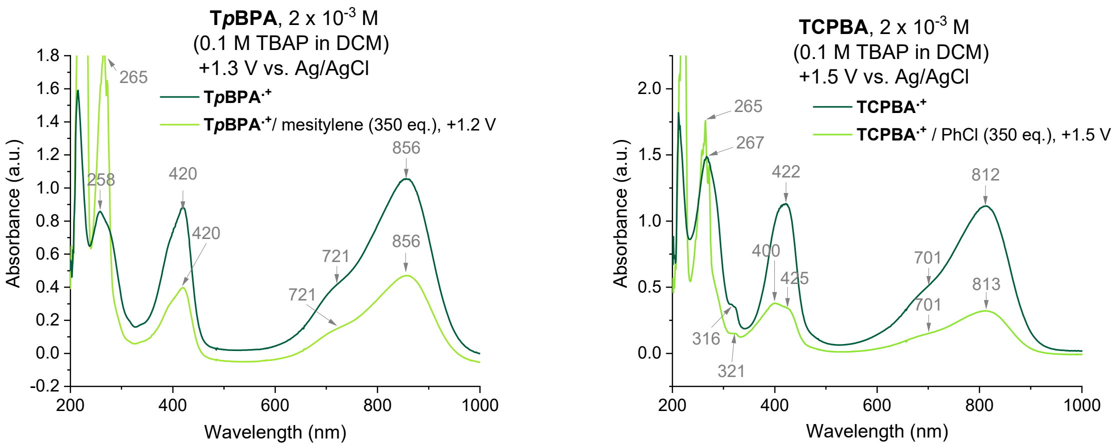


Figure S22. UV-Vis of **T*p*BPA** in the presence of 350 eq. Mesitylene at +1.2 V (left) and **TCPBA** in the presence of 350 eq. PhCl at +1.5 V. Potentials vs. Ag/AgCl.

A difference can be seen in the spectroelectrochemistry of **TCPBA** when in the presence of 350 eq. PhCl (**Figure S22**). This difference cannot be observed for **T*p*BPA**. The UV-vis spectra of electrogenerated **TCPBA**$^{\cdot+}$ in the presence of 350 eq. PhCl resembles the UV-vis spectra of isolated **TCPBA**$^{\cdot+}$ in the presence of 350 eq. PhCl (**Figure S8**).

9. LUMINESCENCE SPECTROSCOPY OF TPA$^{\cdot+}$S

Luminescence (fluorescence) and Time-Correlated Single Photon Counting (TCSPC) measurements were acquired at Technische Universität München (TUM) using an Edinburgh Instruments Spectrofluorimeter FS5. For specifications, see: https://www.edinst.com/products/fs5-spectrofluorometer/

Fluorescence employed a 150 W CW Ozone-free xenon arc lamp, 230 - 1000 nm (dual grating) excitation source and a R928P photomultiplier tube. Depending on the species of interest, the excitation monochromator was set between 250-550 nm and emission set to measure 400 - 750 nm. The integration time was set at 0.1 s and the slit widths were 1 nm (**TCPBA**$^{\cdot+}$) and 5 nm (**T*p*BPA**$^{\cdot+}$) for both excitation and emission. For all fluorescence (excitation emission matrices or, 'EEM') and time-correlated single-photon counting measurements (TCSPC), **T*p*BPA**$^{\cdot+}$$\cdot PF_6$ and **TCPBA**$^{\cdot+}$$\cdot PF_6$ were prepared in anhydrous DCM at 1.7 x 10^{-5} M and 1.8 x 10^{-5} M, respectively.

Prior to measurements, stability of isolated TPA$^{\cdot+}$s was checked by their UV-visible absorption spectra were obtained on a PerkinElmer UV/VIS Lambda 365 instrument to (**Figure S26**). For UV-vis absorption measurements, **T*p*BPA**$^{\cdot+}$$\cdot PF_6$ and **TCPBA**$^{\cdot+}$$\cdot PF_6$ were prepared in anhydrous DCM at 8.3 x 10^{-5} M and 8.9 x 10^{-5} M, respectively (in appropriate sized cuvettes). The UV-vis spectra perfectly matched those of previous isolated batches of TPA$^{\cdot+}$s recorded on another spectrometer in DCM containing 0.1 M TBAP (**Figure S6**).

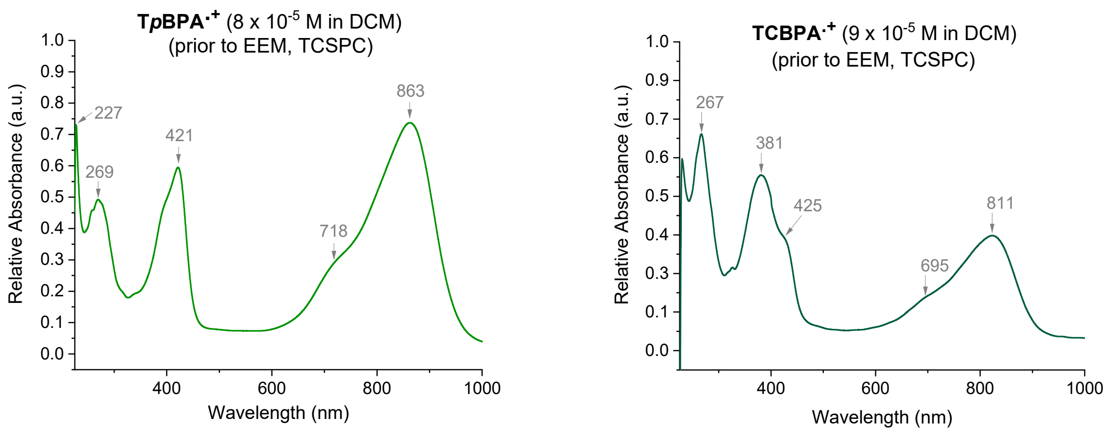


Figure S23. UV-vis spectra for isolated **T*p*BPA**$^{\cdot+}$ (left) and from **TCPBA**$^{\cdot+}$ (right) prior to EEM and TSCPC measurements.

9.1. Luminescence Excitation Emission Matrices

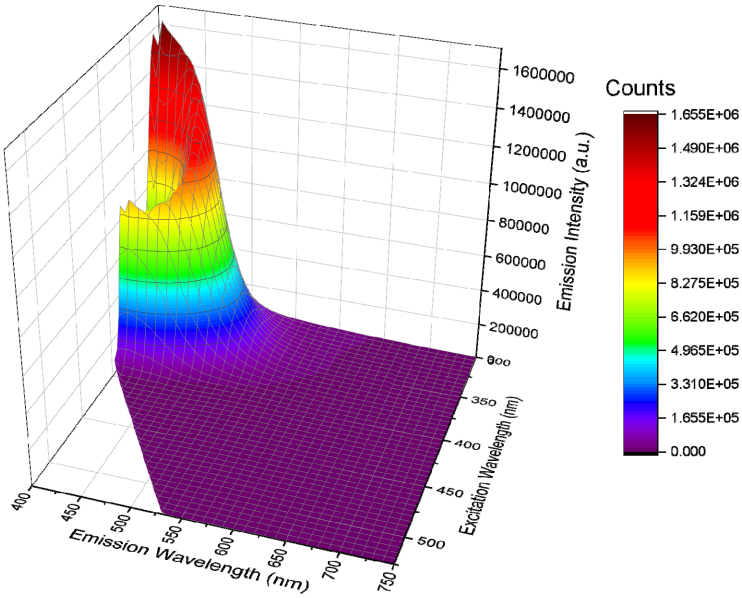


Figure S24. Excitation-Emission Matrix for **T*p*BPA$^{\cdot+}$**.

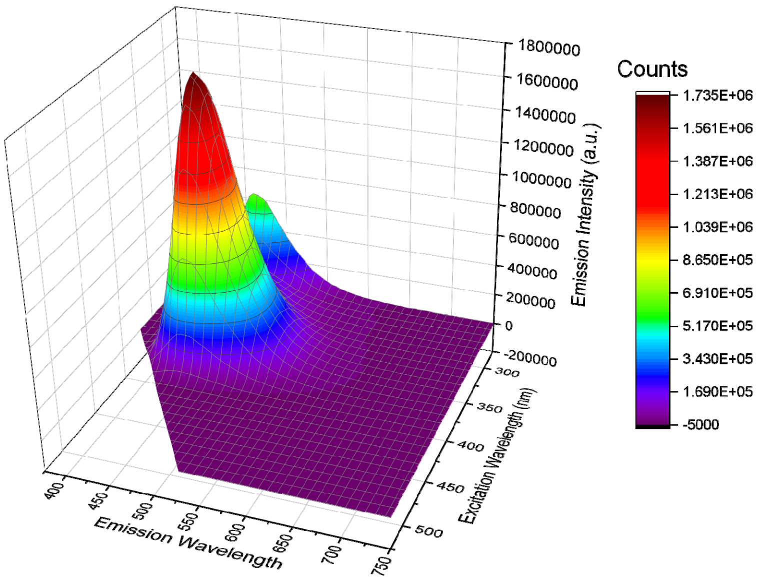


Figure S25. Excitation-Emission Matrix for **TCPBA$^{\cdot+}$**.

9.2. Time-correlated Single Photon Counting Luminescence Measurements

For TCSPC, the excitation source was an Edinburgh Instruments EPL-375 picosecond pulsed diode laser (TCSPC, pulsed excitation at 375 nm at a pulse period of 50 ns). For specifications, see: https://www.edinst.com/wp-content/uploads/2015/08/EPL-Series_Datasheet.pdf

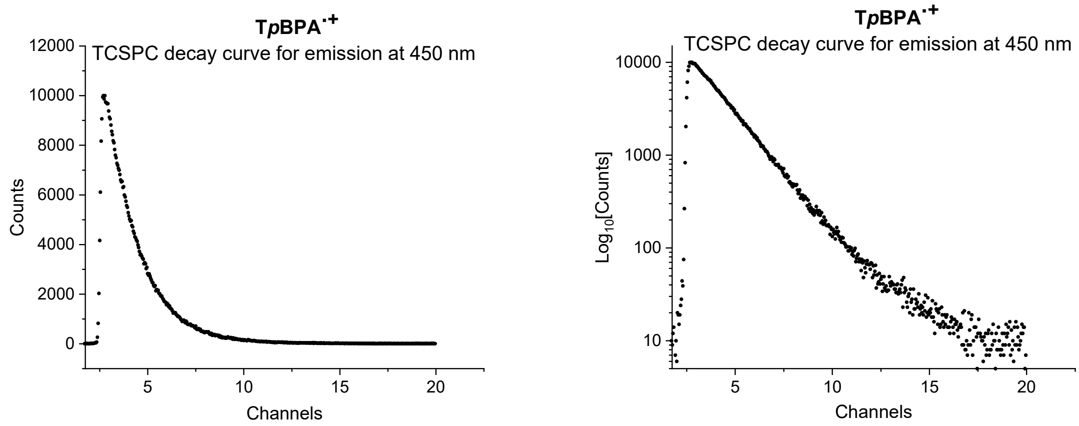


Figure S26. TCSPC of the emitting species at 450 nm present in **T*p*BPA**$^{\cdot+}$.

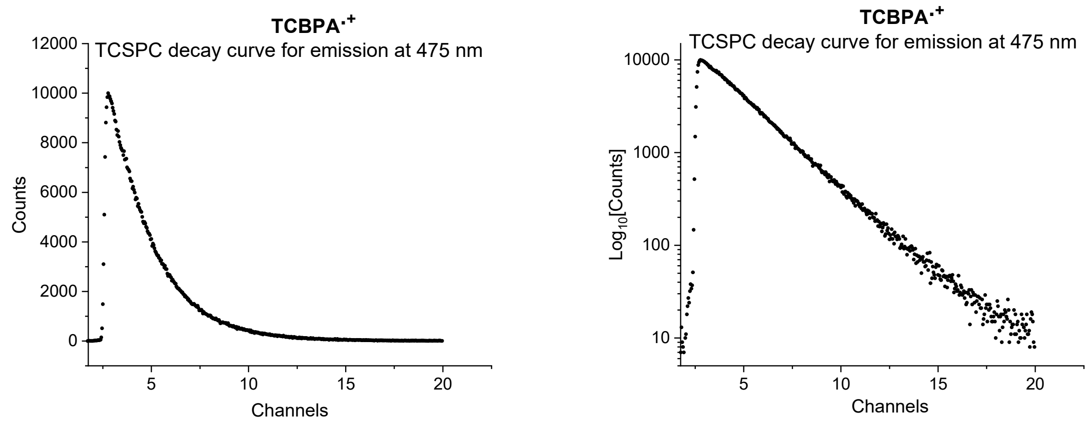


Figure S27. TCSPC of the emitting species at 475 nm present in **TCPBA**$^{\cdot+}$.

Sample	Solvent	Emission detector λ (nm)	Lifetime τ (ns)	χ^2	τ error
T*p*BPA$^{\cdot+}$	DCM	450	1.7	2.02	0.002682
TCBPA$^{\cdot+}$	DCM	475	2.2	1.47	0.003619
T*p*BPA	MeCN	430	1.8	-	-

The Excitation-Emission Matrices (EEMs) for **T*p*BPA**$^{\cdot+}$ and **TCPBA**$^{\cdot+}$ both reveal an emitting species below excitation of 395 nm (Section 9.1). The lifetime of the species emitting at 450 nm in **T*p*BPA**$^{\cdot+}$ was almost identical to the lifetime of **T*p*BPA** itself (measured in MeCN solvent), indicating that a trace amount of the neutral compound was present in the **T*p*BPA**$^{\cdot+}$ sample. The same is presumably true of the 475 nm emitting species in **TCPBA**$^{\cdot+}$.

As per the control reactions with a 365 nm LED involving **T*p*BPA** and **TCBPA**, product yields were only 11% and 8%, respectively (see Section S4 and manuscript). This could arise from excitation of the tail-end of the TPAs$^{\cdot+}$, or from excitation of the TPA followed by a conPET-type mechanism. The productive photochemistry of interest in this study occurs only upon excitation with 395 nm LEDs.

10. TRANSIENT ABSORPTION SPECTROSCOPY OF TPA$^{\cdot+}$S

Transient absorption spectroscopy was performed at the Fakültat für Chemie, Technische Universität München using a similar configuration as previously reported in Prof. Juergen Hauer's group.[18] **T*p*BPA**$^{\cdot+}$·PF_6 and **TCBPA**$^{\cdot+}$·PF_6 were prepared in anhydrous DCM as solvent at a concentration providing an optical density (OD) of 0.2-0.3. The concentrations employed were 8.9 x 10^{-4} M (OD = 0.3) and 8.3 x 10^{-4} M (OD = 0.2), respectively.

The Pump-Probe setup in consists of a commercial titanium: sapphire laser amplifier (Coherent Legend Elite Duo), delivering 25 fs laser pulses at 800 nm central wavelength with 2.4 mJ per pulse at 5 kHz repetition rate. After the appropriate beam splitters, pointing deviations of pulses with around 1 mJ of energy are minimized in a beam stabilization unit to then pump a commercial 1 m Hollow-Core Fiber (HCF, Ultrafast Innovations) with a diameter of 250 μM. This fiber was kept under static 1 atm pressure of Argon. The 800 nm pulses are focused into the fiber using a 1 m lens. Typical HCF output spectra are shown in **Figure S28**.

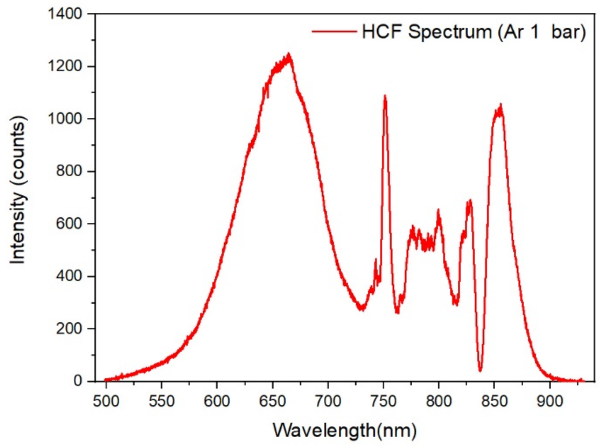


Figure S28. Typical HCF output spectrum using 1 mJ/25 fs pulses at 800 nm for pumping.

The HCF output beam is collimated using a spherical mirror with 1 m focal length. At the exit of the HCF, we obtain 130 μJ per pulse. The pulses are then compressed with a chirped mirror compressor which consists of two pairs of chirped mirrors (PC70 from Ultrafast Innovation) with 500-1050 nm of acceptance bandwidth. Using transient grating frequency resolved optical gating,[19] we obtain 6 fs pulses after the HCF and 8 fs pulses at the sample position. For the current experiment, we chose longer probe pulses (60 fs pulse duration for both pump and probe) to minimize the coherent artefact around Δt = 0 fs. After compression, (see **Figure S29** for a sketch of the experiment) an uncoated fused silica wedge pair is used as a broadband beamsplitter. The reflection from the first surface of the wedge pair serves as the probe pulse. The beam transmitted through the wedge pair serves as the pump pulse. Using a broadband half-wave plate, the polarization of the pump pulse is kept at magic angle (54.7°) with respect to the probe pulse, polarized parallel to the laser table. A telescope consisting of two focusing mirrors with focal lengths of 100 and 200 mm was employed to increase the probe beam's diameter, which in turn reduces its diameter at the sample position. A double chopping scheme is used instead of typical single chopping in order to record the probe-transmission with and without the pump pulse present (ΔOD).[20] Double chopping suppresses scattering from the pump pulse, whose spectrum is identical to the probe's in our setup. Both pump and probe pulses pass by a folding mirror to then hit a spherical mirror under 0°. The folding mirror then reflects the two pulses back, to make them pass through a hole in the spherical mirror with 300 mm focal length. This optical setup minimizes image errors such as astigmatism at the sample positon.[21] The diameter of the focused pump and probe beam at the sample position is 240 and 135 µm respectively, as determined by a beam profiler (Cinogy CMOS-1201). To control the intensity of pump and probe pulses, two identical round continuously variable metallic neutral density filters were used. For the present experiment, we work with 800 nJ per pulse for the pump pulse and 45 nJ per pulse for the probe. A motorized linear stage (Newport, IMS300CCHA) with a minimum step size of 8 fs and a maximal delay of two nano seconds delays the pump beam before the focusing mirror. After the sample, the transmitted probe pulse is collimated using a 200 mm lens and then detected in spectral dispersion using a CMOS camera (ANDOR Kymera 328i). The spectrometer is equipped with two gratings blazed at 500 nm and 800 nm. In combination, the spectral range between 250-1050 nm is covered. The camera allows us to record the transmitted probe with in shot-to-shot detection mode at the laser's repetition rate of 5 kHz.

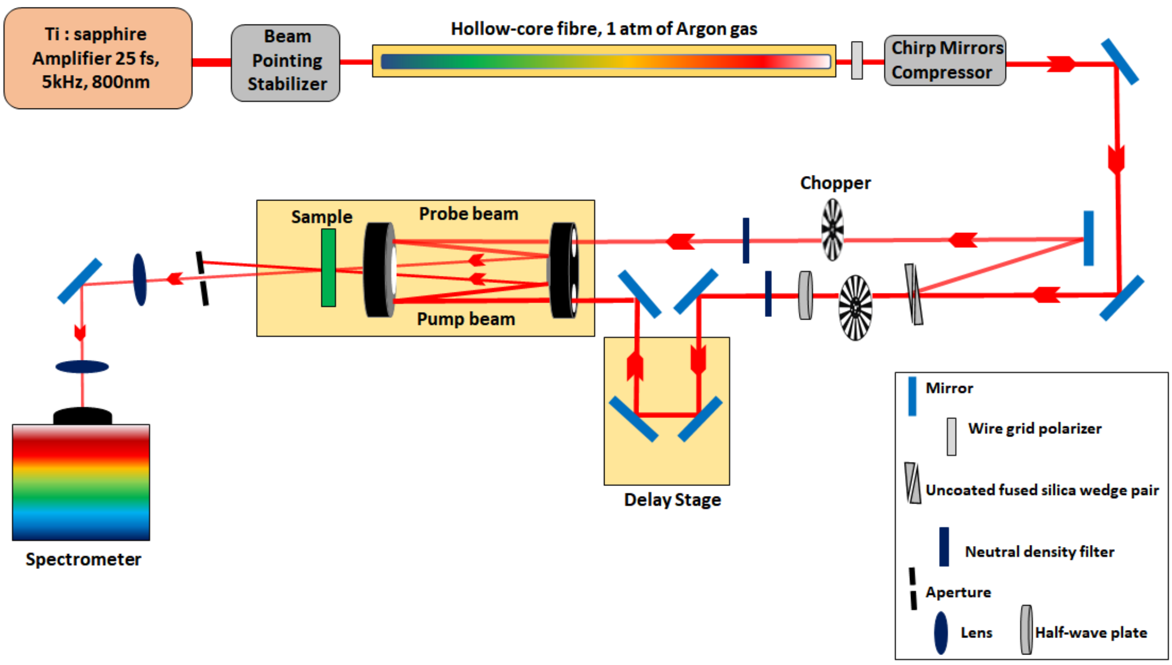


Figure S29. Sketch of the transient absorption experiment.

Measurements for the **T*p*BPA$^{\cdot+}$** and **TCBPA$^{\cdot+}$** were done in a 0.2 mm and 1 mm path-length cuvette, respectively. Both the samples are pumped throughout the measurements in a closed environment using a microgear pump (HNP mzr-S02). For Pump-Probe measurements, the maximal optical density for both samples in the spectral range of the excitation pulses was kept below 0.35 OD. For

T*p*BPA$^{\cdot+}$, after global fitting, three lifetimes are detected from pumping at 860 nm: 1.07 ps (red line), 4.60 ps (pink line), 32.00 ps (green line). The last number is not reliable due to the 50 ps range of acquisition time. The black line is attributed to Stokes-shift/vibrational cooling of the first excited state, while the red line is attributed to the relaxed excited state. The first excited state of **T*p*BPA**$^{\cdot+}$ (D_1) is therefore attributed a lifetime of **4.60 ps**.

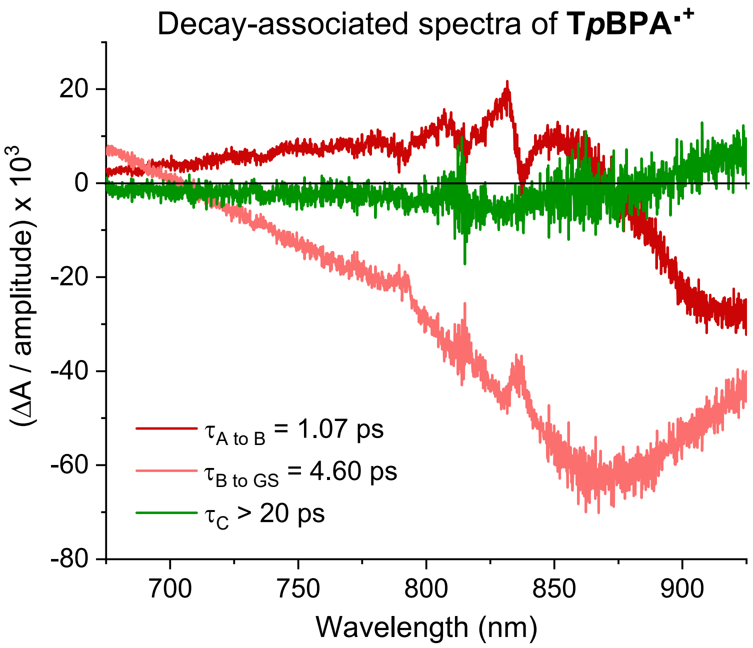


Figure S30. Transient Absorption Spectroscopy of **T*p*BPA**$^{\cdot+}$ (untreated data).

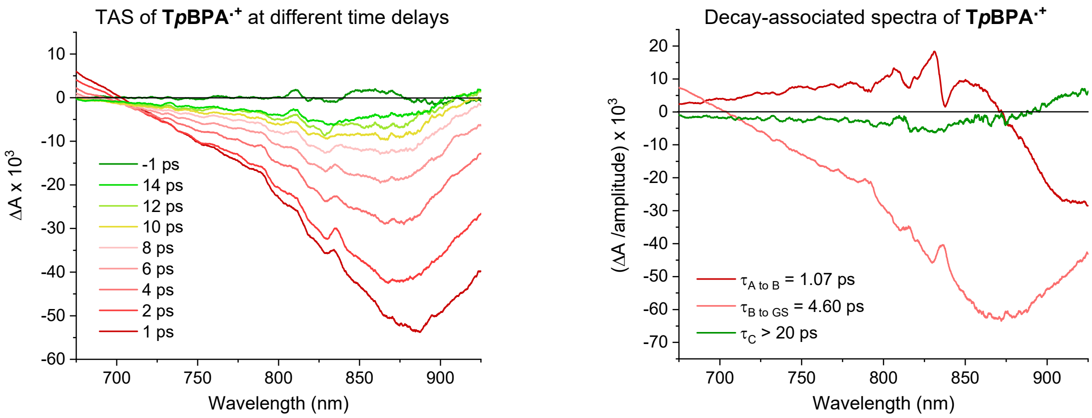


Figure S31. Transient Absorption Spectroscopy of **T*p*BPA**$^{\cdot+}$ (data fitted by a smoothing function for visualization).

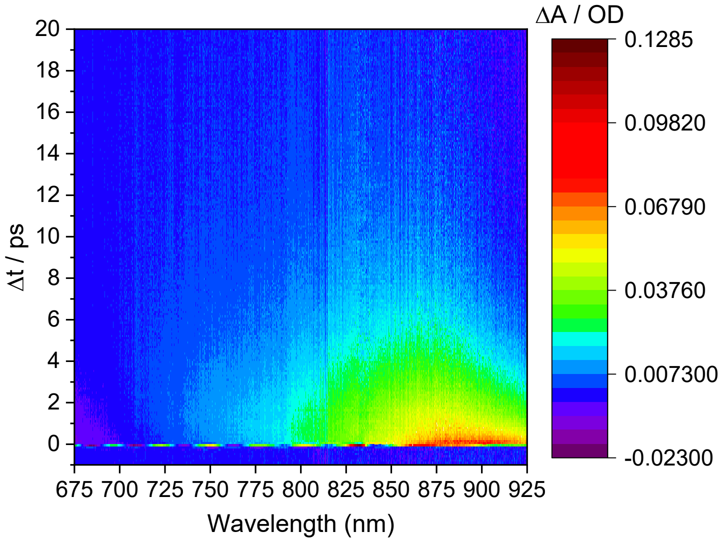


Figure S32. Transient Absorption Map of **T*p*BPA$^{\cdot+}$**.

For **TCBPA$^{\cdot+}$**, after global fitting, three lifetimes are detected from pumping at 860 nm: 1.29 ps (black line), 8.59 ps (red line), 22.47 (blue line). The last number is not reliable due to the 50 ps range of acquisition time. The black line is attributed to Stokes-shift/vibrational cooling of the first excited state, while the red line is attributed to the relaxed excited state. The first excited state of **TCBPA$^{\cdot+}$** (D1) is attributed a lifetime of **8.59 ps**.

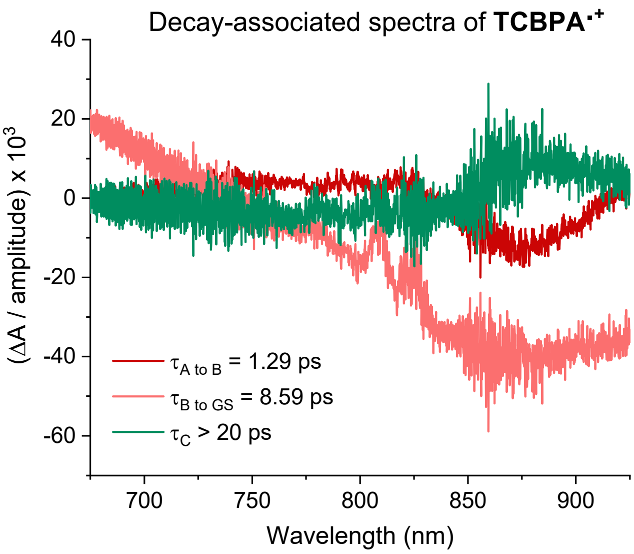


Figure S33. Transient Absorption Spectroscopy of **TCBPA$^{\cdot+}$** (untreated data).

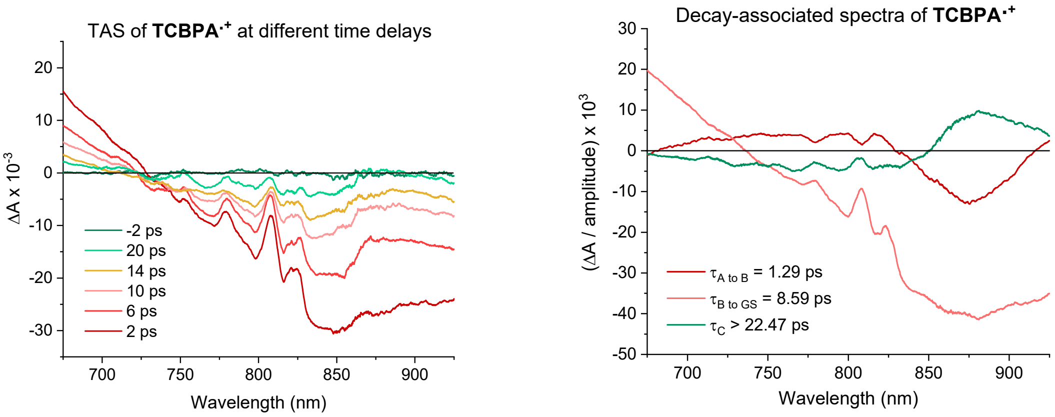


Figure S34. Transient Absorption Spectroscopy of **TCBPA**$^{\cdot+}$ (data fitted by a smoothing function for visualization).

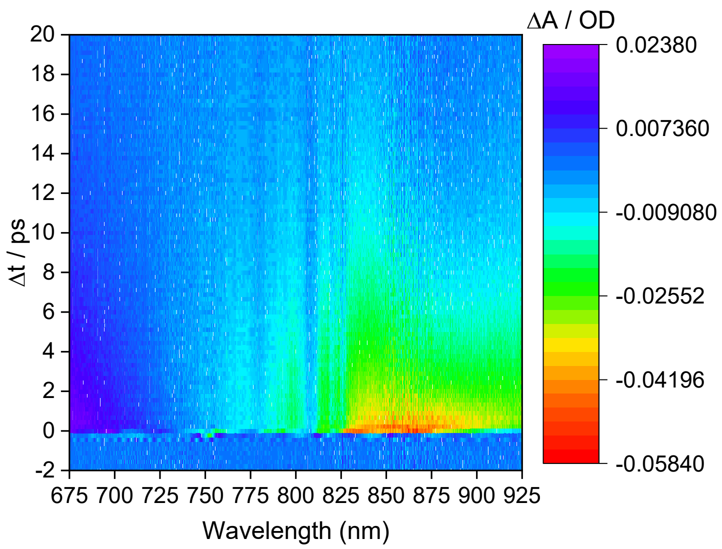


Figure S35. Transient Absorption Map of **TCBPA**$^{\cdot+}$.

The lifetimes of 4.6 and 8.6 ps for **T*p*BPA**$^{\cdot+}$ and **TCBPA**$^{\cdot+}$ are consistent with those reported for similar triarylamine radical cations and phenothiazine radical cations reported in the literature of the order of picoseconds.[22]

11. Emission spectra of LEDs

A BWTEK Inc. Examplar LS optical fiber spectrometer was clamped at a fixed 30 cm distance, positioning ~vertically above the measured LED. The LED was then switched on. The LED was shifted slightly until the maximum possible emitted intensity was detected (when the position was exactly vertical) and this was recorded. Although blue and green (440 nm, 519 nm) LEDs were not used in this study, measurements were repeated with different batches of OSRAM Oslon (SSL 80 LDCQ7P-2U3U LT1960) LEDs in order to demonstrate the reproducibility of the method. Considering the total peak area of their emission spectra, the emitted intensities of all LEDs used in the study at a fixed distance are similar. Minor differences in LED radiant intensities at different wavelengths cannot rationalize the drastic differences in yields of the photoelectrochemical reactions. *This supports the conclusion of higher order photoexcited state participation to rationalize wavelength dependence on yield*.

Table S11. Characterization of LEDs used in this study and their measured wavelengths, optical powers and relative emitting intensities.

Manufacturer	Model/ Brand	LEDs per plate	Input Power (W)	Input Power per LED (W)	LED λ_{max} (nm)	Luminous Flux	Peak intensity, directly above LED[a] (a.u.) at λ_{max}	Peak area, directly above LED[a] (a.u.)
CCS (Creating Customer Satisfaction) Inc.	LDL-71X12UV12-365-N	5	7.6	1.5	366	[70 mW / cm^2][b]	57834[c]	1657892[c]
LED Engin	LZ440UB00-00U4	4	62	10.4	394	3.8 W @ 700 mA	56960	1930122
OSRAM Oslon (batch 1)	Oslon SSL 80 LDCQ7P-2U3U LT1960	6	20	3.3	440	1.5 W @ 1000 mA	32040	1605358
OSRAM Oslon (batch 2)	Oslon SSL 80 LDCQ7P-2U3U LT1960	6	20	3.3	440	1.5 W @ 1000 mA	31542	1645527
OSRAM Oslon (batch 1)	Oslon SSL 80 LDCQ7P-2U3U LT1960	6	20	3.3	440	1.5 W @ 1000 mA	27445	1656573
OSRAM Oslon	Oslon SSL 80 LDCQ7P-2U3U LT1966	6	15	2.5	519	202 lm @ 1000 mA	13851	1404694
LED Engin	LZ4-00R308	4	25	6.3	729	2.1 W @ 700 mA	8920	1309336
LED Engin	LZ4-00R608	4	35	8.7	854	3.8 W @ 700 mA	2965	1065474

[a]Measured by a BWTEC optical fiber spectrometer at a distance of 30 cm directly above the LED. The maximum observed intensity was recorded. [b]Maximum intensity (mW / cm^2) reported by supplier at a 3 cm distance from LED. [c]The mean average value of BRT105 and BRT80 (BRT95) was taken to provide *ca.* the same radiant intensity as the 395 nm LED.

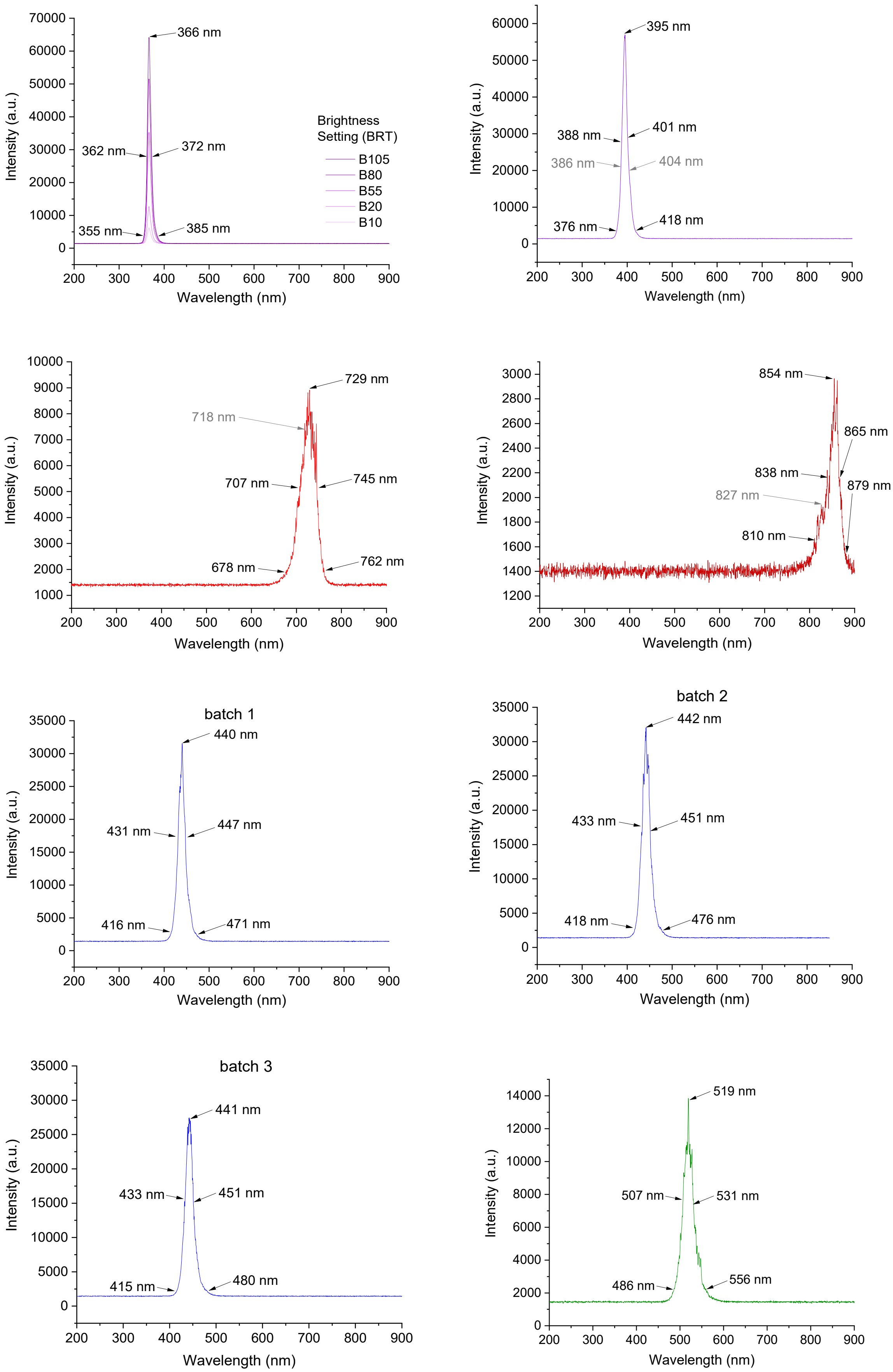


Figure S36. Emission spectra of LEDs used throughout the study at a fixed measurement distance.

12. Electron Paramagnetic Spectroscopy Investigations

As close as possible, EPR samples were prepared to mimic the photoelectrochemical reaction conditions. DCM was chosen as the solvent for its excellent solubility of neutral TPAs and so that conditions were comparable to UV-vis spectroscopic measurements (the photoelectrochemical reaction was confirmed to proceed in DCM in excellent yield, see **Table S7**, entry 2). EPR spectra were measured with a Bruker EMX spectrometer which is a continuous-wave (CW) X-Band (9-10 GHz) spectrometer equipped with an ER 083 (200/60) power source electromagnet (0-600 mT). For the measurements, an ER 4104 OR/9009 resonant cavity with a resonance frequency of 9.66 GHz was used. If not stated otherwise, the spectra were measured with a modulation frequency of 100 kHz, a modulation amplitude of 8.0 G, a centre field of 3453 G, a sweep width of 120 G, a conversion time of 15.00 ms, a time constant of 163.84 ms, a receiver gain of 5.023773×10^2, and an X-axis resolution of 1028. The microwave frequency and power are intrinsically different for every sample and are reported for each individual sample in **Table S12**. Samples in DCM as solvent were measured in Wilmad® quartz EPR tubes (O.D. = 1 mm, I.D. = 0.8 mm), samples using acetonitrile as solvent and placed inside a regular EPR tube. Unless stated otherwise, all solutions were prepared under inert atmosphere (N_2) using anhydrous (MBraun MB SPS) and degassed (freeze-pump-thaw) solvent at 25 °C. The solutions included 100 mM $^nBu_4NPF_6$, 5 mM $TPA^{\cdot+}$s (PF_6 salt) and 1750 mM arene substrate (= 350 equiv.). Hyperfine couplings for N atoms were extracted from simulations done in WINSIM2002 (fitting correlation = >0.995 in each case) and plotted on spectra below.[23] Simulations are shown in Section 12.1. As per **Figure S37**, the presence of electrolyte did not affect the EPR signal (shift in G), but merely changed the intensity presumably due to an effect on **T*p*BPA**$^{\cdot+}$ solubility.

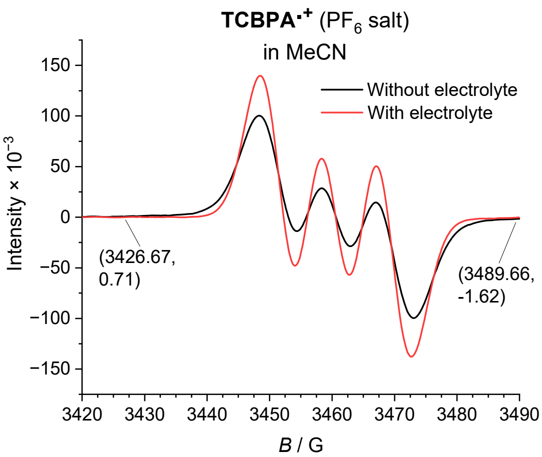


Figure S37. Impact of the presence or absence of electrolyte on the EPR signal.

Table S12. Parameters used for EPR sample measurements.

Sample	Deviation in Conditions	Microwave power / mW	Microwave frequency / GHz
T*p*BPA$^{\cdot+}$ [a]	-	2.110 × 10^{1}	9.642351
T*p*BPA$^{\cdot+}$ [b]	MeCN solvent, no $^{n}Bu_4NPF_6$	2.120 × 10^{1}	9.648397
T*p*BPA$^{\cdot+}$ [c]	MeCN solvent	2.132 × 10^{1}	9.648229
T*p*BPA$^{\cdot+}$ [a]	with 1,3,5-TMB (350 eq.)	2.097 × 10^{1}	9.631667
T*p*BPA$^{\cdot+}$ [a]	with PhI (350 eq.)	2.142 × 10^{1}	9.635545
TCBPA$^{\cdot+}$ [a]	-	6.377 × 10^{1}	9.641069
TCBPA$^{\cdot+}$ [a]	with PhCl (350 eq.)	2.110 × 10^{1}	9.628465
TCBPA$^{\cdot+}$ [d]	with PhBr (350 eq.)	2.112 × 10^{1}	9.631634
TCBPA$^{\cdot+}$ [e]	with 1,2-PhClCl (350 eq.)	2.068 × 10^{1}	9.638088
TCBPA$^{\cdot+}$ [e]	with 1,3-PhClCl (350 eq.)	2.066 × 10^{1}	9.630983
TCBPA$^{\cdot+}$ [d]	with 1,4-PhClCl (350 eq.)	2.078 × 10^{1}	9.634744

[a]Measured with a time constant of 81.82 ms and a conversion time of 100.00 ms. [b]Measured in acetonitrile without electrolyte. [c]Measured in acetonitrile with electrolyte. [d]Measured with a receiver gain of 1.415892 × 10^{2}. [e]Measured with a receiver gain of 5.023773 × 10^{2}.

12.1. EPR spectra of TPA$^{\cdot+}$s

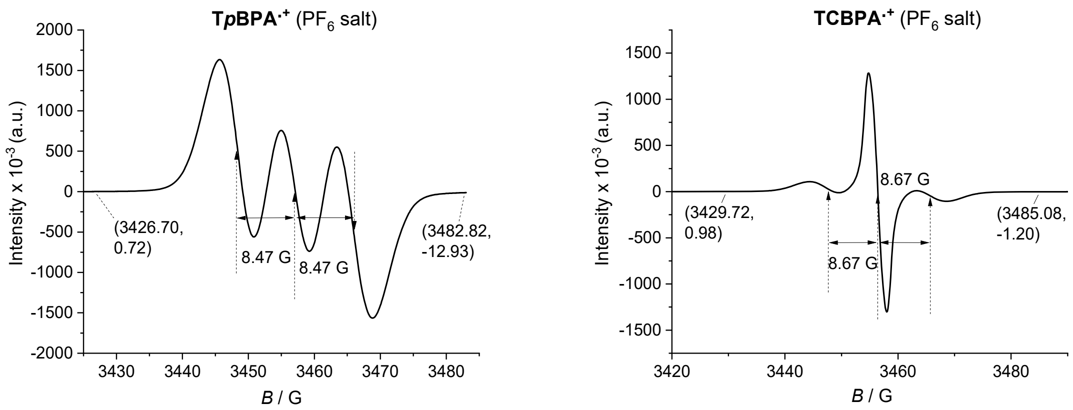


Figure S38. EPR spectra of the isolated **T*p*BPA**$^{\cdot+}$ (left) and **TCBPA**$^{\cdot+}$ (right), as their PF_6 salts.

12.2. EPR spectra of TPA$^{\cdot+}$s in the presence of substrates

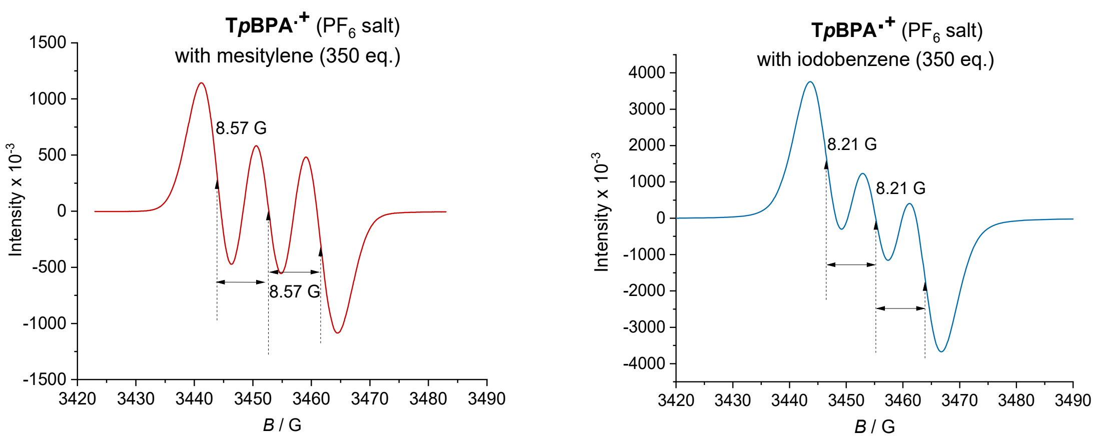


Figure S39. EPR spectra of **T*p*BPA**$^{\cdot+}$ (PF_6 salt) in the presence of mesitylene (left) and PhI (right).

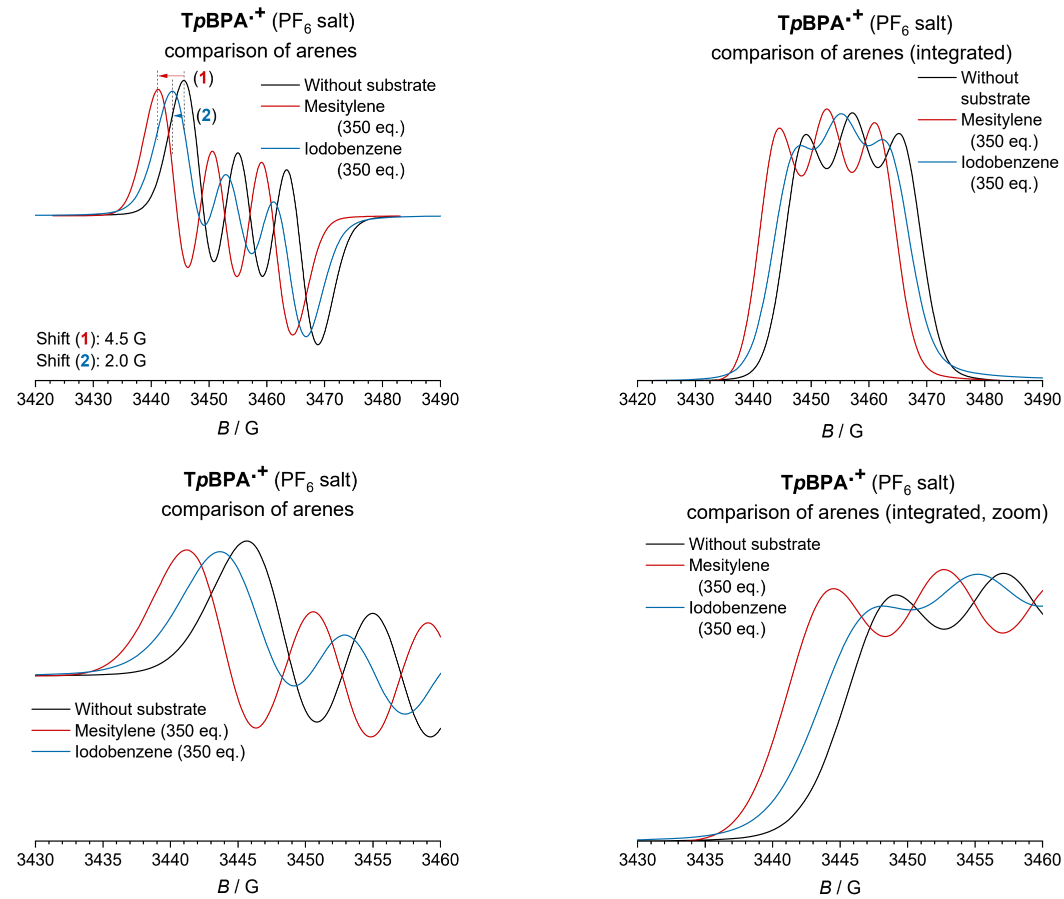


Figure S40. Comparison of EPR spectra of **TCBPA**$^{\cdot+}$ (PF_6 salt) in the presence of arenes.

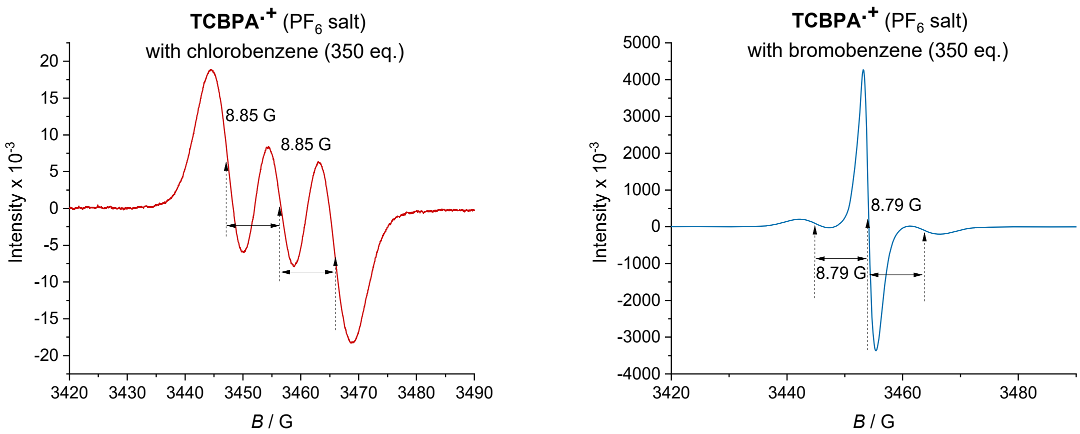


Figure S41. EPR spectra of **TCBPA**$^{\cdot+}$ (PF_6 salt) in the presence of PhCl (left) and PhBr (right).

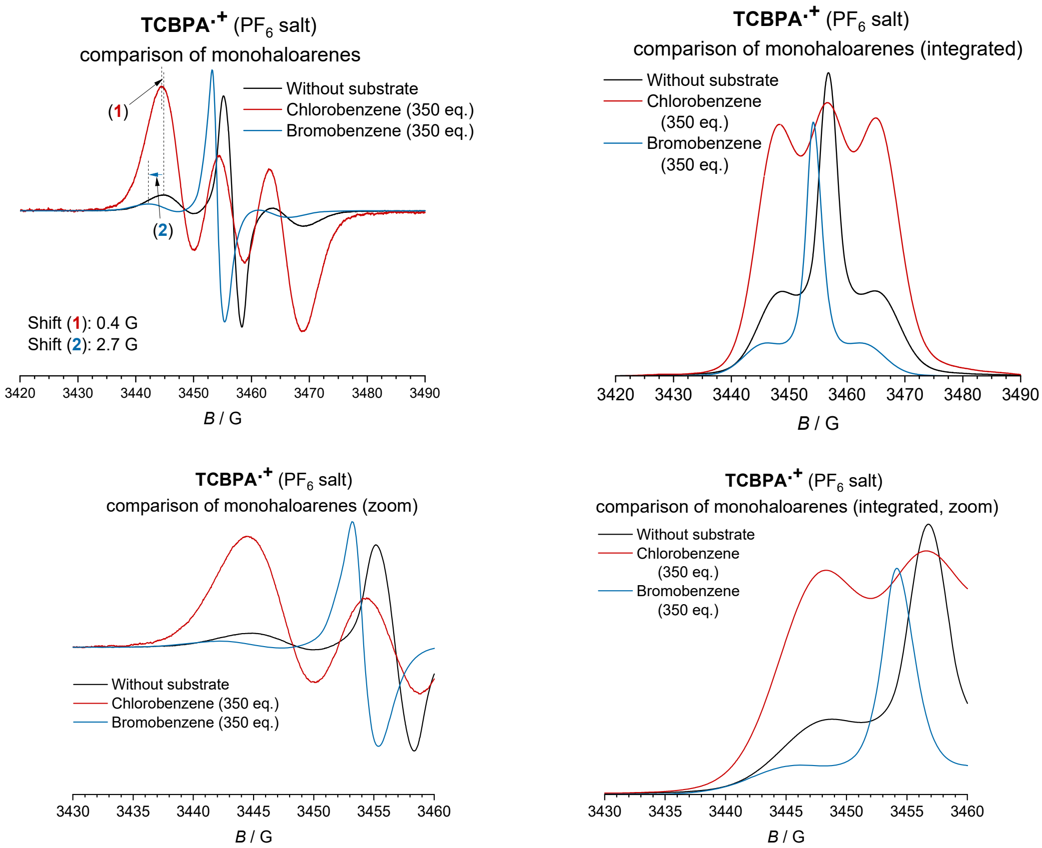


Figure S42. Comparison of EPR spectra of **TCBPA$^{\cdot+}$** (PF₆ salt) in the presence of monohaloarenes.

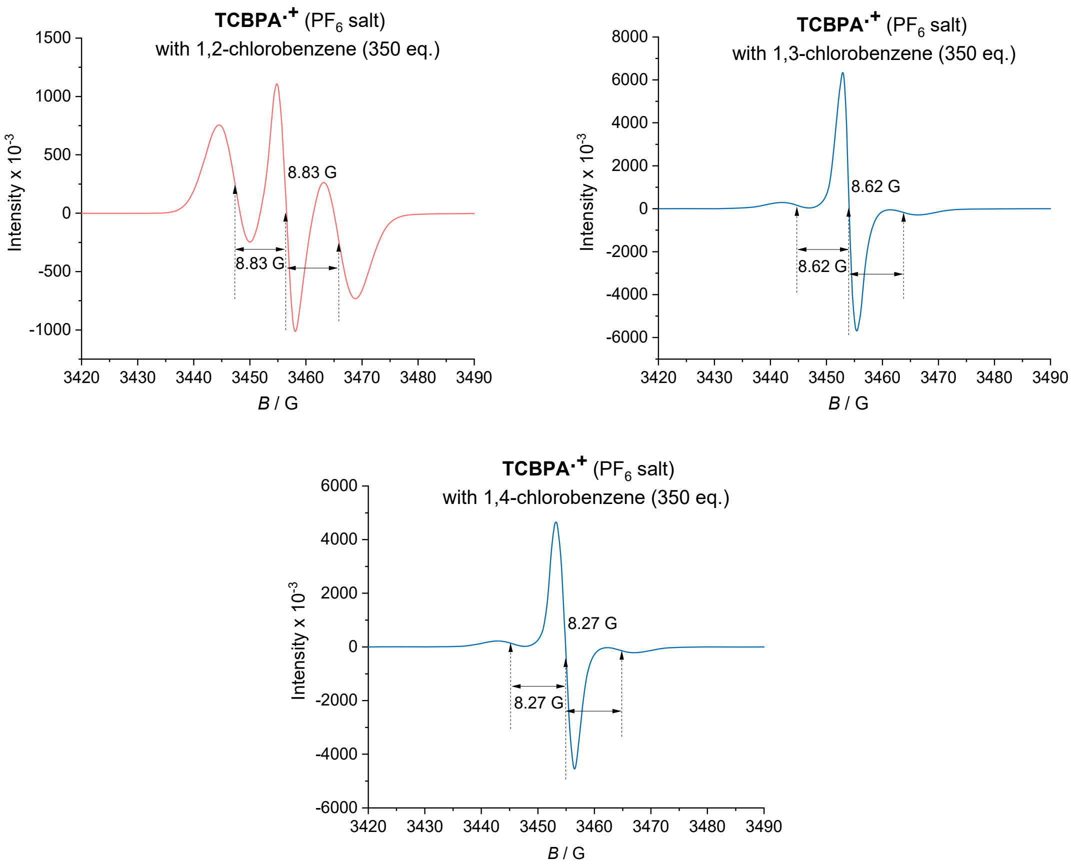


Figure S43. EPR spectra of **TCBPA$^{\cdot+}$** (PF₆ salt) in the presence of dichloroarenes.

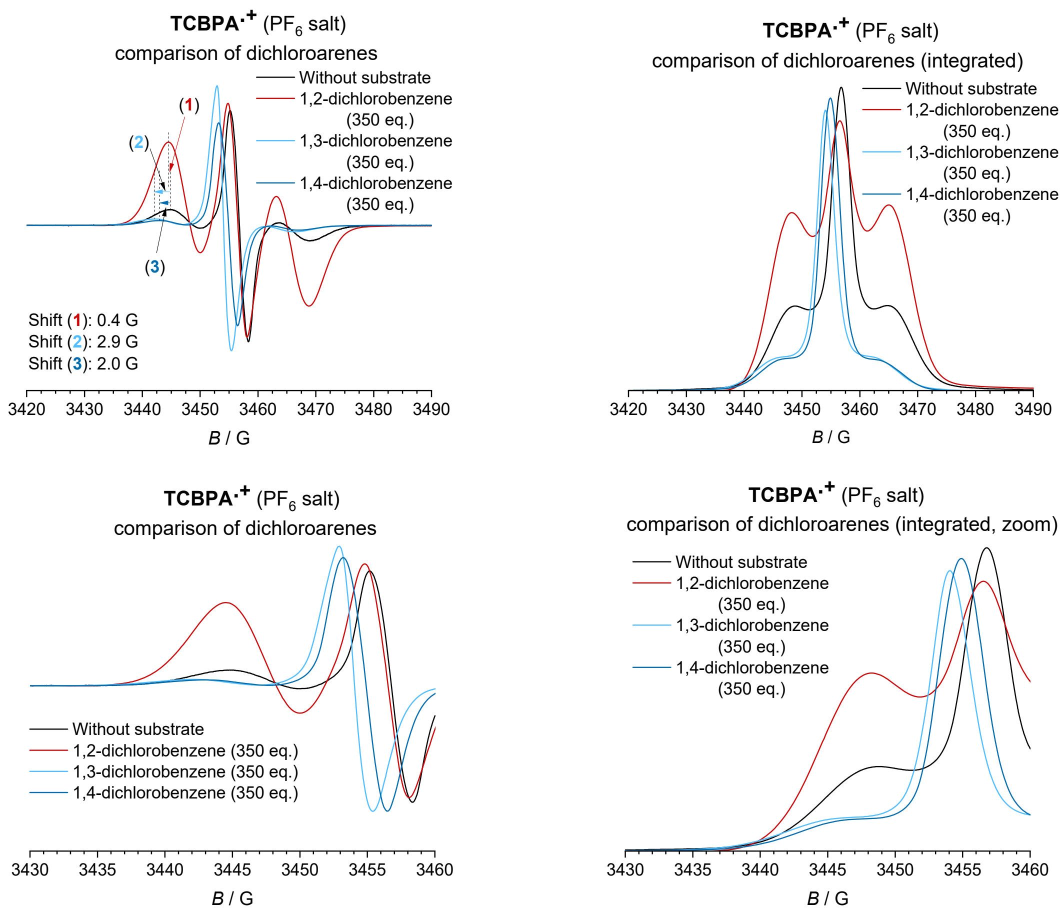


Figure S44. Comparison of EPR spectra of the **TCBPA**$^{\cdot+}$ (PF_6 salt) in the presence of dichloroarenes.

12.3. Simulation of EPR spectra measured

Table S13. Simulated fitting of various EPR spectra and extracted Nitrogen hyperfine couplings.

TPA$^{\cdot+}$	Substrate (350 eq.)	Triplet (%)	Singlet (%)	α(N) (Triplet)	Reaction Yield[b]	Reaction Yield[c]
T*p*BPA$^{\cdot+}$	-	100	N/A	8.47	-	-
T*p*BPA$^{\cdot+}$	1,3,5-TMB	100	N/A	8.57	80	-
T*p*BPA$^{\cdot+}$	PhI	95	5	8.21	n.r.	-
TCBPA$^{\cdot+}$	-	67	33	8.67	-	-
TCBPA$^{\cdot+}$	PhCl	100	N/A	8.85	65	-
TCBPA$^{\cdot+}$	PhBr	33	67	8.79	22	-
TCBPA$^{\cdot+}$	1,2-PhClCl	94	4	8.83	17	31
TCBPA$^{\cdot+}$	1,3-PhClCl	31	69	8.62	20	27
TCBPA$^{\cdot+}$	1,4-PhClCl	45	54	8.27	6	11

n.r. = no reaction. [a]Determined using WINSIM2002 by simulation of the spectrum (single or two species), fitting R > 0.995 in each case;[23] [b]Using ethyl 3-pyrazolecarboxylate as a nucleophile, see main manuscript for exact conditions employed. [c]Using **TdCBPA** as a catalyst.

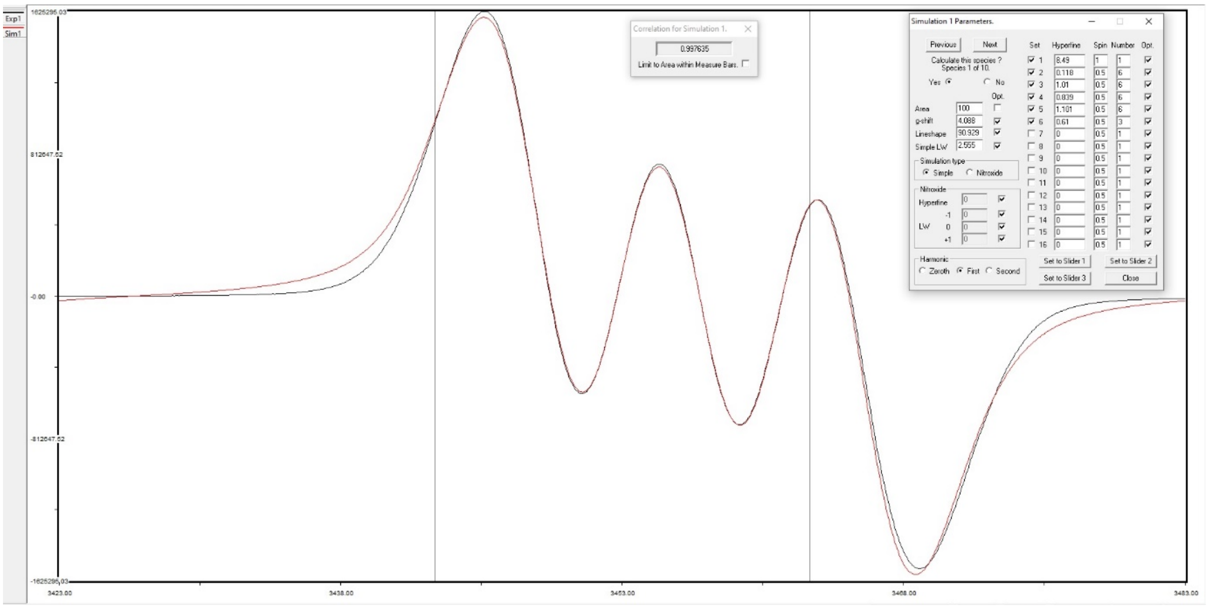


Figure S45. Simulation of the EPR spectrum of **T*p*BPA**$^{\cdot+}$.

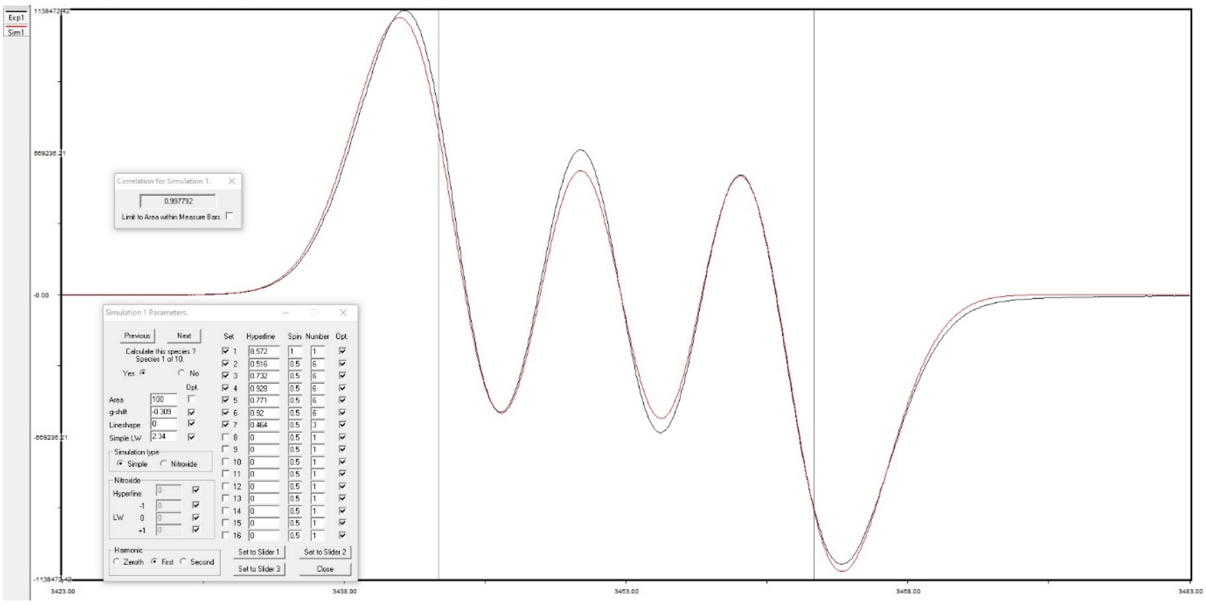


Figure S46. Simulation of the EPR spectrum of **T*p*BPA**$^{\cdot+}$ + Mesitylene (350 eq.).

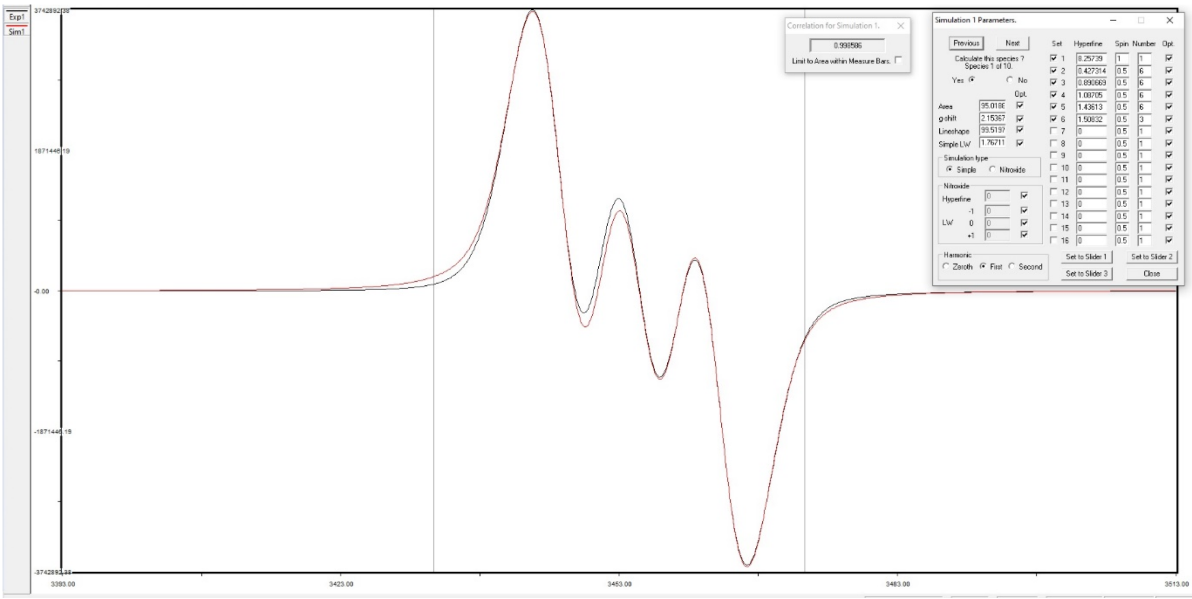


Figure S47. Simulation of the EPR spectrum of **T*p*BPA**$^{\cdot+}$ + **I**odobenzene (350 eq.); parameters of species 1.

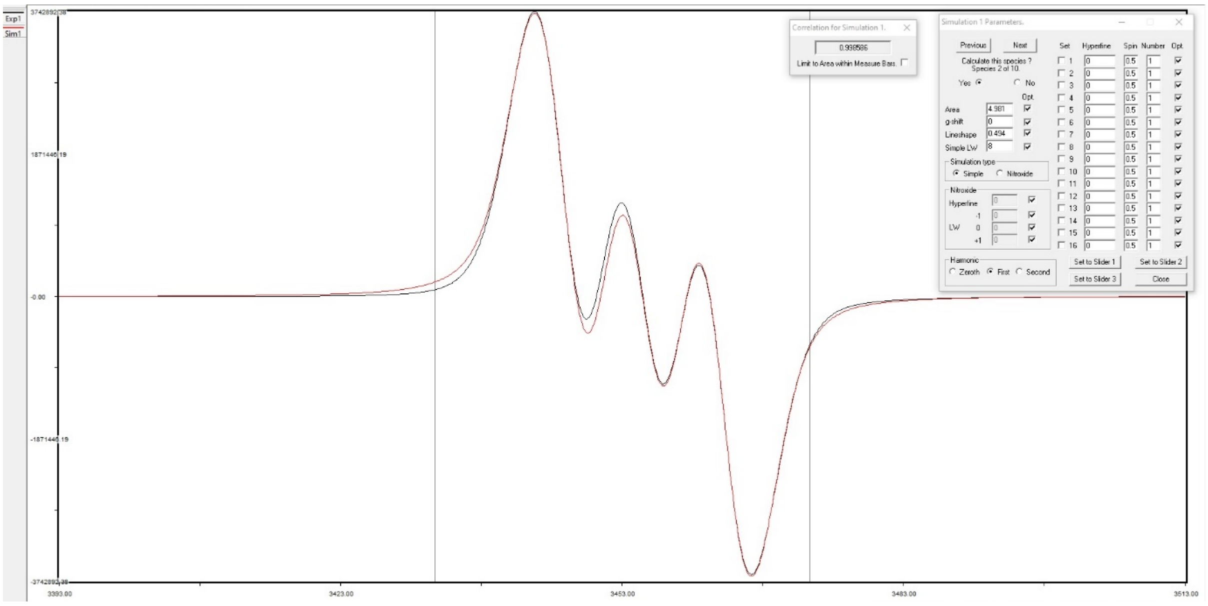


Figure S48. Simulation of the EPR spectrum of **T*p*BPA**$^{\cdot+}$ + **I**odobenzene (350 eq.); parameters of species 2.

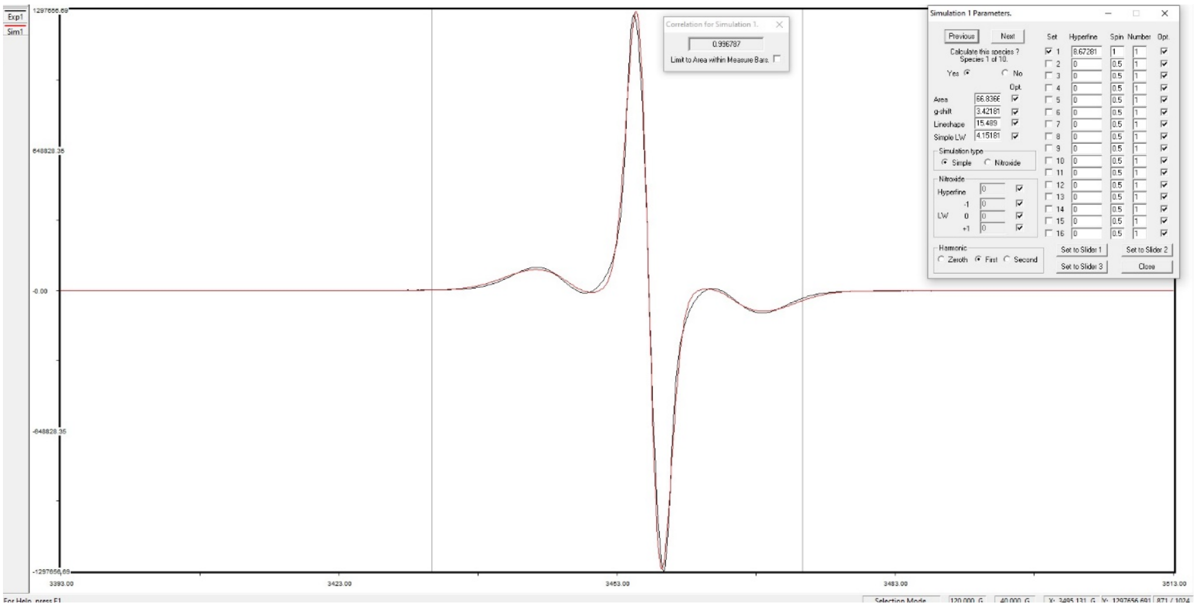


Figure S49. Simulation of the EPR spectrum of **TCBPA**$^{\cdot+}$; parameters of species 1.

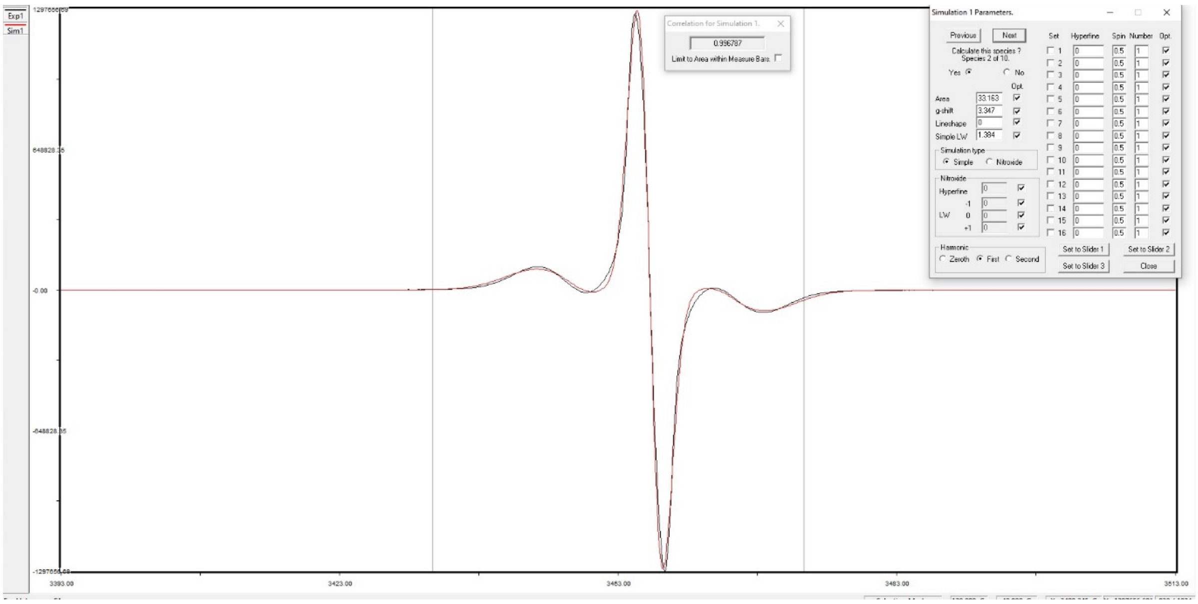


Figure S50. Simulation of the EPR spectrum of **TCBPA**$^{\cdot+}$; parameters of species 2.

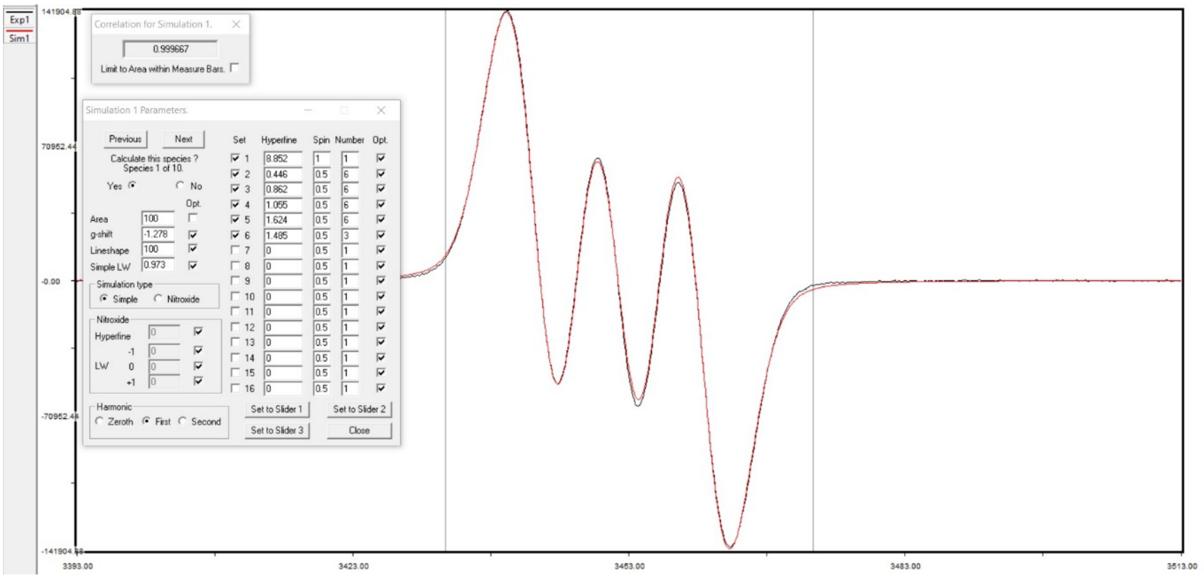


Figure S51. Simulation of the EPR spectrum of **TCBPA**$^{\cdot+}$ + chlorobenzene (350 eq.).

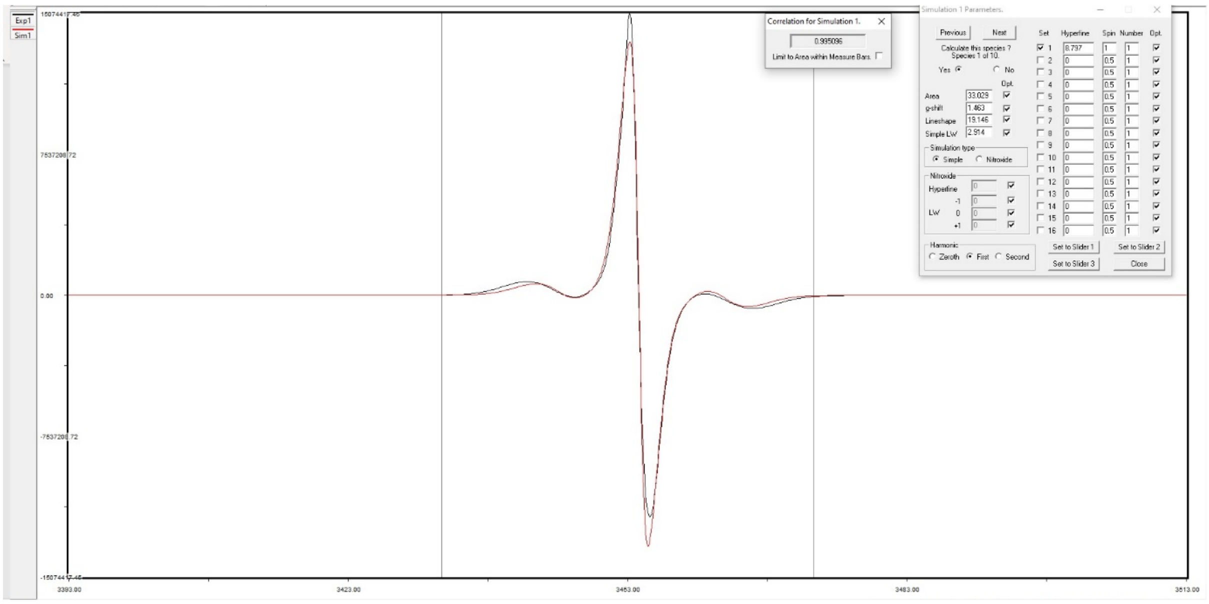


Figure S52. Simulation of the EPR spectrum of **TCBPA**$^{\cdot+}$ + bromobenzene (350 eq.), parameters of species 1.

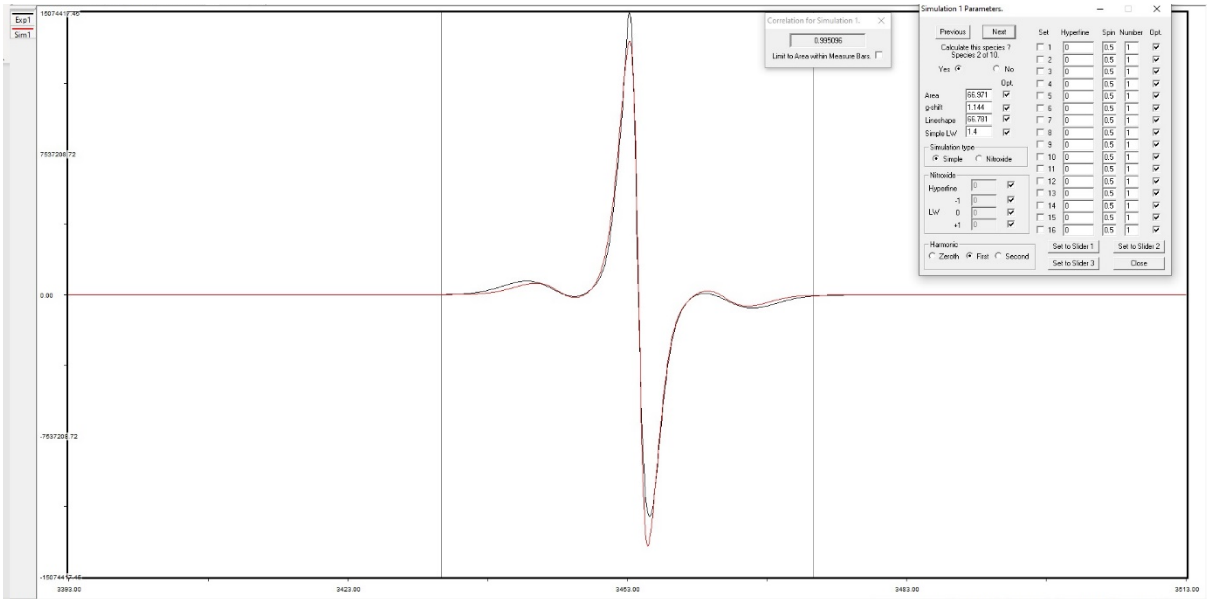


Figure S53. Simulation of the EPR spectrum of **TCBPA**$^{\cdot+}$ + bromobenzene (350 eq.), parameters of species 2.

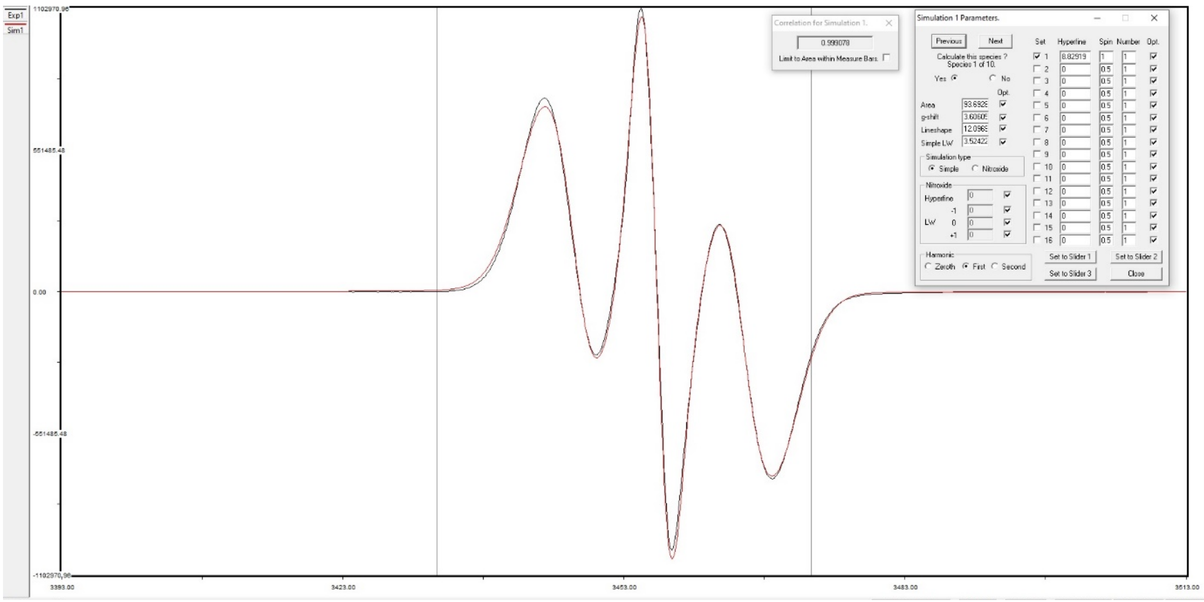


Figure S54. Simulation of the EPR spectrum of **TCBPA**$^{\cdot+}$ + 1,2-dichlorobenzene (350 eq.), parameters of species 1.

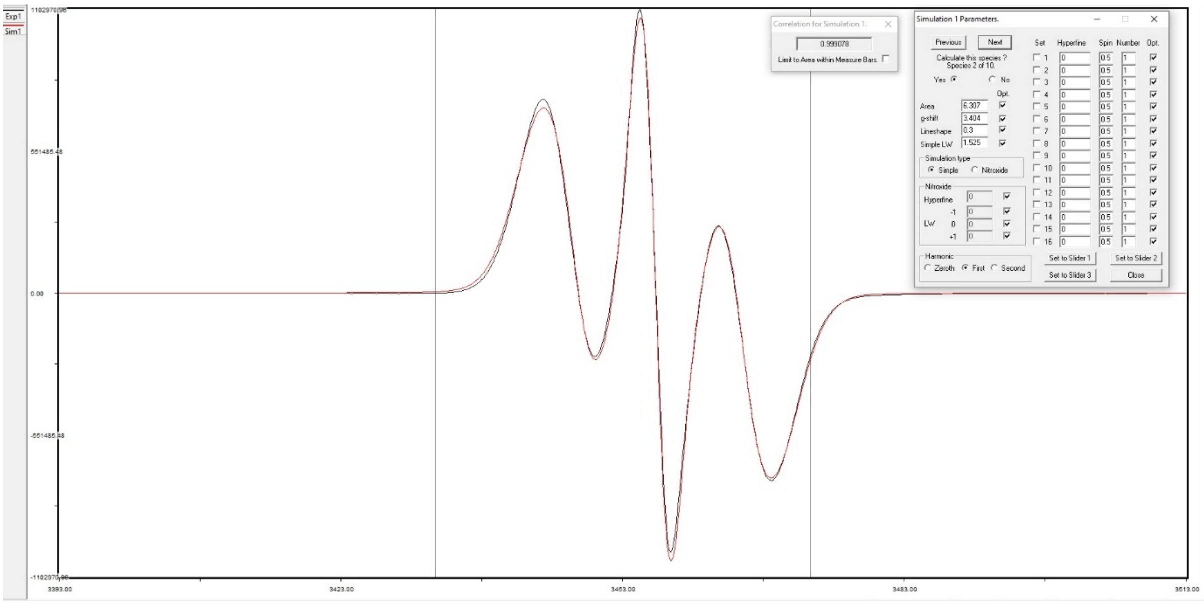


Figure S55. Simulation of the EPR spectrum of **TCBPA**$^{\cdot+}$ + 1,2-dichlorobenzene (350 eq.), parameters of species 2.

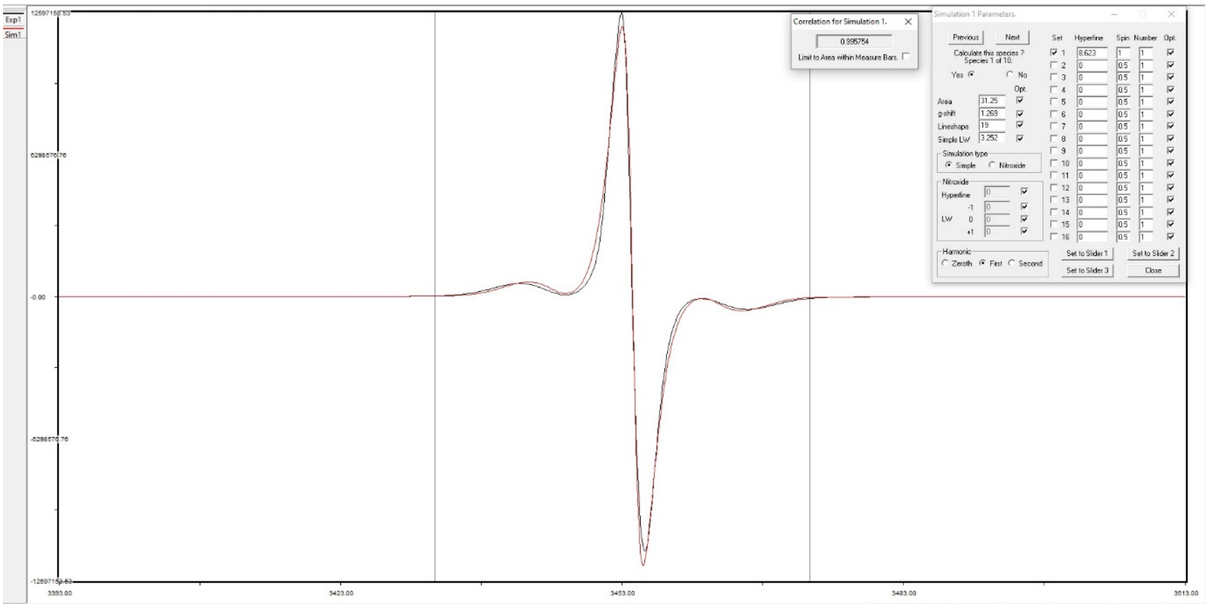


Figure S56. Simulation of the EPR spectrum of **TCBPA**$^{\cdot+}$ + 1,3-dichlorobenzene (350 eq.), parameters of species 1.

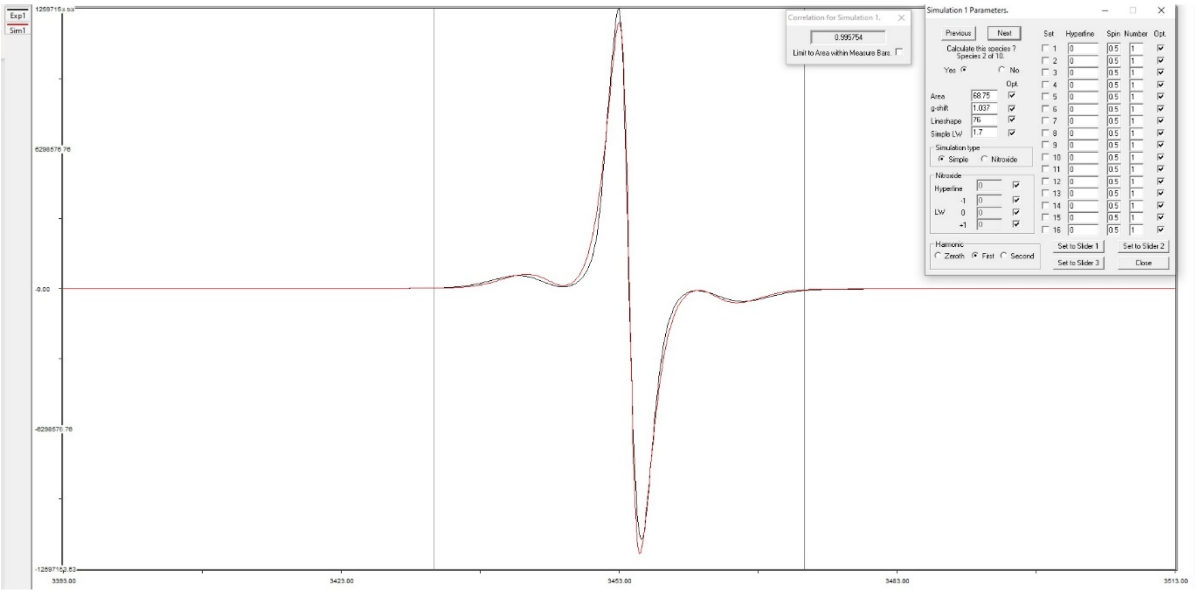


Figure S57. Simulation of the EPR spectrum of **TCBPA$^{\cdot+}$** + 1,3-dichlorobenzene (350 eq.), parameters of species 2.

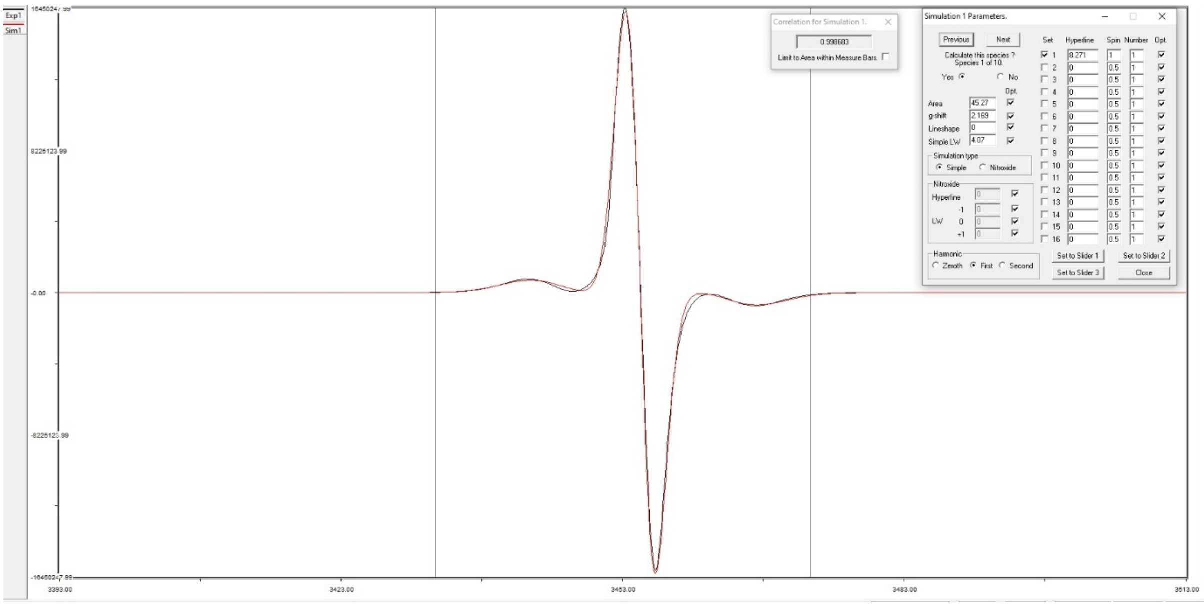


Figure S58. Simulation of the EPR spectrum of **TCBPA$^{\cdot+}$** + 1,4-dichlorobenzene (350 eq.), parameters of species 1.

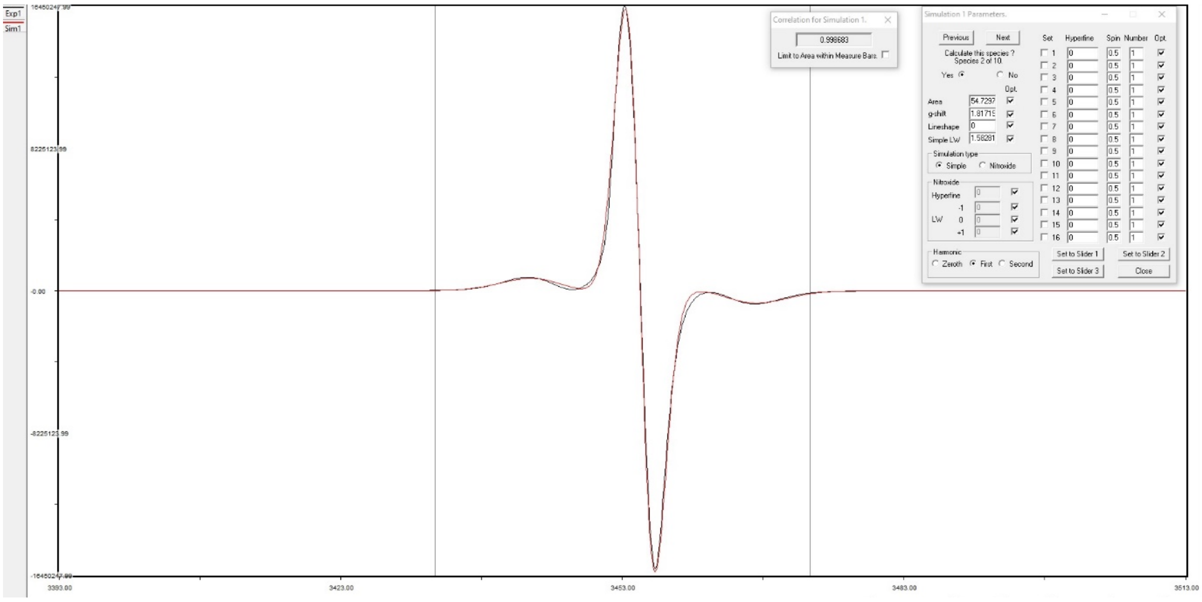


Figure S59. Simulation of the EPR spectrum of **TCBPA$^{\cdot+}$** + 1,4-dichlorobenzene (350 eq.), parameters of species 2.

12.4. Interpretation of EPR spectra of TPA$^{\cdot+}$s in the presence of substrates

EPR spectroscopy of the isolated **T*p*BPA$^{\cdot+}$**$\cdot PF_6$ gave a triplet with a^N = 8.47 G (**Figure S38, left**), consistent with the previously-reported literature for this radical cation ($SbCl_6$ salt) in DCM[24] Indications of hypercoupling were previously observed for **T*p*BPA$^{\cdot+}$**$\cdot PF_6$ salt by us in MeCN[2] The triplet is characteristic of a Nitrogen atom that is not in conjugation with the surrounding aromatic rings, which indicates a 'propellor'-type structure for the TPA$^{\cdot+}$ in solution, consistent with predictions from DFT calculations and from XRD of the solid-state TPA$^{\cdot+}\cdot PF_6$ salts (see **Section S13.2** and **Section S15**). EPR spectroscopy of the isolated **TCBPA$^{\cdot+}$** (PF_6 salt) gave what appeared to be a superposition of two radical species (**Figure S38, right**); a 'masked' triplet and a large central singlet; making interpretations of a^N values and DFT simulation of the EPR signals difficult (a^N = 8.67 G). This could indicate two rotational conformers in solution (**Figure S60**), one 'propeller'-type form (a triplet) and one form in which the N radical cation falls into conjugation with one of the aromatic systems (a broad singlet). We note that the existence of two similar conformers (point groups C_3 and C_2 symmetry) have been proposed for the tri(*p*-chloro)phenylaminium radical cation.[25] The hindered rotation of the biphenyl unit of the TPA$^{\cdot+}$ is reported previously in the literature for a similar dimeric TPA$^{\cdot+}$, with coplanarity of the biphenyl unit being responsible for driving changes in the EPR spectra.[26] Consistent with this, DFT calculations (scanning the dihedral of the biphenyl unit bridge) predicted rotational barriers of 1.48 kcal mol^{-1} and 1.29 kcal mol^{-1} for rotations of the peripheral rings of **T*p*BPA$^{\cdot+}$** and **TCBPA$^{\cdot+}$** (**Figure S61**), confirming that the latter had a higher barrier. Although the difference is very small, and both barriers are thermally accessible at rt, the difference may be a sufficient enough influence on the position of equilibrium to results in different EPR signals. We emphasize the importance the relative difference, since DFT modelled only the naked salts and without explicit solvation.

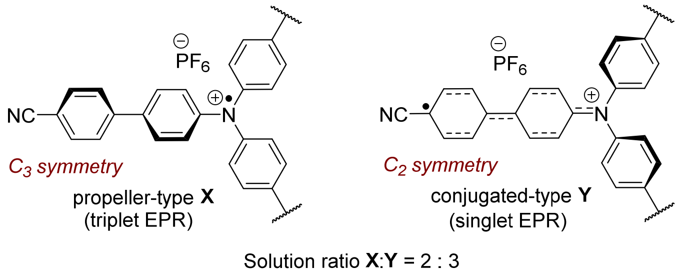
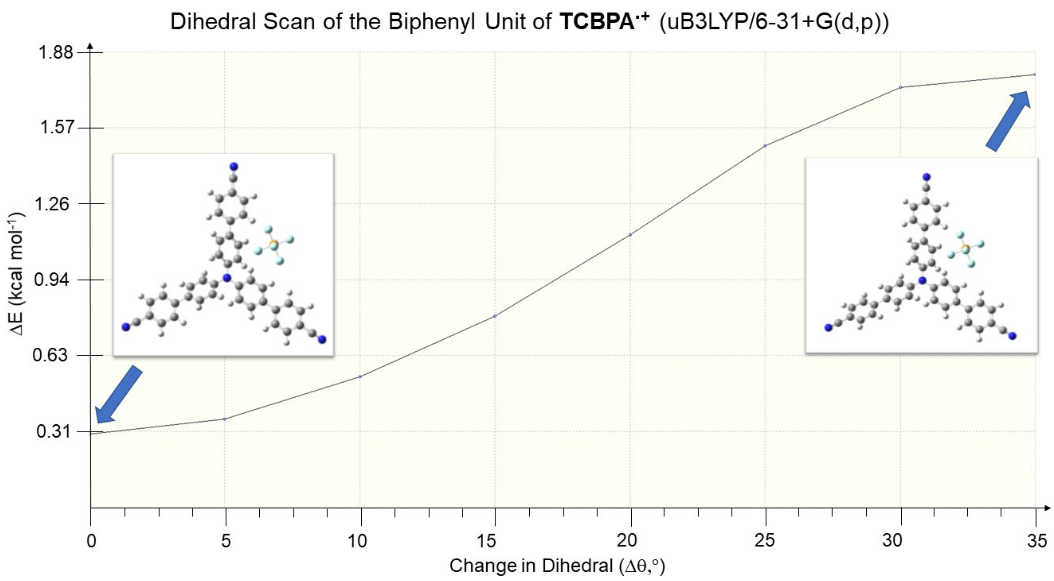


Figure S60. Proposed symmetry-broken rotamers of **TCBPA**$^{\cdot+}$ in solution (top).



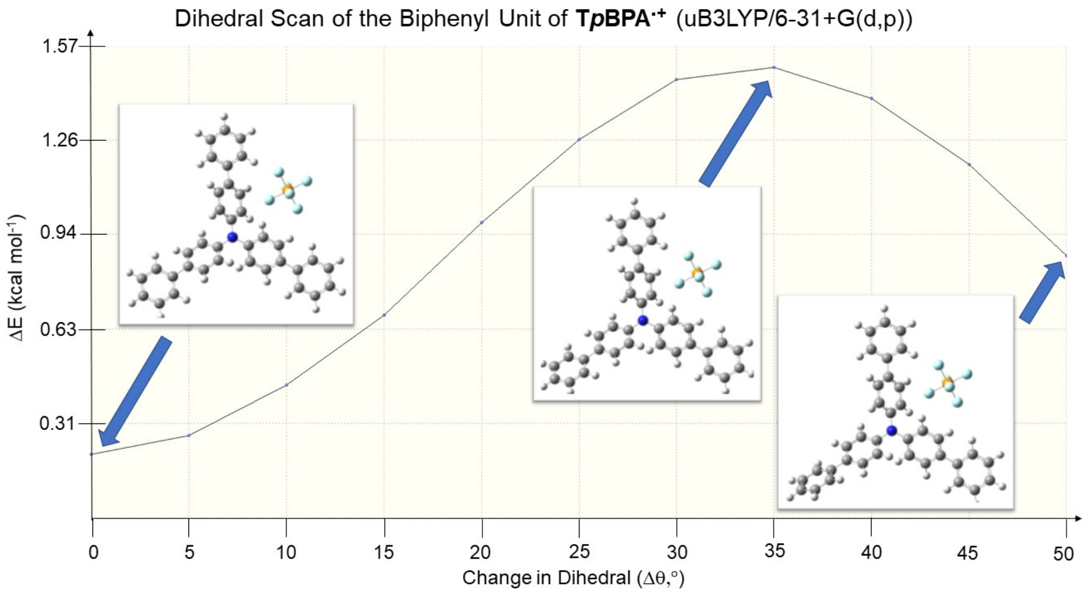


Figure S61. Dihedral scan of the biphenyl units of **TCBPA**$^{\cdot+}$ (top) and **T*p*BPA**$^{\cdot+}$ (bottom) to estimate rotational barrier (bottom), at the uB3LYP/6-31+G(d,p) level, see **Section S13** for details.

In the presence of mesitylene, a large shift in the G values of the signal occurred (**Figures S39-40**), while the shape of the signal remained comparable (a^N = 8.57 G) to the uncomplexed **T*p*BPA$^{\cdot+}$** (**Figure S38, left**). This indicates that the geometry and spin density of the mesitylene-complexed **T*p*BPA$^{\cdot+}$** and uncomplexed **T*p*BPA$^{\cdot+}$** are very similar, and is consistent with the lack of change in UV-vis spectroscopy (**Figures S7-8**) and findings from DFT calculations that a T-π complex *does not* alter the spin density with respect to the uncomplexed **T*p*BPA$^{\cdot+}$** (**Figure S62**).

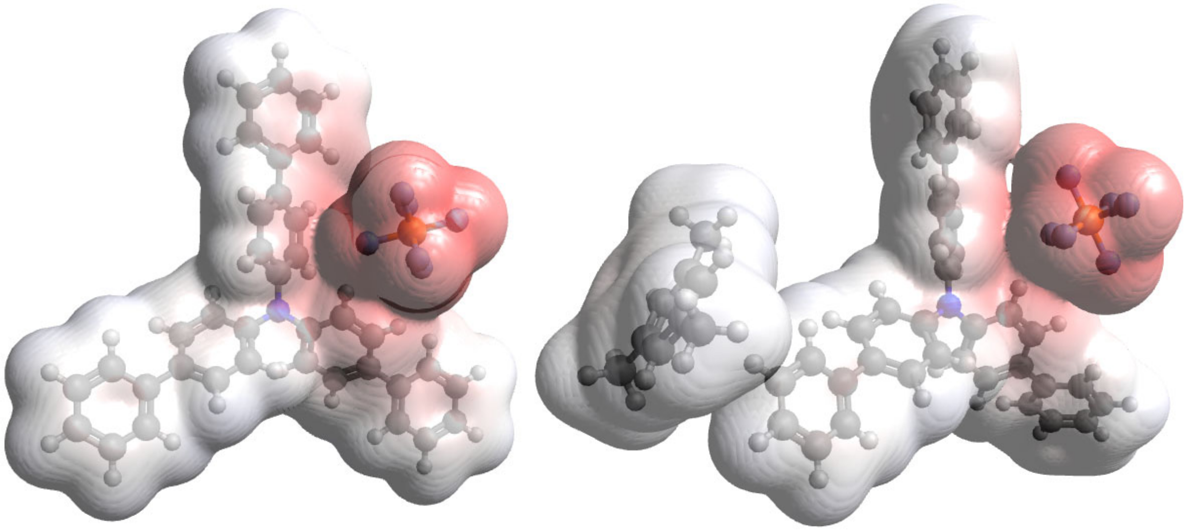


Figure S62. DFT-computed Spin Densities for uncomplexed **T*p*BPA$^{\cdot+}$** (left) and a T-π precomplex **T*p*BPA$^{\cdot+}$** + mesitylene (right). See **Section S13** for details.

In the presence of iodobenzene, a smaller shift in the G values of the signal occurred, and the shape of the signal changed with respect to the uncomplexed **T*p*BPA$^{\cdot+}$** (**Figure S38, left**), as seen by a slight flattening of the triplet 'shoulders' (a^N = *ca.* 8.2 G). Since iodobenzene gave no reaction, this suggests a different geometry of precomplex that is 'unreactive' in the photoelectrochemical reaction. The minor change in EPR signal shape reflects a minor change in spin density consistent with DFT calculations which predict a π-π complex (see **Section S13.3**) that may be formed in small concentrations. Since the reaction of mesitylene proceeded successfully where iodobenzene did not, the 'reactive' precomplex must resemble the geometry of the uncomplexed **T*p*BPA$^{\cdot+}$**. This is consistent with the proposal for a T-π type geometry as found by DFT calculations (see **Section S13.3**). Changes in the EPR spectra were very pronounced in the case of **TCBPA$^{\cdot+}$** (PF_6 salt). In the presence of chlorobenzene (**Figure S41, left**), the G values of the signal were relatively unchanged but the signal shape completely changed to give a triplet (a^N = 8.85 G) resembling that observed for that of uncomplexed **T*p*BPA$^{\cdot+}$** (**Figure S38, left**). This indicates that the geometry and spin density of the chlorobenzene-complexed **TCBPA$^{\cdot+}$** and uncomplexed **TCBPA$^{\cdot+}$** are different, or that complexation drives the solution equilibrium in favour of the 'propeller'-type conformer (Figure S63). The change in spin density would be expected to manifest in a change in the UV-vis spectra, consistent with aforementioned results (**Figures S7-8**) and findings from DFT calculations that a T-π complex (in which the Cl atom faces "in" to the N radical cation) *does* alter the spin density with respect to the uncomplexed **TCBPA**$^{\cdot+}$ (Figure S64).

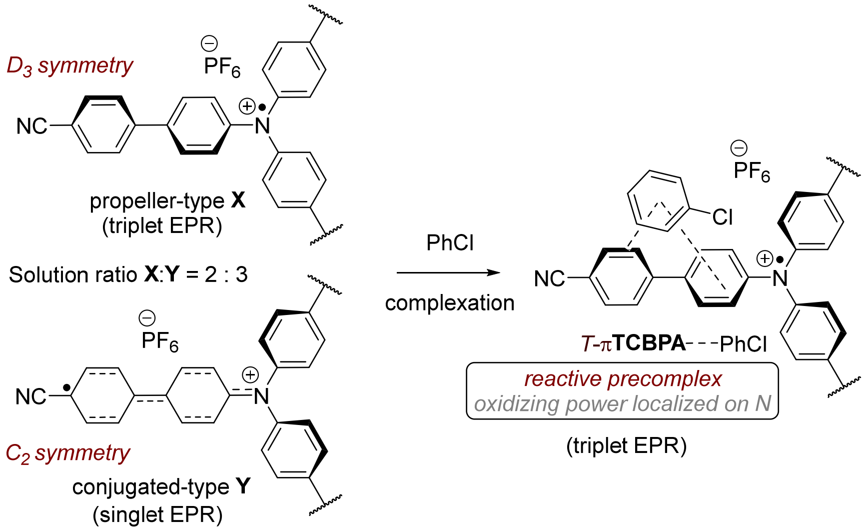


Figure S63. Precomplexation of **TCBPA**$^{\cdot+}$ with chlorobenzene drives the solution equilibrium of rotamers **X** and **Y** formation of the T-π complex.

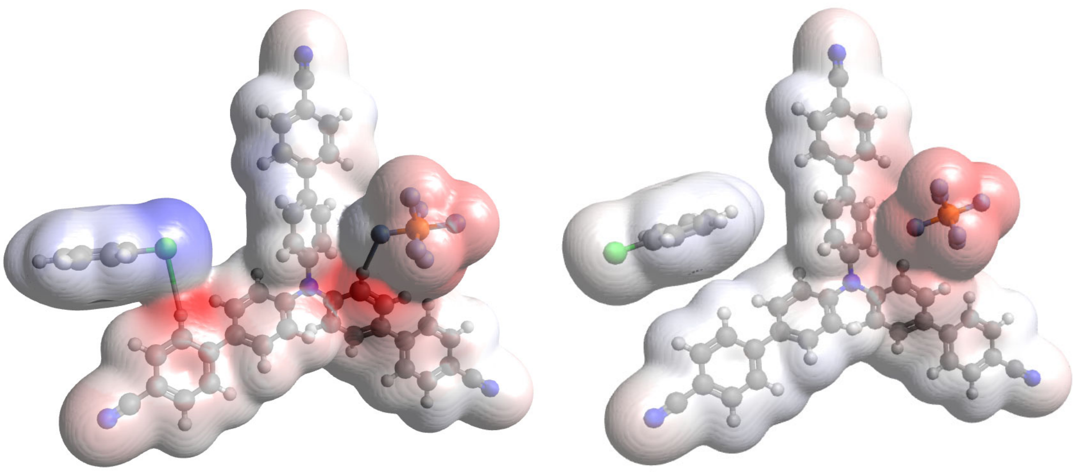


Figure S64. DFT-computed Spin Densities for uncomplexed **TCBPA**$^{\cdot+}$ (top) and T-π precomplexes **TCBPA**$^{\cdot+}$ + PhCl with the Cl atom facing 'in' (bottom, left) or 'out' (bottom, right). See **Section S13** for details.

In order to confirm the presence of two EPR-active species in the spectrum of **TCBPA**$^{\cdot+}$ and to rule out a 'pure triplet signal in which the shoulder resonances are suppressed', we checked the EPR spectra i) with different microwave powers (Figure S65) and ii) at a lower (8x) modulation value (1.0 G) and at the second derivative (harmonic) (Figure S66). In the former case, the microwave power made no difference to the signal shape, all peak intensities increased by the same corresponding fraction. In the latter case, the lower modulation clearly confirmed two radical species, a triplet and overlapping broad singlet. The second derivative spectrum also clearly confirms two overlapping species. Regardless of these parameters, the spectra show the same trend; 1,2-dichlorobenzene favors the triplet representation, while 1,4-dichlorobenzene favors the singlet representation.

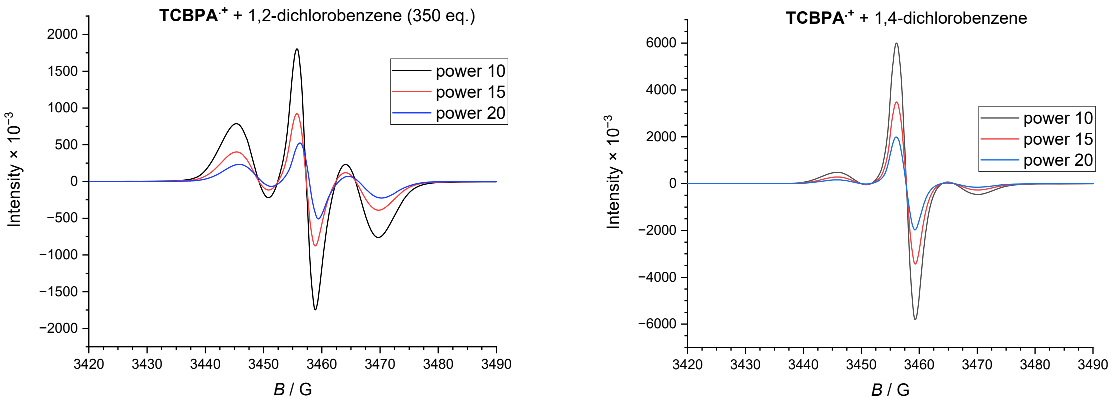


Figure S65. Examination of EPR samples displayed in Figure S44 at different powers.

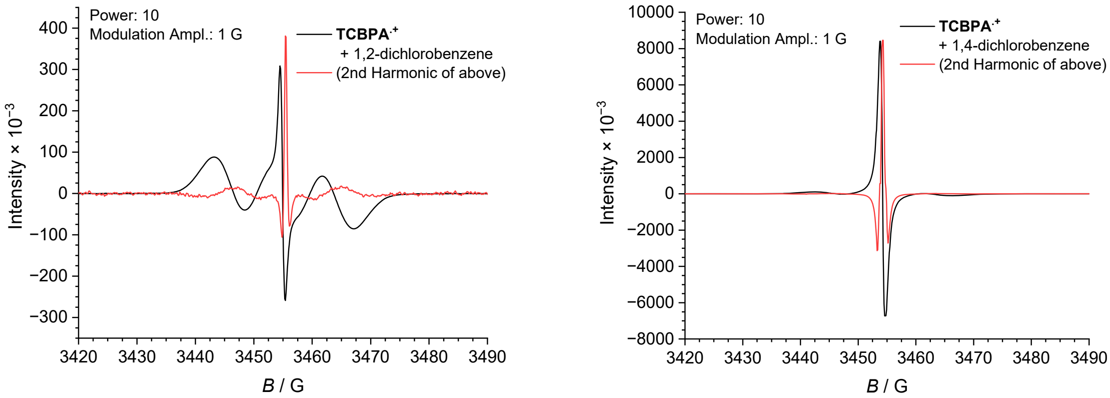


Figure S66. Examination of EPR samples displayed in Figure S44 at a lower modulation amplitude and with the second harmonic.

In the presence of bromobenzene, a small shift in the G values of the signal occurred and the shape of the signal changed with respect to the uncomplexed **TCBPA**$^{\cdot+}$, as seen by a pronounced flattening of the triplet 'shoulders' (a^N = 8.79 G). Together with the poor performance of bromobenzene as a substrate compared to chlorobenzene, this suggests a different geometry of precomplex that is *'unreactive'* to the photoelectrochemical reaction. In the presence of 1,2-dichlorobenzene, the signal shifted in the direction of the triplet observed for chlorobenzene ('propeller'-type complex, a^N = 8.83 G), but to a lesser extent. In the presence of 1,3- or 1,4-dichlorobenzene, the signal shifted in the direction of the 'unreactive' complex (a^N = *ca.* 8.62 G, *ca.* 8.27 G, respectively).

Overall, candidates for the unreactive complex (singlet EPR signal) could include i) formation of the proposed π-π stacked complex, which forces the N radical cation into conjugation with an aromatic system, likely to drastically decrease the oxidizing power of the radical cation in the excited state, ii) a halogen-π complex; since halogen-π interactions are a well-known dispersion interaction in the literature.[27] The former candidate seems more likely, given the shift in the N radical cation's EPR signal shape away from a triplet and towards a singlet.

We note that changes in EPR spectra can arise from changes in temperature and a solvent effect (namely, viscosity) affecting the tumbling of radicals in solution. In this case, anisotropy could result – the separation of the high field line from the central component would differ from that of the low field line in the integrated spectra. Given that all samples were measured at 25 °C, we compared the viscosities of arene substrates (350 eq., ~1 : 4 arene : DCM by volume) to see if they could account for profound changes in EPR spectra (Table S14). Noticeable anisotropy was not present in any of the spectra, despite the different viscosities of arene substrates added. Moreover, viscosity values of these arenes do not correlate with the changes in signal shape towards singlet or triplet representations. Given that the arene is present in ~1 : 4 arene : DCM by volume in the EPR sample, clearly, the viscosity of all samples represents that of DCM and thus 'solvent effects' unrelated to precomplexation cannot account for the profound changes in EPR spectra demonstrated herein.

Table S14. Comparison of known viscosities and difference between low and high-field shoulders from central component to check for solvent-dependent anisotropy.

TPA$^{\cdot+}$	Arene	Viscosity (mPa·s), 25 °C	Signal shape change w.r.t. uncomplexed **TPA$^{\cdot+}$**	Δlow field shoulder	Δhigh field shoulder
- (DCM)	-	0.437[a]	-	-	-
T*p*BPA$^{\cdot+}$	-	-	-	8.04	8.03
T*p*BPA$^{\cdot+}$	Mesitylene	0.661[b]	Triplet (no change)	8.22	8.21
T*p*BPA$^{\cdot+}$	Iodobenzene	1.504[c]	→Singlet (weak)	7.04	7.04
TCBPA$^{\cdot+}$	-	-	-	7.99	7.98
TCBPA$^{\cdot+}$	Chlorobenzene	0.806[b]	→Triplet (strong)	8.28	8.38
TCBPA$^{\cdot+}$	1,2-dichlorobenzene	1.324[b]	→Triplet (strong)	8.45	8.44
TCBPA$^{\cdot+}$	1,3-dichlorobenzene	1.044[b]	→Singlet (strong)	N.D.	N.D.
TCBPA$^{\cdot+}$	1,4-dichlorobenzene	0.839[d]	→Singlet (strong	N.D.	N.D.

Viscosities were obtained from the following references: [a]Rossberg, M.; Lendle, W.; Pfleiderer, G.; Tögel, A.; Torkelson, T. R.; Beutel, K. K. *Chloromethanes* in *Ullmann's Encyclopedia of Industrial Chemistry 7th Edition*, **1999-2014**; [b]Lide, D. R. *CRC Handbook of Chemistry and Physics 89th Edition,* CRC Press, **2009**; [c]Viswanath, D.S.; Natarajan, G. *Data Book on the Viscosity of Liquids*, Hemisphere Publishing, **1989**; [d]Dean, J. A. *Handbook of Organic Chemistry. McGraw-Hill Book Co.* **1987**. [a]Measured at 20 °C; [c]Measured at 32.65 °C. [d]Measured at 55 °C. N.D. not determined, shoulders are too flat to measure a maximum height.

12.5. Comparison of DFT calculated and measured EPR spectra of $TPA^{\cdot+}$s.

A reasonable agreement was found between EPR spectra simulated by DFT at two different theory levels for the case of **TpBPA**$^{\cdot+}$·PF_6 (**Figure S67**). However, for **TCBPA**$^{\cdot+}$·PF_6 the agreement was poor (**Figure S68**), since the calculation assumes only the propeller-type (symmetry C_3) rotamer. Attempts to optimize for the other symmetry C_2 rotamer all converged to give the symmetry C_3 rotamer. For details of the levels of theory and software employed for DFT calculations, see **Section S13**.

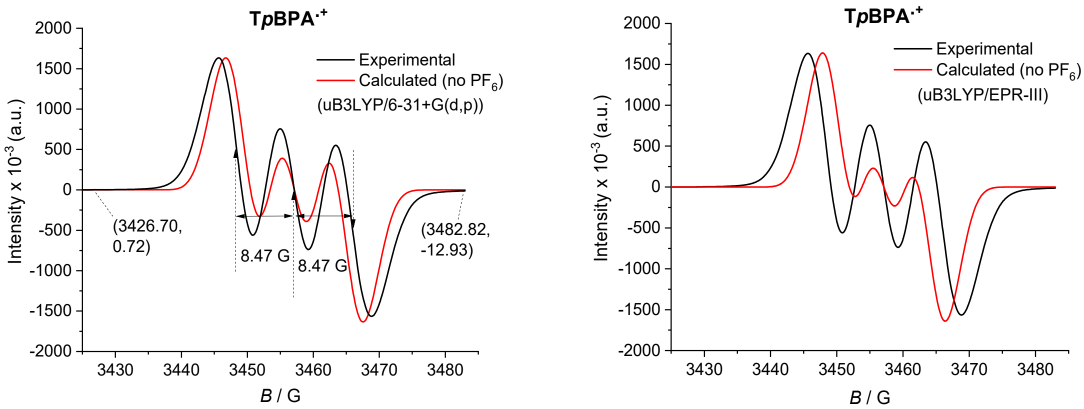


Figure S67. EPR spectra of the isolated **T*p*BPA**$^{\cdot+}$ (PF_6 salt). Calculated EPR spectra (without PF_6 salt) at the uB3LYP/6-31+G(d,p) theory level (left) and at the uB3LYP/EPR-III theory level (right). Solvation was modelled implicitly using a C-PCM solvent model for DCM.

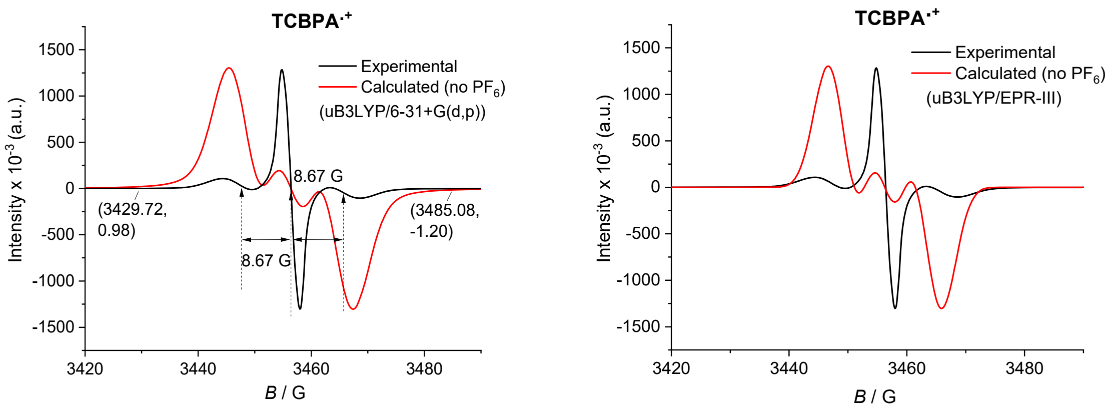


Figure S68. EPR spectra of the isolated **TCBPA**$^{\cdot+}$ (PF_6 salt). Calculated EPR spectra (without PF_6 salt) at the uB3LYP/6-31+G(d,p) theory level (left) and at the uB3LYP/EPR-**III** theory level (right). Solvation was modelled implicitly using a C-PCM solvent model for DCM.

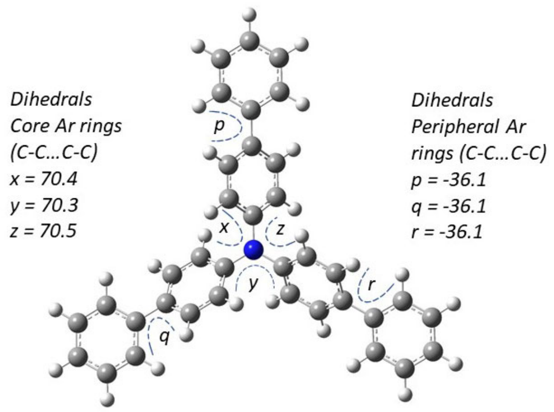
13. Computational Investigations of TPAs, TPA$^{\cdot+}$s and TPA$^{\cdot+}$ Precomplexes

All calculations were performed using Density Functional Theory (DFT)[28] using the Gaussian16 software package.[29] All minima (reactants, intermediates, products) and maxima (transition states) were optimized using the uB3LYP[30] functional with a 6-31+G(d,p) basis set[31] on all atoms. Solvation was modelled implicitly using the Conductor-like Polarisable Continuum Model (CPCM)[32] for a solvent of acetonitrile, in which e-PRC reactions were performed. Frequency calculations were performed on all optimized structures in order to characterize minima (zero imaginary frequencies). GaussView 5.0.9 was used for the visualisation of structures. Spin densities and molecular orbitals were obtained from formcheck (.fchk) files from Gaussian calculations and visualized in Avogadro.[33] Dihedral scans were performed using uB3LYP/6-31+G(d,p) with a step size of 5 degrees and terminated when barrier was detected. Calculation of EPR hyperfine couplings (isotropic fermi constants) was done using uB3LYP either with 6-31+G(d,p) or EPR-III[34,35] as a basis set.

13.1. Computation of Neutral TPAs, XYZ Co-ordinates

Geometries of **T*p*BPA** and **TCBPA** were computed to compare conformations (dihedral angles) with XRD crystallographic data (Section S15).

T*p*BPA in MeCN (uB3LYP)



64

-1442.515977 [uB3LYP/6-31G(d,p)]

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C	-1.12952800	-0.86253300	0.00062500
C	-1.15471600	-2.01672700	0.80158000
C	-2.26191500	-2.86189600	0.79201100
C	-4.57381200	-3.48637900	-0.00081800
C	-5.87922100	-2.96947100	-0.10957500
C	-6.99060200	-3.81539800	-0.11169800
C	-6.82415100	-5.19975900	-0.00105500
C	-5.53394300	-5.72853800	0.10947100
C	-4.42274200	-4.88233500	0.10747300
H	-4.19503500	-1.18889700	-1.44256500

H	-2.24445000	0.29645700	-1.44029000
H	-0.30859800	-2.24601300	1.44105400
H	-2.25871800	-3.73221800	1.44142400
H	-6.02820500	-1.89555100	-0.17106400
H	-7.98755900	-3.39094800	-0.18986900
H	-7.68820300	-5.85765400	-0.00115200
H	-5.39007500	-6.80248800	0.18748300
H	-3.42714700	-5.31168300	0.16889900
C	-0.18078300	1.40818200	0.00150500
C	0.61879100	2.23604600	-0.80439800
C	-1.16348300	2.00700800	0.80772600
C	0.44231500	3.61774500	-0.79580100
H	1.37312300	1.79412900	-1.44713500
C	-1.34260000	3.38835100	0.79856800
H	-1.78168500	1.38868200	1.45032400
C	-0.54371000	4.22916000	0.00108400
H	1.06048500	4.22612200	-1.44921900
H	-2.09501400	3.82062200	1.45141800
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C	0.18634100	7.96080800	-0.11834100
H	1.36977900	6.16880500	-0.18140200
C	-2.19723900	7.65329400	0.11605000
H	-2.88676700	5.61961000	0.18233700
C	-1.09584600	8.50742300	-0.00170500
H	1.05115400	8.61293000	-0.20202300
H	-3.19929900	8.06456500	0.19911800
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C	7.72889600	-1.92330500	0.11333300
C	7.91789500	-3.30453100	-0.00026700
C	6.80330100	-4.14194400	-0.11380800
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H	3.13090100	-3.03420000	-1.44694300
H	6.31247500	-0.30917000	0.17532700
H	8.58608400	-1.26080900	0.19383500
H	8.92018400	-3.72267500	-0.00027400
H	6.93556000	-5.21721200	-0.19424900
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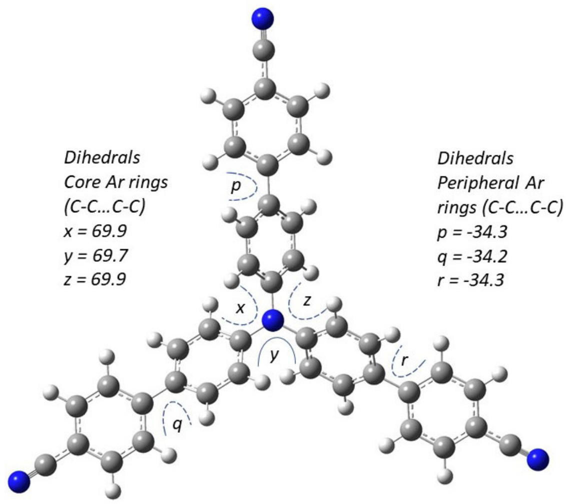
N	0.00028600	-0.00114500	0.00104200

TCBPA in MeCN (uB3LYP)



67

-1719.279809 [uB3LYP/6-31G(d,p)]

Charge = 0; Multiplicity = 1

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C	-0.38155900	2.29174500	-0.79417800
C	-1.13078400	3.46458600	-0.78492300
C	-3.09348800	4.83392400	0.00036900
C	-4.49575200	4.79448100	0.13892700
C	-5.25440100	5.95961300	0.14191900
C	-4.62044500	7.20759200	-0.00014700
C	-3.22189600	7.26700600	-0.14208600
C	-2.47610100	6.09354200	-0.13871300
H	-3.53453300	2.54524900	1.43513800
H	-2.21005700	0.48531000	1.43544500
H	0.49383700	2.21830200	-1.43068100
H	-0.82643900	4.28094500	-1.43252500
H	-5.00347000	3.83952100	0.22275300
H	-6.33325000	5.90799400	0.24234100
H	-2.72758200	8.22732500	-0.24253800
H	-1.39657300	6.15948500	-0.22220500
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C	-0.17838600	-2.31393900	0.80114800
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C	-0.81893300	-3.54951300	0.79091200
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C	-2.42617500	-2.71147500	-0.79372300
H	-2.14931200	-0.68376800	-1.44296800
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H	-0.44552800	-4.33432800	1.44143700
H	-3.28251800	-2.85530000	-1.44522300
C	-2.64627700	-5.09109700	-0.00108200
C	-1.91921800	-6.28996300	0.14396300
C	-4.04579800	-5.17743500	-0.14591400
C	-2.55701000	-7.52548200	0.14713700
H	-0.83849700	-6.25861600	0.23267100
C	-4.69713600	-6.40581000	-0.14883800

H	-4.63633600	-4.27180900	-0.23473500
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C	2.18178100	-0.81082900	-0.79562200
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C	3.49178200	1.06752500	0.78873300
C	5.74168600	0.25671800	0.00020600
C	6.52001500	-0.91044100	-0.13809300
C	7.90931600	-0.85592300	-0.14231600
C	8.56121200	0.38292700	-0.00165000
C	7.80124600	1.55855100	0.13983000
C	6.41260400	1.48874700	0.13776800
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H	1.67891300	-1.53067900	-1.43262700
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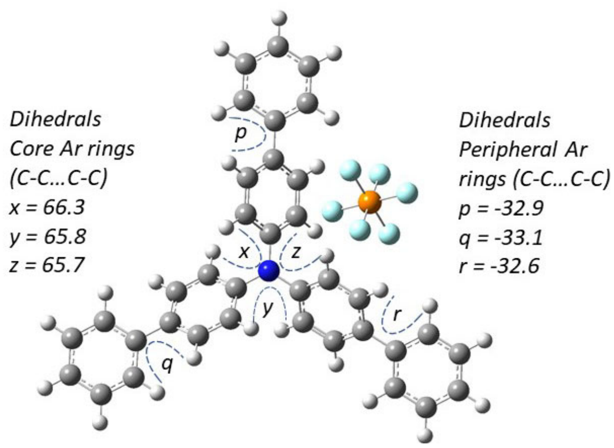
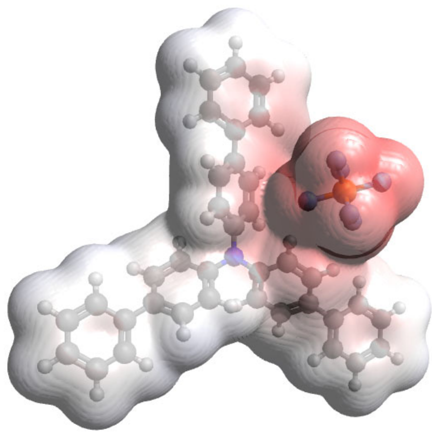
H	8.49059800	-1.76625600	-0.24264200
H	8.29916900	2.51710500	0.23924800
H	5.84234100	2.40780500	0.22108300
N	0.00600900	0.00090900	0.00195200
C	-4.61875800	-8.86044700	-0.00079500
C	9.99181400	0.44711400	-0.00268900
C	-5.39533100	8.41186500	0.00007000
N	11.15605400	0.49984500	-0.00371400
N	-5.15934600	-9.89291700	-0.00077500
N	-6.02599900	9.39192000	0.00028300

13.2. Computation of $TPA^{\cdot +}$s

T*p*BPA$^{\cdot +}$·PF_6 (uB3LYP/6-31+G(d,p))



71



Spin Density, iso = 0.0005

-2383.130662 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

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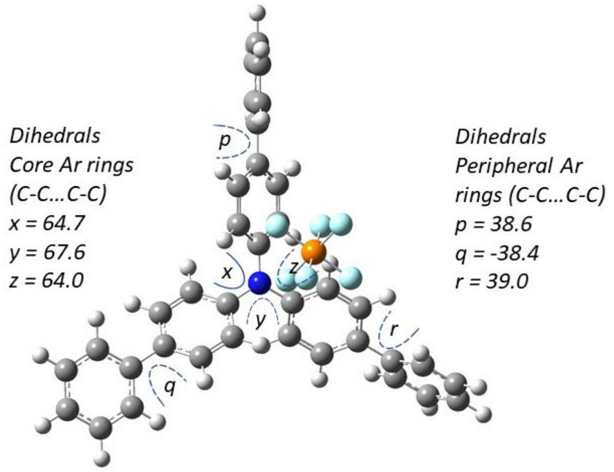
C	0.56002700	-2.27099100	0.06925300
C	0.36861400	-1.14334700	-0.75491100
C	-0.63027500	-1.17172100	-1.74931200
C	-1.41250600	-2.30439800	-1.91091800
C	-2.08337100	-4.64492900	-1.26697800
C	-1.56611000	-5.93254700	-1.02079800
C	-2.36159800	-7.06614200	-1.18910200
C	-3.69236600	-6.93815700	-1.60127300
C	-4.22045000	-5.66609600	-1.84646800
C	-3.42480700	-4.53181700	-1.68392700
H	-0.10345500	-4.23092900	0.57598900
H	1.29877700	-2.24331700	0.86217000
H	-0.75761700	-0.32425900	-2.41320700
H	-2.14468900	-2.32112500	-2.71062200
H	-0.52928600	-6.05126700	-0.72234700
H	-1.94006700	-8.04974500	-1.00490000
H	-4.31162600	-7.82075000	-1.72981200
H	-5.25496800	-5.55578300	-2.15735700
H	-3.85713600	-3.55120500	-1.85560200
C	2.54528400	-0.13094500	-0.29377500
C	3.16708500	0.74055200	0.62323900
C	3.30607400	-1.14088900	-0.91688900
C	4.51623300	0.59669500	0.90761600
H	2.58067400	1.49402600	1.13661600
C	4.65589500	-1.26703100	-0.62754400
H	2.84531200	-1.79060400	-1.65226700
C	5.29612000	-0.40641100	0.29115500
H	4.96407000	1.24856600	1.64954100
H	5.23206800	-2.02172700	-1.15136000
C	6.73649100	-0.55153000	0.59793400
C	7.52800800	0.57467800	0.89948800
C	7.35124300	-1.81957000	0.59598900
C	8.88650300	0.43717400	1.18566100
H	7.08627800	1.56602900	0.88405200
C	8.70866300	-1.95592700	0.88776500
H	6.76031500	-2.70690400	0.39202100
C	9.48263200	-0.82842900	1.18248500
H	9.48081600	1.31924400	1.40438300
H	9.16011300	-2.94347800	0.89189100
H	10.53953500	-0.93493200	1.40744300
C	-0.55317400	3.85912000	-0.94023300
C	0.74153900	3.59057400	-1.43859300
C	1.31420100	2.33403400	-1.32305300
C	0.59690500	1.28947700	-0.70339000
C	-0.69850800	1.53574600	-0.20316800
C	-1.25352000	2.80036400	-0.32072400
C	-1.15486100	5.20499200	-1.06313400
C	-0.35262200	6.36295600	-1.01765600
C	-0.92190700	7.63155000	-1.13013500
C	-2.30392500	7.77139500	-1.29664700
C	-3.11273200	6.63095700	-1.34649300
C	-2.54580000	5.36192100	-1.22794900
H	1.29130200	4.36684400	-1.95922500
H	2.29352900	2.14245000	-1.74662400
H	-1.24438100	0.75413100	0.31308100
H	-2.23231000	2.97357500	0.11209500
H	0.71842200	6.27375000	-0.86591200
H	-0.28700000	8.51105700	-1.08070500
H	-2.74609900	8.75902900	-1.38636200
H	-4.18536200	6.72870500	-1.48424100

H	-3.18495800	4.48704700	-1.29071900
N	1.17041500	0.00594900	-0.58514400
P	-4.22802600	-0.01207000	2.09633300
F	-3.98825700	1.39161700	1.26854000
F	-2.71210700	-0.51156900	1.68337900
F	-3.62482700	0.68895000	3.45742600
F	-4.46396300	-1.41499500	2.92291100
F	-5.74047800	0.48768800	2.50839600
F	-4.82880800	-0.71252100	0.73418500

T*p*BPA$^{\cdot+}$·PF_6 (ωb97xd/6-31+G(d,p))



71

-2382.442852 [ωb97xd/6-31+G(d,p)]

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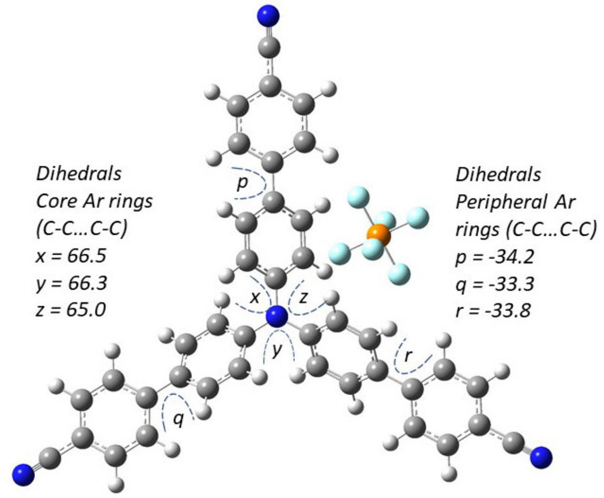
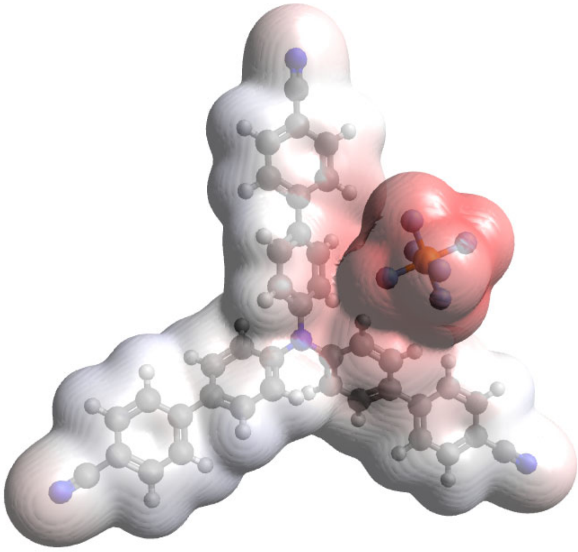
C	-1.49842300	-1.57515500	-0.34668200
C	-1.00308800	-0.45528400	-1.03574300
C	-1.86116400	0.30617000	-1.84864700
C	-3.19178900	-0.05000600	-1.95769100
C	-5.13789400	-1.52299300	-1.37145100
C	-5.84022500	-1.98010300	-0.24765200
C	-7.18771900	-2.31578500	-0.34315900
C	-7.85297600	-2.20494700	-1.56359100
C	-7.16294100	-1.75325800	-2.68797900
C	-5.81677600	-1.41184100	-2.59271500
H	-3.20300300	-2.77783200	0.07592300
H	-0.84804200	-2.13786900	0.31145600
H	-1.47511400	1.15403000	-2.40301800
H	-3.84697100	0.54939800	-2.58048100
H	-5.33811700	-2.05033000	0.71256200
H	-7.71973900	-2.65816600	0.53862500
H	-8.90309400	-2.46860200	-1.63790900
H	-7.67152600	-1.67124300	-3.64319600
H	-5.28519300	-1.07981700	-3.47941400
C	1.33057700	-1.08582600	-0.77451000
C	2.39183700	-0.89783900	0.12339300
C	1.25562700	-2.25669800	-1.54369100
C	3.35953200	-1.87810800	0.24965900
H	2.42355800	-0.01011200	0.74451900
C	2.23623500	-3.22368600	-1.41070800

H	0.45568900	-2.38284700	-2.26474000
C	3.30319400	-3.05651200	-0.51287000
H	4.15314200	-1.74222600	0.97637100
H	2.19114800	-4.10752500	-2.03775100
C	4.34646100	-4.10003900	-0.37388900
C	5.69095500	-3.74614000	-0.19678300
C	4.00646600	-5.45903900	-0.41733300
C	6.67069800	-4.72686900	-0.06900500
H	5.97736100	-2.69882300	-0.18193000
C	4.98640000	-6.43894600	-0.28511900
H	2.96756800	-5.75343100	-0.53200000
C	6.32154300	-6.07616400	-0.11154500
H	7.70855000	-4.43604100	0.05797900
H	4.70521500	-7.48685100	-0.31144400
H	7.08536400	-6.84040200	-0.01003600
C	1.46722400	3.95854500	-0.84510400
C	2.24648000	3.00723100	-1.52432700
C	1.88453900	1.67234700	-1.54653400
C	0.71508100	1.26214700	-0.88730700
C	-0.07866000	2.19747700	-0.20671500
C	0.30337500	3.52692700	-0.18901600
C	1.86715500	5.38569900	-0.81819100
C	2.41104000	5.99667800	-1.95622500
C	2.78423400	7.33768100	-1.93032300
C	2.62434500	8.08740600	-0.76559200
C	2.08656800	7.48831200	0.37289700
C	1.70839200	6.14876800	0.34669900
H	3.15443300	3.31439300	-2.03216300
H	2.48780300	0.95038100	-2.08548300
H	-0.95978000	1.86894900	0.33189400
H	-0.31646900	4.24310400	0.33984500
H	2.52176600	5.42839700	-2.87485900
H	3.19476100	7.79831800	-2.82315500
H	2.91722500	9.13221900	-0.74520600
H	1.96617500	8.06251100	1.28594300
H	1.30932500	5.68782800	1.24524600
N	0.34196500	-0.09379800	-0.90551900
P	-1.29026700	0.29231500	3.12177600
F	-0.71948400	1.82323800	3.22126200
F	-2.22200300	0.72868000	1.84539700
F	-0.06887400	-0.09401400	2.10105900
F	-1.86067100	-1.23629200	3.01862700
F	-0.35993800	-0.13781900	4.39740200
F	-2.50988600	0.68023100	4.14177000

TCBPA$^{\cdot+}\cdot PF_6$ (uB3LYP/6-31+G(d,p))





74

Spin Density: iso = 0.0005

-2659.886522 [uB3LYP/6-31+G(d,p)]

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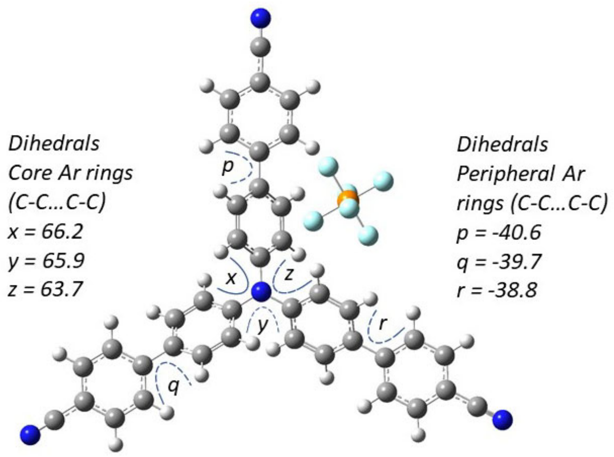
C	-1.30942700	-3.47577400	-0.81076400
C	-0.22343100	-3.42474600	0.08942300
C	0.56937900	-2.29320600	0.19683900
C	0.29084000	-1.16384700	-0.60030500
C	-0.78917300	-1.19817000	-1.50629300
C	-1.57014800	-2.33856400	-1.60504400
C	-2.15190200	-4.68758300	-0.91763200
C	-1.59331100	-5.97024000	-0.75119800
C	-2.37939000	-7.11241000	-0.85165000
C	-3.75494100	-6.99082600	-1.11858400
C	-4.32904900	-5.71774000	-1.28512500
C	-3.53100900	-4.58365500	-1.18680000
H	-0.02239500	-4.26563300	0.74374500
H	1.37204000	-2.26034000	0.92439200
H	-0.98266900	-0.34982300	-2.15243500
H	-2.37037500	-2.35992900	-2.33640000
H	-0.53027400	-6.08036500	-0.56668400
H	-1.93398500	-8.09374800	-0.73147500
H	-5.39116500	-5.62226500	-1.48173000
H	-3.99176600	-3.60784100	-1.29476100
C	2.48241200	-0.12060100	-0.30339900
C	3.15314800	0.75203100	0.57684900
C	3.20928700	-1.10892500	-0.99690800
C	4.52246800	0.63105200	0.75618700
H	2.59278500	1.48689500	1.14328100
C	4.57924500	-1.21334100	-0.81179000
H	2.70581300	-1.75663400	-1.70538800
C	5.26732000	-0.34993100	0.06720400
H	5.01368800	1.28230600	1.47060700
H	5.12778500	-1.95033900	-1.38758700
C	6.72998500	-0.46900400	0.26128600
C	7.51890900	0.67336700	0.50089800
C	7.36432500	-1.72604900	0.21132100
C	8.89316800	0.57017200	0.68339600
H	7.06026500	1.65589100	0.51991300

C	8.73716200	-1.84362700	0.39644400
H	6.77878200	-2.62498000	0.05225200
C	9.51010300	-0.69273900	0.63330100
H	9.48903300	1.45943500	0.85672600
H	9.21022600	-2.81890600	0.36595600
C	-0.71168100	3.81745500	-0.71769300
C	0.54890000	3.57307000	-1.30561100
C	1.14706000	2.32538400	-1.23185800
C	0.48953200	1.27175100	-0.56296100
C	-0.76949100	1.49769700	0.03098300
C	-1.35237800	2.75257200	-0.04839100
C	-1.34448900	5.15222900	-0.80342800
C	-0.56140300	6.32367600	-0.80291200
C	-1.15103900	7.58002100	-0.88333400
C	-2.55051800	7.68901900	-0.97145000
C	-3.34711100	6.52989700	-0.97480700
C	-2.74520300	5.27979800	-0.88914700
H	1.04803700	4.35719400	-1.86394100
H	2.09558500	2.14808400	-1.72545900
H	-1.26436900	0.70932900	0.58655000
H	-2.30145500	2.91031300	0.45134900
H	0.51731700	6.25676300	-0.71321900
H	-0.53614400	8.47312500	-0.87136900
H	-4.42568600	6.61233900	-1.05068200
H	-3.37094700	4.39452100	-0.91525000
N	1.08688600	-0.00401900	-0.48980000
C	10.92629300	-0.80683500	0.82314100
C	-3.16496600	8.98109100	-1.05771300
C	-4.57125400	-8.16465100	-1.22025100
N	-3.66421200	10.03109600	-1.12782500
N	12.07703500	-0.89972000	0.97740200
N	-5.23426300	-9.11872600	-1.30269400
P	-4.46521700	0.00385400	2.01777600
F	-4.13728200	1.57964200	1.66538900
F	-2.85132200	-0.33467100	1.99067800
F	-4.36554300	0.34339400	3.62422400
F	-4.78808200	-1.57072300	2.36898200
F	-6.07447400	0.34352200	2.04493100
F	-4.56099900	-0.33456000	0.41046800

TCBPA$^{\cdot+}\cdot$PF$_6$ (ωb97xd/6-31+G(d,p))



Solvent = MeCN (CPCM)

74

-2659.090856 [ωb97xd/6-31+G(d,p)]

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C	-0.05419400	1.01508200	-0.58778100
C	1.03967600	0.83113300	-1.44974300
C	2.00833300	1.81097400	-1.53734800
C	2.98231500	4.01055800	-0.84863400
C	2.66372700	5.37488700	-0.85583600
C	3.66353700	6.33465500	-0.92441100
C	5.00293800	5.93111000	-0.98150400
C	5.33587800	4.57119900	-0.96885200
C	4.32722900	3.62060800	-0.90431200
H	0.73243500	4.05448100	0.68193700
H	-1.00153400	2.32285700	0.85208800
H	1.10581800	-0.06113400	-2.06164700
H	2.84022100	1.67104000	-2.21809100
H	1.62630600	5.69144900	-0.82960800
H	3.41062200	7.38871500	-0.93966600
H	6.37517700	4.26432600	-1.00150900
H	4.58549700	2.56802300	-0.86045300
C	-2.37826600	0.34947100	-0.31094500
C	-3.18506900	-0.37658900	0.57781400
C	-2.91575900	1.41576700	-1.04717700
C	-4.51690400	-0.03143800	0.72411400
H	-2.75751600	-1.17551700	1.17298600
C	-4.25062200	1.74520400	-0.89242600
H	-2.29816800	1.95076000	-1.75973300
C	-5.07180100	1.03072900	-0.00650300
H	-5.12476200	-0.57265200	1.44090800
H	-4.66758500	2.54618200	-1.49312700
C	-6.50057700	1.39162300	0.15415400
C	-7.47551500	0.39372800	0.28551000
C	-6.89482800	2.73608800	0.17610300
C	-8.81484100	0.72573500	0.43261700
H	-7.19146900	-0.65270300	0.25017900
C	-8.23042400	3.08156800	0.32544900
H	-6.15121200	3.52207200	0.09827500
C	-9.19305900	2.07332800	0.45274900
H	-9.56414800	-0.05224100	0.52473200
H	-8.52616400	4.12425600	0.34979000
C	0.14830700	-4.02478200	-0.52917200
C	-1.04967600	-3.61972000	-1.14102600
C	-1.44588700	-2.29528600	-1.12176300
C	-0.63423500	-1.34167700	-0.48526800
C	0.56684800	-1.72897600	0.13150000
C	0.94464200	-3.05895500	0.10557500
C	0.56468100	-5.44664200	-0.55463000
C	-0.38278100	-6.46817700	-0.40393900
C	0.00150300	-7.80128500	-0.42609400
C	1.35133100	-8.12671100	-0.60379600
C	2.30955900	-7.11769500	-0.75635600
C	1.91255000	-5.78841000	-0.72956800
H	-1.66086500	-4.34319400	-1.66949000
H	-2.35315200	-1.98852300	-1.62959600

H	1.17583500	-0.99944100	0.65392100
H	1.85619900	-3.35029300	0.61548800
H	-1.42735400	-6.22238900	-0.24505800
H	-0.73655200	-8.58532700	-0.30045400
H	3.35303400	-7.37396200	-0.90030400
H	2.65713800	-5.01173500	-0.86825300
N	-1.02156700	0.00798400	-0.46532300
C	-10.57815700	2.42360200	0.60441600
C	1.75567400	-9.50505300	-0.62979400
C	6.04269000	6.92001700	-1.05317600
N	2.08192800	-10.61818700	-0.65104300
N	-11.69666900	2.70642100	0.72649100
N	6.88208100	7.71879400	-1.11255600
P	4.06598300	0.07645100	1.71912500
F	3.88484400	-0.12623400	3.33291500
F	2.49531400	0.52917800	1.60294300
F	4.49756000	1.63469500	1.95967200
F	4.24756600	0.27319800	0.10491900
F	5.63214500	-0.38185400	1.83950500
F	3.62659000	-1.48414100	1.47608200

13.3. Computation of $TPA^{\cdot+}$ precomplexes, XYZ Co-ordinates

All calculations were performed using Density Functional Theory (DFT)[28] using the Gaussian16 software package.[29] All minima (reactants, intermediates, products) and maxima (transition states) were optimized using the uB3LYP[30] functional with a 6-31+G(d,p) basis set on all atoms[31], except bromine and iodine for which the Stuttgart/Dresden Effective Core Potentials MWB28 and MWB46 (respectively) and associated valence basis sets were used.[41] Solvation was modelled implicitly using the Conductor-like Polarisable Continuum Model (CPCM)[32] for a solvent of acetonitrile, in which e-PRC reactions were performed. Frequency calculations were performed on all optimized structures in order to characterize minima (zero imaginary frequencies). All calculations were repeated (optimization and frequency) at the ωb97xd functional[37] with a 6-31+G(d,p) basis set on all atoms[31], except bromine and iodine which used the pseudopotential specified above. Solvation was modelled implicitly using the CPCM as specified above. This was deemed an acceptable working level of theory used by related studies. GaussView 5.0.9 was used for the visualisation of structures. Spin densities and molecular orbitals were obtained from formcheck (.fchk) files from Gaussian calculations and visualized in Avogadro.[33]
In modelling the precomplexes, inspiration was taken from the orientations originally described by Hunter and Sanders.[38] Many different orientations were attempted; sandwich π-stacking, parallel-displaced π-stacking and T-type π-stacking; only the latter two yielded convergence when arenes were placed around the peripheral aromatic rings of the $TPA^{\cdot+}$. Placing the arene ring close to the core aromatic rings of the $TPA^{\cdot+}$ generally led either i) to dissociation or ii) rearrangement to a complex around the peripheral aromatic rings.

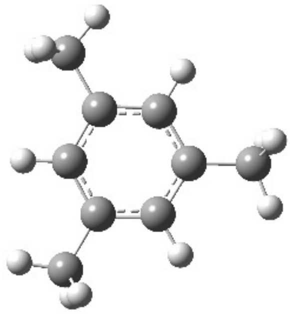
The use of DFT to model dispersion interactions may not be as optimal as MP2 and coupled-cluster methods typically employed for precise determinations of binding energies.[39] However, the computational cost of such methods for complexes of the size studies herein is prohibitively expensive. We note the successful use of DFT to model π-stacking interactions of similar or very large systems at similar levels of theory to ours, which often gave endergonic ΔG values.[40] We note that the ωb97xd functional which was used for comparison includes empirical atom-atom dispersion corrections[37] and generally gives comparable results to more expensive MP2 or coupled-cluster calculations for dispersion-type calculations.[41] In fact, uB3LYP/6-31+(d,p) was found to yield results more comparable to expectations from EPR experiments in this particular case (when ωb97xd was applied to calculate input structures of T-π complexes, they often rearranged to π-π complexes). The intermolecular distances were difficult to characterize compared to the original Hunder-Sanders mode[38] (centroid-to-centroid of the aromatic rings), since arenes were often staggered across both aromatic rings of the $TPA^{\cdot+}$ biphenyl unit. Hence, we give a range of intermolecular distances as defined in the footnote of Table S15 (see diagrams of complexes of interest for the distances).

Table S15. Precomplexation energies and intermolecular distances for the T-π or π-π interaction.

Components	Complex orientation[a]	Complexation free energy ΔG (kcal mol^{-1})		Intermolecular distance (Å)[b]	
		uB3LYP /6-31+G(d,p)	ωb97xd /6-31+G(d,p)	uB3LYP /6-31+G(d,p)	ωb97xd /6-31+G(d,p)
T*p*BPA$^{\cdot+}$/mesitylene	T-π (N/A)	+7.2	+4.9 (→π-π)	3.3 - 5.5	3.6 - 4.2 (π-π)[c]
T*p*BPA$^{\cdot+}$/PhI	T-π “OUT”	+28.4	-	4.7 - 6.5	-
T*p*BPA$^{\cdot+}$/PhI	T-π “IN”	+28.1	-	3.8 - 6.2	-
T*p*BPA$^{\cdot+}$/PhI	π-π “OUT”	+28.3	-	5.2 - 5.5	-
T*p*BPA$^{\cdot+}$/PhI	π-π “IN”	+26.1	-	6.2 - 6.8	-
TCBPA$^{\cdot+}$/PhCl	T-π “OUT”	+4.5	+3.5	4.5 - 6.8	3.2 - 5.3
TCBPA$^{\cdot+}$/PhCl	T-π “IN”	+5.1	+2.9 (→π-π)	4.8 - 7.4	3.7 - 4.3 (π-π)[c]
TCBPA$^{\cdot+}$/1,2-PhClCl	T-π “OUT”	+4.5	-	4.2 - 6.4	-
TCBPA$^{\cdot+}$/1,2-PhClCl	T-π “IN”	+4.7	-	4.6 - 6.9	-
TCBPA$^{\cdot+}$/1,2-PhClCl	π-π “OUT”	+6.6	-	5.3 - 5.7	-
TCBPA$^{\cdot+}$/1,2-PhClCl	π-π “IN”	N.D.	-	N.D.	-
TCBPA$^{\cdot+}$/1,3-PhClCl	T-π “OUT”	+4.9	-	5.3 - 6.7	-
TCBPA$^{\cdot+}$/1,3-PhClCl	T-π “IN”	+5.2	-	4.9 - 7.4	-
TCBPA$^{\cdot+}$/1,3-PhClCl	π-π “OUT”	*Dissociated*	-	*Dissociated*	-
TCBPA$^{\cdot+}$/1,3-PhClCl	π-π “IN”	*Dissociated*	-	*Dissociated*	-
TCBPA$^{\cdot+}$/1,4-PhClCl	T-π (N/A)	*Dissociated*	-	*Dissociated*	-
TCBPA$^{\cdot+}$/1,4-PhClCl	π-π (N/A)	+4.2	-	5.5 - 5.8	-
TCBPA$^{\cdot+}$/PhBr	T-π “OUT”	+30.8	-	3.4 - 6.2	-
TCBPA$^{\cdot+}$/PhBr	T-π “IN”	+31.4	-	3.7 - 6.9	-
TCBPA$^{\cdot+}$/PhBr	π-π “OUT”	+29.7	-	4.9 - 5.4	-
TCBPA$^{\cdot+}$/PhBr	π-π “IN”	N.D.	-	N.D.	-

N.D., not determined - these complexes could not be converged. [a]“IN” and “OUT” refer to the orientation of the halogen atom with respect to the TPA$^{\cdot+}$ N atom. [b]For T-π complexes: the distances between the aromatic centerpoints of each biphenyl to the centerpoint of the arene were averaged and taken as the upper value. The distances between the closest biphenyl C atom and i) the arene C atom closest to the TPA$^{\cdot+}$ N atom and ii) the arene C atom furthest from the TPA$^{\cdot+}$ N atom were averaged and taken as the lower value. For π-π complexes: the distances between the aromatic centerpoints of each biphenyl to the centerpoint of the arene were averaged and taken as the upper value. The distances between the closest biphenyl ring-junction C atom and i) the arene C atom closest to the TPA$^{\cdot+}$ N atom and ii) the arene C atom furthest from the TPA$^{\cdot+}$ N atom were averaged and taken as the lower value. [c]The T-π complex rearranged to the π-π complex using this functional.

Mesitylene (uB3LYP/6-31+G(d,p))



Solvent = MeCN (CPCM)

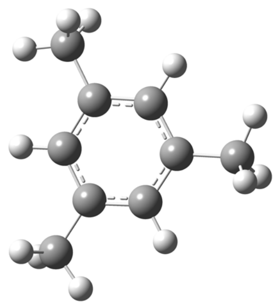
21

-350.089555 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 1

C	0.08293500	1.41031800	0.00003000
C	-1.16521200	0.76103300	-0.00000400
C	-1.26280700	-0.63340900	0.00000500
C	-0.07650500	-1.38978000	0.00001700
C	1.17990100	-0.77698900	0.00002000
C	1.24176000	0.62855500	0.00007000
H	-2.07484100	1.35870500	-0.00000100
H	-0.13932100	-2.47634000	0.00003000
H	2.21422200	1.11731900	0.00008800
C	2.45083700	-1.59709700	-0.00004800
H	3.06527400	-1.37740600	-0.88102100
H	3.06508600	-1.37788000	0.88118900
H	2.23343100	-2.66890200	-0.00033000
C	-2.60867200	-1.32379300	-0.00001100
H	-2.72571300	-1.96600800	-0.88077800
H	-2.72627000	-1.96490400	0.88148800
H	-3.42790000	-0.59928500	-0.00075800
C	0.15778400	2.92105700	-0.00002200
H	-0.33907600	3.34329400	-0.88135900
H	-0.33974700	3.34345700	0.88083600
H	1.19472800	3.26857500	0.00027800

Mesitylene (ωb97xd/6-31+G(d,p))



Solvent = MeCN (CPCM)

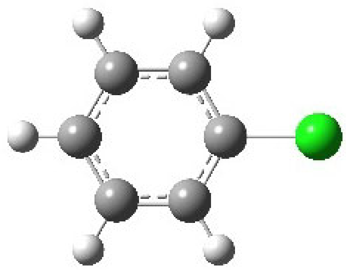
21

-349.966825 [ωb97xd/6-31+G(d,p)]

C	1.10061300	-0.87728500	0.00452400
C	-0.21175800	-1.37159700	0.00696000
C	-1.31005300	-0.51464100	0.00166300

C	-1.08201100	0.86902400	-0.00407700
C	0.20931400	1.39163900	-0.00425600
C	1.29362300	0.50233800	-0.00059800
H	-0.37301600	-2.44791300	0.01255700
H	-1.93345100	1.54692400	-0.00729600
H	2.30643300	0.90078200	-0.00122900
C	0.45092500	2.88126900	0.00231400
H	0.93517400	3.19437700	0.93337400
H	1.10913200	3.17694500	-0.82081700
H	-0.48522000	3.43715800	-0.09386100
C	-2.72091300	-1.05011000	-0.00147500
H	-3.28885300	-0.66602700	0.85202000
H	-3.25318600	-0.74565100	-0.90871700
H	-2.73280100	-2.14197000	0.04668300
C	2.27012800	-1.83090400	-0.00326700
H	2.18943100	-2.55980600	0.80929100
H	2.30870700	-2.39401800	-0.94185000
H	3.21844500	-1.29920000	0.10912200

PhCl (uB3LYP/6-31+G(d,p))



Solvent = MeCN (CPCM)

12

-697.885158 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 1

C	-1.57114100	-1.20427300	0.00000300
C	-0.17891700	-1.21267200	0.00000500
C	0.49717800	-0.00001300	-0.00003100
C	-0.17891400	1.21266400	-0.00000700
C	-1.57111800	1.20428900	0.00001500
C	-2.26922400	0.00000200	-0.00000600
H	-2.10664900	-2.14583200	0.00001200
H	0.36954800	-2.14510000	0.00000600
H	0.36958800	2.14507300	-0.00000700
H	-2.10664400	2.14583700	0.00002600
H	-3.35204500	0.00002300	-0.00000800
Cl	2.26229500	0.00000100	0.00000600

PhCl (ωb97xd/6-31+G(d,p))

Solvent = MeCN (CPCM)

12

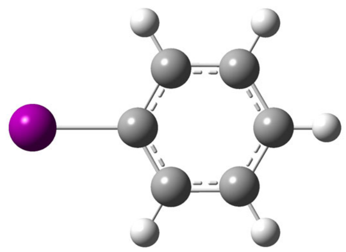
-691.702102 [ωb97xd/6-31+g(d,p)]

Charge = 0; Multiplicity = 1

C	1.57014300	1.20640300	-0.00001300

C	0.17596700	1.21538800	0.00002000
C	-0.50098100	0.00001900	0.00005000
C	0.17596500	-1.21537000	0.00001700
C	1.57013300	-1.20642300	-0.00001200
C	2.26857500	-0.00000800	-0.00000500
H	2.10762500	2.14902100	-0.00003000
H	-0.37333800	2.15018900	0.00000400
H	-0.37338500	-2.15014800	0.00000500
H	2.10757900	-2.14906000	-0.00002300
H	3.35345300	0.00000800	-0.00002600
Cl	-2.25769100	-0.00000300	-0.00001600

PhI (uB3LYP/6-31+G(d,p))



Solvent = MeCN (CPCM)

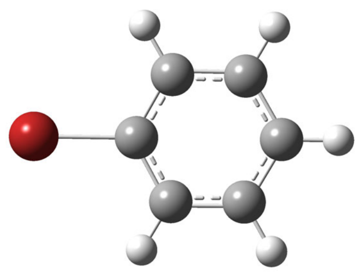
12

-243.016257 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 1

C	3.36745000	0.00000800	-0.00000100
C	2.66603700	1.20947600	0.00000200
C	1.26571600	1.21837500	-0.00000200
C	0.58474600	-0.00002300	0.00000200
C	1.26572900	-1.21838500	0.00000300
C	2.66607600	-1.20945300	-0.00000300
H	4.45317800	0.00004200	0.00000300
H	3.20208300	2.15417300	-0.00000200
H	0.72711500	2.15951300	0.00000100
H	0.72718500	-2.15955600	0.00000900
H	3.20210600	-2.15415900	-0.00000600
I	-1.56992800	0.00000000	0.00000000

PhBr (uB3LYP/6-31+G(d,p))



Solvent = MeCN (CPCM)

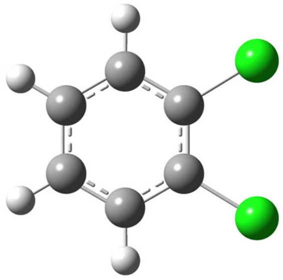
12

-244.977983 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 1

C	2.90150900	0.00000300	-0.00000100
C	2.20086200	1.21026100	0.00000800
C	0.80068200	1.22045800	-0.00000600
C	0.12889000	-0.00001400	0.00000600
C	0.80068600	-1.22046500	0.00000900
C	2.20088600	-1.21024500	-0.00000900
H	3.98709700	0.00002900	0.00000000
H	2.73746000	2.15441900	0.00000100
H	0.25486500	2.15725300	-0.00000600
H	0.25491300	-2.15728600	0.00001600
H	2.73746600	-2.15441400	-0.00001600
Br	-1.83351100	0.00000000	-0.00000100

1,2-dichlorobenzene "1,2PhClCl" (uB3LYP/6-31+G(d,p))



Solvent = MeCN (CPCM)

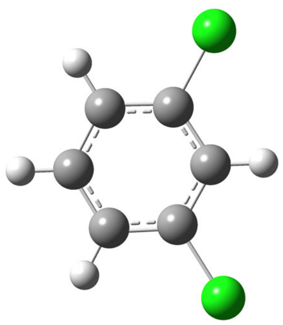
12

-1151.406326 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 1

C	-2.39539200	0.69868200	0.00001300
C	-2.39538700	-0.69866600	-0.00000300
C	-1.18748700	-1.39785400	-0.00000700
C	0.02342000	-0.70074600	-0.00002300
C	0.02340700	0.70074800	-0.00002600
C	-1.18748100	1.39786700	0.00000800
H	-3.33061000	1.24820800	0.00002500
H	-3.33061600	-1.24817800	0.00000100
H	-1.17594800	-2.48178500	-0.00001300
H	-1.17595400	2.48180000	0.00003900
Cl	1.52135700	-1.61356100	0.00001200
Cl	1.52138700	1.61354700	-0.00000100

1,3-dichlorobenzene "1,3PhClCl" (uB3LYP/6-31+G(d,p))



Solvent = MeCN (CPCM)

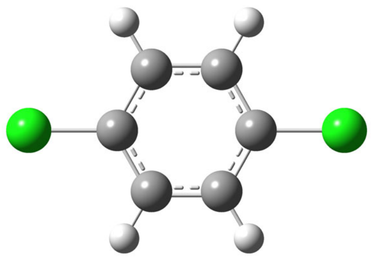
12

-1151.409910 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 1

C	1.21622100	1.39536100	-0.00001400
C	1.19527100	0.00046000	-0.00008000
C	-0.00000200	-0.71993200	-0.00003100
C	-1.19528600	0.00048100	-0.00002700
C	-1.21622000	1.39536100	-0.00002300
C	0.00001400	2.08309300	0.00003700
H	2.15820200	1.93136900	0.00002400
H	-0.00002700	-1.80301400	-0.00001200
H	-2.15817500	1.93141400	0.00000100
H	-0.00000100	3.16836600	0.00008800
Cl	-2.71652100	-0.88697300	0.00001800
Cl	2.71652100	-0.88697300	0.00002400

1,4-dichlorobenzene “1,4PhClCl” (uB3LYP/6-31+G(d,p))



Solvent = MeCN (CPCM)

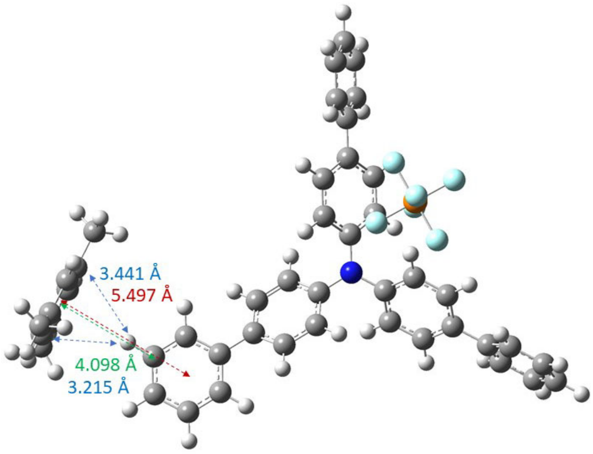
12

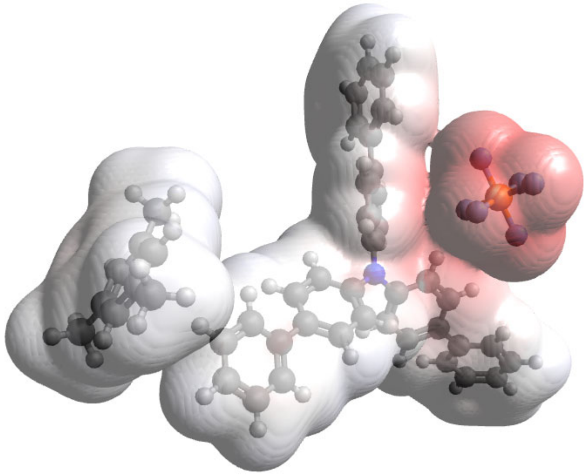
-1151.410145 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 1

C	0.69852900	-1.21643300	0.00000800
C	-0.69853100	-1.21643700	-0.00000700
C	-1.38163600	-0.00000900	0.00001400
C	-0.69852200	1.21642500	0.00000700
C	0.69852400	1.21642900	-0.00000500
C	1.38163600	-0.00001100	0.00001800
H	1.24167400	-2.15475500	-0.00000500
H	-1.24167900	-2.15475500	-0.00000800
H	-1.24169000	2.15473300	0.00000600
H	1.24169700	2.15473300	-0.00002300
Cl	-3.14328000	0.00000800	-0.00000500
Cl	3.14328000	0.00000700	-0.00000500

T*p*BPA$^{\cdot+}\cdot PF_6$ + Mesitylene (uB3LYP/6-31+G(d,p))





Solvent = MeCN (CPCM)

Spin Density, iso = 0.0005

92

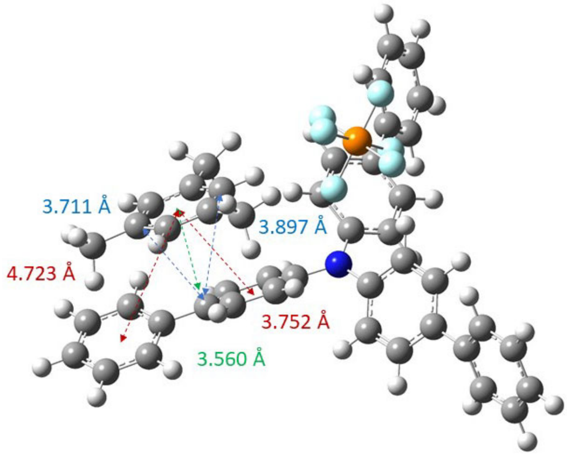
-2733.208722 [uB3LYP/6-31+G(d,p)]

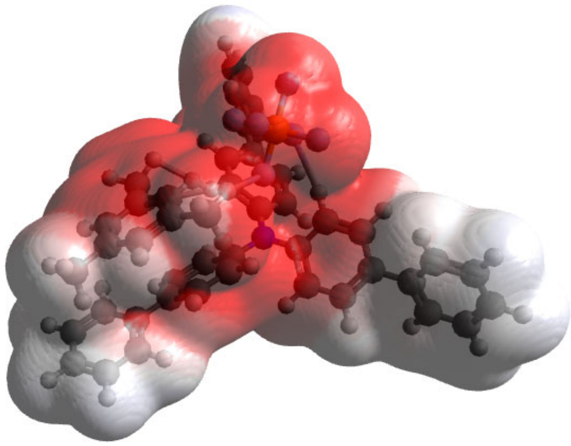
Charge = 0; Multiplicity = 2

C	1.95326100	3.35525000	-1.59330800
C	1.05057600	2.96497100	-0.58008200
C	0.79295400	1.62865800	-0.31674700
C	1.44809000	0.62728000	-1.06188500
C	2.35659200	0.99676500	-2.07447300
C	2.59455700	2.33768800	-2.33309800
C	2.21842300	4.78480400	-1.87050200
C	2.20420800	5.73634700	-0.83112300
C	2.45698000	7.08319800	-1.09236200
C	2.72344700	7.50989600	-2.39770800
C	2.73823900	6.57690400	-3.43998600
C	2.49200800	5.22861200	-3.17971000
H	0.53500000	3.71940900	0.00391300
H	0.10866300	1.35358900	0.47768600
H	2.85096900	0.23344200	-2.66437300
H	3.30019400	2.60005000	-3.11368700
H	2.02266400	5.41884300	0.19072400
H	2.45317000	7.79808300	-0.27504600
H	2.91781100	8.55872300	-2.60064200
H	2.93499700	6.89963200	-4.45795700
H	2.48482800	4.52180400	-4.00335500
C	-0.11204900	-1.16852900	-0.49564100
C	-0.32507300	-2.16296500	0.48093700
C	-1.21744100	-0.60913300	-1.16893200
C	-1.61438700	-2.57830900	0.77460600
H	0.51547100	-2.57017200	1.03126300
C	-2.49990800	-1.04078400	-0.86929500
H	-1.06060400	0.12653100	-1.94958500
C	-2.73437800	-2.03192200	0.10950600
H	-1.75818700	-3.31075600	1.56117500
H	-3.33150900	-0.62957800	-1.43080200
C	-4.10757600	-2.48144000	0.42764000
C	-4.36144000	-3.81272300	0.81419400
C	-5.19509200	-1.58818200	0.35275000
C	-5.65742800	-4.23512800	1.11110800
H	-3.54683300	-4.52875800	0.85709200

C	-6.49007100	-2.01016200	0.65502100
H	-5.02485100	-0.55066600	0.08332600
C	-6.72652300	-3.33603900	1.03410800
H	-5.83305300	-5.26817900	1.39591400
H	-7.31250600	-1.30278300	0.60247900
H	-7.73457100	-3.66527100	1.26756900
C	4.38088600	-3.52850000	-0.92299400
C	3.10830600	-3.85093100	-1.44316000
C	2.05945800	-2.94542500	-1.39901100
C	2.25817200	-1.66877300	-0.83540300
C	3.52172100	-1.32517000	-0.31352800
C	4.55644200	-2.24746500	-0.35616700
C	5.49498100	-4.50210700	-0.97132800
C	5.61817300	-5.40614800	-2.04530000
C	6.67055800	-6.32086300	-2.09205200
C	7.61876700	-6.35719500	-1.06415700
C	7.50754100	-5.46771100	0.00984000
C	6.45969200	-4.54775200	0.05487900
H	2.93432400	-4.82888100	-1.87851400
H	1.09544400	-3.20971700	-1.81847400
H	3.67972400	-0.35442900	0.14307100
H	5.52217500	-1.96343600	0.04738300
H	4.90464700	-5.37591200	-2.86264300
H	6.75374300	-7.00047300	-2.93488900
H	8.43611000	-7.07113100	-1.09983000
H	8.23334700	-5.49402500	0.81707900
H	6.37593300	-3.88021700	0.90658800
N	1.19713100	-0.73649800	-0.79604400
P	4.78169300	2.02332000	2.82820600
F	5.28598300	0.49603900	3.17715200
F	4.43300600	1.55468300	1.28630600
F	3.25424900	1.62492200	3.29347400
F	4.27698700	3.54941300	2.47690600
F	5.13027300	2.49104700	4.36691400
F	6.30872300	2.42029200	2.36093800
C	-10.19736400	-0.22815400	-0.79770400
C	-9.35921000	0.77796300	-1.28703200
C	-8.70295000	1.67282800	-0.42222800
C	-8.90367500	1.53863700	0.95475700
C	-9.74091000	0.53798000	1.48117600
C	-10.37802000	-0.33415100	0.59355100
H	-9.21103900	0.87231600	-2.36114800
H	-8.40226800	2.22402700	1.63550600
H	-11.02930900	-1.11243900	0.98682900
C	-9.94389800	0.42000700	2.97536900
H	-10.37451900	1.33855800	3.39097600
H	-10.61486800	-0.40762800	3.22202500
H	-8.99296200	0.24942900	3.49349800
C	-10.89919500	-1.18634500	-1.73425900
H	-10.58622300	-2.22116500	-1.55159900
H	-11.98609800	-1.15171100	-1.59651200
H	-10.68413100	-0.95032500	-2.78023400
C	-7.80962200	2.75817200	-0.98074400
H	-8.37778600	3.45474500	-1.60864600
H	-7.33747100	3.33610600	-0.18130200
H	-7.01566300	2.33675700	-1.60797000

T*p*BPA$^{\cdot+}$·PF_6 + Mesitylene, π-π-type, (ωb97xd/6-31+G(d,p))





Solvent = MeCN (CPCM)

Spin Density, iso = 0.0005

92

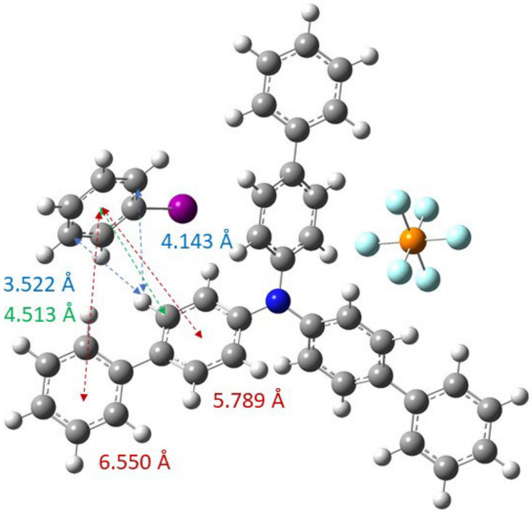
-2732.401836 [ωb97xd/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	2.06112400	3.51711900	-1.49559300
C	0.88573600	3.25101400	-0.77657100
C	0.38738300	1.96688100	-0.67882300
C	1.05990600	0.91059400	-1.30837700
C	2.23544300	1.15581600	-2.03460600
C	2.72167500	2.44746800	-2.12324900
C	2.59927000	4.89530700	-1.58160600
C	2.55911000	5.74477000	-0.46742900
C	3.06735100	7.03850900	-0.54469200
C	3.61923100	7.50482000	-1.73732900
C	3.66259900	6.66803000	-2.85191200
C	3.15937100	5.37230400	-2.77446900
H	0.35811500	4.05888200	-0.28102700
H	-0.49327000	1.76185500	-0.08362100
H	2.74483700	0.34222800	-2.53867700
H	3.63510100	2.62864900	-2.67953300
H	2.15054700	5.38481800	0.47213800
H	3.03770200	7.68038300	0.32992200
H	4.01363100	8.51410200	-1.79768300
H	4.08383800	7.02578000	-3.78598600
H	3.18093000	4.73644400	-3.65448400
C	-0.84021800	-0.59751000	-1.26606000
C	-1.44309700	-1.58479500	-0.47107700
C	-1.62595500	0.17931500	-2.13423100
C	-2.80702700	-1.79148700	-0.55423900
H	-0.84539900	-2.14720300	0.23742300
C	-2.98627300	-0.04674200	-2.20962200
H	-1.15863400	0.91680600	-2.77691900
C	-3.60663600	-1.03619500	-1.42743800
H	-3.26444800	-2.52131600	0.10379300
H	-3.57039700	0.52808700	-2.91958900
C	-5.06179500	-1.28512900	-1.54530700
C	-5.58291500	-2.57609500	-1.38534300
C	-5.94614000	-0.23699300	-1.83537700
C	-6.94919000	-2.81255800	-1.51585900

H	-4.91733400	-3.40931000	-1.18218800
C	-7.31029200	-0.47288400	-1.96616200
H	-5.57082900	0.77706800	-1.92812400
C	-7.81752900	-1.76235600	-1.80865000
H	-7.33327000	-3.82044900	-1.39560500
H	-7.97995100	0.35424500	-2.17887300
H	-8.88235100	-1.94634800	-1.90910600
C	3.15583000	-3.66576200	-0.79224100
C	2.00159200	-3.76555400	-1.58634500
C	1.13745300	-2.69472700	-1.72847500
C	1.41848700	-1.48594700	-1.07159000
C	2.57267200	-1.36355100	-0.28247800
C	3.42199600	-2.44679800	-0.14792100
C	4.07307400	-4.81989300	-0.63762800
C	4.36114400	-5.65521500	-1.72554800
C	5.22605000	-6.73628600	-1.57895700
C	5.81216400	-7.00250100	-0.34208400
C	5.52967100	-6.17938500	0.74737400
C	4.66896800	-5.09507800	0.60081400
H	1.77156500	-4.69700600	-2.09244800
H	0.26086300	-2.78092400	-2.36050500
H	2.77450100	-0.43701800	0.24142800
H	4.31193300	-2.34142100	0.46338600
H	3.92668500	-5.44603700	-2.69848400
H	5.44668200	-7.36744900	-2.43383400
H	6.48495400	-7.84639500	-0.22788500
H	5.97525000	-6.38430200	1.71553300
H	4.44089200	-4.47293600	1.46106200
N	0.54640700	-0.39228600	-1.20940500
P	1.77494600	1.05805100	2.83984100
F	2.73964500	-0.23612200	3.11593800
F	2.70721400	1.46981400	1.55769200
F	0.83262800	0.14197200	1.86207700
F	0.81003300	2.34803200	2.56218100
F	0.84969000	0.64088900	4.12305300
F	2.71880200	1.97061900	3.81672800
C	-5.26035400	0.06893000	1.70573900
C	-4.79648800	1.23831800	1.09915700
C	-3.45049900	1.60718000	1.16180600
C	-2.56004500	0.78308800	1.85569300
C	-2.99348900	-0.39550900	2.46830500
C	-4.34527500	-0.73616700	2.38702500
H	-5.49907700	1.87492200	0.56502000
H	-1.50960200	1.05667900	1.92261800
H	-4.69290000	-1.65167100	2.86330900
C	-2.02345800	-1.30554600	3.17880400
H	-1.04030700	-0.84205900	3.27467700
H	-2.38553000	-1.56758300	4.17812400
H	-1.90150100	-2.24411900	2.62504600
C	-6.70925600	-0.33644300	1.61185400
H	-7.08878900	-0.67692300	2.58016200
H	-7.33397000	0.49182900	1.26779200
H	-6.83143000	-1.15977000	0.89943100
C	-2.97027500	2.85961300	0.47099300
H	-3.74417000	3.63216800	0.46336500
H	-2.08342200	3.27188000	0.96147000
H	-2.70914400	2.64998300	-0.57356200

T*p*BPA$^{\cdot+}$·PF_6 + Iodobenzene, T-π-type, I atom pointing 'in' (uB3LYP)



83

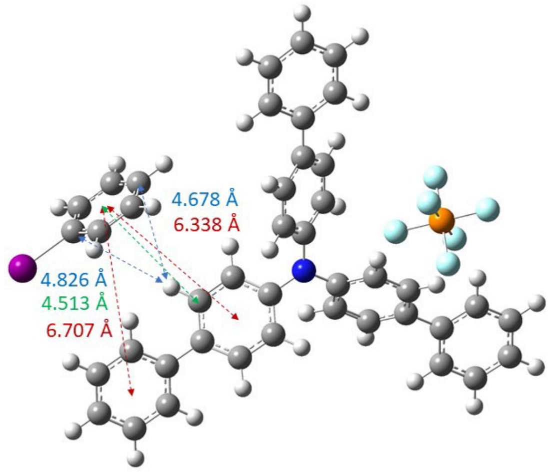
-2626.102094 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	-0.37901500	3.25985400	-0.15613500
C	0.15933900	2.51869100	-1.23171900
C	0.15240500	1.13249000	-1.22966500
C	-0.40743000	0.43379000	-0.13997200
C	-0.95135600	1.15614000	0.94226300
C	-0.93051500	2.54205100	0.92846400
C	-0.36563200	4.73918200	-0.16481400
C	0.68704000	5.44880800	-0.77728800
C	0.70022500	6.84412300	-0.78208100
C	-1.39347200	6.86947400	0.42909800
C	-1.40569000	5.47419000	0.43922400
H	0.55285800	3.03598800	-2.09996700
H	0.53654200	0.58624800	-2.08376900
H	-1.34719200	0.62739000	1.80198500
H	-1.31419700	3.07714300	1.79025700
H	1.51288300	4.90819700	-1.22905400
H	1.52638800	7.37156200	-1.24974500
H	-2.21034100	7.41671300	0.89025200
H	-2.24181100	4.95347100	0.89539800
C	0.67784400	-1.69958500	-0.64019600
C	0.47010800	-2.87271400	-1.39410900
C	1.99292600	-1.25267600	-0.39841100
C	1.55657500	-3.57401800	-1.89438800
H	-0.53876400	-3.20087100	-1.61794800
C	3.06933100	-1.96882900	-0.89977300
H	2.16318300	-0.37443200	0.21416500
C	2.88162100	-3.14407900	-1.66069900
H	1.37334100	-4.44812500	-2.50976900
H	4.07302400	-1.63137600	-0.66490200
C	4.03539800	-3.90043300	-2.19628300
C	3.98566200	-5.30372600	-2.31815200
C	5.21103700	-3.23519900	-2.59854500
C	5.07463000	-6.01617500	-2.82210700
H	3.10214200	-5.84401300	-1.99254000
C	6.29702500	-3.94865400	-3.10744500

H	5.26771700	-2.15284800	-2.53823500
H	5.01981400	-7.09820900	-2.89730400
H	7.18934700	-3.41574000	-3.42245400
C	-3.78561800	-3.04842900	1.40334800
C	-2.47212700	-3.51412800	1.63819400
C	-1.36757200	-2.84447800	1.13544600
C	-1.54442900	-1.66716300	0.37876300
C	-2.84687900	-1.18345000	0.13628100
C	-3.94114600	-1.86996400	0.63994400
C	-4.95945300	-3.77188400	1.93960200
C	-4.94515600	-5.17509900	2.07356100
C	-6.05402700	-5.85622400	2.57717500
C	-7.22694800	-3.75688200	2.83791100
C	-6.12107300	-3.07476900	2.32921100
H	-2.31233200	-4.39099900	2.25617800
H	-0.36794000	-3.19968100	1.35948800
H	-2.99944900	-0.30315300	-0.47824100
H	-4.93270500	-1.50234700	0.40068900
H	-4.07378100	-5.74000400	1.75716500
H	-6.02642000	-6.93862300	2.66155800
H	-8.10783100	-3.19953500	3.14263600
H	-6.15083500	-1.99189900	2.25944500
N	-0.42444200	-0.97717700	-0.13265800
P	-5.40478200	1.82824400	-1.95021600
F	-5.49963600	0.84929700	-3.26948700
F	-3.79982900	1.47860600	-1.80758200
F	-5.03943900	3.10417600	-2.92231500
F	-5.30818000	2.80555000	-0.62995100
F	-7.00662000	2.17591000	-2.09217200
F	-5.76762100	0.54970900	-0.97714100
C	7.03663100	0.19246000	-0.12422600
C	6.32639300	0.21855400	1.08237500
C	5.40252400	1.24243700	1.29850500
C	5.17354400	2.23369100	0.34271900
C	5.89164400	2.19294800	-0.85881200
C	6.82180800	1.17605700	-1.09441500
H	7.75781500	-0.60081700	-0.29815000
H	6.49790100	-0.54595300	1.83212400
H	4.45440200	3.02555500	0.52069200
H	5.71853200	2.96131300	-1.60669400
H	7.37617300	1.15060700	-2.02764700
C	-0.34022000	7.56066400	-0.18014600
H	-0.33048700	8.64657200	-0.18601800
C	6.23438400	-5.34200900	-3.22040500
H	7.08066600	-5.89674700	-3.61463300
C	-7.19911800	-5.15039600	2.96303800
H	-8.06102500	-5.68086300	3.35683700
I	4.31018600	1.29726400	3.15275200

T*p*BPA$^{\cdot+}\cdot$PF$_6$ + Iodobenzene, T-π-type, I atom pointing ‘out’ (uB3LYP)



83

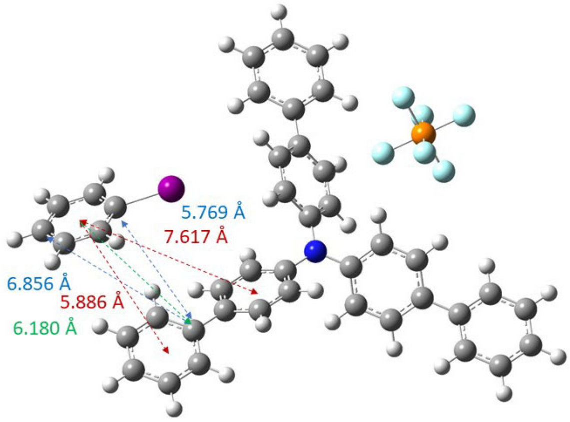
-2626.101654 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	1.14799200	3.23786300	-1.01442400
C	0.35415900	2.59346300	-0.03932300
C	0.37775800	1.21634100	0.11740000
C	1.21400200	0.42968600	-0.70161700
C	2.01587700	1.05479700	-1.67888700
C	1.97530700	2.43230300	-1.82832800
C	1.11380700	4.70782600	-1.17850000
C	-0.07199700	5.43354300	-0.94575600
C	-0.10388800	6.81963900	-1.10320200
C	2.23400600	6.80444200	-1.72372000
C	2.26634900	5.41776900	-1.57161100
H	-0.26044900	3.18311900	0.63211300
H	-0.21222100	0.74803000	0.89720100
H	2.63111000	0.45445800	-2.33954900
H	2.56690700	2.88813400	-2.61467900
H	-0.98078600	4.90973100	-0.66639400
H	-1.03066600	7.35850600	-0.92949200
H	3.13625400	7.33345200	-2.01614100
H	3.19968600	4.88759500	-1.73321800
C	0.05653000	-1.67912000	-0.26686400
C	0.06469900	-2.75115500	0.64842000
C	-1.14784300	-1.31859500	-0.90448600
C	-1.10888900	-3.43930700	0.91699900
H	0.97850300	-3.00852500	1.17226600
C	-2.31133800	-2.02183900	-0.63153100
H	-1.15438900	-0.52062700	-1.63855500
C	-2.32477400	-3.09668900	0.28494000
H	-1.09012000	-4.23108300	1.65797700
H	-3.21678200	-1.75781200	-1.16694200
C	-3.57199800	-3.83978400	0.57236300
C	-3.53979600	-5.21628900	0.87369100
C	-4.82205500	-3.18901100	0.55078000
C	-4.71662900	-5.91692200	1.14122200
H	-2.59369000	-5.74858600	0.87279400
C	-5.99746400	-3.88992400	0.82352100
H	-4.87485200	-2.12429500	0.34630400
H	-4.67056900	-6.97965800	1.36019700

H	-6.94854900	-3.36575300	0.81224400
C	4.91342500	-3.06282500	-0.91266900
C	3.71026400	-3.60500200	-1.41857200
C	2.50630900	-2.92908700	-1.29791600
C	2.46860700	-1.66868000	-0.66521200
C	3.65883500	-1.10877000	-0.15582500
C	4.85354800	-1.80131400	-0.27944500
C	6.19343800	-3.79307400	-1.04260300
C	6.22903700	-5.20189000	-1.00850800
C	7.43727500	-5.88933500	-1.12939400
C	8.61529800	-3.78631300	-1.33089400
C	7.40863800	-3.09718600	-1.20419100
H	3.72516100	-4.55083100	-1.94911000
H	1.60293200	-3.34722000	-1.72752900
H	3.63761300	-0.16121200	0.37086000
H	5.74593500	-1.36852800	0.15878900
H	5.31165500	-5.76287000	-0.85945400
H	7.44383800	-6.97459800	-1.08908800
H	9.53883200	-3.23109900	-1.46605300
H	7.40787400	-2.01303900	-1.25806200
N	1.24768200	-0.97209500	-0.54398800
P	5.51148500	2.26854600	2.07338500
F	5.55556400	1.33372500	3.42693200
F	3.98547300	1.73224000	1.75376000
F	4.88966700	3.51245400	2.95252700
F	5.46598700	3.20155400	0.71900900
F	7.03491100	2.80217500	2.39149300
F	6.13109400	1.02128000	1.19371500
C	-4.99665800	2.52947100	0.59302200
C	-6.15327900	1.79374300	0.87915000
C	-6.87303900	1.23209100	-0.17678000
C	-6.46642500	1.38829300	-1.50299000
C	-5.30775000	2.12715400	-1.77219100
C	-4.57254400	2.69739200	-0.72858900
H	-4.43205300	2.96919700	1.41006400
H	-6.47817500	1.66751700	1.90603300
H	-7.03327100	0.94874900	-2.31629500
H	-4.98589800	2.25286400	-2.80192700
H	-3.67539600	3.26971500	-0.94393600
C	1.04893200	7.51144300	-1.49139600
H	1.02407000	8.59046100	-1.61154800
C	-5.95037100	-5.25696000	1.11864900
H	-6.86558600	-5.80246400	1.32885600
C	8.63544300	-5.18504500	-1.29280700
H	9.57519100	-5.72070500	-1.38923700
I	-8.65602300	0.10290800	0.24962600

T*p*BPA$^{\cdot+}$·PF_6 + Iodobenzene, π-π type, I atom pointing 'in' (uB3LYP)



83

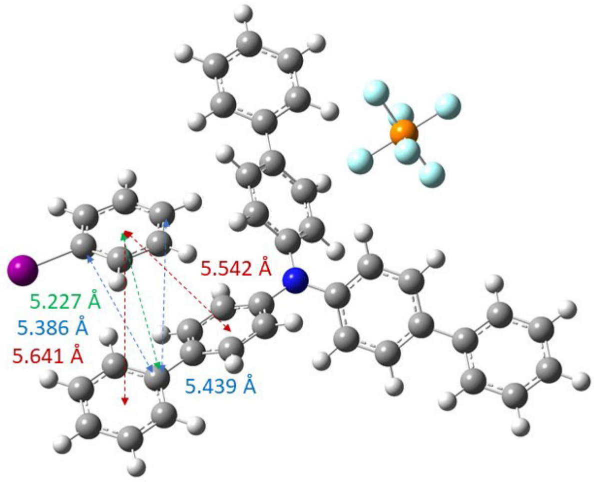
-2626.105314 [uB3LYP/6-31G(d,p)]

Charge = 0; Multiplicity = 2

C	1.45627500	3.17626900	-2.04074900
C	0.38780000	2.67285700	-1.26541600
C	0.26904300	1.31940400	-0.99042300
C	1.23202700	0.41444700	-1.48329300
C	2.30621300	0.89808400	-2.25883800
C	2.40745100	2.25356900	-2.53037600
C	1.57557100	4.62214000	-2.33037800
C	0.42761700	5.42365800	-2.49313000
C	0.54133500	6.78692000	-2.76827000
C	2.95231900	6.59719900	-2.71903200
C	2.84047400	5.23270800	-2.44937000
H	-0.33772700	3.35641900	-0.83804000
H	-0.53786500	0.96190500	-0.36083400
H	3.02836700	0.20524000	-2.67575700
H	3.21715500	2.59849700	-3.16409000
H	-0.55874200	4.97459100	-2.43128400
H	-0.35573000	7.38443700	-2.90128300
H	3.93634500	7.05031100	-2.79512700
H	3.74107600	4.64449900	-2.30336500
C	-0.14745700	-1.58235100	-1.18532800
C	-0.45052600	-2.55391900	-0.20988300
C	-1.12027300	-1.23289800	-2.14377300
C	-1.70006500	-3.15510300	-0.19834400
H	0.27791600	-2.79882600	0.55500800
C	-2.36259800	-1.84865200	-2.12364300
H	-0.88213500	-0.51494000	-2.92059000
C	-2.68652600	-2.82237500	-1.15298800
H	-1.92791300	-3.86651600	0.58792900
H	-3.08040800	-1.59788900	-2.89706400
C	-4.01555700	-3.47343800	-1.13752700
C	-4.15875100	-4.81310600	-0.72356300
C	-5.16953700	-2.77023500	-1.53783900
C	-5.41149600	-5.42784500	-0.71311800
H	-3.28366700	-5.38634400	-0.43356300
C	-6.42210900	-3.38518000	-1.52302600
H	-5.09247600	-1.72976300	-1.83757100
H	-5.49814600	-6.46442500	-0.40093300

H	-7.29994700	-2.82211200	-1.82582400
C	4.59956300	-3.24723000	-0.40061000
C	3.53434200	-3.78222800	-1.15985200
C	2.39144100	-3.04322700	-1.42221700
C	2.28005400	-1.72465900	-0.93323300
C	3.33291400	-1.17135700	-0.17507900
C	4.46605400	-1.92698900	0.08415700
C	5.81461700	-4.04419300	-0.12269800
C	5.74143700	-5.44271700	0.03855000
C	6.88811200	-6.19252900	0.30322100
C	8.22202500	-4.17549400	0.24619300
C	7.07547700	-3.42350500	-0.01249600
H	3.61958600	-4.77685500	-1.58377500
H	1.60368000	-3.46125300	-2.03885200
H	3.24253400	-0.17516300	0.24346300
H	5.24106300	-1.49336700	0.70615500
H	4.78012500	-5.94408400	-0.01590200
H	6.80799700	-7.26748800	0.43556200
H	9.18529400	-3.67882000	0.31602000
H	7.16483200	-2.35129500	-0.15625100
N	1.12237200	-0.96356700	-1.20126600
P	4.74997700	2.20816400	2.34221300
F	4.25271400	1.25643100	3.58911500
F	3.37681200	1.83279400	1.51006400
F	3.98584900	3.49736500	3.02085900
F	5.24592100	3.15797500	1.09380600
F	6.12091500	2.58091900	3.17217900
F	5.51212500	0.91587000	1.66204200
C	-8.56581300	1.49089200	-0.51045600
C	-7.32057800	1.66755000	0.10532000
C	-6.99514600	0.87424500	1.20678800
C	-7.87930500	-0.08486200	1.70351900
C	-9.12063100	-0.24872900	1.07643700
C	-9.46580700	0.53580000	-0.02816200
H	-8.82546100	2.10493000	-1.36794500
H	-6.62663500	2.41016600	-0.27273900
H	-7.61710900	-0.69592700	2.56015800
H	-9.81340800	-0.99321900	1.45794200
H	-10.42998300	0.40394100	-0.50971500
C	1.80377700	7.38008800	-2.88094600
H	1.89160700	8.44161300	-3.09257900
C	-6.54877500	-4.71668700	-1.11177500
H	-7.52365800	-5.19507500	-1.10204000
C	8.13355600	-5.56283700	0.40666300
H	9.02590100	-6.14725000	0.61047500
I	-5.08413200	1.13799000	2.16387500

T*p*BPA$^{\cdot+}\cdot PF_6$ + Iodobenzene, π-π type, I atom pointing 'out' (uB3LYP)



83

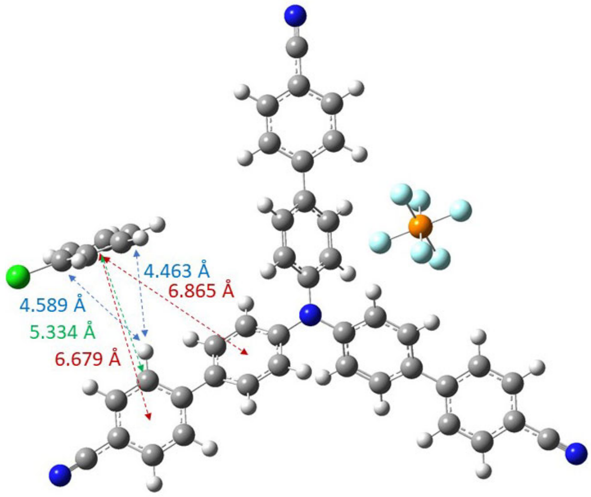
-2626.101810 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	1.94160400	3.25352100	-1.97141700
C	0.79718500	2.82247800	-1.26391700
C	0.55397000	1.47745000	-1.03269300
C	1.46404800	0.50781600	-1.50206900
C	2.61320100	0.91843700	-2.20880600
C	2.83874100	2.26685100	-2.43777400
C	2.19250100	4.69094700	-2.21616100
C	1.12317700	5.58859800	-2.41017300
C	1.36121400	6.94353900	-2.64387800
C	3.74339400	6.55316000	-2.48920000
C	3.50732900	5.19703300	-2.26078900
H	0.10872300	3.55367000	-0.85457900
H	-0.31130700	1.17357500	-0.45447800
H	3.29700100	0.17763200	-2.60760700
H	3.70571500	2.55795600	-3.02071700
H	0.10143700	5.22190000	-2.40542200
H	0.52350400	7.61632800	-2.80212900
H	4.76372300	6.92459300	-2.50830900
H	4.34877400	4.53299800	-2.08953400
C	-0.08644800	-1.37546800	-1.34007400
C	-0.52300200	-2.34658500	-0.41606500
C	-0.97138200	-0.91817300	-2.33771400
C	-1.81685200	-2.83962700	-0.49135100
H	0.13842600	-2.67450300	0.37801700
C	-2.26003800	-1.42582200	-2.40388400
H	-0.63079700	-0.20117400	-3.07627900
C	-2.71798900	-2.39519200	-1.48416700
H	-2.14682300	-3.55192300	0.25708000
H	-2.91013300	-1.09295800	-3.20572400
C	-4.09736700	-2.92645200	-1.55727900
C	-4.37774400	-4.26066600	-1.19991800
C	-5.16382400	-2.11022700	-1.98509700
C	-5.67854300	-4.76099300	-1.27095100
H	-3.57156200	-4.91858400	-0.89061000
C	-6.46484200	-2.61053300	-2.05043400
H	-4.98101800	-1.07131600	-2.24145700

H	-5.87133700	-5.79532000	-1.00178700
H	-7.27395800	-1.96128500	-2.37161600
C	4.46062700	-3.43766000	-0.33461500
C	3.40295700	-3.86709700	-1.16802000
C	2.33924200	-3.03274100	-1.47386300
C	2.30354900	-1.72150900	-0.95477600
C	3.35052900	-1.27249400	-0.12316000
C	4.40331000	-2.12260700	0.17853900
C	5.59049800	-4.33600400	-0.01034700
C	5.39902900	-5.72809500	0.10243000
C	6.46528700	-6.57352800	0.41128300
C	7.95302400	-4.66831300	0.49707700
C	6.88675700	-3.82092500	0.19384000
H	3.43418900	-4.85494400	-1.61458900
H	1.55859600	-3.37163600	-2.14569400
H	3.31392700	-0.28264900	0.31782200
H	5.17227400	-1.76751800	0.85548300
H	4.40699700	-6.15008500	-0.02461600
H	6.29362600	-7.64181300	0.50480300
H	8.94578400	-4.25175800	0.63964200
H	7.06812500	-2.75585500	0.08911500
N	1.22753400	-0.86320800	-1.26558200
P	4.82932100	1.97537400	2.51945000
F	4.30273800	1.02637000	3.75638700
F	3.44771700	1.64720100	1.68125800
F	4.10068100	3.27918200	3.20926900
F	5.35446500	2.92263500	1.28115100
F	6.20863500	2.30102100	3.35533600
F	5.55559100	0.66846100	1.82822900
C	-4.10522000	0.21303300	2.43489900
C	-5.48531700	0.00952100	2.31309500
C	-6.23509000	0.91235900	1.55738700
C	-5.64153000	2.00564100	0.92434300
C	-4.26028500	2.19474100	1.05607600
C	-3.49148100	1.30240700	1.80932000
H	-3.51575700	-0.48545000	3.02174700
H	-5.95610200	-0.83705500	2.80059900
H	-6.23315300	2.70155400	0.33981300
H	-3.79224900	3.04406300	0.56691200
H	-2.42110700	1.45512700	1.90858100
C	2.67193700	7.43216000	-2.68295800
H	2.85651900	8.48716900	-2.86244700
C	-6.72789000	-3.93821600	-1.69530500
H	-7.74028800	-4.32754100	-1.74815800
C	7.74715300	-6.04798100	0.60861300
H	8.57697400	-6.70669500	0.84701300
I	-8.35947600	0.61405300	1.36682000

TCBPA$^{•+}$·PF_6 + PhCl, Cl atom facing outward (uB3LYP/6-31+G(d,p))



Solvent = MeCN (CPCM)

86

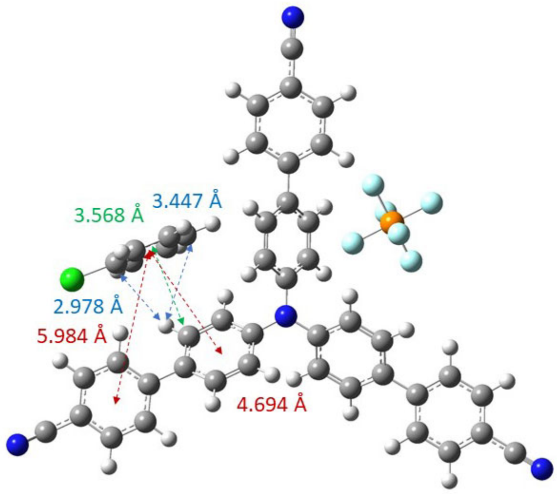
-3351.684452 [uB3LYP/6-31+G(d,p)]

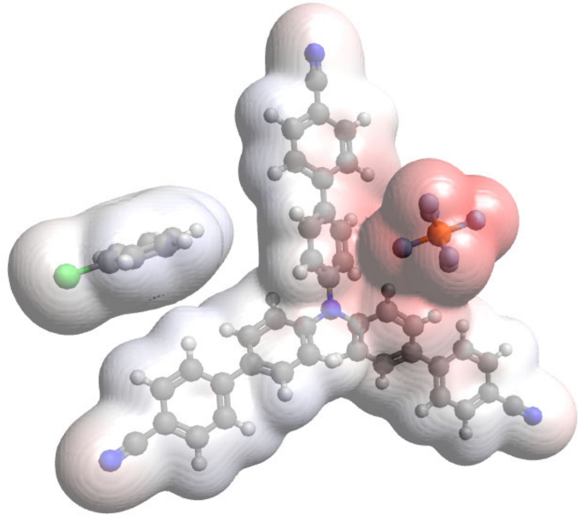
Charge = 0; Multiplicity = 2

C	0.32705400	3.35880800	-0.84945000
C	-0.47758300	2.66096200	0.07696800
C	-0.41469000	1.28105800	0.18808200
C	0.47049000	0.55121800	-0.63179700
C	1.28152200	1.23204400	-1.56294300
C	1.20388300	2.61185700	-1.66524800
C	0.25402900	4.83239700	-0.96231800
C	-0.96400900	5.51115900	-0.76018000
C	-1.03914500	6.89516800	-0.86683000
C	0.11657200	7.63438000	-1.17668200
C	1.34104000	6.97277700	-1.37925200
C	1.40167100	5.58791000	-1.27420600
H	-1.13016900	3.20787900	0.74837000
H	-1.01107400	0.76869600	0.93410900
H	1.93260100	0.67389000	-2.22572100
H	1.80452500	3.11310200	-2.41598700
H	-1.86793500	4.95273100	-0.54312000
H	-1.98560000	7.40337400	-0.71912700
H	2.23478500	7.54233100	-1.60872300
H	2.35739200	5.09374000	-1.40997100
C	-0.62921600	-1.60721700	-0.30250400
C	-0.60923800	-2.70933900	0.57583900
C	-1.82540400	-1.26107400	-0.96260500
C	-1.76618600	-3.44357500	0.78620100
H	0.29686100	-2.95477600	1.11781700
C	-2.97260900	-2.00846700	-0.74626900
H	-1.83708200	-0.43974500	-1.66985700
C	-2.97206700	-3.11375200	0.13133200
H	-1.74236600	-4.26001500	1.49933400
H	-3.87138700	-1.75399600	-1.29683100
C	-4.20258200	-3.90452800	0.35800700
C	-4.13426700	-5.29189100	0.59386800
C	-5.46863700	-3.28647100	0.34209300
C	-5.28664700	-6.04064200	0.80411900
H	-3.17509300	-5.79806600	0.58756600

C	-6.62832600	-4.02288900	0.55526300
H	-5.54927100	-2.21607100	0.18787800
C	-6.54237600	-5.40746400	0.78676100
H	-5.21934900	-7.10956200	0.97376300
H	-7.59517500	-3.53201700	0.55059700
C	4.28218200	-2.80650700	-0.84203900
C	3.11820300	-3.37012100	-1.40916100
C	1.88955300	-2.73813100	-1.30494000
C	1.79168700	-1.50536000	-0.62662800
C	2.94358100	-0.92564500	-0.05593000
C	4.16396800	-1.57385200	-0.16470100
C	5.58955900	-3.49023000	-0.95501000
C	5.66917900	-4.89702100	-0.95637800
C	6.89431400	-5.54553000	-1.06042600
C	8.07573000	-4.79040900	-1.17100900
C	8.01422700	-3.38524000	-1.17298500
C	6.78303100	-2.74908000	-1.06350600
H	3.18242000	-4.29356300	-1.97383400
H	1.01549000	-3.16693800	-1.78145100
H	2.87268100	-0.00114900	0.50586900
H	5.02662500	-1.13022200	0.31933600
H	4.76917300	-5.49253100	-0.84898000
H	6.94122300	-6.62882300	-1.04932000
H	8.92328500	-2.80149400	-1.26652400
H	6.74940000	-1.66541700	-1.08832100
N	0.54501200	-0.85321800	-0.52028400
C	-7.73450700	-6.17257400	1.00561900
C	9.34173900	-5.45337000	-1.28148100
C	0.04613500	9.06179900	-1.28632900
N	10.37029500	-5.99248900	-1.37141900
N	-8.70335200	-6.79405700	1.18373000
N	-0.01169800	10.22167000	-1.37576400
P	4.61128300	2.41931500	2.34619000
F	4.65009100	1.45613900	3.67971300
F	3.12141700	1.82538500	1.96240400
F	3.90618300	3.61469500	3.22922700
F	4.57041100	3.37985800	1.01108000
F	6.09828900	3.00974300	2.72785800
F	5.31297100	1.21981900	1.46145500
C	-6.45016700	1.83812100	0.60766900
C	-7.72581500	1.35614700	0.91848900
C	-8.64079400	1.16168000	-0.11695700
C	-8.31467500	1.43554800	-1.44577000
C	-7.03478800	1.91713200	-1.73912200
C	-6.10190900	2.11895700	-0.71718600
H	-5.73166800	1.99274000	1.40691500
H	-8.00216600	1.13666500	1.94400900
H	-9.04282000	1.27718700	-2.23372900
H	-6.77221800	2.13347200	-2.77023500
H	-5.11056600	2.49377700	-0.95164900
Cl	-10.25588900	0.55462000	0.26486400

TCBPA$^{\cdot+}$$\cdot$PF$_6$ + PhCl, Cl atom facing outward (ωb97xd/6-31+G(d,p))





Solvent = MeCN (CPCM)

Spin Density: iso = 0.00050

86

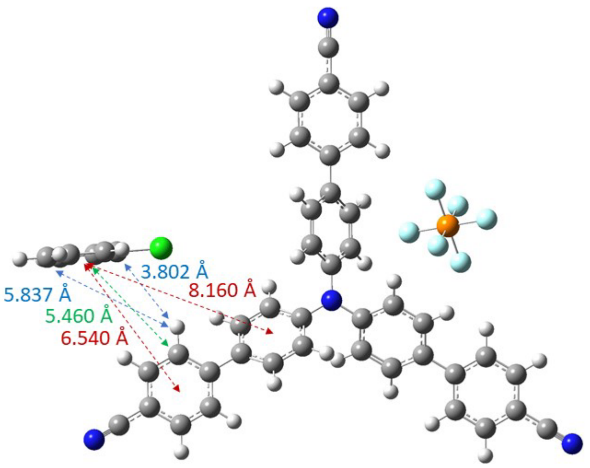
-3350.787340 [ωb97xd/6-31+G(d,p)]

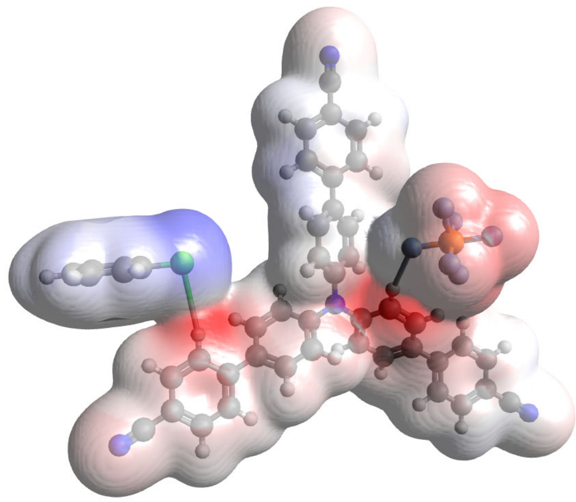
Charge = 0; Multiplicity = 2

C	0.52638900	3.20262800	-0.36656500
C	-0.31155100	2.60816200	0.58842100
C	-0.46902200	1.23531600	0.63738500
C	0.23581700	0.43121200	-0.26957800
C	1.07490000	1.00794200	-1.23224400
C	1.20784200	2.38333700	-1.27758000
C	0.69745700	4.67348700	-0.40589600
C	-0.40064400	5.52372700	-0.22149500
C	-0.24248300	6.90186100	-0.25873500
C	1.02985300	7.44300500	-0.47874000
C	2.13657300	6.60477000	-0.65990900
C	1.96529600	5.22823900	-0.62449200
H	-0.81641300	3.22515900	1.32414900
H	-1.09613700	0.77986500	1.39565000
H	1.58805500	0.38088300	-1.95267300
H	1.83670600	2.82823000	-2.04023200
H	-1.39111200	5.10804800	-0.06759600
H	-1.09705900	7.55525900	-0.12446900
H	3.12125400	7.02978800	-0.81847400
H	2.82676100	4.57776900	-0.73108100
C	-1.19401800	-1.50677600	-0.02462300
C	-1.39986900	-2.58442600	0.84887600
C	-2.27361300	-0.92839000	-0.70626900
C	-2.68499300	-3.06022300	1.04424800
H	-0.56768000	-3.00708200	1.40057400
C	-3.55047900	-1.41624100	-0.50310100
H	-2.10227600	-0.12213100	-1.40929600
C	-3.77893100	-2.48263100	0.38007200
H	-2.84472900	-3.86410200	1.75454500
H	-4.37345100	-0.97658600	-1.05732800
C	-5.15527000	-2.97891200	0.61395700
C	-5.40977000	-4.34869700	0.76126300
C	-6.22292400	-2.07531200	0.69258600

C	-6.70048000	-4.80939900	0.98002300
H	-4.59882000	-5.06502500	0.68268700
C	-7.51768600	-2.52193200	0.91136300
H	-6.03949200	-1.01027300	0.59950300
C	-7.75674700	-3.89358900	1.05586600
H	-6.89169700	-5.87139900	1.08452800
H	-8.33647800	-1.81412700	0.97510000
C	3.46272100	-3.44562700	-0.53196500
C	2.21541000	-3.87007000	-1.02222500
C	1.09907100	-3.06317400	-0.92001800
C	1.21273500	-1.79660600	-0.31638000
C	2.45536800	-1.35597600	0.17660200
C	3.55987900	-2.17809500	0.06541000
C	4.65354000	-4.31919400	-0.64314500
C	4.54015200	-5.70292700	-0.45133200
C	5.65270800	-6.52614300	-0.54962700
C	6.90031600	-5.96597600	-0.84821000
C	7.02934200	-4.58603600	-1.04496400
C	5.90990100	-3.77307000	-0.93963100
H	2.12727300	-4.82745800	-1.52390100
H	0.15307700	-3.38342300	-1.34119600
H	2.53932400	-0.39676100	0.67524200
H	4.50233000	-1.84057600	0.48181800
H	3.57993900	-6.14060000	-0.19986800
H	5.55882800	-7.59427300	-0.39030700
H	7.99603200	-4.15728000	-1.28331300
H	6.01311700	-2.70705000	-1.11185100
N	0.09356500	-0.96987000	-0.20801600
C	-9.09502200	-4.36453700	1.28217300
C	8.05596700	-6.81323000	-0.95240900
C	1.20085900	8.86896700	-0.51699800
N	8.98886800	-7.49777500	-1.03597700
N	-10.17573300	-4.74488100	1.46484200
N	1.33845500	10.02060500	-0.54813800
P	4.35794300	2.21337500	1.51319800
F	4.60210400	1.88118700	3.09698600
F	2.84152000	1.60282500	1.62182800
F	3.79004700	3.69461700	1.90773900
F	4.11856000	2.54123000	-0.07181600
F	5.87521300	2.81720400	1.40856500
F	4.92116000	0.72581900	1.11676300
C	-3.93127500	2.34836900	-0.13770800
C	-5.25531100	1.95919800	0.05866600
C	-5.99468400	1.52184300	-1.03632200
C	-5.44127600	1.45392000	-2.31144700
C	-4.11594700	1.84834200	-2.49033100
C	-3.36183100	2.30006700	-1.40839800
H	-3.34811700	2.69055400	0.71080000
H	-5.70497000	1.99736400	1.04464500
H	-6.03414600	1.10406700	-3.14908200
H	-3.67593400	1.80030400	-3.48089200
H	-2.32966500	2.60333800	-1.55441500
Cl	-7.66863700	1.04771800	-0.80589700

TCBPA$^{\cdot+}\cdot PF_6$ + PhCl, Cl atom facing inward (uB3LYP/6-31+G(d,p))





Solvent = MeCN (CPCM)

Spin Density, iso = 0.0005

86

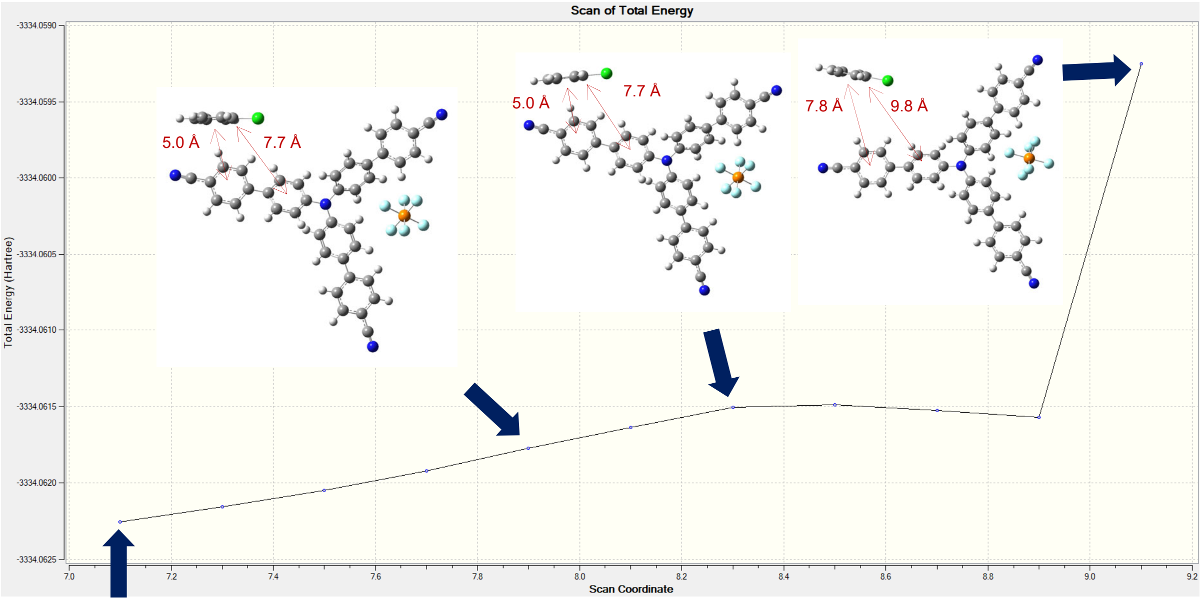
-3351.683498 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	0.54528800	3.46471000	-0.96377500
C	-0.30060900	2.81311000	-0.04057100
C	-0.30361200	1.43270600	0.08144200
C	0.55457300	0.65572100	-0.72365600
C	1.40744000	1.29015000	-1.65009900
C	1.39561500	2.67130800	-1.76355600
C	0.53976000	4.93896400	-1.09086400
C	-0.65060100	5.67211500	-0.91596200
C	-0.66311200	7.05694200	-1.03663400
C	0.52900400	7.74179000	-1.33325800
C	1.72659800	7.02537600	-1.50849800
C	1.72460700	5.64028300	-1.38970400
H	-0.93411300	3.39568500	0.61902100
H	-0.93148800	0.95437000	0.82417800
H	2.03883600	0.69674500	-2.30120100
H	2.02703400	3.13819000	-2.51120800
H	-1.58165400	5.15559700	-0.70962600
H	-1.58868200	7.60752600	-0.90982500
H	2.64828900	7.55285100	-1.72794800
H	2.65978900	5.10326300	-1.50464500
C	-0.65297400	-1.44369400	-0.39210500
C	-0.69552900	-2.54006600	0.49273400
C	-1.82469400	-1.04303600	-1.06527600
C	-1.88934100	-3.21444200	0.69722500
H	0.19251400	-2.82671400	1.04428900
C	-3.00935400	-1.73119600	-0.85485400
H	-1.78976600	-0.22651300	-1.77730600
C	-3.07172700	-2.82906800	0.02986200
H	-1.91228300	-4.02640700	1.41544900
H	-3.88969200	-1.43581600	-1.41453500
C	-4.34249400	-3.55521400	0.25047700
C	-4.34600200	-4.94205500	0.49892100
C	-5.57576800	-2.87444900	0.21583300
C	-5.53641700	-5.63057500	0.70257400
H	-3.41339100	-5.49550800	0.50776500

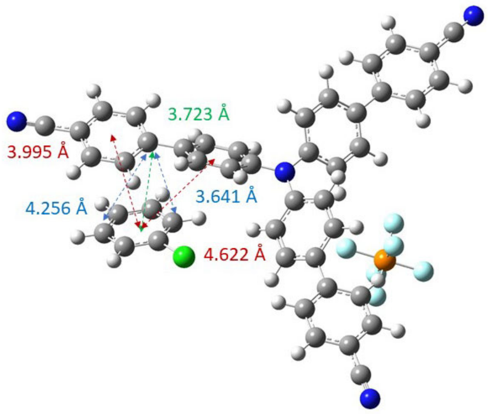
C	-6.77278600	-3.55067800	0.42240600
H	-5.60207200	-1.80240500	0.05265700
C	-6.75868800	-4.93582300	0.66580100
H	-5.52452900	-6.69993600	0.88192800
H	-7.71376900	-3.01219400	0.40298500
C	4.19705400	-2.88997300	-0.86483300
C	3.01343600	-3.39893900	-1.44255800
C	1.81703400	-2.70499700	-1.35839400
C	1.77311200	-1.46347400	-0.69040900
C	2.94567400	-0.93789400	-0.10963300
C	4.13299700	-1.64781800	-0.19772600
C	5.46985200	-3.63912100	-0.95558800
C	5.48026800	-5.04798300	-0.93732300
C	6.67330900	-5.75677500	-1.01999400
C	7.89125600	-5.06174100	-1.12855600
C	7.89862700	-3.65543900	-1.15032500
C	6.69902900	-2.95863000	-1.06194100
H	3.03804300	-4.32928100	-1.99901500
H	0.92824600	-3.09321400	-1.84237000
H	2.91531100	-0.00589200	0.44346500
H	5.00983000	-1.24572400	0.29688200
H	4.55106500	-5.59713100	-0.83093900
H	6.66708800	-6.84083800	-0.99378200
H	8.83607400	-3.11824800	-1.24260100
H	6.71831800	-1.87506400	-1.10188000
N	0.55900700	-0.74990500	-0.60267500
C	-7.98953400	-5.63916500	0.87722100
C	9.12462800	-5.78671000	-1.21628700
C	0.52262000	9.16976900	-1.45737300
N	10.12675800	-6.37605800	-1.28752700
N	-8.98984300	-6.21056300	1.04913600
N	0.51683000	10.33010100	-1.55853700
P	4.82980700	2.17387200	2.46725500
F	4.29343900	1.39263100	3.81221200
F	3.37505100	1.91066000	1.73654300
F	4.26884400	3.59811400	3.06924500
F	5.36392200	2.95260300	1.11985900
F	6.28138700	2.43431900	3.19585200
F	5.38826100	0.74690400	1.86239700
C	-10.11423100	0.94787200	-1.10149000
C	-8.72224400	1.05566800	-1.18443700
C	-7.98584500	1.15846200	-0.00379300
C	-8.60112000	1.15791000	1.24849100
C	-9.99402700	1.04935400	1.31325300
C	-10.75201500	0.94433100	0.14290200
H	-10.69598000	0.86709800	-2.01468200
H	-8.22151400	1.05922700	-2.14644500
H	-8.00738000	1.23981100	2.15234900
H	-10.48191900	1.04762900	2.28322000
H	-11.83274600	0.86056500	0.20021500
Cl	-6.22578300	1.29568300	-0.09711800

To confirm that the converged precomplex structure was the local minima, we ran a scan moving the PhCl partner away from the initial geometry of the our converged precomplex (structure shown above) across a co-ordinate of the biphenyl unit to which it was originally precomplexed, reoptimizing and calculating the total energy (*E*) at each step. As can be seen below, the energy *increases* as the PhCl partner is moved away from the discovered converged geometry above. The energy is higher when the two components are separated. Endergonic values for precomplexation are a result of the CPCM model for acetonitrile as confirmed by comparing the zero point energies for precomplexation vs. the Gibbs free energies involving the CPCM model.



Initial precomplex geometry (see above)

TCBPA$^{\cdot+}$·PF_6 + PhCl, Cl atom facing inward (ωb97xd/6-31+G(d,p))



Solvent = MeCN (CPCM)

86

-3350.788360 [ωb97xd/6-31+G(d,p)]

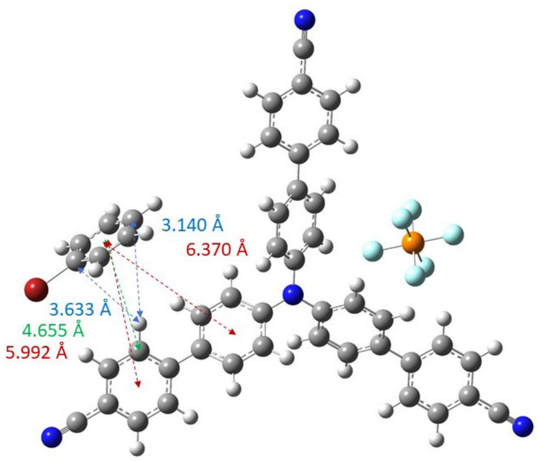
Charge = 0; Multiplicity = 2

C	-1.50528000	-3.20704700	-1.10074000
C	-0.33011700	-2.94994000	-0.37756800
C	0.19490000	-1.67376100	-0.30824700
C	-0.45725000	-0.62144600	-0.97197400
C	-1.62044500	-0.86804100	-1.71931300
C	-2.13117900	-2.14958000	-1.77788300
C	-2.08922600	-4.56731500	-1.13313000
C	-1.26774500	-5.69649600	-1.24750200
C	-1.81648400	-6.97079900	-1.27437700
C	-3.20487100	-7.12494300	-1.18074800
C	-4.03714300	-6.00549100	-1.06074000
C	-3.47726800	-4.73621600	-1.03942000
H	0.15257700	-3.74817600	0.17599700
H	1.07504300	-1.47845700	0.29308600
H	-2.09638900	-0.06244300	-2.26657900

H	-3.01945100	-2.33680100	-2.37032800
H	-0.19274000	-5.58036900	-1.33752000
H	-1.17705800	-7.84075700	-1.37226100
H	-5.11068400	-6.13124200	-0.97667200
H	-4.11811100	-3.87053200	-0.91125100
C	1.43402200	0.90384100	-0.86707400
C	1.98417100	1.88092400	-0.02227800
C	2.26644600	0.14022100	-1.69938800
C	3.35281000	2.07272900	-0.00563800
H	1.34441900	2.44506300	0.64673700
C	3.63298300	0.35042200	-1.67462600
H	1.83716900	-0.58595500	-2.38021800
C	4.20225800	1.30874400	-0.82226700
H	3.77050400	2.78981500	0.69200900
H	4.26140800	-0.22534400	-2.34469700
C	5.67114500	1.48289500	-0.75068900
C	6.23330200	2.74069200	-0.49168000
C	6.52019400	0.38063800	-0.90961800
C	7.60744400	2.89557600	-0.38409800
H	5.59679400	3.61297900	-0.38902600
C	7.89548300	0.52054500	-0.80195700
H	6.10609900	-0.60737000	-1.07586800
C	8.44117000	1.78094500	-0.53622400
H	8.03421300	3.87255700	-0.18771000
H	8.54203600	-0.34335300	-0.90590400
C	-2.60991900	3.92145500	-0.54881600
C	-1.43009100	4.03987300	-1.30182600
C	-0.54814000	2.98086000	-1.41332800
C	-0.84046600	1.76904500	-0.76663100
C	-2.01638500	1.63203900	-0.01141800
C	-2.88519900	2.70320900	0.09120100
C	-3.54785300	5.06300900	-0.43337100
C	-3.06273600	6.37104100	-0.30014800
C	-3.93582800	7.44383800	-0.19012400
C	-5.31647900	7.21434200	-0.21561500
C	-5.81648900	5.91369200	-0.34921700
C	-4.93269600	4.84928200	-0.45526100
H	-1.21698200	4.95942700	-1.83591600
H	0.34016400	3.07142000	-2.02810300
H	-2.22599200	0.70758200	0.51546900
H	-3.77199400	2.59572900	0.70592000
H	-1.99411500	6.55338000	-0.25923000
H	-3.55257600	8.45181200	-0.07901200
H	-6.88641300	5.74115800	-0.37557300
H	-5.32622800	3.84592100	-0.57823200
N	0.04598200	0.68426000	-0.87527800
C	9.86452800	1.93177900	-0.41494200
C	-6.22637300	8.32055700	-0.10415600
C	-3.77912100	-8.44159400	-1.20536300
N	-6.96125300	9.21379700	-0.01449100
N	11.01409400	2.05334800	-0.31567100
N	-4.24268100	-9.50502700	-1.22519000
P	-4.35467000	-1.43454800	1.75814600
F	-4.08200200	-1.22726200	3.35852400
F	-2.75389800	-1.24785400	1.46407700
F	-4.13678300	-3.04588900	1.92591000
F	-4.63086300	-1.63636000	0.15799900
F	-5.95357900	-1.61379800	2.05640900
F	-4.56724300	0.18207800	1.58739300
C	7.03238200	-1.29759100	2.17042200

C	6.17782800	-2.17500100	1.50586900
C	4.83673300	-1.82941300	1.37005000
C	4.33305600	-0.64095000	1.88604900
C	5.20202300	0.22769000	2.54402100
C	6.54949300	-0.09607600	2.68641900
H	8.08154700	-1.55409100	2.27402100
H	6.54911500	-3.10663700	1.09359000
H	3.28473700	-0.39023100	1.76851000
H	4.81894200	1.16324500	2.93864800
H	7.22240400	0.58726300	3.19358100
Cl	3.75484800	-2.91584600	0.51447900

TCBPA$^{\cdot+}$$\cdot$PF$_6$ + PhBr, T-π-type, Br atom pointing 'out' (uB3LYP)



86

-2904.815381 [uB3LYP/6-31+G(d,p)]

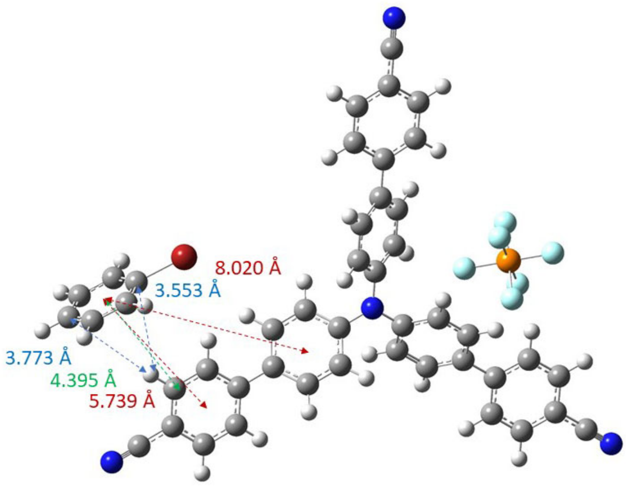
Charge = 0; Multiplicity = 2

C	1.08474700	3.43684600	-0.89492600
C	0.20396600	2.83156200	0.02764800
C	0.12186700	1.45278700	0.14466800
C	0.93324600	0.63091900	-0.66461900
C	1.81892800	1.21843300	-1.59138200
C	1.88604800	2.59871800	-1.70010700
C	1.16586100	4.90961700	-1.01495200
C	0.02177600	5.71122700	-0.82961100
C	0.09067300	7.09540600	-0.94261000
C	1.32015500	7.71012400	-1.24205700
C	2.47240100	6.92475900	-1.42832500
C	2.38900600	5.54121900	-1.31666800
H	-0.39400700	3.44728900	0.69051700
H	-0.53115800	1.00812900	0.88692300
H	2.41423000	0.59192700	-2.24574800
H	2.54171100	3.03157100	-2.44752800
H	-0.93722700	5.24963000	-0.62052800
H	-0.79994200	7.69940700	-0.80751600
H	3.42268000	7.39800200	-1.65033400
H	3.29028300	4.95043700	-1.43991500
C	-0.39238700	-1.39633800	-0.34024100
C	-0.50117400	-2.48978400	0.54289000
C	-1.53719700	-0.92556900	-1.01485600
C	-1.73378600	-3.09207800	0.74488400

H	0.36754700	-2.82992100	1.09510200
C	-2.76163600	-1.54175500	-0.80655500
H	-1.45216500	-0.11135700	-1.72557500
C	-2.89030300	-2.63506700	0.07700600
H	-1.80662600	-3.90255600	1.46171300
H	-3.62241000	-1.19341100	-1.36660800
C	-4.20291400	-3.28260700	0.29750000
C	-4.29208100	-4.66834200	0.53740700
C	-5.39123200	-2.52554600	0.27243500
C	-5.52294900	-5.28205400	0.74263800
H	-3.39558200	-5.27895100	0.53833700
C	-6.62800600	-3.12615100	0.48079400
H	-5.35003700	-1.45301500	0.11541400
C	-6.69953000	-4.51128900	0.71598100
H	-5.57808100	-6.35131800	0.91548500
H	-7.53288400	-2.52843600	0.46948500
C	4.37246700	-3.11226300	-0.80761000
C	3.15991000	-3.55975900	-1.37712400
C	2.00362200	-2.80033500	-1.29370600
C	2.03031700	-1.55363000	-0.63351700
C	3.23287100	-1.08919900	-0.06074400
C	4.37960800	-1.86325500	-0.14972400
C	5.60177600	-3.93087400	-0.89774100
C	5.53434800	-5.33827300	-0.86805200
C	6.68628400	-6.11276900	-0.94961500
C	7.94056700	-5.48669200	-1.06831200
C	8.02563000	-4.08278100	-1.10172200
C	6.86635300	-3.31986400	-1.01477900
H	3.13130100	-4.49401300	-1.92709600
H	1.09311600	-3.14235500	-1.77235000
H	3.25567700	-0.15374800	0.48691800
H	5.28061600	-1.50492400	0.33536100
H	4.57649000	-5.83420300	-0.75330000
H	6.62023200	-7.19474800	-0.91471900
H	8.99137100	-3.59939300	-1.20177300
H	6.94493400	-2.23920900	-1.06435700
N	0.85834400	-0.77341700	-0.54705700
C	-7.97117700	-5.13766300	0.92939100
C	9.13185300	-6.27947700	-1.15412500
C	1.39814900	9.13689300	-1.35744900
N	10.09955800	-6.92414900	-1.22352600
N	-9.00429200	-5.64706000	1.10279300
N	1.46097800	10.29622800	-1.45146700
P	5.23344400	2.07968600	2.29598400
F	5.10830700	1.15937600	3.65390300
F	3.68747700	1.67921600	1.88375900
F	4.67321500	3.38380200	3.12729600
F	5.35648500	2.99751800	0.93638800
F	6.77609200	2.47691500	2.70600000
F	5.79040400	0.77171200	1.46308700
C	-9.91346500	-0.02061900	-1.27527400
C	-8.66780200	0.61878300	-1.28207400
C	-8.08174800	0.94193900	-0.06021200
C	-8.69126200	0.65224500	1.15853800
C	-9.93662700	0.01235100	1.14532200
C	-10.54787500	-0.32435400	-0.06655400
H	-10.38224300	-0.27865400	-2.22027400
H	-8.17309200	0.85576900	-2.21738100
H	-8.21477200	0.91529600	2.09633500
H	-10.42336000	-0.22008500	2.08788700

H	-11.51361600	-0.82048100	-0.06896100
Br	-6.33743600	1.83706600	-0.05558600

TCBPA$^{\cdot+}$$_{\cdot}PF_6$ + PhBr, T-π-type, Br atom pointing 'in' (uB3LYP)



86

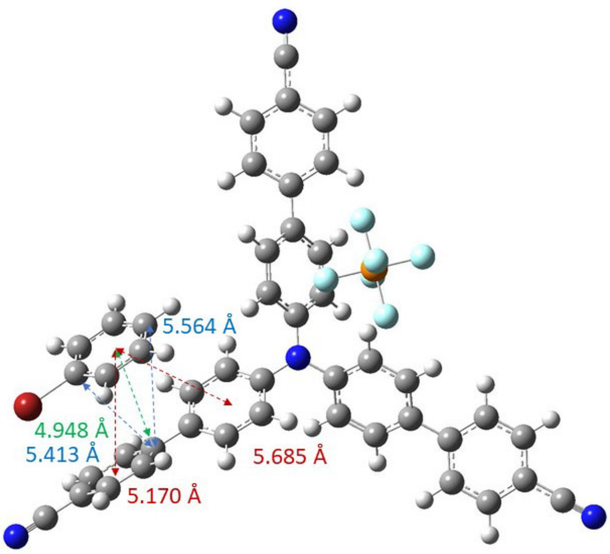
-2904.814500 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	1.04832600	3.42933500	-0.86705600
C	0.17450200	2.81252000	0.05451900
C	0.10399100	1.43259300	0.16553700
C	0.92068200	0.62114300	-0.64882300
C	1.79905300	1.22013100	-1.57519400
C	1.85444700	2.60139300	-1.67796300
C	1.11797400	4.90327800	-0.97957700
C	-0.03087900	5.69562900	-0.78388000
C	0.02740800	7.08087100	-0.88946800
C	1.25079500	7.70619900	-1.19187800
C	2.40768700	6.93024800	-1.38843900
C	2.33488400	5.54552500	-1.28411900
H	-0.42706100	3.42016900	0.72157700
H	-0.54383600	0.97928400	0.90712500
H	2.39812500	0.60151100	-2.23361200
H	2.50490000	3.04285400	-2.42488800
H	-0.98544900	5.22614100	-0.57225200
H	-0.86681800	7.67762200	-0.74629600
H	3.35337600	7.41154600	-1.61270300
H	3.23990400	4.96221300	-1.41519400
C	-0.38597700	-1.41951500	-0.33059200
C	-0.48384600	-2.51642100	0.54948600
C	-1.53532000	-0.95841500	-1.00406400
C	-1.71020900	-3.13209300	0.74913100
H	0.38820400	-2.84918200	1.10097300
C	-2.75330200	-1.58816900	-0.79842400
H	-1.45836600	-0.14124000	-1.71230600
C	-2.87105200	-2.68560400	0.08157900
H	-1.77484100	-3.94534500	1.46357700
H	-3.61711000	-1.24764900	-1.35859600
C	-4.17663800	-3.34846700	0.29841100
C	-4.25007800	-4.73545000	0.53664700

C	-5.37400800	-2.60591400	0.27126700
C	-5.47405200	-5.36406900	0.73771000
H	-3.34648400	-5.33547200	0.53925800
C	-6.60429900	-3.22133400	0.47496200
H	-5.34578000	-1.53287500	0.11577900
C	-6.65971800	-4.60744100	0.70860500
H	-5.51676800	-6.43409000	0.90930100
H	-7.51619800	-2.63409800	0.46116200
C	4.39396000	-3.08937500	-0.81091300
C	3.18457900	-3.54634700	-1.37968200
C	2.02138400	-2.79811400	-1.29158300
C	2.03761100	-1.55339300	-0.62722000
C	3.23681100	-1.07970500	-0.05493000
C	4.39057300	-1.84262000	-0.14868800
C	5.63079600	-3.89593400	-0.90626100
C	5.57690100	-5.30401200	-0.88131600
C	6.73605200	-6.06712100	-0.96792100
C	7.98400300	-5.42861400	-1.08716000
C	8.05553100	-4.02385300	-1.11598500
C	6.88919500	-3.27241200	-1.02390300
H	3.16370300	-4.47894900	-1.93279500
H	1.11327100	-3.14708400	-1.76975700
H	3.25187100	-0.14601500	0.49598100
H	5.28903900	-1.47755200	0.33607600
H	4.62408300	-5.80950600	-0.76628700
H	6.68045900	-7.14980500	-0.93657700
H	9.01635000	-3.53086800	-1.21657500
H	6.95732300	-2.19089500	-1.06993300
N	0.85874000	-0.78428100	-0.53637600
C	-7.92412700	-5.24978400	0.91771500
C	9.18271100	-6.20953400	-1.17820900
C	1.31787500	9.13409100	-1.29983900
N	10.15652300	-6.84445500	-1.25190100
N	-8.95097800	-5.77279600	1.08771500
N	1.37176500	10.29434900	-1.38781600
P	5.20160600	2.09987000	2.31319200
F	5.08554500	1.17268300	3.66720600
F	3.65828200	1.68903600	1.90122900
F	4.63231400	3.39589400	3.15097400
F	5.31552300	3.02457100	0.95744800
F	6.74165200	2.50738000	2.72277500
F	5.76769300	0.79998100	1.47381400
C	-5.91332500	2.28338700	0.65811100
C	-7.07974200	1.56006600	0.93529700
C	-7.84147900	1.09467800	-0.13429300
C	-7.48270200	1.32518200	-1.46055400
C	-6.31325700	2.05083200	-1.71818300
C	-5.52895800	2.52921500	-0.66381500
H	-5.30974800	2.65225200	1.48213700
H	-7.38124200	1.36835900	1.95903800
H	-8.09338100	0.95323800	-2.27567500
H	-6.02161900	2.23863000	-2.74730100
H	-4.62389500	3.09176300	-0.87125800
Br	-9.47846000	0.08273500	0.24044300

TCBPA$^{\cdot+}$$\cdot$PF$_6$ + PhBr, π-π-type, Br atom pointing 'out' (uB3LYP)



86

-2904.817215 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

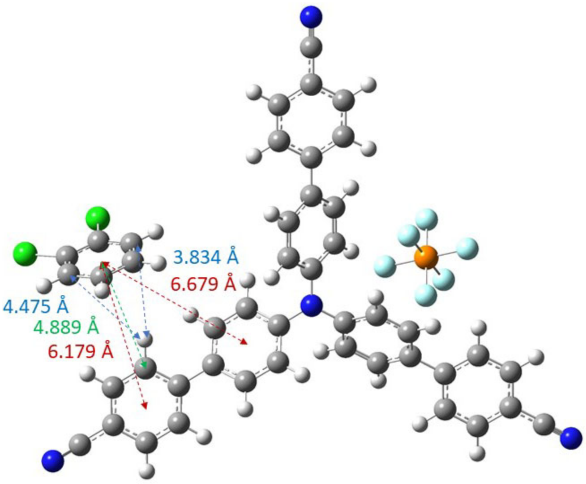
C	1.98246600	3.43419900	-1.70921600
C	0.82415800	3.01799700	-1.01739400
C	0.52798600	1.67396700	-0.85483700
C	1.39582600	0.69533900	-1.38301400
C	2.55697300	1.09333700	-2.07802300
C	2.83714700	2.44143800	-2.23596200
C	2.29429300	4.87094900	-1.87605000
C	1.26359100	5.81899500	-2.03384600
C	1.55130800	7.16996700	-2.19403100
C	3.93087900	6.66962000	-2.03517200
C	3.62974400	5.32109300	-1.88024500
H	0.16964000	3.75415100	-0.56375400
H	-0.34278800	1.37474500	-0.28288800
H	3.20500300	0.34773000	-2.52428500
H	3.71085800	2.72829900	-2.81068300
H	0.22801900	5.49709800	-2.05805500
H	0.74872500	7.88759100	-2.32508300
H	4.96284400	7.00304900	-2.02601300
H	4.44135700	4.61640100	-1.73473000
C	-0.23493700	-1.12460400	-1.29879800
C	-0.69987600	-2.11625300	-0.41165600
C	-1.10711900	-0.58608700	-2.26623100
C	-2.01437500	-2.55084200	-0.49255900
H	-0.03928000	-2.51877200	0.34782900
C	-2.41517200	-1.04046400	-2.34292600
H	-0.74912300	0.16148700	-2.96486400
C	-2.89970600	-2.02819500	-1.45919300
H	-2.35383000	-3.31653100	0.19638400
H	-3.07263200	-0.61298000	-3.09211700
C	-4.29919200	-2.50451300	-1.54497800
C	-5.00805300	-2.87052100	-0.38340900
C	-4.95119500	-2.60268700	-2.79035600
C	-6.32300500	-3.31673500	-0.45729200
H	-4.53959200	-2.78105100	0.59075000

C	-6.26404200	-3.05260900	-2.87854300
H	-4.42147500	-2.35136700	-3.70285300
H	-6.86013200	-3.58442700	0.44602300
H	-6.74936900	-3.13382500	-3.84504100
C	4.22222500	-3.44779100	-0.53530800
C	3.13033200	-3.77476500	-1.36879200
C	2.10263300	-2.87230500	-1.59309500
C	2.14290800	-1.59938900	-0.98690300
C	3.22505100	-1.25410400	-0.15067600
C	4.24239900	-2.17113700	0.06659100
C	5.31492900	-4.41758900	-0.29948300
C	5.05102100	-5.80080000	-0.24429800
C	6.07299600	-6.71696000	-0.02158800
C	7.67455000	-4.88415400	0.09301300
C	6.64260100	-3.97812600	-0.12566800
H	3.10552600	-4.73102300	-1.87961900
H	1.29316300	-3.12711400	-2.26769500
H	3.24080900	-0.29628200	0.35745500
H	5.04440900	-1.90639000	0.74696800
H	4.03483200	-6.16513900	-0.34980800
H	5.85384800	-7.77794600	0.02899300
H	8.69332300	-4.53241200	0.21410300
H	6.87761400	-2.92102200	-0.18731200
N	1.10230700	-0.67409500	-1.21918400
P	3.28133000	1.97334700	3.23085200
F	1.65603800	1.96413000	2.97210800
F	3.53577200	1.61584900	1.64053000
F	3.32929000	3.57894300	2.87523800
F	4.90683200	1.98133900	3.48728400
F	3.02846700	2.33073200	4.81706100
F	3.23384700	0.36652200	3.58324100
C	-4.99183700	1.11993300	2.99795000
C	-6.29166200	0.60654100	2.91184700
C	-7.01631400	0.82803900	1.74276200
C	-6.49195000	1.53768100	0.66462700
C	-5.19075800	2.04408000	0.76940100
C	-4.44093000	1.83751200	1.93160800
H	-4.41561100	0.95538400	3.90360500
H	-6.72228800	0.05126200	3.73761400
H	-7.07595600	1.69642200	-0.23510600
H	-4.76958600	2.60025000	-0.06290800
H	-3.43338400	2.23476900	2.00651000
C	2.89000800	7.60250700	-2.19463700
C	-6.95810900	-3.41175500	-1.70884800
C	7.39331700	-6.26151200	0.14714100
Br	-8.83963800	0.11923300	1.61158500
C	8.45163200	-7.20157900	0.37373500
C	-8.31236200	-3.87443900	-1.79198800
C	3.19350500	8.99402500	-2.35767900
N	-9.41248200	-4.25131500	-1.85986800
N	3.44000600	10.12469000	-2.49056900
N	9.31115900	-7.96602100	0.55723300

TCBPA$^{\cdot+}\cdot PF_6$ + PhBr, π-π-type, Br atom pointing ‘out’ (uB3LYP)

(COULD NOT BE CONVERGED).

TCBPA$^{•+}$·PF_6 + 1,2-dichlorobenzene, T-π type, Cl atoms pointing 'out' (uB3LYP)



86

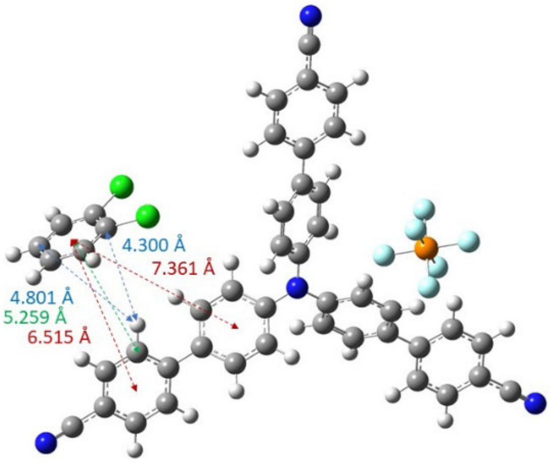
-3811.285602 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	0.55626800	3.34555500	-0.87547100
C	-0.24050800	2.63830700	0.05061900
C	-0.15934700	1.25955100	0.16379300
C	0.73677000	0.54037400	-0.65368200
C	1.54028000	1.23070600	-1.58436800
C	1.44437500	2.60921100	-1.68872000
C	0.46381500	4.81788100	-0.99044700
C	-0.76343600	5.48063000	-0.79093900
C	-0.85682200	6.86338700	-0.89946100
C	0.28940700	7.61753600	-1.20854400
C	1.52283300	6.97200500	-1.40857100
C	1.60177300	5.58821300	-1.30163400
H	-0.90154300	3.17735600	0.72012300
H	-0.74990300	0.74034700	0.90971000
H	2.19988300	0.68045300	-2.24531700
H	2.03941300	3.11739400	-2.43926400
H	-1.66023800	4.91051600	-0.57461800
H	-1.81018100	7.35910700	-0.75382400
H	2.40922700	7.55313500	-1.63752000
H	2.56419300	5.10664200	-1.43530900
C	-0.33518200	-1.63147800	-0.32263900
C	-0.30228800	-2.73184200	0.55753200
C	-1.53502900	-1.30101600	-0.98411100
C	-1.45081700	-3.47877300	0.76961400
H	0.60658200	-2.96577100	1.09996500
C	-2.67363400	-2.06088700	-0.76596000
H	-1.55598100	-0.48151500	-1.69328000
C	-2.66059300	-3.16349600	0.11484500
H	-1.41766800	-4.29353600	1.48432100
H	-3.57539400	-1.81812500	-1.31693000
C	-3.88288500	-3.96576500	0.34549900
C	-3.80109900	-5.35222800	0.58201400
C	-5.15444300	-3.35903100	0.33362600
C	-4.94599200	-6.11123000	0.79658000

H	-2.83727400	-5.84947800	0.57292700
C	-6.30667600	-4.10577300	0.55112500
H	-5.24504400	-2.28945000	0.17917000
C	-6.20743100	-5.48939700	0.78304200
H	-4.86854300	-7.17940800	0.96660000
H	-7.27785800	-3.62354500	0.54958000
C	4.59215900	-2.76783100	-0.85379800
C	3.43669100	-3.34663200	-1.42307500
C	2.19977500	-2.73048600	-1.32163800
C	2.08470900	-1.49876000	-0.64418500
C	3.22783500	-0.90391500	-0.07147900
C	4.45663200	-1.53653400	-0.17724100
C	5.90851600	-3.43467500	-0.96347300
C	6.00598700	-4.84033400	-0.96590900
C	7.23951300	-5.47326700	-1.06654300
C	8.41165400	-4.70316900	-1.17239000
C	8.33238700	-3.29888900	-1.17328600
C	7.09289100	-2.67838300	-1.06744800
H	3.51389400	-4.26944700	-1.98715800
H	1.33221900	-3.17075300	-1.79962600
H	3.14381600	0.01994300	0.48958700
H	5.31242300	-1.08174000	0.30856200
H	5.11323900	-5.44725100	-0.86210600
H	7.30001700	-6.55589300	-1.05638300
H	9.23435100	-2.70369200	-1.26316700
H	7.04573300	-1.59519300	-1.09153000
N	0.82949100	-0.86279200	-0.54037000
C	-7.39190700	-6.26498300	1.00669300
C	9.68631200	-5.34995400	-1.27920500
C	0.20028700	9.04378700	-1.31986500
N	10.72188300	-5.87598300	-1.36614200
N	-8.35456200	-6.89486000	1.18884200
N	0.12728600	10.20270100	-1.41060900
P	4.84625500	2.45872700	2.33869200
F	4.88548300	1.49294100	3.67035500
F	3.36411400	1.85234200	1.94446500
F	4.12508400	3.64573100	3.21993500
F	4.80499300	3.42183300	1.00544800
F	6.32556000	3.06159300	2.73081700
F	5.56407900	1.26757400	1.45574600
C	-7.05246200	0.94903900	2.29242700
C	-8.24784400	0.70003000	1.61745500
C	-8.30828000	0.83795800	0.22770400
C	-7.16665100	1.22596600	-0.48630700
C	-5.97067200	1.47501600	0.19319800
C	-5.91396400	1.33612700	1.58033900
H	-7.01564600	0.83949500	3.37132800
H	-9.13771000	0.39902100	2.15924800
H	-5.09418700	1.77584200	-0.37003000
H	-4.98110500	1.53173100	2.09891900
Cl	-9.82869300	0.51753000	-0.58484200
Cl	-7.20016000	1.41517700	-2.22936900

TCBPA$^{\cdot+}$$\cdot$PF$_6$ + 1,2-dichlorobenzene, T-π type, Cl atoms pointing 'in' (uB3LYP)



86

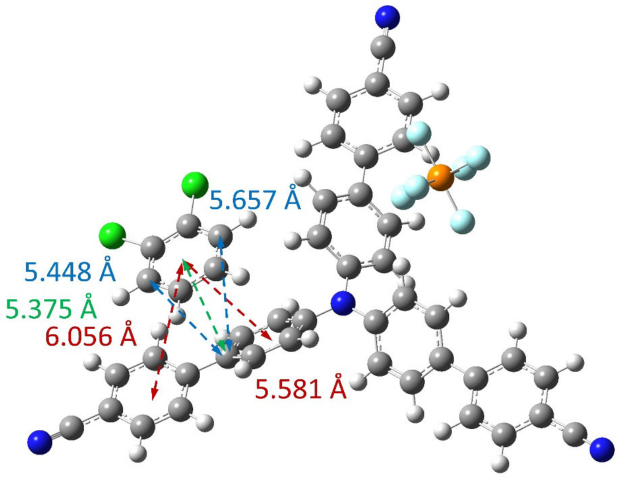
-3811.285387 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	0.27937200	3.27107500	-0.75856800
C	-0.46621600	2.52479300	0.17940900
C	-0.32769600	1.14952200	0.27770000
C	0.57658100	0.47352400	-0.56724600
C	1.32970500	1.20328700	-1.51005700
C	1.17641200	2.57765800	-1.59932800
C	0.12568600	4.73943400	-0.85733500
C	-1.12156200	5.35097000	-0.62132500
C	-1.27233100	6.72978700	-0.71411800
C	-0.16484400	7.53162400	-1.04380400
C	1.08783800	6.93759400	-1.28044200
C	1.22416600	5.55716800	-1.18892700
H	-1.13211800	3.03124000	0.86912400
H	-0.87915100	0.60082800	1.03239000
H	1.99503100	0.68579700	-2.19144900
H	1.73238800	3.11558500	-2.35906200
H	-1.98943600	4.74388500	-0.38822900
H	-2.24056600	7.18603000	-0.54032100
H	1.94437900	7.55572400	-1.52566500
H	2.20122300	5.11538200	-1.35079500
C	-0.40043800	-1.74145200	-0.22983100
C	-0.30304500	-2.84609300	0.64007900
C	-1.62824000	-1.45292800	-0.85884900
C	-1.41659700	-3.63783000	0.87500000
H	0.62750200	-3.04891000	1.15777000
C	-2.73134900	-2.25711700	-0.61807400
H	-1.69813600	-0.62982300	-1.56067100
C	-2.65389400	-3.36419200	0.25382500
H	-1.33423300	-4.45579300	1.58206200
H	-3.65543100	-2.04480600	-1.14417800
C	-3.83881100	-4.21313800	0.51112900
C	-3.69959700	-5.59724500	0.73411900
C	-5.13158000	-3.65379100	0.53956600
C	-4.80936700	-6.39945100	0.97469100
H	-2.71875500	-6.05829000	0.69411300
C	-6.24905900	-4.44387000	0.78349300
H	-5.26527500	-2.58727600	0.39614400

C	-6.09264800	-5.82445600	1.00173700
H	-4.68820800	-7.46524500	1.13394300
H	-7.23687300	-3.99764600	0.81309300
C	4.55443300	-2.67539900	-0.89166100
C	3.40926900	-3.29554200	-1.43782600
C	2.15148700	-2.73071600	-1.30004400
C	2.00389600	-1.51036100	-0.60851300
C	3.13604900	-0.87529700	-0.05765000
C	4.38619700	-1.45694600	-0.19937600
C	5.89399600	-3.28601600	-1.04139800
C	6.04941800	-4.68628500	-1.06394000
C	7.30506600	-5.26621800	-1.20310800
C	8.44136900	-4.44685400	-1.32800800
C	8.30423700	-3.04717400	-1.30895000
C	7.04324300	-2.48000000	-1.16483700
H	3.50898100	-4.20961400	-2.01258700
H	1.29074300	-3.20159000	-1.76086300
H	3.02907900	0.03982400	0.51378600
H	5.23451200	-0.97235400	0.27032400
H	5.18534000	-5.33081500	-0.94598600
H	7.41035500	-6.34545100	-1.20841100
H	9.17859600	-2.41434500	-1.41325600
H	6.95087600	-1.39949700	-1.17410900
N	0.72742000	-0.92567900	-0.46906700
C	-7.24116900	-6.64463100	1.25247800
C	9.73859900	-5.03848700	-1.47493500
C	-0.31287200	8.95414100	-1.13856000
N	10.79251500	-5.51974600	-1.59463500
N	-8.17475400	-7.31051600	1.45657500
N	-0.43361600	10.11004100	-1.21582300
P	4.72324700	2.51625900	2.34428600
F	4.77332500	1.55236400	3.67699500
F	3.24783300	1.89331700	1.95109900
F	3.98942200	3.69633400	3.22430600
F	4.67123800	3.47738100	1.00988800
F	6.19597500	3.13569200	2.73548700
F	5.45412000	1.33217000	1.46248500
C	-9.07846900	0.00253400	0.73894100
C	-7.98457700	0.73752400	1.19703200
C	-7.09104800	1.30439300	0.28369500
C	-7.29552000	1.13347900	-1.09205500
C	-8.39251700	0.39654700	-1.54749700
C	-9.28239900	-0.16788700	-0.63308800
H	-9.76667500	-0.43343000	1.45569100
H	-7.81605800	0.87694800	2.25917000
H	-8.54055500	0.27137600	-2.61443900
H	-10.13112800	-0.73805000	-0.99638400
Cl	-5.72914800	2.22278100	0.89764700
Cl	-6.20028300	1.82947400	-2.27167100

TCBPA$^{\cdot+}\cdot PF_6$ + 1,2-dichlorobenzene, 'π-π' complex, Cl atoms pointing 'out' (UB3LYP)



86

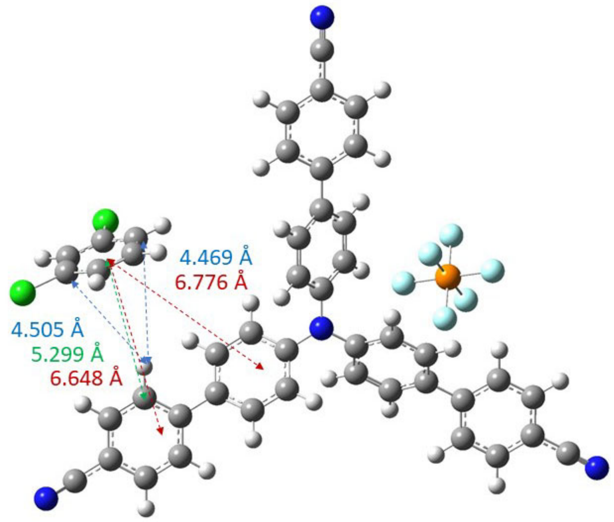
-3811.282264 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	1.58066600	3.44148300	-1.73653500
C	0.39665400	3.13702200	-1.03073300
C	-0.06144000	1.83365300	-0.92295200
C	0.66435300	0.78364100	-1.52193400
C	1.85083500	1.06906500	-2.22834500
C	2.29359500	2.37822900	-2.33115300
C	2.05962700	4.83692800	-1.85094700
C	1.14585200	5.90629500	-1.93300300
C	1.58762600	7.21966500	-2.04328500
C	2.96738600	7.49114400	-2.06934600
C	3.89327700	6.43566900	-1.98598100
C	3.43832700	5.12624000	-1.88035600
H	-0.15101900	3.92468700	-0.52549400
H	-0.95105100	1.61667300	-0.34323100
H	2.39131900	0.27201100	-2.72566000
H	3.18407100	2.58249400	-2.91505400
H	0.07923300	5.71047100	-1.93765700
H	0.87265200	8.03170700	-2.11602700
H	4.95736900	6.64440700	-1.99658400
H	4.16419600	4.32514700	-1.79382700
C	-1.17748000	-0.82382500	-1.49183300
C	-1.74734700	-1.80695700	-0.65783200
C	-1.99354900	-0.12044900	-2.40096300
C	-3.10564800	-2.07256900	-0.73419800
H	-1.13290800	-2.32234900	0.07126800
C	-3.34951800	-0.40053700	-2.46872500
H	-1.55487000	0.60684500	-3.07441700
C	-3.93765600	-1.37874200	-1.63859200
H	-3.53272200	-2.80041200	-0.05337200
H	-3.95295100	0.11965100	-3.20436700
C	-5.38727100	-1.66807800	-1.71387000
C	-5.87307400	-2.97446100	-1.50826300
C	-6.31202300	-0.64261900	-1.99348200
C	-7.23321900	-3.25284300	-1.58083800
H	-5.18172600	-3.78751400	-1.31526400
C	-7.67509600	-0.90664600	-2.06413700

H	-5.96792500	0.37666600	-2.13132200
C	-8.14310400	-2.21699300	-1.85892900
H	-7.59166200	-4.26531400	-1.43115000
H	-8.37619400	-0.10525100	-2.26935700
C	2.97116700	-3.70104000	-0.88429200
C	1.84311600	-3.85879800	-1.71893600
C	0.93023100	-2.83128200	-1.89494400
C	1.12697000	-1.59943100	-1.23696100
C	2.24819500	-1.42255100	-0.40049900
C	3.14855500	-2.46271500	-0.23063500
C	3.94168700	-4.80313500	-0.70135100
C	3.51824300	-6.14704600	-0.71373000
C	4.42557000	-7.18617700	-0.54199800
C	5.78960100	-6.89738600	-0.35713700
C	6.22963300	-5.56158800	-0.34358400
C	5.31135100	-4.53163200	-0.51190400
H	1.70014200	-4.78214000	-2.26921000
H	0.09243900	-2.95827000	-2.57087600
H	2.38638700	-0.49574400	0.14479700
H	3.97808100	-2.31766900	0.45190800
H	2.46686000	-6.38481500	-0.83278200
H	4.08346400	-8.21519600	-0.54332500
H	7.28213000	-5.33778000	-0.20939200
H	5.66892600	-3.50789800	-0.52162800
N	0.20496400	-0.54612500	-1.41622300
C	-9.54701700	-2.49666900	-1.93359100
C	6.73120700	-7.96395200	-0.18305000
C	3.42905700	8.84350000	-2.18155600
N	7.49656600	-8.83057100	-0.04208000
N	-10.68771200	-2.72407100	-1.99461100
N	3.80352700	9.94260600	-2.27311800
P	4.34856600	1.18321600	2.52403500
F	3.50866100	0.42493000	3.71847800
F	2.97881600	1.25402400	1.60833100
F	3.97862000	2.64174900	3.18835800
F	5.18617300	1.93945700	1.32694300
F	5.71507200	1.11017900	3.43677700
F	4.71494800	-0.27784700	1.85651100
C	-5.89031600	-0.49097800	3.36955800
C	-5.51461400	0.81768400	3.05294500
C	-4.18443800	1.22381300	3.22458000
C	-3.23671500	0.31931200	3.71220000
C	-3.61514600	-0.98629600	4.02649400
C	-4.94157800	-1.39141600	3.85501200
Cl	-3.67186000	2.85691700	2.84349200
H	-5.24287400	-2.40516800	4.09785900
H	-6.92274900	-0.79360200	3.23353600
H	-2.87227700	-1.68123000	4.40417900
H	-2.21054000	0.64521700	3.84171200
Cl	-6.73611100	1.92141500	2.44918600
H	-4.55941529	-0.10129500	3.54499444
H	-6.76538406	-1.94253584	-1.78567655
H	-2.55698139	-1.10316692	-1.56689470

TCBPA$^{\cdot+}$·PF_6 + 1,3-dichlorobenzene, T-π-type, Cl atoms pointing 'out' (uB3LYP)



86

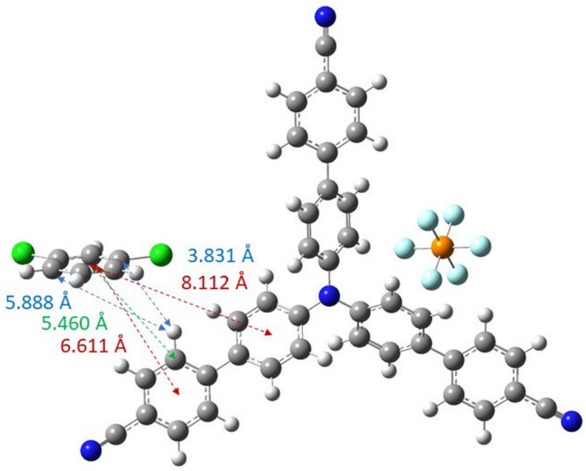
-3811.288657 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	0.38376900	3.32371100	-0.80541100
C	-0.37035700	2.57647800	0.12498100
C	-0.23360000	1.20095800	0.22248300
C	0.67750200	0.52558600	-0.61556500
C	1.43894800	1.25619600	-1.55096900
C	1.28727500	2.63079100	-1.63964400
C	0.23244900	4.79240900	-0.90299800
C	-1.01565800	5.40517800	-0.67481900
C	-1.16422600	6.78427700	-0.76689600
C	-0.05363700	7.58525300	-1.08810400
C	1.19995700	6.99005100	-1.31676700
C	1.33410100	5.60936900	-1.22590000
H	-1.04164700	3.08236400	0.80990000
H	-0.79162800	0.65155100	0.97181300
H	2.10972500	0.73920800	-2.22738100
H	1.84996400	3.16928200	-2.39400800
H	-1.88580100	4.79887000	-0.44827600
H	-2.13309400	7.24142400	-0.59911400
H	2.05887400	7.60747100	-1.55537300
H	2.31180300	5.16675400	-1.38145500
C	-0.30191500	-1.68997800	-0.28811700
C	-0.21056700	-2.79615900	0.58056900
C	-1.52538100	-1.40051400	-0.92518900
C	-1.32567600	-3.58830500	0.80642400
H	0.71631300	-2.99975500	1.10449300
C	-2.63015400	-2.20496700	-0.69322100
H	-1.59036100	-0.57643100	-1.62634100
C	-2.55876300	-3.31351100	0.17738100
H	-1.24813800	-4.40746700	1.51263200
H	-3.55060700	-1.99175200	-1.22529300
C	-3.74547200	-4.16267800	0.42536600
C	-3.60779200	-5.54710600	0.64734800
C	-5.03838800	-3.60326900	0.44604100
C	-4.71916200	-6.34958100	0.87945100
H	-2.62674700	-6.00818200	0.61316300
C	-6.15746000	-4.39360600	0.68178100

H	-5.17117900	-2.53655800	0.30310000
C	-6.00254100	-5.77451100	0.89905500
H	-4.59911900	-7.41561300	1.03794600
H	-7.14547300	-3.94748200	0.70554400
C	4.65862700	-2.62185000	-0.90725100
C	3.51915200	-3.24035600	-1.46704100
C	2.25990800	-2.67611400	-1.34038200
C	2.10538100	-1.45787400	-0.64679100
C	3.23166800	-0.82430900	-0.08247000
C	4.48319500	-1.40567500	-0.21273200
C	5.99960700	-3.23219900	-1.04496500
C	6.15506000	-4.63242000	-1.06978700
C	7.41200900	-5.21217000	-1.19747700
C	8.54965800	-4.39264000	-1.30823000
C	8.41252100	-2.99300000	-1.28676600
C	7.15016100	-2.42601400	-1.15425400
H	3.62491500	-4.15271900	-2.04342400
H	1.40382300	-3.14580100	-1.81103100
H	3.11811300	0.08846200	0.49137500
H	5.32652600	-0.92339800	0.26830900
H	5.28970100	-5.27711700	-0.96261100
H	7.51718800	-6.29139900	-1.20469500
H	9.28800600	-2.36003000	-1.38020600
H	7.05803800	-1.34547100	-1.16161400
N	0.82741800	-0.87371800	-0.51769000
C	-7.15259400	-6.59507600	1.14140800
C	9.84828700	-4.98405600	-1.44320700
C	-0.19944300	9.00803400	-1.18233700
N	10.90334700	-5.46512800	-1.55316200
N	-8.08722500	-7.26153500	1.33869500
N	-0.31840900	10.16414000	-1.25921200
P	4.68375900	2.46502500	2.51763700
F	4.62823600	1.38425800	3.75704700
F	3.23554900	1.90208500	1.96440200
F	3.89752000	3.57185400	3.44646600
F	4.73718400	3.54310700	1.27615800
F	6.12915300	3.02469700	3.06850400
F	5.46680700	1.35425100	1.58646000
C	-6.03493200	1.73163800	0.84537200
C	-7.20213500	1.22023000	1.41851600
C	-8.21883400	0.76983400	0.57616200
C	-8.10104600	0.81669800	-0.81365300
C	-6.92120800	1.33331800	-1.35074900
C	-5.88194500	1.79383200	-0.54212900
H	-5.23525800	2.08627200	1.48768600
H	-7.31876100	1.17332300	2.49509200
H	-8.89955900	0.46351700	-1.45466500
H	-4.97604000	2.19165700	-0.98463800
Cl	-9.69948600	0.12313200	1.27726100
Cl	-6.74992600	1.40390600	-3.10245700

TCBPA$^{\cdot+}\cdot PF_6$ + 1,3-dichlorobenzene, T-π-type, Cl atoms pointing 'in (uB3LYP)



86

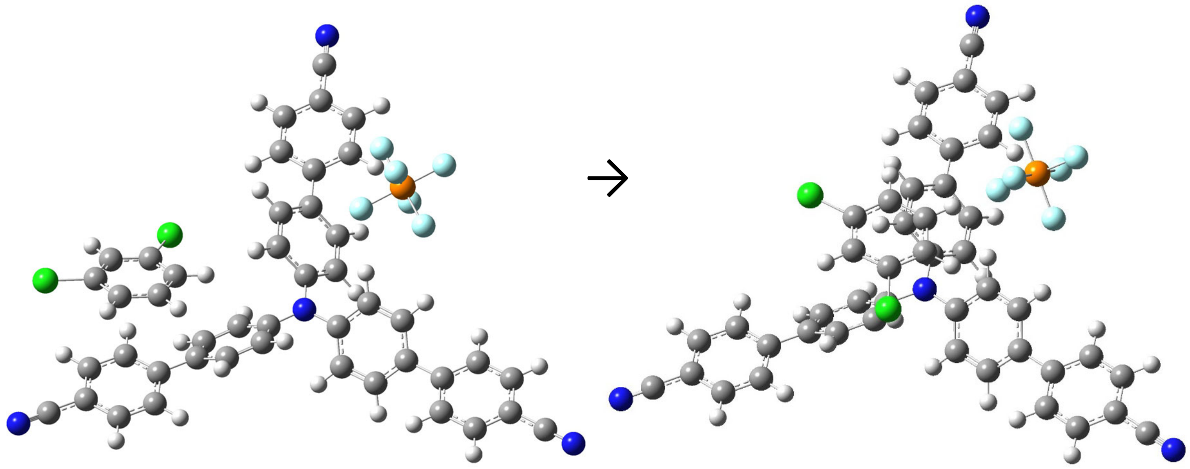
-3811.288068 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	0.79905300	3.45435600	-1.04768400
C	-0.02329500	2.76366300	-0.13149100
C	0.04224300	1.38552300	-0.00354200
C	0.94666300	0.64914000	-0.79673100
C	1.77698200	1.32331300	-1.71606200
C	1.69700300	2.70158000	-1.83496200
C	0.72297600	4.92609900	-1.17907500
C	-0.50239700	5.60163600	-1.01402800
C	-0.58067200	6.98396300	-1.13834900
C	0.57916400	7.72468700	-1.42864200
C	1.81094000	7.06630200	-1.59391800
C	1.87473700	5.68304600	-1.47165400
H	-0.69272300	3.31532500	0.51920500
H	-0.56747900	0.88003800	0.73630300
H	2.44489500	0.76072500	-2.35806300
H	2.31294400	3.19657200	-2.57752600
H	-1.40897100	5.04154100	-0.81268100
H	-1.53254200	7.48960900	-1.01939300
H	2.70763800	7.63720100	-1.80803800
H	2.83540300	5.19135400	-1.57830100
C	-0.15271200	-1.50822300	-0.45568100
C	-0.13669800	-2.59937500	0.43636000
C	-1.34432600	-1.17433200	-1.13027600
C	-1.29420800	-3.33163000	0.64991300
H	0.76640300	-2.83625100	0.98702400
C	-2.49191500	-1.92024400	-0.91112900
H	-1.35220500	-0.36301300	-1.84913600
C	-2.49658100	-3.01159600	-0.01629600
H	-1.27379700	-4.13776100	1.37476700
H	-3.38752800	-1.67514000	-1.47084400
C	-3.72927000	-3.79654500	0.21848100
C	-3.66423600	-5.17870300	0.48407500
C	-4.99437300	-3.17690900	0.18324300
C	-4.81863300	-5.92112500	0.70524100
H	-2.70599400	-5.68659300	0.49336300

C	-6.15591300	-3.90719900	0.40752900
H	-5.07346200	-2.10968400	0.00620000
C	-6.07330800	-5.28667100	0.66890100
H	-4.75361900	-6.98622900	0.89822600
H	-7.12188400	-3.41492700	0.38808500
C	4.76065400	-2.71199400	-0.92505900
C	3.60792700	-3.26988100	-1.51988800
C	2.37854500	-2.63570900	-1.43757900
C	2.27014500	-1.40584200	-0.75657500
C	3.41066000	-0.83027800	-0.16059300
C	4.63129600	-1.48212300	-0.24488900
C	6.06811800	-3.39991300	-1.01105500
C	6.14254400	-4.80692600	-1.01985600
C	7.36752100	-5.45936700	-1.09814900
C	8.55403000	-4.70804200	-1.17435700
C	8.49784600	-3.30270000	-1.16810700
C	7.26662100	-2.66262400	-1.08482600
H	3.68197500	-4.19097200	-2.08716100
H	1.51266500	-3.06048000	-1.93246700
H	3.32935400	0.09306200	0.40187200
H	5.48364600	-1.04526400	0.26291500
H	5.23800600	-5.39970300	-0.93849300
H	7.41031900	-6.54287700	-1.09322400
H	9.41108400	-2.72183100	-1.23507300
H	7.23763700	-1.57869000	-1.10285600
N	1.02119200	-0.75309100	-0.67071900
C	-7.26750200	-6.04506200	0.89943200
C	9.81987200	-5.37518900	-1.25816800
C	0.50558300	9.15049100	-1.55597500
N	10.84833000	-5.91770200	-1.32629300
N	-8.23814500	-6.66092400	1.08713400
N	0.44512400	10.30902400	-1.65982700
P	4.96605500	2.27777500	2.62418700
F	4.44113800	1.32231900	3.85676400
F	3.57893800	1.96007600	1.79024300
F	4.24523200	3.57964100	3.32477800
F	5.48881000	3.23084200	1.38895100
F	6.35007700	2.59255700	3.45581600
F	5.68417900	0.97328700	1.92017800
C	-9.72655200	0.70621400	-0.21302300
C	-8.38995400	0.78243000	-0.60693100
C	-7.42165600	0.89255500	0.39184100
C	-7.75705000	0.92843800	1.74532100
C	-9.10562100	0.85018400	2.10253800
C	-10.10254600	0.73845500	1.12993100
H	-8.11306800	0.75669800	-1.65377000
H	-6.98527900	1.01461300	2.50147500
H	-9.38295100	0.87645500	3.15146000
H	-11.14783300	0.67798900	1.40997500
Cl	-5.72720000	0.99013400	-0.08158600
Cl	-10.96718400	0.56626200	-1.45540300

TCBPA$^{\cdot+}$·PF_6 + 1,3-dichlorobenzene, from 'π-π' complex Cl atoms pointing 'out' → dissociated to a structure that is not a π-π complex, (uB3LYP)



(Input structure) (Converged structure)

86

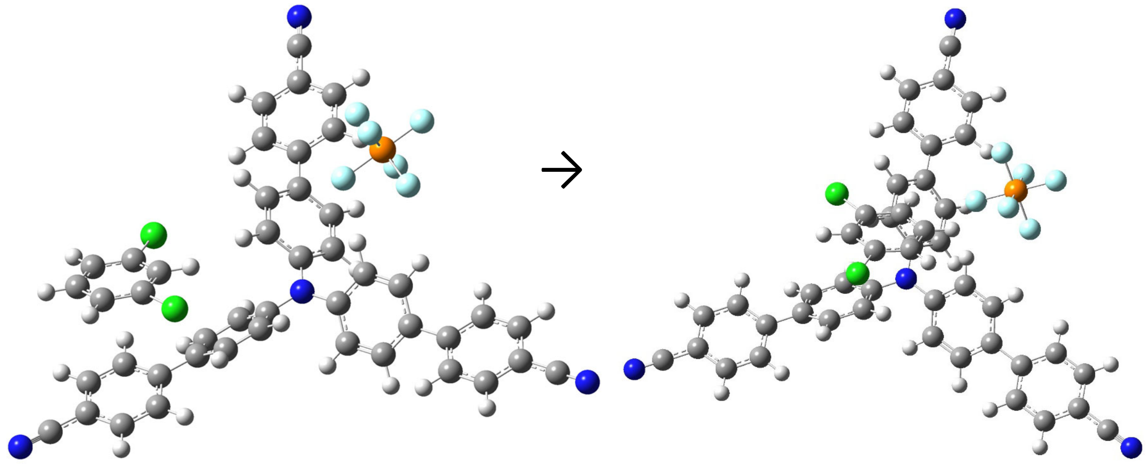
-3811.286857 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	2.34007600	3.47809100	-1.38637800
C	1.16736300	3.49631800	-0.60107900
C	0.25109400	2.45789800	-0.65312700
C	0.48805100	1.35592800	-1.50025600
C	1.65418900	1.32107900	-2.29182200
C	2.55878600	2.36933800	-2.23197600
C	3.31425100	4.59023900	-1.32397400
C	2.88246100	5.91586400	-1.12071100
C	3.79286300	6.96489000	-1.06313900
C	5.16765900	6.70346400	-1.20434200
C	5.61575000	5.38551600	-1.40508700
C	4.69465500	4.34607700	-1.46523200
H	0.99053900	4.31291800	0.08995800
H	-0.62215700	2.47110800	-0.01119400
H	1.82154000	0.49697500	-2.97567700
H	3.42801900	2.34523300	-2.87971600
H	1.82399600	6.13522100	-1.03234700
H	3.44547700	7.98172800	-0.91712000
H	6.67604200	5.18133800	-1.50465900
H	5.05638300	3.33217000	-1.59672300
C	-1.82373300	0.56177400	-1.50625100
C	-2.68225500	-0.27774500	-0.76812500
C	-2.35339800	1.67206000	-2.19426800
C	-4.04049800	-0.00420200	-0.72156700
H	-2.27589600	-1.10877400	-0.20325100
C	-3.71455500	1.92946900	-2.14237300
H	-1.70453000	2.29760100	-2.79638800
C	-4.58844500	1.10186400	-1.40539600
H	-4.67833100	-0.63459100	-0.11205500
H	-4.10962000	2.76213500	-2.71376200
C	-6.03952200	1.38820000	-1.34924600
C	-6.97972400	0.34066300	-1.28928500
C	-6.51048800	2.71591800	-1.35349100
C	-8.34379200	0.60470700	-1.23831100

H	-6.64608800	-0.69119300	-1.30874000
C	-7.87148100	2.99368300	-1.29852500
H	-5.80746700	3.54145700	-1.37342100
C	-8.79688300	1.93617900	-1.24179900
H	-9.05703500	-0.21141100	-1.20326100
H	-8.21922000	4.02074900	-1.29177300
C	0.91860700	-3.70358100	-1.83679800
C	-0.22414400	-3.27371600	-2.54655000
C	-0.67447600	-1.96634400	-2.45984600
C	0.01870300	-1.03844800	-1.65452400
C	1.16725700	-1.44711600	-0.94539500
C	1.60098700	-2.76023500	-1.03883700
C	1.38413300	-5.10538900	-1.92383500
C	0.46317700	-6.16065200	-2.07851000
C	0.89153300	-7.48073900	-2.15566500
C	2.26535000	-7.77326700	-2.08316300
C	3.19854800	-6.73194900	-1.93106800
C	2.75658700	-5.41637300	-1.85049300
H	-0.74438600	-3.96096900	-3.20439100
H	-1.53105100	-1.64701300	-3.04237100
H	1.68545400	-0.75434800	-0.29205700
H	2.45805300	-3.06070500	-0.44711700
H	-0.60066500	-5.95306900	-2.11232500
H	0.17003200	-8.28300100	-2.26370700
H	4.25864400	-6.95528800	-1.88355100
H	3.48954000	-4.62287300	-1.75463500
N	-0.43787900	0.29244900	-1.55518200
C	-10.20162000	2.21594000	-1.18742100
C	2.71361200	-9.13237100	-2.16353900
C	6.11194200	7.78015300	-1.14319000
N	3.07740600	-10.23692700	-2.22892200
N	-11.34306800	2.44348300	-1.14336300
N	6.87855900	8.65563000	-1.09343400
P	4.29732600	-0.40012600	2.04352600
F	3.26696100	-0.89108500	3.23088100
F	3.04939700	0.35755000	1.27791300
F	4.61440800	0.97569600	2.88682400
F	5.32304200	0.08999300	0.85481800
F	5.54053100	-1.15830000	2.80729700
F	3.97576700	-1.77688000	1.19814700
C	-2.32496400	-1.94040400	3.90565300
C	-2.98725700	-0.72983000	4.11402800
C	-2.22469700	0.43890900	4.10581200
C	-0.84525100	0.41885100	3.90003500
C	-0.21461900	-0.81133300	3.69436700
C	-0.94724600	-2.00155900	3.69622800
H	-4.05767900	-0.69816800	4.27668500
H	-0.27620600	1.34144600	3.89978800
H	0.85810100	-0.84256500	3.53196100
Cl	-3.03799900	1.97971100	4.36836800
H	-0.45739200	-2.95552200	3.53810100
Cl	-3.26562400	-3.43034700	3.91428300

TCBPA$^{\cdot+}$·PF_6 + 1,3-dichlorobenzene, from 'π-π' complex Cl atoms pointing 'in' → dissociated to a structure that is not a π-π complex, (uB3LYP)



(Input structure) (Converged structure)

86

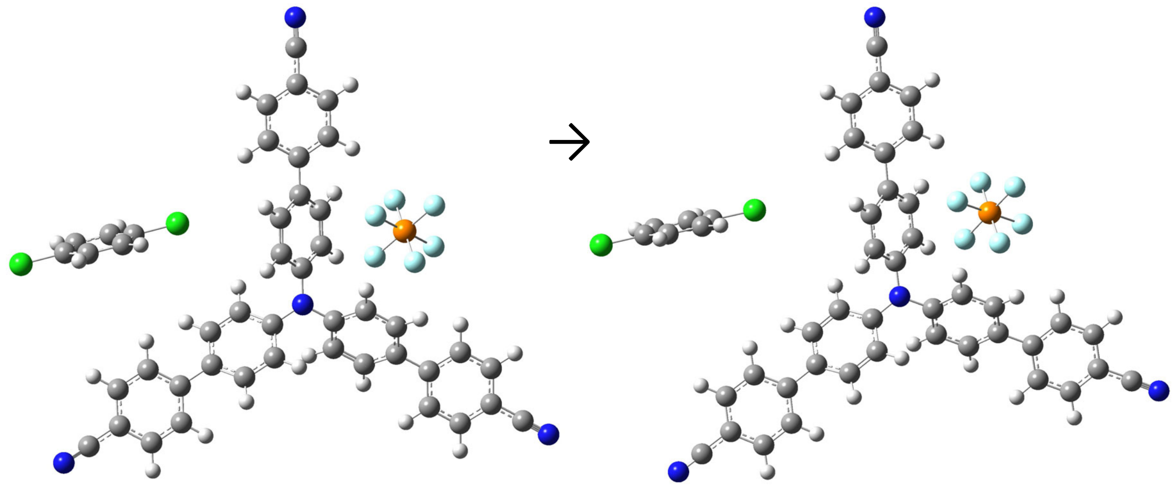
-3811.284234 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	-1.97109700	-3.44015600	-1.56341200
C	-0.80323600	-3.39563800	-0.77183300
C	0.01938300	-2.28026400	-0.76426900
C	-0.31016100	-1.16186200	-1.55724600
C	-1.47320400	-1.18874000	-2.35409100
C	-2.28365600	-2.31276000	-2.35312700
C	-2.84440600	-4.63480800	-1.56484700
C	-2.29934400	-5.92606600	-1.42077600
C	-3.11445500	-7.05219900	-1.42461100
C	-4.50577400	-6.90547400	-1.56918600
C	-5.06665800	-5.62351200	-1.71102300
C	-4.23997500	-4.50586000	-1.71004100
H	-0.55799800	-4.22724900	-0.12074200
H	0.88647600	-2.25051400	-0.11438200
H	-1.71000500	-0.34897300	-2.99709000
H	-3.15049500	-2.33053100	-3.00420300
H	-1.22645600	-6.05638500	-1.33115700
H	-2.68007700	-8.04065200	-1.32389800
H	-6.14007500	-5.50849100	-1.81301600
H	-4.68876600	-3.52244500	-1.79715100
C	1.92167500	-0.16282800	-1.50783400
C	2.69924100	0.72836300	-0.74056800
C	2.55251100	-1.19670400	-2.22946200
C	4.07679300	0.58087300	-0.69920800
H	2.21787800	1.49956800	-0.15042400
C	3.93159400	-1.32868800	-2.18132400
H	1.96468800	-1.85968000	-2.85375100
C	4.72516300	-0.44709600	-1.41653700
H	4.65343800	1.24819200	-0.06838200
H	4.40224400	-2.10242600	-2.77775500
C	6.19691900	-0.59545000	-1.36786800
C	7.03129600	0.53591000	-1.27450800
C	6.79441400	-1.87052600	-1.41303300
C	8.41450600	0.40424100	-1.23000600

H	6.59893700	1.53046600	-1.26243600
C	8.17617700	-2.01626500	-1.36493500
H	6.17496700	-2.75955800	-1.45953400
C	8.99472200	-0.87614800	-1.27400700
H	9.04492100	1.28437700	-1.16878500
H	8.62206400	-3.00442900	-1.38980800
C	-1.22020600	3.83389800	-1.69768200
C	-0.03990200	3.54423300	-2.41638300
C	0.53846100	2.28568300	-2.37101300
C	-0.05944400	1.26797100	-1.59921500
C	-1.23845000	1.53848400	-0.87483000
C	-1.80116600	2.80414900	-0.92708100
C	-1.83305900	5.17970300	-1.75221700
C	-1.03274900	6.33344300	-1.86908100
C	-1.60426900	7.59980200	-1.91850700
C	-3.00269400	7.73667300	-1.85624900
C	-3.81644500	6.59521900	-1.74181300
C	-3.23204500	5.33506700	-1.68838800
H	0.40766000	4.30062700	-3.05149400
H	1.42138000	2.07187700	-2.96229700
H	-1.68123700	0.77766600	-0.24211700
H	-2.68328100	2.99958400	-0.32822700
H	0.04787700	6.24521100	-1.89542300
H	-0.97550300	8.47974600	-1.99752500
H	-4.89514000	6.69871800	-1.70242500
H	-3.87275800	4.46259300	-1.62219700
N	0.51798500	-0.01929900	-1.55321300
C	10.42019300	-1.01863300	-1.22563900
C	-3.59836500	9.03927800	-1.90911900
C	-5.35189000	-8.06246600	-1.57208300
N	-4.08234300	10.09785700	-1.95208500
N	11.57850100	-1.13436200	-1.18627700
N	-6.03917600	-9.00282900	-1.57472200
P	-4.19403100	0.08172100	2.08705600
F	-3.41340600	1.03561900	3.17900500
F	-2.74096800	-0.45609200	1.52239100
F	-4.22265100	-1.14617600	3.18054700
F	-4.97077100	-0.87019000	0.99373500
F	-5.64200600	0.62109100	2.64979900
F	-4.16015300	1.31152300	0.99193200
C	2.24232600	0.98088000	4.68925300
C	2.62345000	-0.26416100	4.18723200
C	1.66843800	-1.00396800	3.48851400
C	0.37105800	-0.53336500	3.28767900
C	0.02421900	0.71759300	3.80561900
C	0.95422000	1.48584500	4.51094900
H	3.62714300	-0.64363700	4.33516700
H	-0.35460700	-1.12375400	2.74051400
H	-0.98396400	1.09044400	3.65722600
Cl	2.12708100	-2.58044900	2.84695700
H	0.68371200	2.45543500	4.91312200
Cl	3.43042500	1.93426400	5.57496000

$TCBPA^{\cdot+}\cdot PF_6$ + 1,4-dichlorobenzene, from 'T-π' type complex → dissociated (uB3LYP)



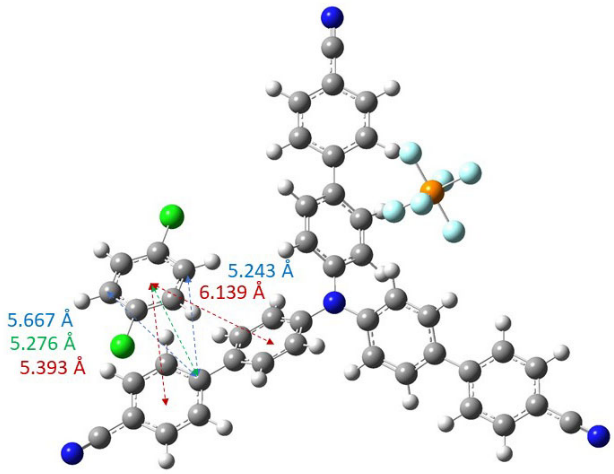
86

(DISSOCIATED) [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

(DISSOCIATED)

$TCBPA^{\cdot+}\cdot PF_6$ + 1,4-dichlorobenzene, π-π type (uB3LYP)



86

-3811.289982 [uB3LYP/6-31+G(d,p)]

Charge = 0; Multiplicity = 2

C	-1.77765500	-3.42536900	-1.52828200
C	-0.59013900	-3.08337300	-0.84592100
C	-0.16524800	-1.76735500	-0.75700100
C	-0.92941900	-0.74224400	-1.35142200
C	-2.11950600	-1.06536800	-2.03506800
C	-2.52860900	-2.38673700	-2.11943700
C	-2.22206100	-4.83381400	-1.62137800

C	-1.28268900	-5.88043500	-1.70728500
C	-1.69248000	-7.20573500	-1.79634000
C	-3.06507300	-7.51256500	-1.79657400
C	-4.01618100	-6.48003000	-1.70986700
C	-3.59321500	-5.15837200	-1.62586800
H	-0.01280000	-3.85173800	-0.34402700
H	0.72838800	-1.52177100	-0.19508800
H	-2.68981800	-0.28744500	-2.52937200
H	-3.42314100	-2.61987100	-2.68600300
H	-0.22160100	-5.65785200	-1.73145900
H	-0.95814200	-7.99997200	-1.87235300
H	-5.07464100	-6.71566100	-1.70112400
H	-4.33797800	-4.37508800	-1.53671700
C	0.86877000	0.91365900	-1.36796900
C	1.43080300	1.91164600	-0.54654200
C	1.68273400	0.23019000	-2.29376100
C	2.77994800	2.21204800	-0.65245500
H	0.81901600	2.41149000	0.19557300
C	3.02918800	0.54529100	-2.39135500
H	1.24816500	-0.50929900	-2.95650600
C	3.60957100	1.53950300	-1.57495000
H	3.20317600	2.95101100	0.01877300
H	3.62972400	0.04002400	-3.13962600
C	5.04886900	1.86760300	-1.68375100
C	5.50373500	3.18678100	-1.48964800
C	5.99431400	0.86757300	-1.98536100
C	6.85361800	3.50218500	-1.59528000
H	4.79540600	3.98074100	-1.27965400
C	7.34752300	1.16871500	-2.08938000
H	5.67516400	-0.16086600	-2.11475900
C	7.78436800	2.49153600	-1.89590900
H	7.18777700	4.52412700	-1.45403200
H	8.06498300	0.38652900	-2.31154400
C	-3.34367100	3.68344500	-0.69790600
C	-2.23269200	3.86821400	-1.54981500
C	-1.29593900	2.86451400	-1.73709500
C	-1.45037300	1.62970300	-1.07303700
C	-2.55398900	1.42629800	-0.21907400
C	-3.47884900	2.44277600	-0.03855800
C	-4.33959500	4.76044500	-0.50290500
C	-3.95138600	6.11484800	-0.52421600
C	-4.88271200	7.13044400	-0.34053900
C	-6.23583000	6.80676700	-0.13437200
C	-6.64084500	5.46006300	-0.11204400
C	-5.69876600	4.45392400	-0.29247000
H	-2.12243300	4.79349800	-2.10430000
H	-0.47215700	3.01141100	-2.42604300
H	-2.65957400	0.49813400	0.33114900
H	-4.29434300	2.27789500	0.65634800
H	-2.90850300	6.37968900	-0.65982000
H	-4.56747900	8.16798100	-0.34905900
H	-7.68500900	5.20918100	0.03840900
H	-6.02976100	3.42123200	-0.29482300
N	-0.50445800	0.60039100	-1.26334200
C	9.17771400	2.80971500	-2.00569700
C	-7.20188000	7.84903600	0.05252900
C	-3.49376500	-8.87747800	-1.88584200
N	-7.98690900	8.69608500	0.20387800
N	10.30984600	3.06832100	-2.09527500
N	-3.84146000	-9.98673600	-1.95864800

P	-4.67905200	-1.28929400	2.60081800
F	-3.99455900	-0.60820100	3.93278700
F	-3.22793200	-1.21648500	1.82013400
F	-4.29729400	-2.78521800	3.16832500
F	-5.36102200	-1.96821500	1.26645600
F	-6.12650200	-1.35961100	3.37925200
F	-5.05711000	0.20932300	2.03055800
C	7.70383700	-1.14150700	2.31772700
C	6.92172300	-2.20297000	1.85596900
C	5.53808800	-2.15732000	2.02849700
C	4.91929000	-1.07443700	2.65361800
C	5.70145100	-0.01297500	3.11525600
C	7.08501900	-0.05788700	2.94167800
H	8.78028600	-1.16391600	2.19030200
H	7.38955000	-3.05144900	1.36944700
H	3.84295900	-1.05284500	2.78199100
H	5.23374200	0.83482800	3.60308600
Cl	4.55187200	-3.49689200	1.44800900
Cl	8.07151100	1.27941700	3.52608700

14. Computational Investigation of TPA$^{\cdot+}$ Excited States

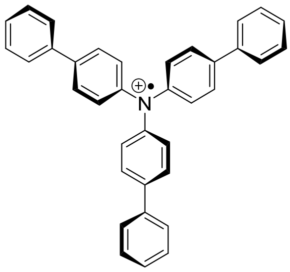
All calculations were performed using Time-Dependent Density Functional Theory (TD-DFT)[42] using the Gaussian16 software package.[29] Ground state geometries of TPAs$^{\cdot+}$ (as isolated radical cations) were obtained from optimization calculations with the CAM-B3LYP functional[43] and a 6-31G(d,p) basis set on all atoms.[31] Solvent was modelled implicitly using the CPCM model[32] for i) a solvent of acetonitrile, which was the reaction solvent or ii) a solvent of dichloromethane, in which UV-vis and other spectroscopic studies were undertaken. Single point TD-DFT calculations on these optimized geometried were performed at the CAM-B3LYP/6-31G(d,p) level of theory. The first 8-10 excited states of TPAs$^{\cdot+}$ are reported, which correspond to their vertical excitation energies. The lowest energy excited state(s) whose absorptions overlay with the purple (λ_{max} = 395 nm) LED used are highlighted in purple. Calculations in dichloromethane were compared to those conducted using the ωb97xd functional[37] and a 6-31G(d,p) basis set, after re-optimization of the ground state geometry at ωb97xd/6-31G(d,p). These levels of theory were in accordance with/similar to previous studies on related compounds and therefore deemed acceptable for the purposes of this study.[6, 22b, 44]

We note that there is a reasonable agreement between all computed and experimental UV-vis spectra, especially in the 400-580 nm region, despite the computational prediction of some transitions that are not present in the experimental spectra. Although reasonable agreement was found between UV-vis spectra in MeCN and calculations (CPCM = MeCN), poor agreement was found for the 580-850 nm region when comparing results in DCM. Due to the interference of charge-transfer interactions, vibrational transitions and symmetry breaking of states as reported for similar TPA$^{\cdot+}$s in the literature,[25] the prediction of transitions beyond 700 nm is challenging with TD-DFT. Our observations are highly consistent with a related study on the TD-DFT of carbazoles.[22b]

Transitions with a negligible coefficient (f < 0.0010) are labelled in red.

14.1. XYZ Co-ordinates and Computed UV-Visible Spectra

T*p*BPA$^{\cdot+}$ <u>in MeCN</u>



64

-1441.431053 [CAM-B3LYP/6-31G(d,p)]

Charge = 1; Multiplicity = 2

C	-2.47464400	-3.40562900	-0.00085000
C	-2.81789100	-2.26438800	-0.74261400
C	-2.01470100	-1.14266100	-0.74554300
C	-0.82456700	-1.13747500	-0.00196800
C	-0.46267300	-2.27098800	0.74207500
C	-1.28269800	-3.38052700	0.74019800
C	-3.34475400	-4.60073200	0.00003700
C	-4.73638800	-4.47113000	-0.07769500
C	-5.55327500	-5.59374900	-0.07454000
C	-4.99416100	-6.86547700	0.00113600
C	-3.61217700	-7.00730300	0.07631200
C	-2.79431700	-5.88539800	0.07833000
H	-3.71179600	-2.27025000	-1.35491500
H	-2.27708800	-0.28494600	-1.35264300
H	0.43418900	-2.25609800	1.34913300
H	-1.01286400	-4.23227900	1.35314400
H	-5.18503300	-3.48416000	-0.11482300
H	-6.63027100	-5.47418700	-0.12560500
H	-5.63275800	-7.74244300	0.00151200
H	-3.16788200	-7.99562000	0.12773100
H	-1.71730300	-6.00964300	0.11495300
C	-0.57086100	1.28284100	-0.00111100
C	0.01510100	2.31500000	-0.74969700
C	-1.72957100	1.53675100	0.74855100
C	-0.55596200	3.57096800	-0.74672700
H	0.88643600	2.11295800	-1.36044400
C	-2.28150100	2.80128500	0.74689200
H	-2.16126700	0.75351900	1.35955000
C	-1.71238000	3.84486600	0.00029200
H	-0.11778100	4.34690500	-1.36311000
H	-3.15090400	2.99421000	1.36413400
C	-2.31449500	5.19502300	0.00067100
C	-1.50922900	6.33682100	-0.08530900
C	-3.70204500	5.35820200	0.08717100
C	-2.07553400	7.60446200	-0.08242400
H	-0.43019900	6.23412400	-0.12852900
C	-4.26729700	6.62630900	0.08496100
H	-4.34613800	4.48640200	0.13047300
C	-3.45623600	7.75360100	0.00135000
H	-1.43561100	8.47854600	-0.13992300
H	-5.34522600	6.73371700	0.14286400
H	-3.89835600	8.74425400	0.00159200
C	4.18870700	-0.43915000	-0.00152200

C	3.56977600	0.58034200	0.73889300
C	2.19889100	0.73460300	0.74041800
C	1.39866500	-0.14684300	-0.00281400
C	1.99944000	-1.17469300	-0.74592600
C	3.37266600	-1.30806100	-0.74289400
C	5.65882900	-0.59380700	0.00035700
C	6.49516300	0.52596500	0.07989000
C	7.87582500	0.37999100	0.07931200
C	8.44528100	-0.88718200	0.00447500
C	7.62459600	-2.00797100	-0.07248000
C	6.24381500	-1.86320700	-0.07703300
H	4.17161700	1.24041100	1.35210100
H	1.73710600	1.50402000	1.34690600
H	1.38865500	-1.83190500	-1.35262700
H	3.82517300	-2.07909100	-1.35510900
H	6.06357200	1.52052100	0.11613700
H	8.50862500	1.25955800	0.13170800
H	9.52414600	-1.00081900	0.00613700
H	8.06057200	-3.00002300	-0.12316600
H	5.61460900	-2.74605800	-0.11442200
N	0.00134200	-0.00079700	-0.00197500

Excited State 1: Doublet 1.4983 eV 827.51 nm f=0.4369
<S**2>=0.823
116B ->125B 0.17271
117B ->125B -0.12698
124B ->125B 0.95494

Excited State 2: Doublet 2.1065 eV 588.57 nm f=0.2015
<S**2>=0.878
114B ->125B 0.20025
118B ->125B -0.51143
122B ->125B 0.78517
123B ->125B 0.15009

Excited State 3: Doublet 2.1949 eV 564.88 nm f=0.0117
<S**2>=0.862
122B ->125B 0.15605
123B ->125B -0.96789
123B ->127B -0.13990

Excited State 4: Doublet 2.3038 eV 538.17 nm f=0.0717
<S**2>=0.878
114B ->125B -0.21395
115B ->125B -0.16899
118B ->125B -0.82146
122B ->125B -0.43624

Excited State 5: Doublet 2.5937 eV 478.02 nm f=0.0052
<S**2>=0.970
122A ->126A 0.10781
124A ->127A -0.12474
125A ->129A -0.10087
111B ->125B -0.13854
116B ->125B 0.11023
117B ->125B -0.36249
121B ->125B -0.84244
122B ->126B -0.11883
124B ->125B -0.13464

Excited State 6: Doublet 2.8419 eV 436.27 nm f=0.0008
<S**2>=0.900
116B ->125B -0.49674
117B ->125B -0.79678
121B ->125B 0.22138

Excited State 7: Doublet 3.0104 eV 411.86 nm f=0.0029
<S**2>=0.890
114B ->125B -0.10383
115B ->125B 0.95176
118B ->125B -0.14310

Excited State 8: Doublet **3.2074 eV** **386.56 nm** f=0.0251
<S**2>=1.824
119A ->127A -0.10301
120A ->132A 0.15289
121A ->133A 0.15344
122A ->126A 0.29422
122A ->134A 0.12630
124A ->127A -0.13087
124A ->129A 0.20138
125A ->127A 0.20463
107B ->125B -0.13232
116B ->125B -0.59075
117B ->125B 0.23186
119B ->131B -0.14038
120B ->132B -0.15039
121B ->127B 0.19698
122B ->126B -0.28537
124B ->130B 0.12169

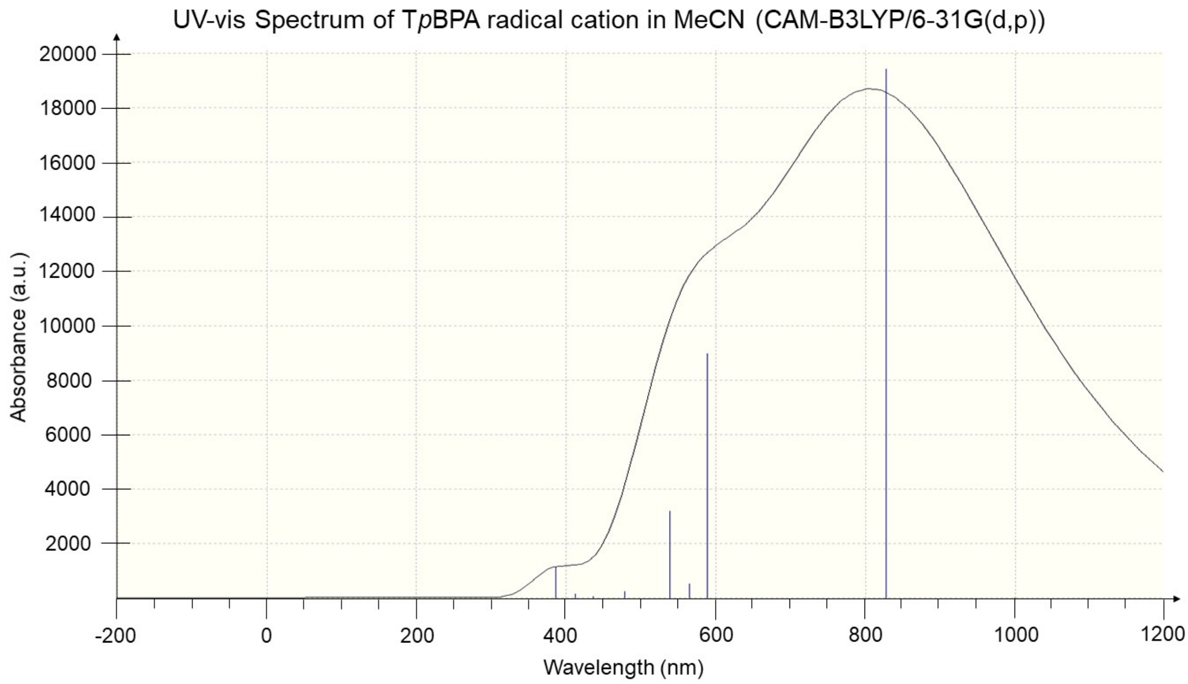


Figure S69. Computed UV-vis spectrum of **T*p*BPA**$^{\cdot+}$ at CAM-B3LYP/6-31G(d,p), CPCM = MeCN.

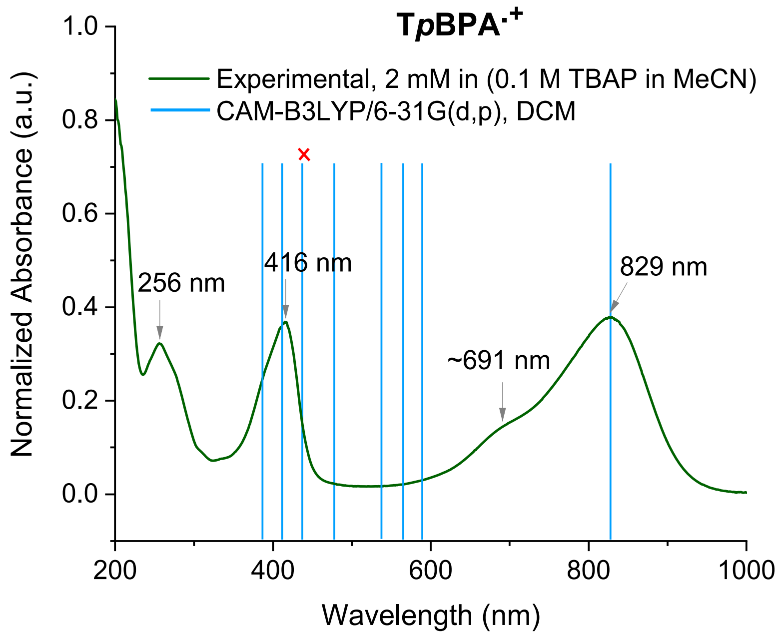
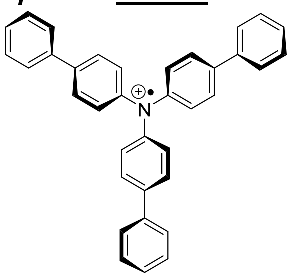


Figure S70. Comparison of experimental UV-vis spectrum of **T*p*BPA$^{\cdot+}$** and computed UV-vis transitions at CAM-B3LYP/6-31G(d,p), CPCM = MeCN.

T*p*BPA$^{\cdot+}$ <u>in DCM</u>



64

-1441.426158 [CAM-B3LYP/6-31G(d,p)]

Charge = 1; Multiplicity = 2

C	0.33224000	4.19657700	-0.00068200
C	-0.66873400	3.55187700	0.74313800
C	-0.78804700	2.17743800	0.74519300
C	0.11073800	1.39987300	-0.00108800
C	1.12056700	2.02644800	-0.74741000
C	1.21905900	3.40253000	-0.74490000
C	0.44929600	5.66998900	-0.00027100
C	-0.69139000	6.47729900	0.08039100
C	-0.58068700	7.86108200	0.07813200
C	0.67141500	8.46237700	0.00082400
C	1.81271500	7.67077100	-0.07708600
C	1.70325000	6.28690000	-0.08042800
H	-1.34173600	4.13731600	1.35823400
H	-1.54347100	1.69581200	1.35394900
H	1.79075800	1.43213600	-1.35637100
H	1.97569000	3.87498200	-1.35993800
H	-1.67445000	6.02025400	0.11819100
H	-1.47579000	8.47159300	0.13099500

H	0.75740900	9.54375400	0.00127900
H	2.79309900	8.13210800	-0.12954100
H	2.60172600	5.68027100	-0.11866200
C	-1.26891500	-0.60514400	-0.00089400
C	-1.49337600	-1.77211300	0.74554800
C	-2.31625900	-0.04358200	-0.74724400
C	-2.74352200	-2.35562600	0.74340000
H	-0.69875200	-2.18580500	1.35433100
C	-3.55741500	-0.64593200	-0.74482700
H	-2.13639700	0.83387800	-1.35627600
C	-3.80206700	-1.81084800	-0.00056600
H	-2.91440100	-3.23103800	1.35859900
H	-4.34474200	-0.22671000	-1.35994400
C	-5.13682000	-2.44572000	-0.00026700
C	-5.26614100	-3.83723700	0.07940000
C	-6.29774000	-1.66765900	-0.07965300
C	-6.52013000	-4.43275200	0.07686500
H	-4.37905800	-4.46048800	0.11647400
C	-7.55116900	-2.26430800	-0.07656900
H	-6.22111800	-0.58624400	-0.11715100
C	-7.66660900	-3.64852400	0.00029200
H	-6.60169800	-5.51320100	0.12888600
H	-8.44065900	-1.64555800	-0.12843800
H	-8.64630600	-4.11432300	0.00048400
C	3.46952000	-2.38669500	0.00088900
C	2.33744600	-2.76002000	-0.74065800
C	1.19470800	-1.98712100	-0.74350600
C	1.15753400	-0.79734600	-0.00012600
C	2.28123400	-0.40576800	0.74392900
C	3.41217800	-1.19582400	0.74213400
C	4.68757400	-3.22387300	0.00103800
C	4.59583100	-4.61859200	-0.07475900
C	5.74028000	-5.40428300	-0.07182700
C	6.99615000	-4.81036700	0.00125200
C	7.10047300	-3.42505500	0.07418300
C	5.95674000	-2.63830500	0.07686900
H	2.36773500	-3.65301700	-1.35354000
H	0.34433800	-2.27227500	-1.35073500
H	2.24235900	0.49060500	1.35070800
H	4.25639400	-0.90404900	1.35547300
H	3.62156500	-5.09434000	-0.10928800
H	5.65049900	-6.48422100	-0.12085600
H	7.89015900	-5.42479300	0.00134200
H	8.07645800	-2.95412400	0.12323900
H	6.05155800	-1.55822400	0.11105300
N	-0.00010500	-0.00101600	-0.00096900

Excited State 1: Doublet 1.8589 eV 666.96 nm f=0.4300
<S**2>=0.853
115B ->125B 0.26233
118B ->125B 0.14772
123B ->125B -0.14634
124B ->125B 0.91410

Excited State 2: Doublet 1.8605 eV 666.41 nm f=0.4288
<S**2>=0.854
114B ->125B -0.26234
117B ->125B -0.14813
123B ->125B 0.91397
124B ->125B 0.14634

```
Excited State   3:      Doublet      2.5691 eV    482.59 nm    f=0.0034
      <S**2>=0.860
  114B ->125B      -0.17076
  117B ->125B       0.95250
  118B ->125B       0.10355

Excited State   4:      Doublet      2.5700 eV    482.43 nm    f=0.0034
      <S**2>=0.860
  115B ->125B      -0.17067
  117B ->125B      -0.10360
  118B ->125B       0.95257

Excited State   5:      Doublet      2.7896 eV    444.46 nm    f=0.0000
      <S**2>=1.132
  123A ->126A       0.12862
  124A ->127A      -0.12850
  125A ->129A       0.16652
  110B ->125B       0.11313
  113B ->125B       0.18672
  122B ->125B       0.87566
  123B ->127B       0.14596
  124B ->126B      -0.14614

Excited State   6:      Doublet      2.8213 eV    439.46 nm    f=0.0035
      <S**2>=0.867
  116B ->125B       0.97597

Excited State   7:      Doublet      3.2220 eV    384.81 nm    f=0.0017
      <S**2>=0.917
  119B ->125B       0.71296
  119B ->126B      -0.15164
  120B ->125B       0.63363
  121B ->125B       0.17687

Excited State   8:      Doublet      3.2228 eV    384.70 nm    f=0.0018
      <S**2>=0.917
  120B ->125B      -0.19404
  120B ->127B      -0.12562
  121B ->125B       0.94841
  121B ->126B       0.10892

Excited State   9:      Doublet      3.2238 eV    384.59 nm    f=0.0002
      <S**2>=0.916
  119B ->125B      -0.65497
  120B ->125B       0.70853
  120B ->127B       0.10149
  121B ->125B       0.10155
  121B ->127B      -0.11698

Excited State  10:      Doublet      3.2887 eV    377.00 nm    f=0.1736
      <S**2>=2.274
  118A ->128A      -0.10804
  119A ->136A       0.15088
  121A ->134A      -0.15257
  122A ->132A      -0.15646
  122A ->134A      -0.10846
  123A ->127A      -0.22914
  124A ->126A       0.23036
  124A ->129A      -0.29500
```

125A ->126A	0.28679
125A ->127A	0.37319
114B ->125B	0.25809
120B ->134B	0.13981
121B ->132B	0.16460
121B ->134B	0.10749
122B ->126B	-0.14068
122B ->127B	0.11564
122B ->136B	-0.12747
123B ->126B	0.18413
123B ->129B	0.22259
124B ->127B	-0.18322
124B ->129B	0.11703

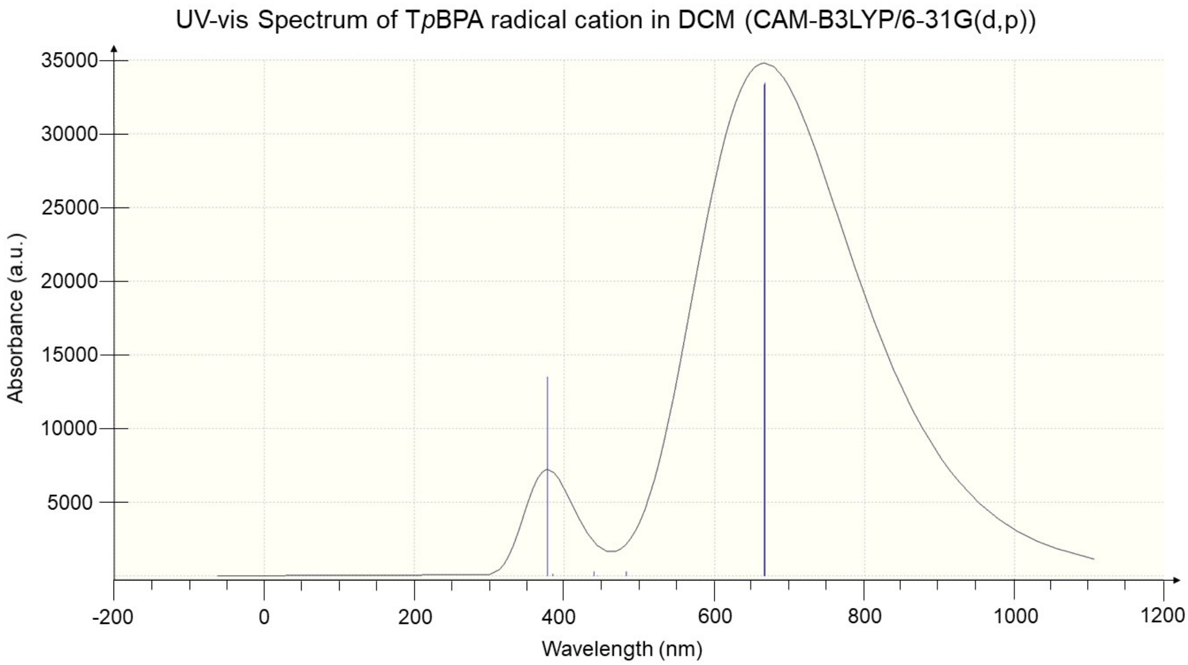


Figure S71. Computed UV-vis spectrum of **T*p*BPA**$^{\cdot+}$ at CAM-B3LYP/6-31G(d,p), CPCM = DCM.

T*p*BPA$^{\cdot+}$ <u>in DCM (ωb97xd)</u>

64

-1441.813421 [ωb97xd/6-31+G(d,p)]

Charge = 1; Multiplicity = 2

C	-2.47269300	-3.40322900	-0.00138800
C	-1.28790300	-3.37586200	0.75404200
C	-0.46609200	-2.26402600	0.75604300
C	-0.82322500	-1.13701700	-0.00230000
C	-2.00552000	-1.14418500	-0.76055300
C	-2.81088000	-2.26802100	-0.75772700
C	-3.34451600	-4.60042200	-0.00032600
C	-2.78892100	-5.88718600	0.01383100
C	-3.60867500	-7.01196500	0.01223200
C	-4.99549800	-6.86824300	0.00214100
C	-5.55834400	-5.59263800	-0.00921800
C	-4.73977200	-4.46697900	-0.01324600
H	-1.02473600	-4.22451000	1.37595000

H	0.42634400	-2.24394200	1.37147000
H	-2.26103500	-0.28887400	-1.37598800
H	-3.69948500	-2.27907000	-1.37939300
H	-1.71032000	-6.01174400	0.00092600
H	-3.16325200	-8.00151100	0.01291600
H	-5.63416600	-7.74558400	0.00312000
H	-6.63687500	-5.47266900	-0.00892200
H	-5.18964400	-3.47875100	-0.00121900
C	1.39918800	-0.14711400	-0.00076500
C	2.19583500	0.72868700	0.75514400
C	1.99780100	-1.16923300	-0.75576100
C	3.56977800	0.57455500	0.75327600
H	1.73146500	1.49274300	1.36844400
C	3.37387400	-1.30310800	-0.75277500
H	1.38576700	-1.82083100	-1.36928600
C	4.18705800	-0.43902700	0.00039000
H	4.17247800	1.22913000	1.37333700
H	3.82844300	-2.06858600	-1.37214400
C	5.66002000	-0.59267300	0.00043800
C	6.49439900	0.53354700	0.01032400
C	6.24455800	-1.86661600	-0.00955400
C	7.87865000	0.38876900	0.00737800
H	6.06102100	1.52906200	-0.00490800
C	7.62899100	-2.00990400	-0.00685300
H	5.61541300	-2.75150500	0.00575800
C	8.45006600	-0.88303900	0.00019800
H	8.51112100	1.27057000	0.00468200
H	8.06638500	-3.00302900	-0.00427100
H	9.52941000	-0.99545900	0.00010300
C	-1.71235700	3.84144500	0.00067500
C	-0.55867200	3.56943100	-0.75442800
C	0.01431600	2.31110200	-0.75764000
C	-0.56955600	1.28203300	-0.00075900
C	-1.72506600	1.53367300	0.75700700
C	-2.27949400	2.80022600	0.75529900
C	-2.31674800	5.19356800	0.00089800
C	-1.50675400	6.33744400	-0.00969000
C	-2.07591700	7.60760500	-0.00680500
C	-3.46246500	7.75412100	0.00102600
C	-4.27721400	6.62270300	0.00879400
C	-3.70940100	5.35197600	0.01153200
H	-0.12462400	4.34561300	-1.37520700
H	0.88362300	2.10665400	-1.37256900
H	-2.15282200	0.74950500	1.37162800
H	-3.14686400	2.99443400	1.37670000
H	-0.42575400	6.23604900	0.00507700
H	-1.43526600	8.48349400	-0.00469400
H	-3.90563300	8.74468700	0.00108100
H	-5.35719600	6.72871900	0.00672300
H	-4.35410700	4.47837200	-0.00334400
N	0.00246000	-0.00076500	-0.00160700

Excited State 1: Doublet 1.9301 eV 642.36 nm f=0.4187
<S**2>=0.845
114B ->125B -0.13019
115B ->125B -0.30613
118B ->125B -0.20907
124B ->125B 0.88794

```
Excited State   2:      Doublet      1.9335 eV    641.24 nm    f=0.4166
      <S**2>=0.846
  114B ->125B      0.30625
  115B ->125B     -0.13036
  117B ->125B     -0.21034
  123B ->125B      0.88746

Excited State   3:      Doublet      2.5560 eV    485.08 nm    f=0.0082
      <S**2>=0.858
  114B ->125B      0.24036
  117B ->125B      0.90705
  118B ->125B     -0.24603
  123B ->125B      0.11087

Excited State   4:      Doublet      2.5567 eV    484.94 nm    f=0.0082
      <S**2>=0.858
  115B ->125B     -0.24011
  117B ->125B      0.24588
  118B ->125B      0.90733
  124B ->125B      0.10987

Excited State   5:      Doublet      2.8196 eV    439.72 nm    f=0.0042
      <S**2>=0.866
  116B ->125B      0.97412

Excited State   6:      Doublet      2.9807 eV    415.95 nm    f=0.0000
      <S**2>=1.225
  123A ->127A     -0.14968
  124A ->126A     -0.15009
  125A ->129A     -0.18201
  110B ->125B      0.15374
  113B ->125B      0.23955
  122B ->125B      0.82236
  123B ->127B      0.18706
  124B ->126B      0.18756

Excited State   7:      Doublet      3.4322 eV    361.24 nm    f=0.1575
      <S**2>=2.205
  119A ->137A     -0.13258
  120A ->134A     -0.15123
  121A ->132A     -0.13778
  123A ->126A     -0.22046
  124A ->127A     -0.22169
  124A ->129A      0.29961
  125A ->126A      0.43844
  125A ->127A     -0.19793
  114B ->125B      0.24974
  115B ->125B      0.17852
  119B ->134B      0.14572
  120B ->132B      0.14022
  122B ->126B      0.19163
  123B ->126B      0.18137
  123B ->129B     -0.10610
  124B ->127B      0.18061
  124B ->129B      0.22088

Excited State   8:      Doublet      3.4326 eV    361.19 nm    f=0.1571
      <S**2>=2.206
  119A ->136A      0.13277
  120A ->133A     -0.12388
```

122A ->132A -0.13939
122A ->133A 0.11816
123A ->127A 0.22110
123A ->129A 0.29973
124A ->126A -0.22084
125A ->126A 0.19735
125A ->127A 0.43841
114B ->125B -0.17654
115B ->125B 0.25078
119B ->133B 0.13178
121B ->132B 0.14261
122B ->127B 0.19152
123B ->127B -0.18096
123B ->129B 0.22083
124B ->126B 0.18061
124B ->129B 0.10639

Excited State 9: Doublet 3.5467 eV 349.57 nm f=0.0055
<S**2>=0.989
119B ->125B 0.40475
119B ->126B 0.13907
120B ->125B 0.57723
120B ->126B 0.10938
121B ->125B 0.63315
121B ->126B 0.13700

Excited State 10: Doublet 3.5497 eV 349.28 nm f=0.0069
<S**2>=0.989
119B ->125B -0.10239
119B ->127B -0.15540
120B ->125B 0.72765
120B ->126B -0.12247
121B ->125B -0.59798
121B ->127B 0.12481

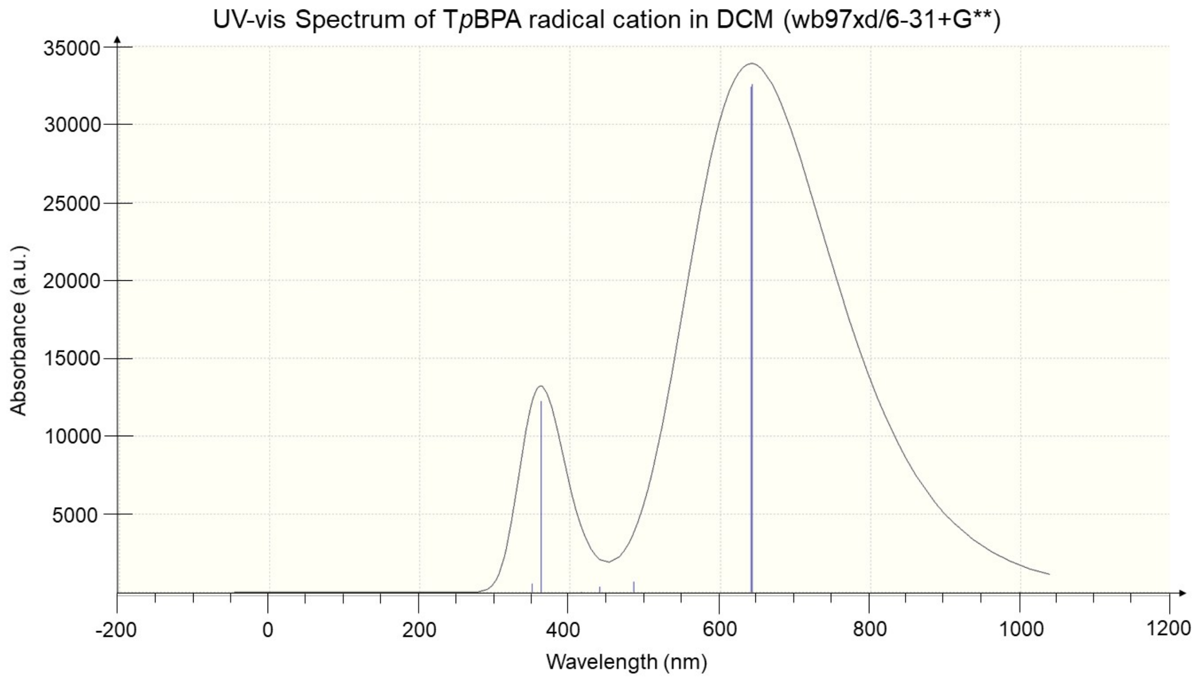


Figure S72. Computed UV-vis spectrum of **T*p*BPA$^{\cdot+}$** at ωb97xd/6-31+G(d,p), CPCM = DCM.

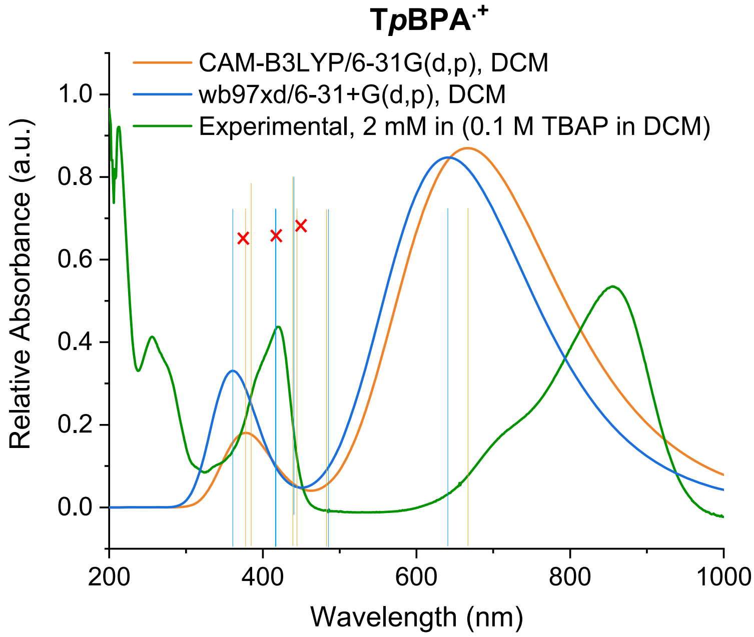
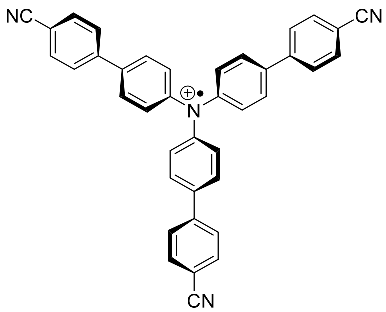


Figure S73. Comparison of experimental UV-vis spectrum of **T*p*BPA$^{\cdot+}$** and computed UV-vis transitions at CAM-B3LYP/6-31G(d,p) and ωb97xd/6-31+G(d,p), CPCM = DCM.

TCBPA$^{\cdot+}$ in MeCN (CAM-B3LYP)



67

-1718.052984 [CAM-B3LYP/6-31G(d,p)]

Charge = 1; Multiplicity = 2

C	-1.37643100	3.96799300	0.00198700
C	-0.24160700	3.60385100	-0.73771100
C	0.22094600	2.30387200	-0.74071800
C	-0.45625700	1.32474100	0.00220200
C	-1.59510800	1.67167900	0.74494700
C	-2.03972200	2.97789400	0.74172400
C	-1.86388500	5.36446800	0.00086300
C	-0.96154500	6.43345300	-0.04724500
C	-1.41188000	7.74252300	-0.04636600
C	-2.78446800	8.00097500	-0.00067400
C	-3.69778200	6.94431200	0.04597100
C	-3.23544800	5.63945400	0.04838700
H	0.26420600	4.34173500	-1.34892100
H	1.07510000	2.02970500	-1.34729100
H	-2.09489000	0.92647900	1.35130300
H	-2.89531300	3.24205800	1.35173200
H	0.10521700	6.24215600	-0.06031000

H	-0.70561400	8.56374500	-0.07453700
H	-4.76163300	7.14794900	0.07368100
H	-3.95127000	4.82570100	0.06262100
C	1.38454700	-0.26799800	0.00219700
C	1.89329700	-1.34373700	-0.74166300
C	2.25497800	0.54283300	0.74659300
C	3.25022900	-1.59401600	-0.73874500
H	1.22848900	-1.94534800	-1.34899000
C	3.60832700	0.27418900	0.74292900
H	1.85997400	1.34760400	1.35409600
C	4.13364800	-0.79454300	0.00162800
H	3.63566200	-2.40089100	-1.35056000
H	4.26490400	0.88179700	1.35415900
C	5.58663800	-1.07166200	0.00047500
C	6.06064300	-2.38775500	-0.04905900
C	6.51135900	-0.02200500	0.04845200
C	7.41936100	-2.65293800	-0.04840700
H	5.36127900	-3.21563500	-0.06322300
C	7.87241700	-0.27463400	0.04567200
H	6.16548300	1.00503600	0.06289800
C	8.33023300	-1.59412300	-0.00184400
H	7.77687500	-3.67537500	-0.07755100
H	8.58092500	0.54469800	0.07361700
C	-2.75000800	-3.17865000	-0.00245700
C	-1.56435600	-3.25900900	0.74263000
C	-0.65251400	-2.22327900	0.74664100
C	-0.91534000	-1.06523100	-0.00069000
C	-2.09776400	-0.96760600	-0.74956400
C	-2.99520200	-2.01574900	-0.74742800
C	-3.72122300	-4.29431900	-0.00155800
C	-3.28137800	-5.62192800	0.05532800
C	-4.18631400	-6.66959100	0.05431800
C	-5.55638700	-6.39949000	-0.00016400
C	-6.01095600	-5.07923700	-0.05498000
C	-5.09646800	-4.04001900	-0.05708500
H	-1.37096900	-4.13006700	1.35724300
H	0.23980000	-2.28364200	1.35735200
H	-2.28262200	-0.09181900	-1.35918400
H	-3.88467400	-1.94551400	-1.36215500
H	-2.22014400	-5.84125400	0.07569300
H	-3.83676700	-7.69461400	0.08924300
H	-7.07391800	-4.87208000	-0.08916400
H	-5.45838500	-3.01857900	-0.07716900
N	0.00477400	-0.00265300	0.00151600
C	9.73978900	-1.86227000	-0.00292900
C	-6.49908200	-7.48111100	0.00055000
C	-3.25775700	9.35539300	-0.00145300
N	-7.25963800	-8.35305200	0.00112700
N	10.87650000	-2.07815800	-0.00365700
N	-3.63976400	10.44754600	-0.00200400

Excited State 1: Doublet 1.7267 eV 718.05 nm f=0.4484
<S**2>=0.850
134B ->143B -0.23141
135B ->143B 0.16928
139B ->143B -0.17188
142B ->143B -0.91616

Excited State 2: Doublet 2.1077 eV 588.25 nm f=0.2059
<S**2>=0.887

132B ->143B -0.19826
138B ->143B 0.58539
141B ->143B 0.74276

Excited State 3: Doublet 2.3009 eV 538.85 nm f=0.1126
<S**2>=0.918
132B ->143B 0.26032
133B ->143B 0.15715
138B ->143B 0.76874
141B ->143B -0.48473

Excited State 4: Doublet 2.6619 eV 465.78 nm f=0.0000
<S**2>=1.009
142A ->145A -0.10344
143A ->146A 0.10480
130B ->143B -0.11172
134B ->143B 0.24909
135B ->143B 0.70358
139B ->143B -0.53562
142B ->143B 0.15575

Excited State 5: Doublet 2.7611 eV 449.04 nm f=0.0014
<S**2>=0.899
140B ->143B 0.97026
140B ->145B -0.13577
140B ->146B 0.13424

Excited State 6: Doublet 2.7729 eV 447.13 nm f=0.0014
<S**2>=1.267
140A ->144A 0.18763
142A ->145A -0.16526
143A ->146A 0.12093
130B ->143B -0.16153
134B ->143B -0.36996
135B ->143B -0.50978
139B ->143B -0.55685
141B ->144B -0.19720
142B ->143B 0.10861
142B ->145B -0.11805

Excited State 7: Doublet 2.8957 eV 428.16 nm f=0.0031
<S**2>=0.904
132B ->143B 0.11806
133B ->143B -0.95199
138B ->143B 0.11745

Excited State 8: Doublet **3.0691 eV** **403.98 nm** f=0.0652
<S**2>=2.220
136A ->150A -0.11646
137A ->151A 0.10114
139A ->145A -0.16348
139A ->153A 0.10158
140A ->144A 0.30518
141A ->154A 0.14858
142A ->146A -0.26935
142A ->153A -0.10198
143A ->145A 0.29470
143A ->146A -0.11970
134B ->143B 0.43941
135B ->143B -0.10185

136B ->149B	0.12266
137B ->148B	-0.10200
139B ->143B	0.10372
139B ->145B	-0.24641
140B ->154B	0.15885
141B ->144B	-0.27612
142B ->146B	-0.25296
142B ->153B	-0.10650

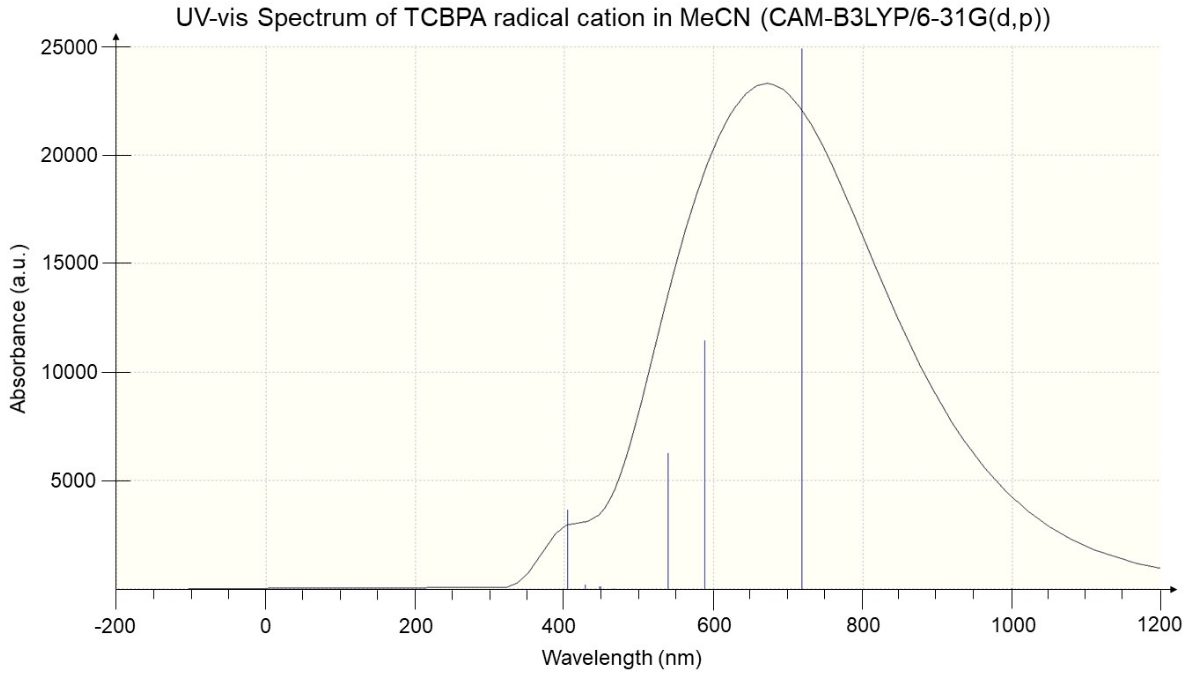


Figure S74. Computed UV-vis spectrum of **TCBPA$^{\cdot+}$** at CAM-B3LYP/6-31G(d,p), CPCM = MeCN.

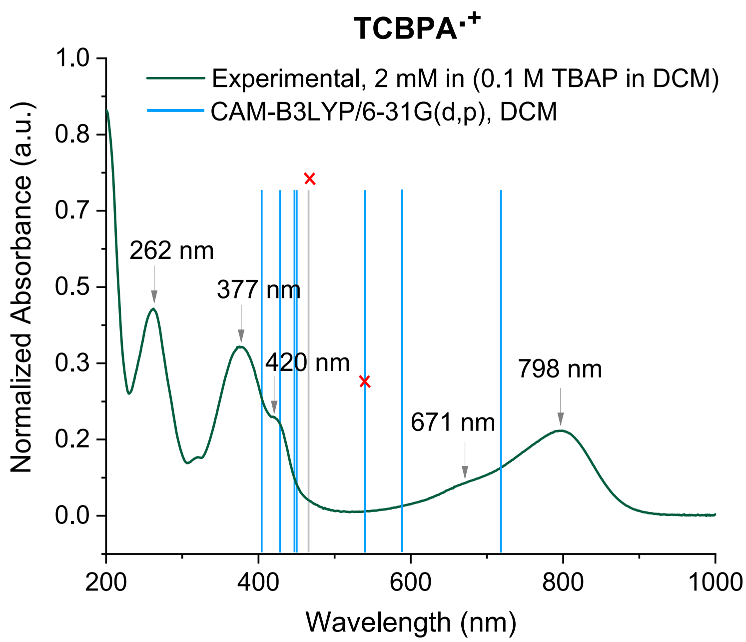


Figure S75. Comparison of experimental UV-vis spectrum of **TCBPA$^{\cdot+}$** and computed UV-vis transitions at CAM-B3LYP/6-31G(d,p), CPCM = MeCN.

TCBPA$^{\cdot+}$ in DCM (CAM-B3LYP)

67

-1718.044170 [CAM-B3LYP/6-31G(d,p)]

Charge = 1; Multiplicity = 2

C	4.20573100	-0.14578200	0.00121600
C	3.45577500	-1.06993400	-0.74133200
C	2.07651500	-1.03190800	-0.74425500
C	1.40765200	-0.04902300	0.00130400
C	2.14291200	0.88498000	0.74733100
C	3.52155000	0.82772400	0.74431900
C	5.68375800	-0.19700400	0.00065900
C	6.35321400	-1.42494300	-0.05345100
C	7.73650900	-1.47924700	-0.05243700
C	8.47474900	-0.29403300	-0.00096800
C	7.82063600	0.93964400	0.05125100
C	6.43688200	0.98154300	0.05388700
H	3.96155400	-1.80640700	-1.35430900
H	1.51272800	-1.72814900	-1.35277000
H	1.62846500	1.61820500	1.35613100
H	4.07703600	1.52722100	1.35760500
H	5.78863100	-2.35002800	-0.07135100
H	8.24678700	-2.43451300	-0.08499600
H	8.39612500	1.85715000	0.08308400
H	5.93789000	1.94359500	0.07200000
C	-0.74148900	-1.19228100	-0.00064400
C	-1.92529900	-1.27991200	-0.74899000
C	-0.30225700	-2.29585900	0.74658400
C	-2.64894400	-2.45475600	-0.74639100
H	-2.24434400	-0.44373200	-1.35884600
C	-1.04225800	-3.46051100	0.74330700
H	0.58898400	-2.21719400	1.35686400
C	-2.22637600	-3.56578700	-0.00149700
H	-3.53851000	-2.52423000	-1.36102800
H	-0.71594600	-4.29089700	1.35808800
C	-3.01194200	-4.81882900	-0.00114900
C	-4.40988800	-4.78201800	-0.05888300
C	-2.37060100	-6.06154000	0.05702100
C	-5.15099500	-5.95126500	-0.05661200
H	-4.92676700	-3.82952500	-0.08043400
C	-3.10118800	-7.23746900	0.05567400
H	-1.28812300	-6.11276900	0.07813100
C	-4.49638500	-7.18442700	-0.00025200
H	-6.23325800	-5.91333100	-0.09200000
H	-2.59633900	-8.19553500	0.09130700
C	-1.97465700	3.71076900	0.00136500
C	-2.47413900	2.63124700	0.74511000
C	-1.83333600	1.40925600	0.74813500
C	-0.65726400	1.24032300	0.00145800
C	-0.14194700	2.31109400	-0.74490800
C	-0.79967400	3.52410300	-0.74195500
C	-2.67091300	5.01558300	0.00080200
C	-4.06808900	5.07690000	0.05706200
C	-4.72537900	6.29527300	0.05469200
C	-3.98578400	7.47953700	-0.00050800
C	-2.59027800	7.43454400	-0.05514400
C	-1.94401100	6.21027300	-0.05632900
H	-3.35751400	2.76173400	1.35877700

H	-2.21009400	0.59686000	1.35722500
H	0.74248100	2.17119400	-1.35413100
H	-0.41582600	4.33028400	-1.35569800
H	-4.65053300	4.16302000	0.07747300
H	-5.80770100	6.33335100	0.08897800
H	-2.01932700	8.35476400	-0.09006700
H	-0.86059300	6.18541400	-0.07664500
N	0.00323600	-0.00026400	0.00072300
C	-5.25907600	-8.39984000	0.00019100
C	-4.66125400	8.74553300	-0.00116800
C	9.90880600	-0.34385100	-0.00177900
N	-5.20610800	9.76608900	-0.00163400
N	-5.87404500	-9.37974300	0.00054800
N	11.06500100	-0.38395700	-0.00245100

Excited State 1: Doublet 1.9290 eV 642.75 nm f=0.4465
<S**2>=0.877
133B ->143B -0.29835
136B ->143B -0.17932
141B ->143B -0.14600
142B ->143B 0.89167

Excited State 2: Doublet 1.9308 eV 642.14 nm f=0.4446
<S**2>=0.877
132B ->143B -0.29819
135B ->143B 0.18002
141B ->143B 0.89146
142B ->143B 0.14601

Excited State 3: Doublet 2.5162 eV 492.74 nm f=0.0066
<S**2>=0.872
132B ->143B 0.20394
135B ->143B 0.83945
136B ->143B 0.43398
141B ->143B -0.10470

Excited State 4: Doublet 2.5169 eV 492.61 nm f=0.0066
<S**2>=0.872
133B ->143B -0.20382
135B ->143B -0.43404
136B ->143B 0.83951
142B ->143B 0.10403

Excited State 5: Doublet 2.7609 eV 449.07 nm f=0.0039
<S**2>=0.870
134B ->143B 0.97584

Excited State 6: Doublet 2.8163 eV 440.23 nm f=0.0000
<S**2>=1.649
137A ->146A -0.11754
141A ->145A 0.22078
142A ->144A 0.22089
143A ->146A 0.22585
131B ->143B 0.20152
140B ->143B 0.71617
140B ->146B 0.16914
141B ->144B -0.22905
142B ->145B -0.22916

Excited State 7: Doublet 3.0943 eV 400.69 nm f=0.1297
<S**2>=2.393
137A ->144A -0.15583
137A ->151A -0.11486
138A ->154A 0.11692
139A ->152A 0.10199
140A ->152A 0.10677
141A ->144A -0.21546
141A ->145A -0.10684
142A ->144A 0.10653
142A ->145A -0.21569
142A ->146A 0.31516
143A ->144A 0.38347
132B ->143B 0.30053
137B ->150B 0.12571
138B ->152B -0.11723
139B ->152B -0.11276
140B ->144B -0.25197
141B ->145B -0.19271
141B ->146B 0.24663
142B ->144B -0.19269
142B ->146B 0.12593

Excited State 8: Doublet 3.0947 eV 400.63 nm f=0.1295
<S**2>=2.393
137A ->145A -0.15619
137A ->150A -0.11480
138A ->153A -0.10800
139A ->152A 0.10603
140A ->152A -0.11093
141A ->144A -0.10701
141A ->145A 0.21362
141A ->146A 0.31556
142A ->144A -0.21615
142A ->145A -0.10622
143A ->145A 0.38283
133B ->143B -0.30191
137B ->151B 0.10103
139B ->152B 0.12668
140B ->145B 0.25273
141B ->144B 0.19331
141B ->146B 0.12603
142B ->145B -0.19056
142B ->146B -0.24709

Excited State 9: Doublet 3.3141 eV 374.11 nm f=0.0000
<S**2>=1.898
134A ->147A -0.12023
137A ->146A 0.16219
138A ->152A -0.12226
141A ->145A -0.24474
142A ->144A -0.24312
143A ->146A -0.20214
131B ->143B 0.20263
137B ->152B -0.11417
140B ->143B 0.59360
140B ->146B -0.21571
141B ->144B 0.23453
142B ->145B 0.23588

Excited State 10: Doublet 3.4809 eV 356.19 nm f=0.0098
<S**2>=1.033
137B ->143B 0.22918
137B ->145B 0.13585
138B ->143B -0.50712
138B ->145B -0.15323
139B ->143B 0.75888
139B ->145B 0.13396

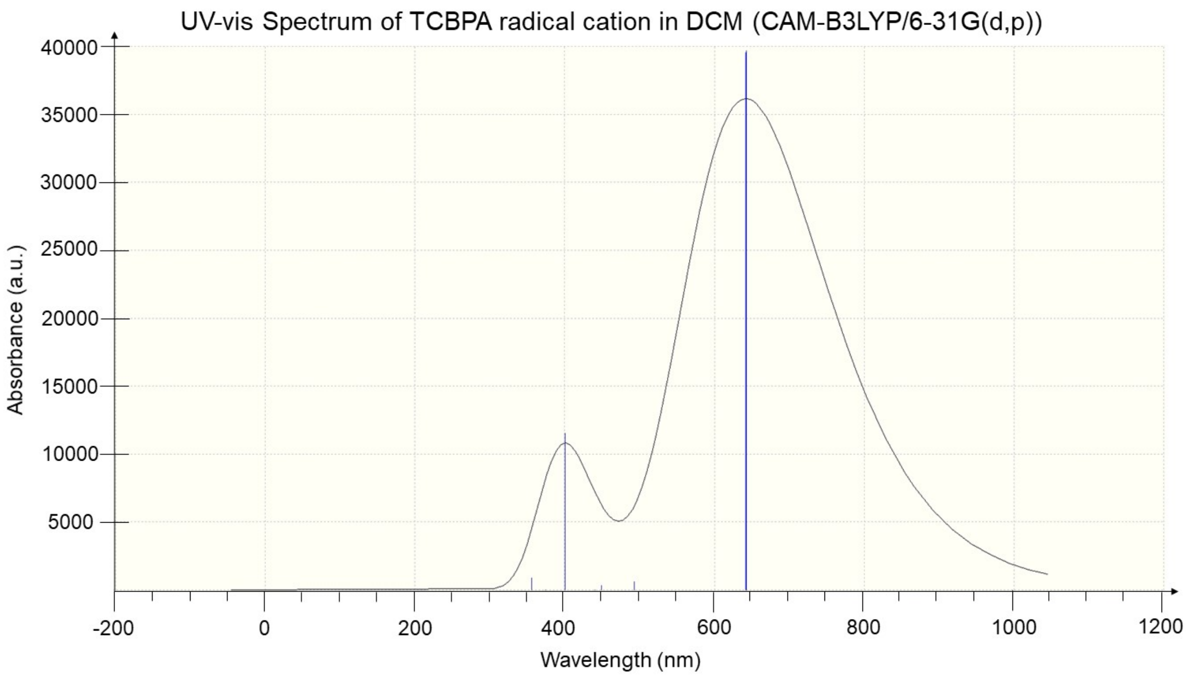


Figure S76. Computed UV-vis spectrum of **T*p*BPA$^{\cdot+}$** at CAM-B3LYP/6-31G(d,p), CPCM = DCM.

TCBPA$^{\cdot+}$ in DCM (ωb97xd)

67

-1718.459448 [ωb97xd/6-31+G(d,p)]

Charge = 1; Multiplicity = 2

C	3.45359800	2.39626600	-0.00704300
C	3.40154000	1.21519100	-0.76491600
C	2.26916000	0.42178000	-0.76955300
C	1.15269900	0.80623200	-0.00954900
C	1.18589500	1.98685300	0.75042200
C	2.32874500	2.76545100	0.74836500
C	4.67552000	3.23488900	-0.00208600
C	5.94372200	2.63922000	0.01473700
C	7.09257100	3.41730400	0.02175000
C	6.98084400	4.81228900	0.00745800
C	5.72103500	5.42190100	-0.01145000
C	4.57945800	4.63289300	-0.01401900
H	4.24482400	0.93167000	-1.38498900
H	2.22629000	-0.46842900	-1.38684900
H	0.33733200	2.26127600	1.36685700
H	2.36162400	3.65304800	1.37053700
H	6.03688800	1.55885900	0.04620900
H	8.07025300	2.94973200	0.04434500

H	5.63927000	6.50272000	-0.03053600
H	3.60664500	5.11155900	-0.05009500
C	0.11611300	-1.39473200	-0.00826900
C	-0.77370300	-2.17141300	-0.76822800
C	1.12317900	-2.01219100	0.75150500
C	-0.65017200	-3.54849600	-0.76328500
H	-1.52392800	-1.69150900	-1.38641500
C	1.22832400	-3.39090600	0.75002800
H	1.78355000	-1.41305800	1.36820400
C	0.34748400	-4.18223100	-0.00496100
H	-1.31552100	-4.13846400	-1.38396200
H	1.98186300	-3.86171800	1.37177800
C	0.46721200	-5.65918900	-0.00048900
C	-0.67980800	-6.46408400	0.01429800
C	1.72848600	-6.26978500	-0.01027500
C	-0.57476600	-7.84762500	0.02003300
H	-1.66410500	-6.00893000	0.04587700
C	1.84646800	-7.65240600	-0.00886700
H	2.62690100	-5.66255000	-0.04284800
C	0.69173800	-8.44316700	0.00697900
H	-1.46626100	-8.46391600	0.04089900
H	2.82505900	-8.11838400	-0.02622400
C	-3.80319200	1.79501800	-0.00222200
C	-3.55917100	0.63236700	0.74652300
C	-2.31206600	0.03538600	0.74787400
C	-1.27228700	0.60366900	-0.00627500
C	-1.49854300	1.76837800	-0.75807800
C	-2.75355000	2.34870900	-0.75309700
C	-5.14361400	2.42673000	0.00107000
C	-6.30108500	1.63690100	-0.01008800
C	-7.55893800	2.22278900	-0.00969400
C	-7.67004300	3.61788800	0.00627900
C	-6.52292800	4.41990100	0.02036600
C	-5.27073800	3.82214500	0.01585600
H	-4.34525400	0.21011900	1.36282600
H	-2.12540200	-0.84040000	1.35890900
H	-0.70578500	2.18387900	-1.36970200
H	-2.93069700	3.22434500	-1.36790500
H	-6.22165000	0.55544000	-0.04266000
H	-8.44996300	1.60571400	-0.02775100
H	-6.61366600	5.49997800	0.04093300
H	-4.38584100	4.44892200	0.04731300
N	-0.00147900	0.00501800	-0.00826000
C	0.80776900	-9.87552300	0.01015200
C	-8.97003200	4.23052000	0.00829100
C	8.16713000	5.62345500	0.01183300
N	-10.01890000	4.72532200	0.00985900
N	0.90186000	-11.03148700	0.01264500
N	9.12469900	6.27769400	0.01532600

Excited State 1: Doublet 1.9911 eV 622.69 nm f=0.4324
<S**2>=0.859
132B ->143B -0.34518
136B ->143B -0.25030
142B ->143B 0.86919

Excited State 2: Doublet 1.9988 eV 620.29 nm f=0.4275
<S**2>=0.860
133B ->143B -0.34564
135B ->143B 0.25579

141B ->143B 0.86715

Excited State 3: Doublet 2.5110 eV 493.75 nm f=0.0159
<S**2>=0.867
133B ->143B 0.28161
135B ->143B 0.90716
136B ->143B -0.16231
141B ->143B -0.14194

Excited State 4: Doublet 2.5132 eV 493.33 nm f=0.0154
<S**2>=0.867
132B ->143B -0.27798
135B ->143B 0.16246
136B ->143B 0.90877
142B ->143B 0.13814

Excited State 5: Doublet 2.7645 eV 448.48 nm f=0.0045
<S**2>=0.868
134B ->143B 0.97304

Excited State 6: Doublet 2.9984 eV 413.50 nm f=0.0000
<S**2>=1.800
137A ->146A 0.13255
141A ->145A 0.24842
142A ->144A 0.25229
143A ->146A -0.23642
131B ->143B -0.24589
140B ->143B 0.63868
140B ->146B 0.18812
141B ->145B -0.27324
142B ->144B -0.27664

Excited State 7: Doublet **3.2290 eV** **383.97 nm** f=0.1075
<S**2>=2.404
137A ->144A -0.16339
137A ->149A -0.12813
138A ->150A -0.13202
141A ->144A -0.14582
141A ->145A 0.19420
142A ->144A -0.19007
142A ->145A -0.14736
142A ->146A -0.33191
143A ->144A 0.38283
132B ->143B 0.30434
137B ->150B -0.15535
138B ->152B 0.10014
140B ->144B -0.26730
141B ->145B -0.18293
142B ->144B 0.17763
142B ->146B 0.27440

Excited State 8: Doublet **3.2311 eV** **383.72 nm** f=0.1058
<S**2>=2.408
137A ->145A -0.16359
137A ->148A -0.12771
139A ->151A 0.13255
139A ->153A -0.10273
140A ->152A -0.13562
141A ->144A 0.19079
141A ->145A 0.14675

141A ->146A -0.33382
142A ->144A -0.14562
142A ->145A 0.19281
143A ->145A 0.38021
133B ->143B 0.30341
138B ->151B 0.15674
139B ->152B -0.13887
140B ->145B -0.26753
141B ->144B -0.17994
141B ->146B 0.27583
142B ->145B -0.18106

Excited State 9: Doublet 3.5329 eV 350.94 nm f=0.0001
<S**2>=1.734
137A ->146A -0.18740
141A ->145A -0.23351
142A ->144A -0.23621
143A ->146A 0.17444
131B ->143B -0.33457
139B ->151B 0.10740
140B ->143B 0.58762
140B ->146B -0.22395
141B ->145B 0.19564
142B ->144B 0.19646

Excited State 10: Doublet 3.6770 eV 337.19 nm f=0.3403
<S**2>=1.593
132A ->144A 0.10101
133A ->145A -0.10162
134A ->154A 0.10304
135A ->147A -0.18287
137A ->144A 0.16326
142A ->156A -0.10768
143A ->144A 0.45183
143A ->149A -0.23153
143A ->153A -0.10808
132B ->143B -0.38555
134B ->154B 0.11609
135B ->147B 0.16292
136B ->143B -0.10919
140B ->144B 0.12600
142B ->143B -0.28343

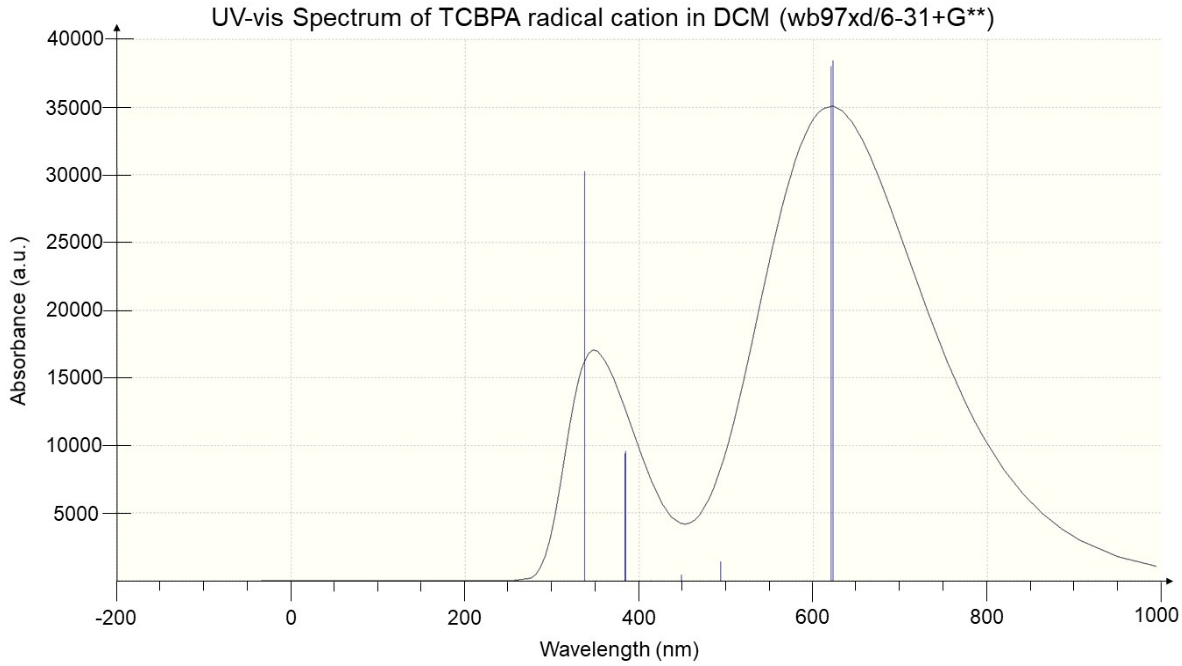


Figure S77. Computed UV-vis spectrum of **TCBPA·+** at ωb97xd/6-31+G(d,p), CPCM = DCM.

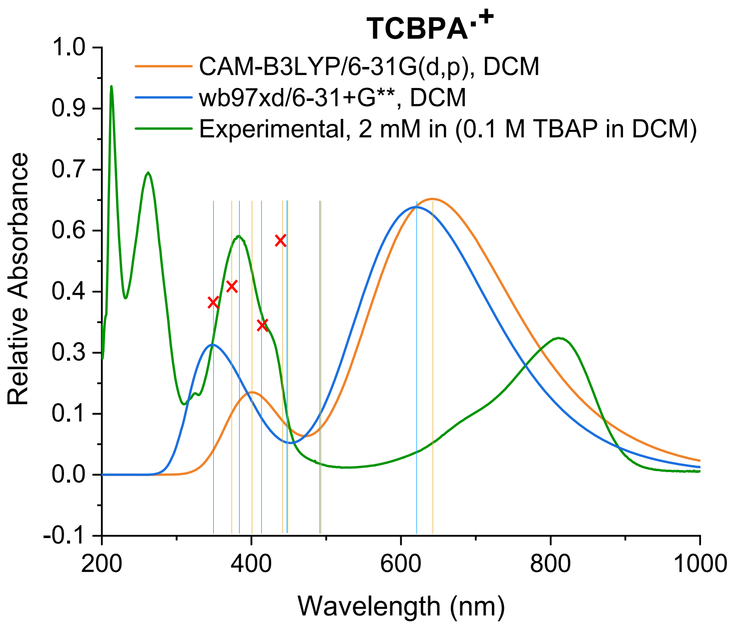
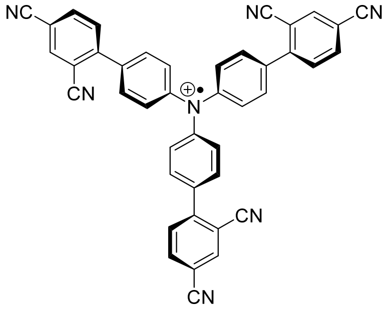


Figure S78. Comparison of experimental UV-vis spectrum of **TCBPA·+** and computed UV-vis transitions at CAM-B3LYP/6-31G(d,p) and ωb97xd/6-31+G(d,p), CPCM = DCM.

TdCBPA·+ in MeCN (CAM-B3LYP)



70

-1994.651364 [CAM-B3LYP/6-31G(d,p)]

Charge = 1; Multiplicity = 2

C	-4.17303400	0.48217600	-0.05569100
C	-3.57500100	-0.55169400	0.67720100
C	-2.20473100	-0.71753900	0.67933100
C	-1.40146900	0.16137100	-0.06286200
C	-1.98808500	1.19657100	-0.80629100
C	-3.36031000	1.34746200	-0.79981400
C	-5.64805100	0.62111100	-0.05775100
C	-6.44343200	-0.50630700	-0.26903800
C	-7.82541800	-0.42092800	-0.28954000
C	-8.44670100	0.81375600	-0.08883900
C	-7.68008600	1.95373200	0.13722200
C	-6.29015800	1.85723200	0.15297100
H	-4.18913200	-1.21283200	1.27726500
H	-1.74972000	-1.49326200	1.28230400
H	-1.37168400	1.84533900	-1.41590100
H	-3.80559500	2.12592400	-1.40721400
H	-5.96780200	-1.46420900	-0.44243200
H	-8.42359800	-1.30680200	-0.46565700
H	-8.15745400	2.91016400	0.30957800
C	0.55696200	-1.28580900	-0.06156800
C	1.71442400	-1.54324700	0.68795400
C	-0.04089700	-2.30921700	-0.81168900
C	2.25616100	-2.81292400	0.68634500
H	2.15500700	-0.76254600	1.29529100
C	0.51541800	-3.57272700	-0.80548500
H	-0.90707800	-2.09781300	-1.42608100
C	1.66605300	-3.84564900	-0.05431100
H	3.13160100	-3.01573400	1.29178900
H	0.06871500	-4.34591200	-1.41815600
C	2.28435800	-5.19230300	-0.05603300
C	3.66061200	-5.31449400	-0.25425500
C	1.53465300	-6.36866600	0.14242300
C	4.27967100	-6.55295500	-0.27293400
H	4.25296900	-4.42219900	-0.41825100
C	2.14818900	-7.61960200	0.12850100
C	3.52113800	-7.71016000	-0.08390800
H	5.34779400	-6.62594200	-0.43800000
H	1.55830700	-8.51301800	0.29067300
C	2.50101400	3.36810300	-0.05684800
C	2.83712400	2.23308400	-0.80612000
C	2.01744000	1.12244100	-0.81213000
C	0.83157800	1.13266100	-0.06278500
C	0.47885300	2.26600800	0.68535600

C	1.31055500	3.36787000	0.68232300
C	3.36342500	4.57296500	-0.05891800
C	4.75571500	4.50483900	0.14591500
C	5.53888200	5.65742000	0.13065900
C	4.93833800	6.89419300	-0.08936300
C	3.55813800	6.97929500	-0.28438300
C	2.78870200	5.82824700	-0.26411700
H	3.73080800	2.22902600	-1.41794800
H	2.26544700	0.26513600	-1.42533400
H	-0.41736900	2.26039100	1.29301300
H	1.05067500	4.22919600	1.28642000
H	6.60673100	5.58835300	0.29731900
H	3.09339300	7.94263700	-0.45614000
H	1.72096500	5.90034700	-0.43351900
N	-0.00505100	0.00318000	-0.06300400
C	4.15512200	-8.99763500	-0.10223900
C	5.74322000	8.08233600	-0.10945600
C	-9.87854400	0.91213300	-0.10914700
N	6.38887300	9.04142500	-0.12608900
N	4.66940800	-10.03317500	-0.11740300
N	-11.03227000	0.98790700	-0.12624300
C	-5.54398500	3.05155700	0.43769000
C	0.12443300	-6.32311900	0.41249000
C	5.41237100	3.25757400	0.42382700
N	5.96717500	2.27024000	0.65758700
N	-1.00935300	-6.31858800	0.64015800
N	-4.97147700	4.02741200	0.67682700

Excited State 1: Doublet 1.9649 eV 630.98 nm f=0.3705
<S**2>=0.861
151B ->161B -0.29342
155B ->161B 0.19227
157B ->161B 0.21466
158B ->161B -0.12416
160B ->161B -0.86730

Excited State 2: Doublet 2.1193 eV 585.03 nm f=0.1130
<S**2>=0.856
150B ->161B -0.13954
156B ->161B -0.72471
159B ->161B -0.63637

Excited State 3: Doublet 2.3462 eV 528.45 nm f=0.1837
<S**2>=0.943
161A ->162A -0.10477
150B ->161B -0.34523
152B ->161B -0.15848
154B ->161B -0.11802
156B ->161B 0.62004
159B ->161B -0.59932

Excited State 4: Doublet 2.5758 eV 481.35 nm f=0.0056
<S**2>=0.883
151B ->161B -0.30332
153B ->161B -0.55481
154B ->161B -0.18077
155B ->161B -0.68277
157B ->161B -0.18320
160B ->161B -0.11519

Excited State 5: Doublet 2.7668 eV 448.12 nm f=0.0029
<S**2>=0.896
150B ->161B -0.13066
152B ->161B 0.95091
156B ->161B 0.11283

Excited State 6: Doublet 2.8648 eV 432.79 nm f=0.0012
<S**2>=1.923
155A ->165A 0.11339
156A ->164A -0.11822
158A ->168A 0.12910
158A ->169A 0.10064
159A ->162A -0.21525
160A ->163A -0.19840
160A ->164A 0.16752
161A ->164A 0.17334
148B ->161B -0.12799
151B ->161B -0.11981
153B ->161B -0.12321
154B ->165B -0.10793
157B ->161B 0.51084
157B ->164B 0.12788
158B ->161B -0.26956
158B ->164B -0.11387
158B ->168B -0.16812
159B ->162B 0.21593
160B ->161B 0.16577
160B ->163B -0.18305
160B ->164B 0.19393

Excited State 7: Doublet **3.0023 eV** **412.97 nm** f=0.0312
<S**2>=2.369
154A ->166A -0.12670
155A ->165A 0.16130
156A ->163A -0.20096
158A ->168A -0.15427
158A ->169A -0.11572
159A ->162A -0.26653
160A ->164A -0.26324
161A ->163A 0.21345
151B ->161B 0.30946
153B ->166B 0.11343
154B ->165B -0.15171
157B ->163B 0.22463
158B ->161B 0.27564
158B ->163B -0.10695
158B ->164B 0.11898
158B ->168B 0.18881
159B ->162B 0.23683
160B ->164B -0.23302

Excited State 8: Doublet **3.0460 eV** **407.04 nm** f=0.0586
<S**2>=2.525
154A ->165A -0.20923
155A ->166A 0.22526
156A ->162A -0.25238
159A ->163A -0.32491
159A ->164A -0.13504
160A ->162A -0.19267
161A ->162A 0.21967

150B ->161B -0.27416
150B ->163B -0.11461
151B ->162B 0.11276
153B ->165B 0.19226
154B ->161B -0.11180
154B ->163B -0.11651
154B ->164B -0.10199
154B ->166B -0.21145
155B ->162B -0.14981
155B ->165B -0.13790
157B ->162B 0.26225
159B ->163B 0.26995
159B ->164B 0.10935
160B ->162B -0.11478

Excited State 9: Doublet **3.1773 eV** **390.22 nm** f=0.0081
<S**2>=1.122
160A ->164A -0.13572
161A ->164A -0.10919
157B ->161B -0.23341
158B ->161B -0.87024
158B ->168B 0.13000
160B ->164B -0.14411

Excited State 10: Doublet 3.2793 eV 378.08 nm f=0.0224
<S**2>=1.626
156A ->163A 0.10085
157A ->172A 0.12348
158A ->168A -0.16066
158A ->169A -0.12495
160A ->163A 0.11977
160A ->164A -0.17340
161A ->163A 0.10645
161A ->164A -0.19541
148B ->161B -0.17431
151B ->161B -0.20954
153B ->161B -0.11697
157B ->161B 0.56625
158B ->164B 0.11734
158B ->168B 0.18232
160B ->161B 0.29809
160B ->163B 0.12338
160B ->164B -0.16977

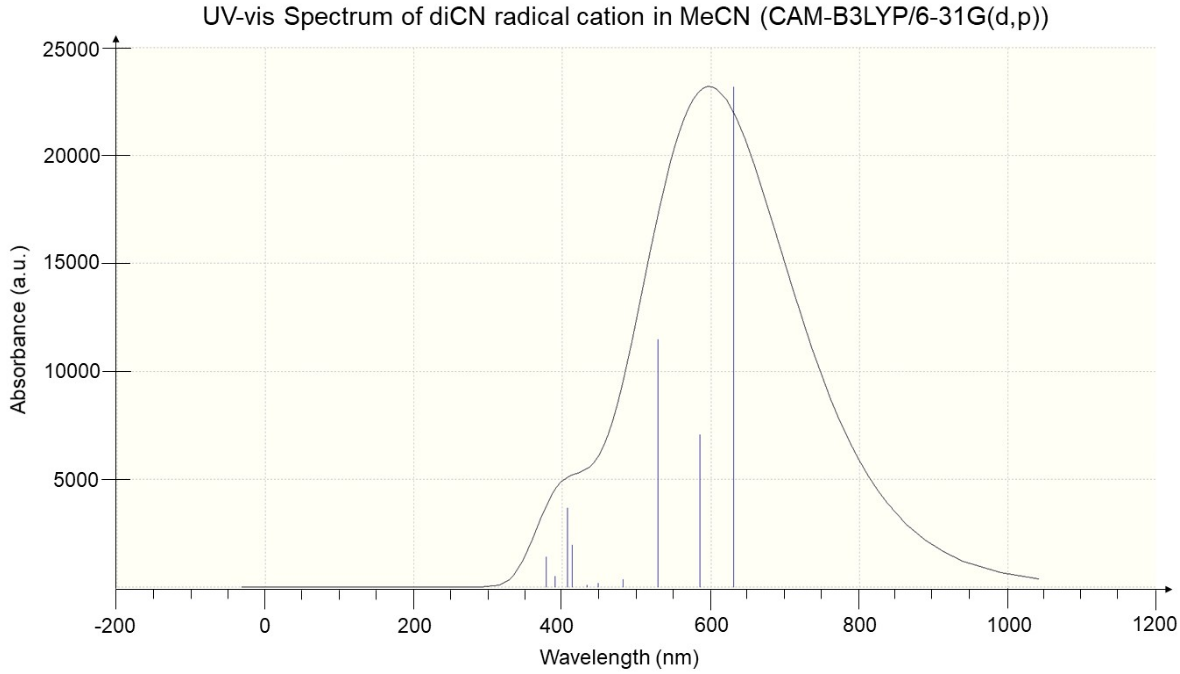


Figure S79. Computed UV-vis spectrum of **TdCBPA$^{\cdot+}$** at CAM-B3LYP/6-31G(d,p), CPCM = MeCN.

TdCBPA$^{\cdot+}$ in DCM (CAM-B3LYP)

70

-1994.642135 [CAM-B3LYP/6-31G(d,p)]

Charge = 1; Multiplicity = 2

C	3.69202100	-2.00171300	0.06077600
C	2.60884900	-2.50669100	-0.67106000
C	1.39036300	-1.85801500	-0.67217600
C	1.23551400	-0.67724400	0.07001500
C	2.30977500	-0.16545300	0.81329300
C	3.52109700	-0.82745700	0.80572300
C	4.98293400	-2.72887900	0.05788800
C	4.99492000	-4.10913700	0.26533800
C	6.17962100	-4.82606200	0.28106300
C	7.39302400	-4.16476800	0.07942000
C	7.41163700	-2.79033200	-0.14275700
C	6.21421300	-2.07796100	-0.15351800
H	2.73381000	-3.39954400	-1.27237000
H	0.57301400	-2.23327300	-1.27515600
H	2.17652800	0.71968200	1.42265700
H	4.33273500	-0.44370000	1.41160600
H	4.05897500	-4.62631000	0.43995300
H	6.16750600	-5.89537000	0.45439400
H	8.34843800	-2.27528200	-0.31498100
C	-1.19937800	-0.73616400	0.06750300
C	-2.29316500	-0.28384700	-0.68565100
C	-1.30025200	-1.91547700	0.82037100
C	-3.46593300	-1.01200900	-0.68535000
H	-2.20376800	0.60660100	-1.29527400
C	-2.48136300	-2.63024000	0.81275500
H	-0.47130700	-2.23900400	1.43739700
C	-3.57823200	-2.19478600	0.05762200

H	-4.29703400	-0.67719200	-1.29478000
H	-2.56103500	-3.51896600	1.42654500
C	-4.85666800	-2.94379800	0.05535700
C	-6.05604500	-2.25543300	0.24505000
C	-4.91423300	-4.33792100	-0.13888900
C	-7.27286200	-2.91632700	0.25870600
H	-6.03192500	-1.18427800	0.40660800
C	-6.13359900	-5.01215400	-0.12984800
C	-7.31266200	-4.29983800	0.07317300
H	-8.19132400	-2.36426000	0.41733200
H	-6.16033200	-6.08291200	-0.28883200
C	-0.11304600	4.19028300	0.05908700
C	-1.03982600	3.45581800	0.81048500
C	-1.00823300	2.07575500	0.81763900
C	-0.03339600	1.40091400	0.06772500
C	0.90653700	2.12445200	-0.68164400
C	0.85961700	3.50415000	-0.68031000
C	-0.12558000	5.67185400	0.05817500
C	-1.30463600	6.41628900	-0.14249100
C	-1.28219400	7.80944400	-0.13080000
C	-0.07865100	8.47675900	0.08129300
C	1.10021500	7.75297300	0.27241000
C	1.06753000	6.36865900	0.25586300
H	-1.77296200	3.96724400	1.42204300
H	-1.70375700	1.51780600	1.43204800
H	1.63590000	1.60370700	-1.28946000
H	1.56657900	4.05861700	-1.28622000
H	-2.19636400	8.36623800	-0.29452800
H	2.03526900	8.27433100	0.43790200
H	1.98335700	5.81388800	0.42189100
N	0.00145100	-0.00449300	0.06901700
C	-8.56984800	-4.99241100	0.08617500
C	-0.05361600	9.91182900	0.09764900
C	8.62577900	-4.89992400	0.09582700
N	-0.03064700	11.06771200	0.11151300
N	-9.58381200	-5.54788500	0.09733000
N	9.61732100	-5.49444100	0.10981300
C	6.27922800	-0.67020000	-0.43290000
C	-3.72951500	-5.10787900	-0.39886800
C	-2.56044900	5.77255500	-0.41181500
N	-3.58173600	5.27916600	-0.63715000
N	-2.79202700	-5.74898700	-0.61645100
N	6.35812700	0.45954500	-0.66672900

Excited State 1: Doublet 2.0489 eV 605.14 nm f=0.3770
<S**2>=0.873
151B ->161B -0.31907
154B ->161B -0.20953
156B ->161B 0.12378
157B ->161B 0.14386
159B ->161B -0.25299
160B ->161B 0.83240

Excited State 2: Doublet 2.0538 eV 603.69 nm f=0.3728
<S**2>=0.875
150B ->161B 0.31821
153B ->161B 0.21700
156B ->161B -0.14387
157B ->161B 0.12308
159B ->161B 0.83081

160B ->161B   0.25244

Excited State   3:   Doublet   2.4496 eV   506.14 nm   f=0.0252
<S**2>=0.880
150B ->161B   -0.26966
153B ->161B   0.80481
154B ->161B   -0.26537
156B ->161B   -0.27648
157B ->161B   0.23056
159B ->161B   -0.14908

Excited State   4:   Doublet   2.4524 eV   505.55 nm   f=0.0247
<S**2>=0.880
151B ->161B   -0.26840
153B ->161B   0.26463
154B ->161B   0.80119
156B ->161B   -0.23713
157B ->161B   -0.28692
160B ->161B   0.14407

Excited State   5:   Doublet   2.6733 eV   463.78 nm   f=0.0045
<S**2>=0.872
152B ->161B   0.97443

Excited State   6:   Doublet   2.8937 eV   428.46 nm   f=0.0000
<S**2>=2.157
153A ->167A   -0.12066
156A ->165A   0.16240
157A ->166A   0.16182
158A ->164A   0.17149
159A ->162A   0.26244
160A ->163A   0.26218
161A ->164A   0.21076
149B ->161B   0.15358
155B ->167B   0.16174
156B ->165B   0.13628
157B ->166B   -0.13611
158B ->161B   0.52538
158B ->164B   0.23162
159B ->162B   -0.25604
160B ->163B   -0.25693

Excited State   7:   Doublet   **3.0233 eV**   **410.10 nm**   f=0.0521
<S**2>=2.526
153A ->163A   -0.10233
156A ->165A   0.13817
156A ->167A   0.10597
157A ->166A   -0.13662
157A ->167A   -0.13077
158A ->162A   0.10079
158A ->163A   -0.15326
158A ->165A   0.10793
158A ->166A   -0.12013
159A ->162A   0.19672
159A ->164A   0.17714
160A ->163A   -0.20084
160A ->164A   -0.23046
161A ->162A   0.13927
161A ->163A   -0.21630
150B ->161B   0.17392

151B ->161B -0.22385
155B ->165B 0.12119
155B ->166B -0.15934
156B ->165B 0.10434
157B ->161B 0.11683
157B ->164B 0.13534
157B ->166B 0.10729
157B ->167B 0.13816
158B ->162B 0.12922
158B ->163B 0.24794
159B ->162B 0.11813
159B ->163B 0.13386
160B ->162B 0.13513
160B ->163B -0.11322
160B ->164B -0.23292

Excited State 8: Doublet **3.0234 eV** **410.08 nm** f=0.0520
<S**2>=2.527
153A ->162A -0.10213
156A ->166A 0.14030
156A ->167A -0.12511
157A ->165A 0.13818
157A ->167A -0.10829
158A ->162A -0.15321
158A ->163A -0.10068
158A ->165A -0.11897
158A ->166A -0.10943
159A ->163A 0.19842
159A ->164A -0.23092
160A ->162A 0.19858
160A ->164A -0.17689
161A ->162A -0.21574
161A ->163A -0.14000
150B ->161B 0.22239
151B ->161B 0.17497
155B ->165B -0.16012
155B ->166B -0.12015
156B ->161B -0.11746
156B ->164B -0.13568
156B ->166B 0.10734
156B ->167B -0.13639
157B ->165B -0.10356
158B ->162B 0.24647
158B ->163B -0.13110
159B ->162B -0.13430
159B ->163B 0.11739
159B ->164B -0.23306
160B ->162B 0.11772
160B ->163B 0.13219

Excited State 9: Doublet 3.3672 eV 368.22 nm f=0.0000
<S**2>=1.436
153A ->167A 0.10164
156A ->165A -0.14595
157A ->166A -0.14429
158A ->164A -0.15658
159A ->162A -0.14783
160A ->163A -0.14626
140B ->161B 0.10393
149B ->161B 0.29963

155B ->161B -0.24818
155B ->167B -0.12953
156B ->165B -0.11792
157B ->166B 0.11694
158B ->161B 0.68616
158B ->164B -0.17653
159B ->162B 0.11592
160B ->163B 0.11686

Excited State 10: Doublet 3.5215 eV 352.08 nm f=0.1849
<S**2>=1.428
152A ->171A 0.12920
154A ->168A -0.15589
155A ->172A 0.10078
161A ->162A -0.36223
161A ->163A 0.11260
161A ->165A 0.11014
161A ->169A -0.19111
151B ->161B -0.29733
153B ->168B -0.13680
156B ->161B 0.43811
157B ->161B 0.27555
159B ->161B 0.13290
160B ->161B -0.29187

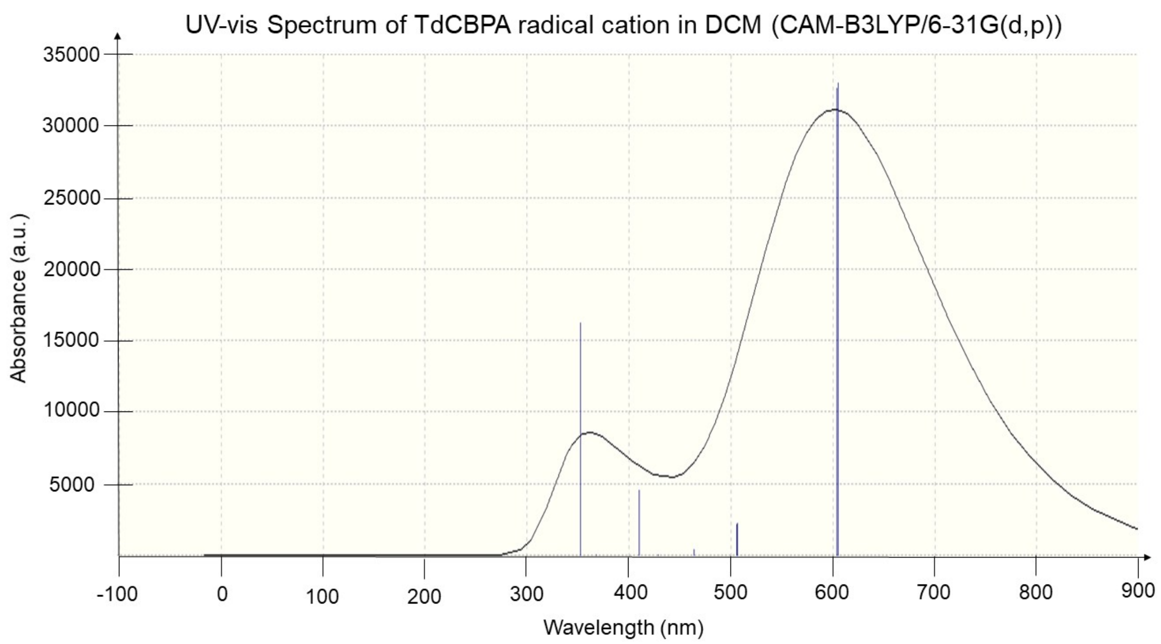
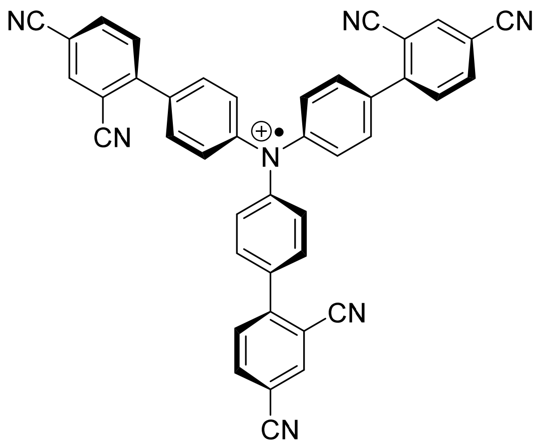


Figure S80. Computed UV-vis spectrum of **TdCBPA**$^{\cdot+}$ at CAM-B3LYP/6-31G(d,p), CPCM = DCM.

TdCBPA$^{\cdot+}$ in DCM (ωb97xd)



70

-1995.088780 [ωb97xd/6-31G(d,p)]

Charge = 1; Multiplicity = 2

C	3.36054900	-2.50664400	0.11125400
C	2.21905000	-2.84605600	-0.62884600
C	1.10346400	-2.02809400	-0.61989100
C	1.12164000	-0.84824400	0.14141400
C	2.25356600	-0.50401300	0.89753200
C	3.36000000	-1.33327700	0.87936000
C	4.54499000	-3.39982700	0.08695900
C	4.39284000	-4.76093300	0.36185900
C	5.48181500	-5.62119600	0.35513500
C	6.75617000	-5.12420900	0.06216400
C	6.93744500	-3.77226600	-0.22863900
C	5.83426800	-2.91748600	-0.21644200
H	2.21742600	-3.74089400	-1.24164700
H	0.23986900	-2.27378600	-1.22715000
H	2.24562500	0.38394000	1.51924700
H	4.21930200	-1.07961800	1.49002500
H	3.40923600	-5.14834300	0.60315900
H	5.34681100	-6.67277700	0.58030100
H	7.92116600	-3.38754000	-0.47039600
C	-1.29409200	-0.55029000	0.13980300
C	-2.30564700	0.05732200	-0.62177100
C	-1.56501000	-1.70229500	0.89610200
C	-3.57277500	-0.49738400	-0.63220900
H	-2.08495400	0.92809900	-1.22820700
C	-2.83790200	-2.24230700	0.87784700
H	-0.79342200	-2.14112600	1.51813800
C	-3.85224300	-1.65467900	0.10821700
H	-4.34564200	-0.04667400	-1.24523400
H	-3.05113900	-3.11192400	1.48926300
C	-5.21895400	-2.23142200	0.08395400
C	-6.32018700	-1.41629100	0.35588400
C	-5.44837000	-3.58940100	-0.21620000
C	-7.61077300	-1.92685900	0.35086800
H	-6.16209400	-0.37011500	0.59326300
C	-6.74119800	-4.11491800	-0.22649900
C	-7.81974700	-3.27967800	0.06321300
H	-8.45283900	-1.28195700	0.57369300
H	-6.90225000	-5.15914400	-0.46611400

C	0.49177600	4.15980800	0.11135200
C	-0.52395600	3.57327400	0.87991400
C	-0.69051300	2.20077500	0.89652700
C	0.17165200	1.39219400	0.13860200
C	1.20223100	1.96579000	-0.62367300
C	1.35470800	3.34080800	-0.63088600
C	0.67454200	5.63197900	0.08777900
C	-0.38613800	6.50821700	-0.21823700
C	-0.19655300	7.89080300	-0.23045800
C	1.06444700	8.40887300	0.06444400
C	2.13053800	7.55265100	0.36044800
C	1.92903400	6.17960300	0.36623600
H	-1.17127700	4.19105300	1.49250200
H	-1.45503900	1.74999000	1.51879600
H	1.84527800	1.34053000	-1.23238200
H	2.13030900	3.78658900	-1.24413000
H	-1.02038300	8.55094500	-0.47523200
H	3.10867900	7.96046000	0.58793300
H	2.75506200	5.52060200	0.60938800
N	-0.00040500	-0.00243800	0.14366700
C	-9.15320100	-3.81621800	0.05992200
C	1.26678100	9.83207900	0.05680600
C	7.88825400	-6.00995200	0.05425100
N	1.43282100	10.97907700	0.05204800
N	-10.22921800	-4.24677500	0.05846000
N	8.79906000	-6.72660800	0.04879900
C	6.04424900	-1.53851300	-0.56825500
C	-4.36085800	-4.46310600	-0.56713800
C	-1.68474500	6.00080800	-0.57232600
N	-2.73454800	5.60852800	-0.86859400
N	-3.49766200	-5.17856500	-0.86143000
N	6.22900900	-0.43248300	-0.86201600

Excited State 1:	Doublet	2.0981 eV	590.94 nm	f=0.3438	<S**2>=0.850
150B -> 161B	-0.32115				
151B -> 161B	0.11187				
155B -> 161B	-0.16117				
156B -> 161B	0.14251				
157B -> 161B	-0.29957				
160B -> 161B	0.82793				
Excited State 2:	Doublet	2.1016 eV	589.95 nm	f=0.3409	<S**2>=0.850
150B -> 161B	-0.11083				
151B -> 161B	-0.32083				
154B -> 161B	-0.16667				
156B -> 161B	0.30278				
157B -> 161B	0.14244				
159B -> 161B	0.82589				
Excited State 3:	Doublet	2.4658 eV	502.82 nm	f=0.0466	<S**2>=0.872
150B -> 161B	-0.34725				
154B -> 161B	0.21618				
155B -> 161B	0.51782				
156B -> 161B	-0.29675				
157B -> 161B	0.61030				
160B -> 161B	0.20446				
Excited State 4:	Doublet	2.4659 eV	502.80 nm	f=0.0473	<S**2>=0.872
151B -> 161B	0.35005				
154B -> 161B	-0.52137				

155B -> 161B 0.21847
156B -> 161B 0.60386
157B -> 161B 0.29473
159B -> 161B -0.20769

Excited State 5: Doublet 2.6844 eV 461.86 nm f=0.0049 <S**2>=0.870
152B -> 161B 0.97078

Excited State 6: Doublet 3.0847 eV 401.94 nm f=0.0000 <S**2>=2.298
153A -> 165A 0.12241
156A -> 166A -0.15565
157A -> 167A 0.15334
158A -> 164A -0.20313
159A -> 163A -0.27078
160A -> 162A -0.27458
161A -> 164A -0.20438
149B -> 161B -0.18059
153B -> 167B -0.14475
154B -> 165B -0.11651
155B -> 166B -0.11571
158B -> 161B 0.44143
158B -> 164B -0.24887
159B -> 163B 0.27072
160B -> 162B 0.27381

Excited State 7: Doublet 3.1745 eV **390.56 nm** **f=0.0337** <S**2>=2.580
153A -> 162A -0.10241
153A -> 166A 0.13601
153A -> 170A -0.10699
156A -> 164A -0.10855
156A -> 165A -0.13054
156A -> 167A -0.13217
157A -> 166A 0.13097
158A -> 162A -0.20894
158A -> 166A -0.13688
159A -> 162A -0.19646
160A -> 163A -0.19847
160A -> 164A -0.29145
161A -> 162A -0.24719
150B -> 161B -0.24461
153B -> 165B -0.19747
156B -> 164B -0.10562
158B -> 162B -0.29220
159B -> 162B 0.16195
160B -> 163B 0.16262
160B -> 164B 0.23508

Excited State 8: Doublet 3.1752 eV **390.48 nm** **f=0.0331** <S**2>=2.582
153A -> 163A -0.10188
153A -> 167A 0.13437
153A -> 169A 0.10625
156A -> 166A -0.12862
157A -> 164A 0.10885
157A -> 165A 0.13323
157A -> 167A -0.12906
158A -> 163A -0.20969
158A -> 167A -0.13899
159A -> 163A 0.19816
159A -> 164A -0.29375
160A -> 162A -0.19443

161A -> 163A	-0.24574
151B -> 161B	-0.24395
153B -> 166B	0.19012
155B -> 166B	0.10160
157B -> 164B	-0.10577
158B -> 163B	-0.29281
159B -> 163B	-0.16336
159B -> 164B	0.23673
160B -> 162B	0.15949

Excited State 9:	Doublet	3.5529 eV	348.97 nm	f=0.0001	<S**2>=1.418
156A -> 166A	0.13250				
157A -> 167A	-0.13160				
158A -> 164A	0.17991				
159A -> 169A	-0.10505				
160A -> 170A	0.10485				
161A -> 174A	-0.11054				
119B -> 161B	-0.10162				
140B -> 161B	0.13922				
149B -> 161B	-0.45853				
153B -> 161B	-0.25018				
153B -> 167B	0.10679				
158B -> 161B	0.56175				
158B -> 164B	0.16523				
159B -> 169B	0.10188				
160B -> 170B	-0.10152				

Excited State 10:	Doublet	3.7106 eV	334.14 nm	f=0.3194	<S**2>=1.711
152A -> 171A	-0.13226				
154A -> 165A	0.11807				
154A -> 168A	-0.14232				
154A -> 171A	-0.11059				
155A -> 172A	-0.11040				
159A -> 163A	0.10331				
160A -> 162A	-0.10480				
161A -> 162A	0.39438				
161A -> 163A	-0.27605				
161A -> 166A	-0.12038				
161A -> 169A	-0.20005				
161A -> 170A	-0.23781				
150B -> 161B	-0.11807				
151B -> 161B	0.13315				
152B -> 171B	0.10902				
152B -> 172B	-0.10035				
156B -> 168B	-0.12788				
157B -> 161B	-0.19413				
159B -> 161B	0.15654				
160B -> 161B	-0.22934				

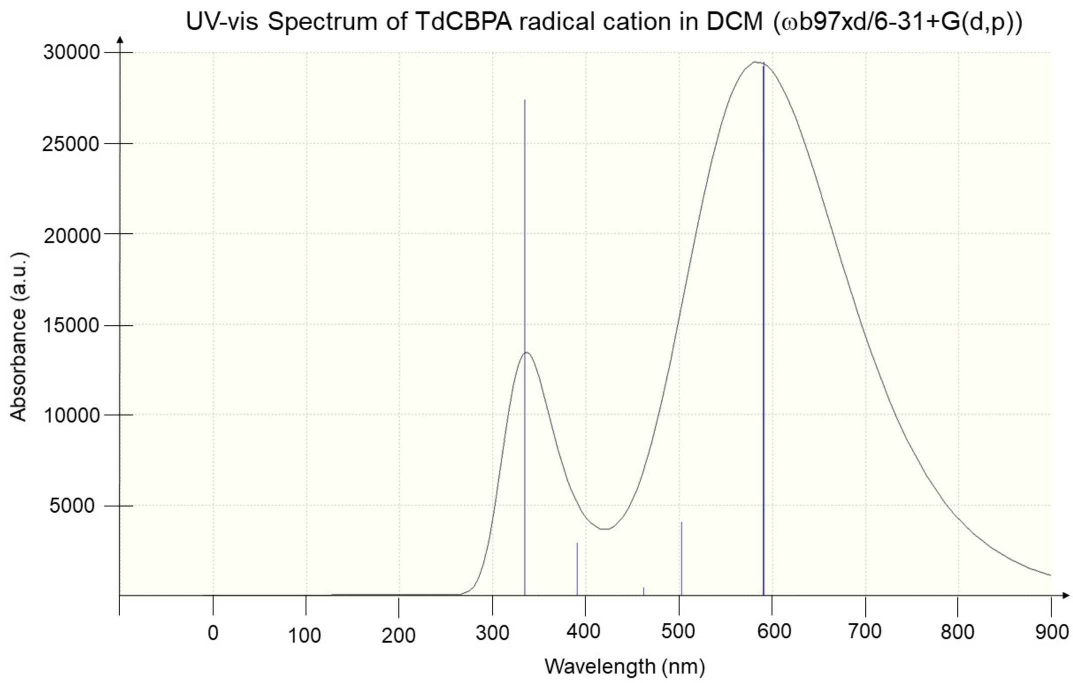


Figure S81. Computed UV-vis spectrum of **TdCBPA**$^{\cdot+}$ at ωb97xd/6-31+G(d,p), CPCM = DCM.

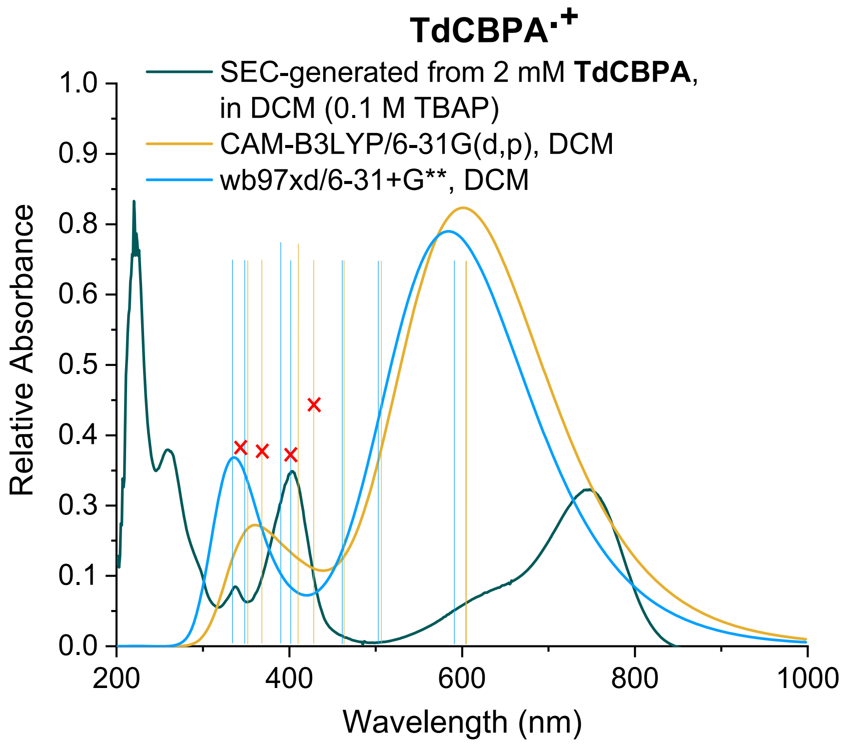


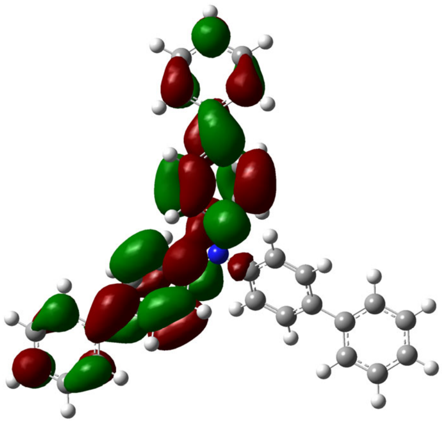
Figure S82. Comparison of experimental UV-vis spectrum of **TdCBPA**$^{\cdot+}$ and computed UV-vis transitions at CAM-B3LYP/6-31G(d,p) and ωb97xd/6-31+G(d,p), CPCM = DCM.

14.2 Molecular orbitals and natural transition orbitals for TPA$^{\cdot+}$ photoexcitations

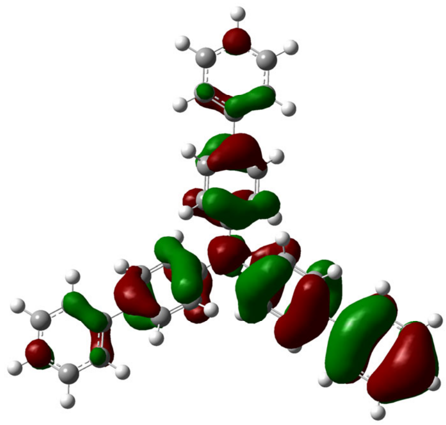
For the first excited state, the ground state MOs (canonical MOs) involved in the transition were visualized, for which a clear dominant transition (probability f = >|0.7|) was observed. For higher order excited states where oftentimes no dominant configuration was present (probability f = <|0.7|), the natural transition orbitals (NTOs) were visualized. NTOs are known to offer intuitive representations of orbitals involved in any *hole-particle* excitation.[45] Calculated canonical MOs resembled those of similar reported compounds.[46]

T*p*BPA$^{\cdot+}$ in MeCN, CAM-B3LYP/6-31G(d,p)

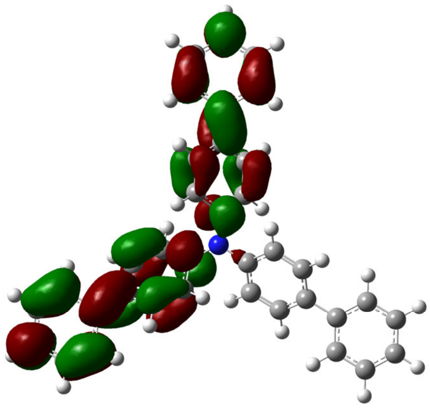
Ground state:



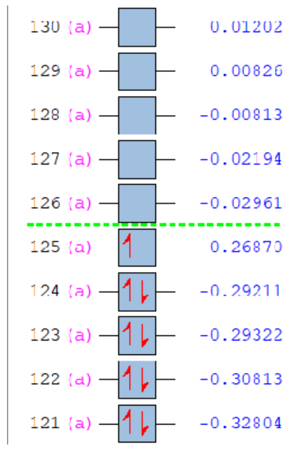
126 (LUMO)



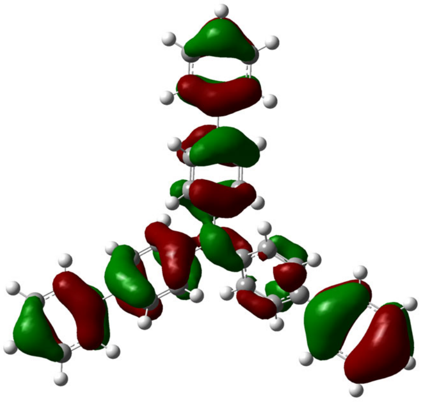
125 (SOMO)



126 (LUMO+1)

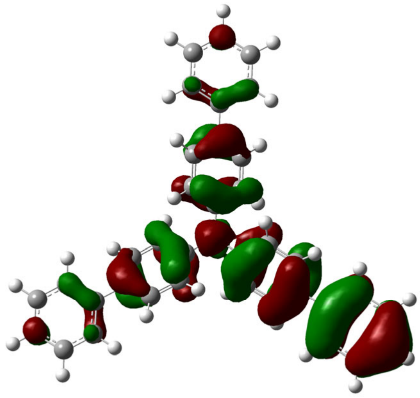


Ground → Excited state 1 MOs:



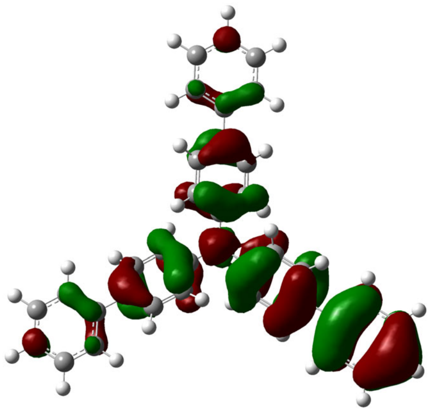
124 (HOMO)

→



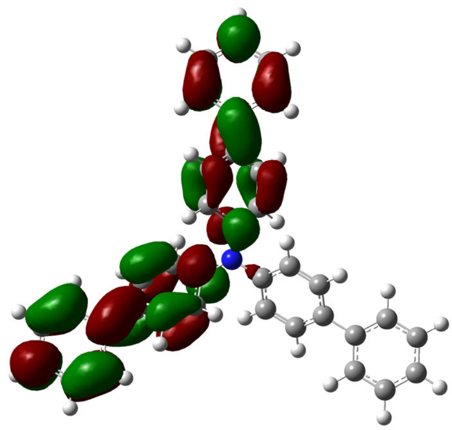
125 (SOMO)

Ground → Excited state 7 MOs:



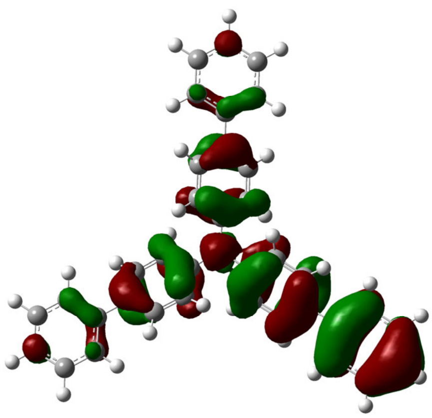
125 (HOMO)

→



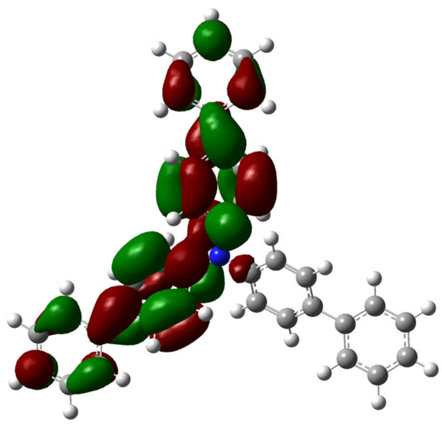
127 (LUMO+1)

Ground → Excited state 8 MOs:



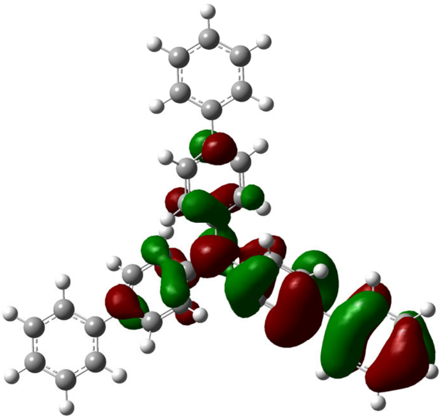
125 (HOMO)

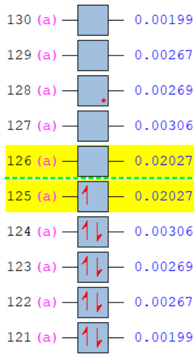
→

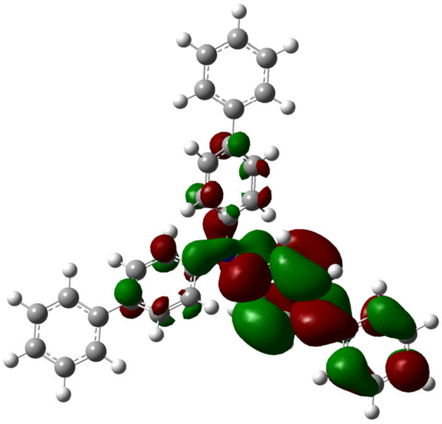


126 (LUMO)

Ground → Excited state 1 NTOs:

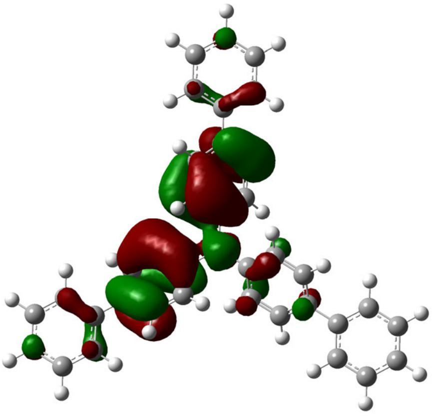


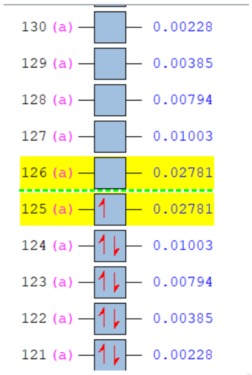


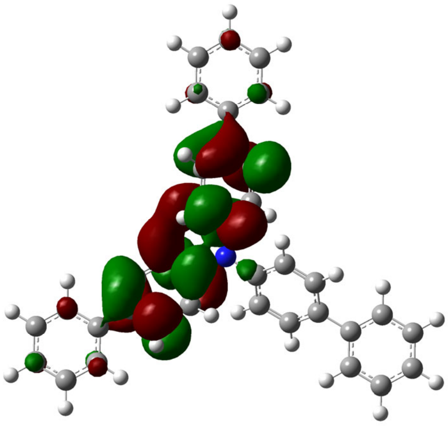


125 (NTO) → 126 (NTO)

Ground → Excited state 7 NTOs:

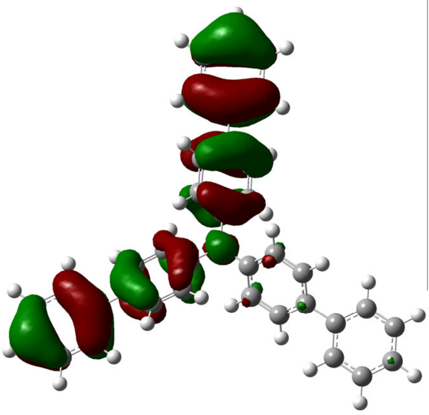


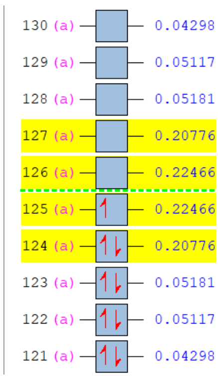


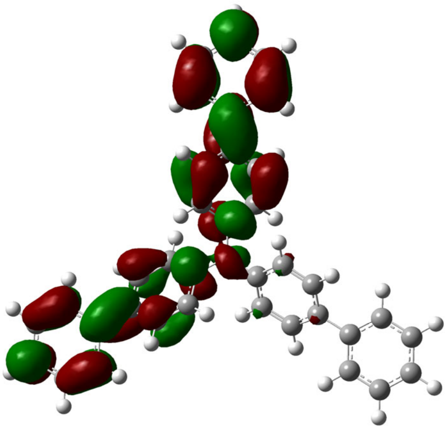


125 (NTO) → 126 (NTO)

Ground → Excited state 8 NTOs:

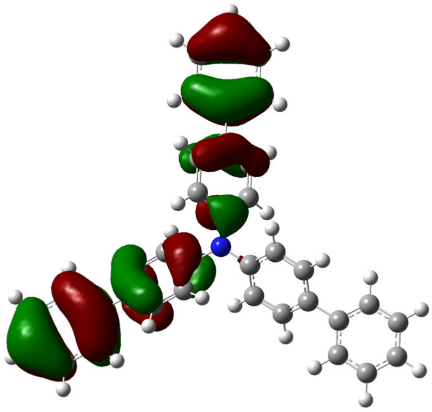






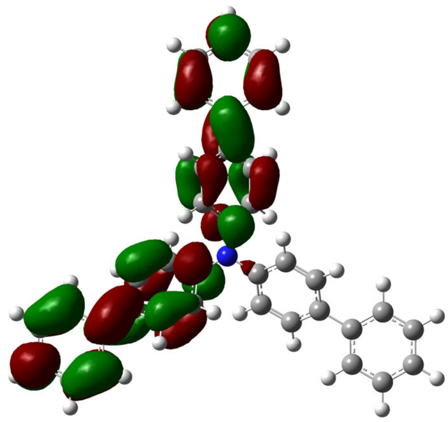
125 (NTO) → 126 (NTO)

and



124 (NTO)

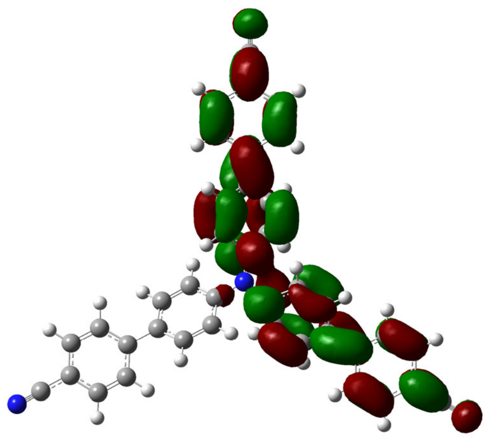
→



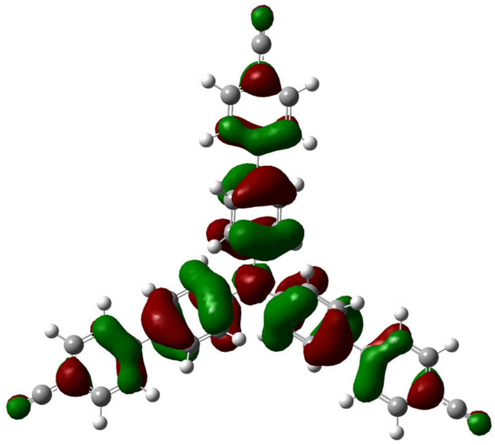
127 (NTO)

TCBPA$^{\cdot +}$ in MeCN, CAM-B3LYP/6-31G(d,p)

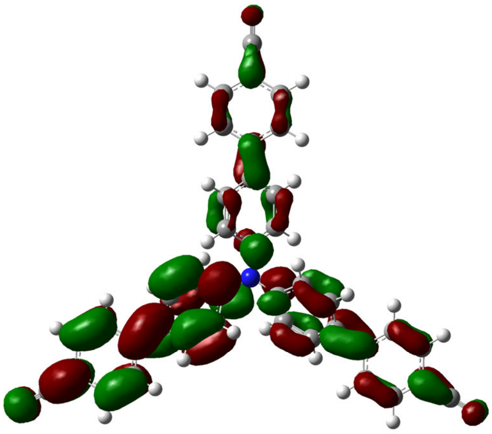
Ground state:



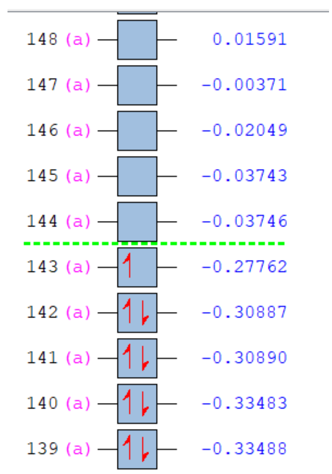
144 (LUMO)



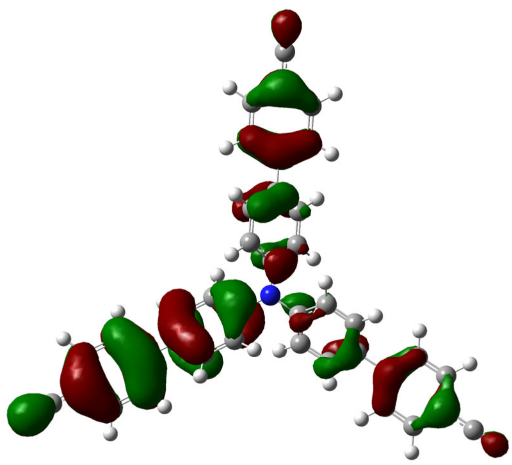
143 (SOMO)



145 (LUMO)

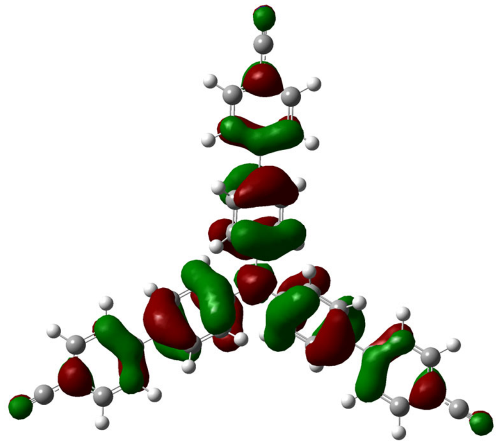


Ground → Excited state 1 MOs:



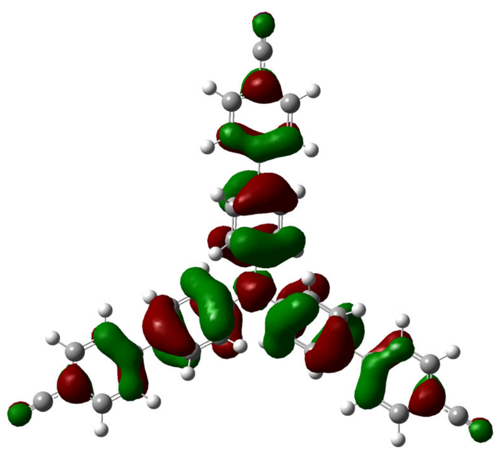
142 (HOMO)

→



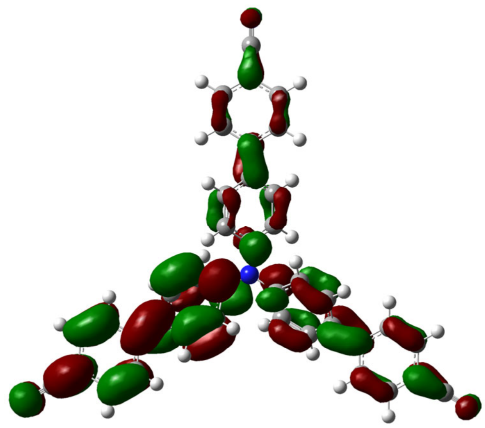
143 (SOMO)

Ground → Excited state 7 MOs:



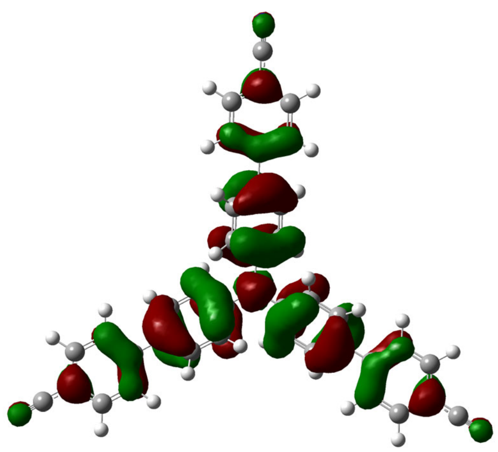
143 (SOMO)

→



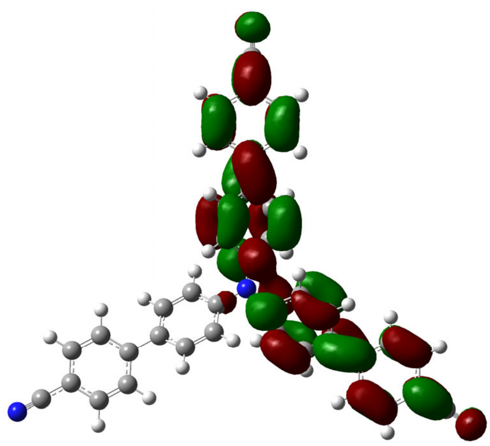
145 (LUMO+1)

Ground → Excited state 8 MOs:



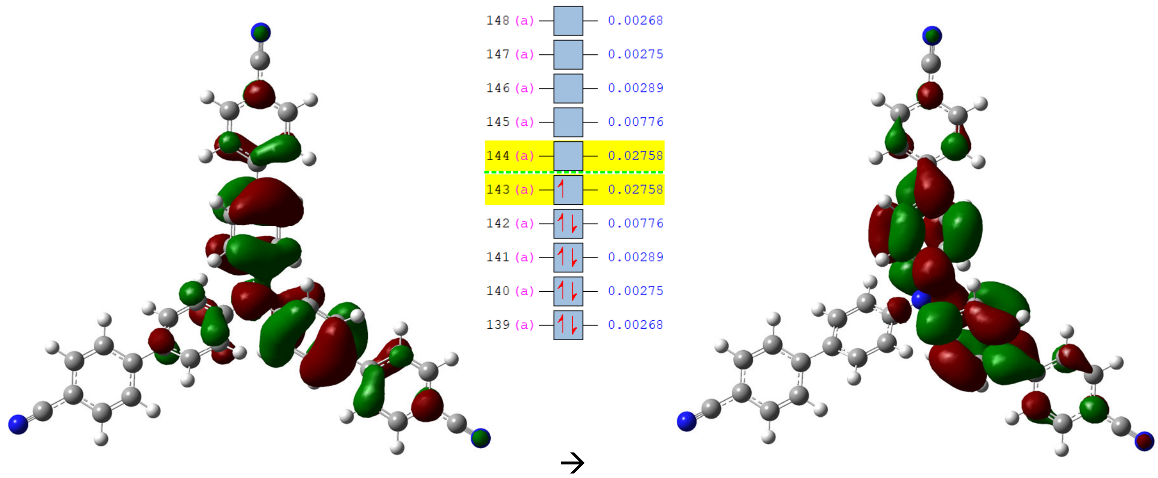
143 (SOMO)

→



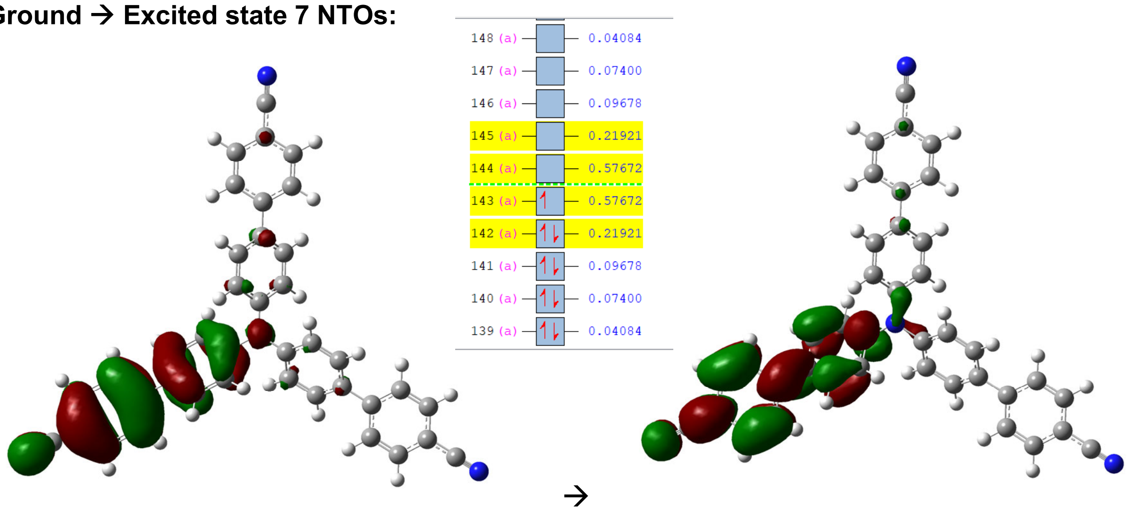
144 (LUMO)

Ground → Excited state 1 NTOs:



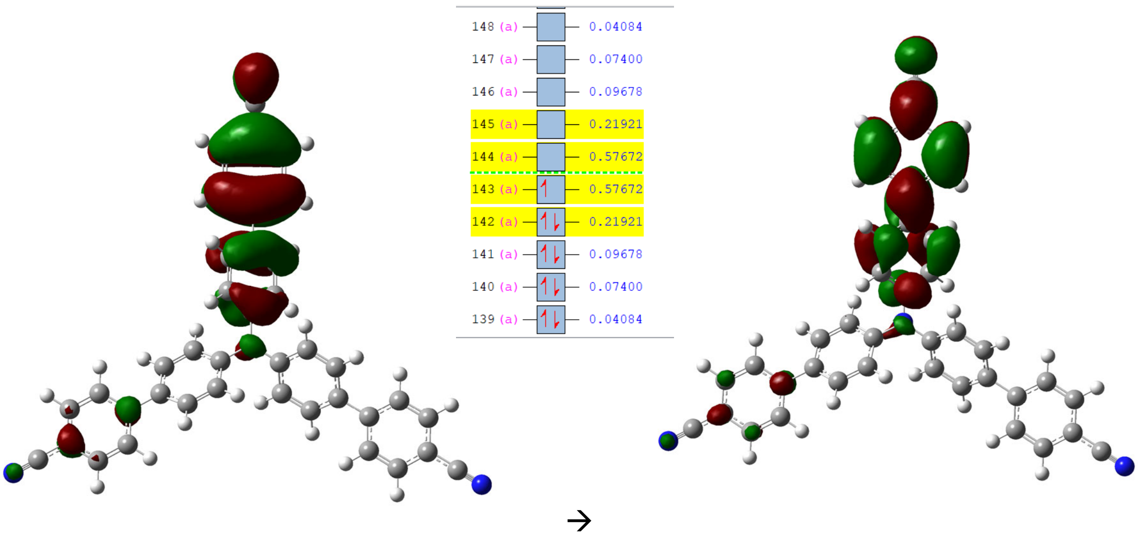
143 (NTO) 144 (NTO)

Ground → Excited state 7 NTOs:



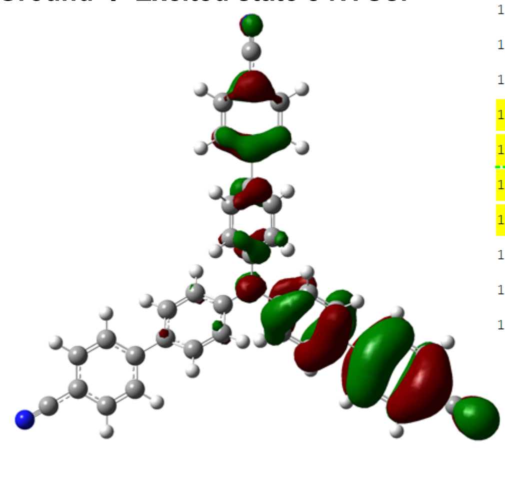
143 (NTO) 144 (NTO)

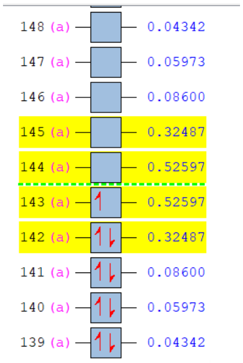
and



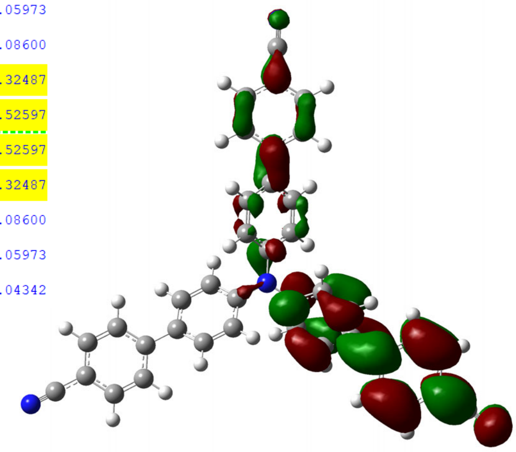
142 (NTO) 145 (NTO)

Ground → Excited state 8 NTOs:



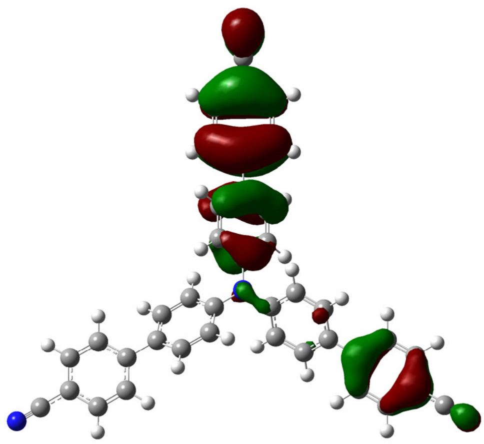


→



143 (NTO) 144 (NTO)

and



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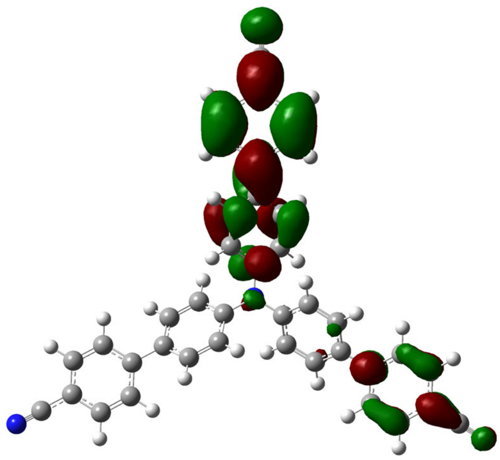
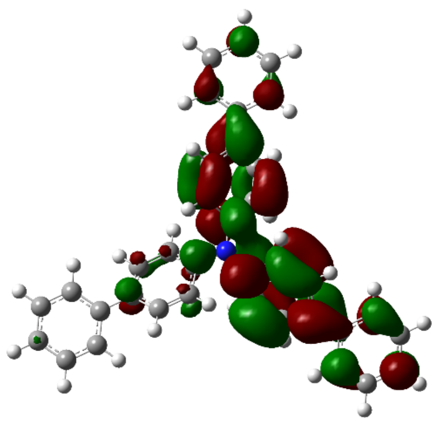
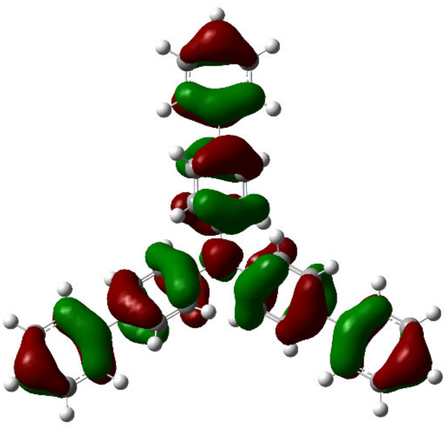


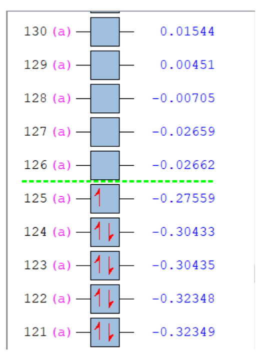
142 (NTO) 145 (NTO)

T*p*BPA$^{\cdot+}$ in DCM, CAM-B3LYP/6-31G(d,p)

Ground state:

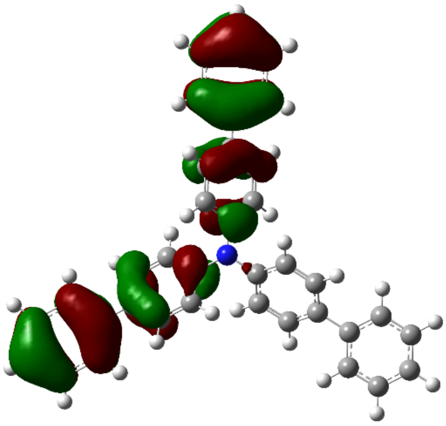






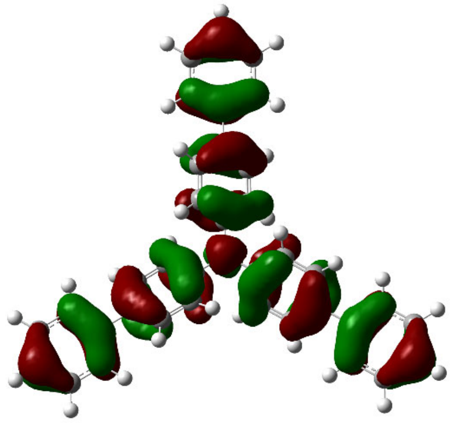
126 (LUMO) 125 (SOMO)

Ground → Excited state 1 MOs:



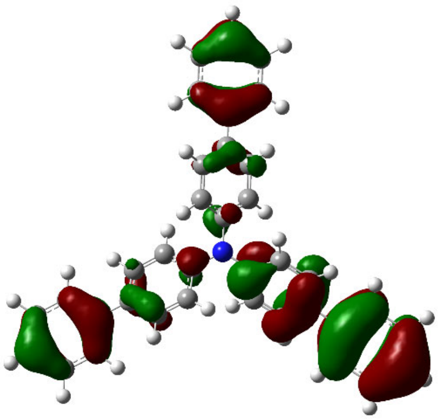
124 (HOMO)

→



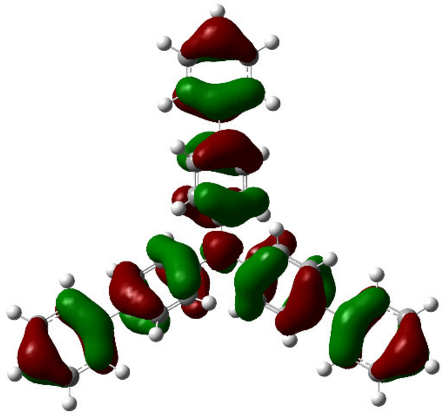
125 (SOMO)

Ground → Excited state 2 MOs:



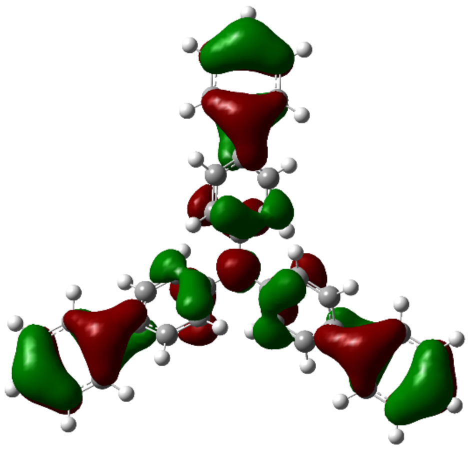
123 (HOMO-1)

→



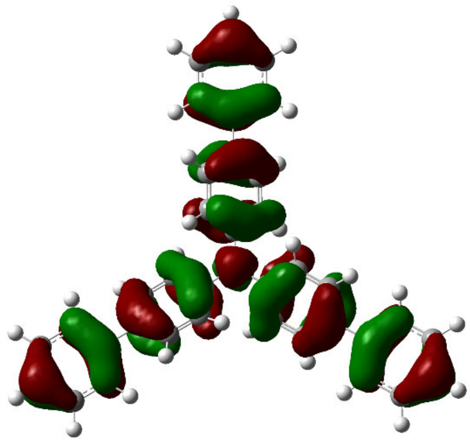
125 (SOMO)

Ground → Excited state 7 (385 nm) MOs:



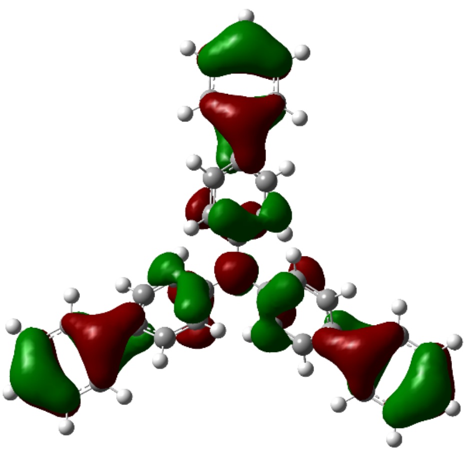
119

→



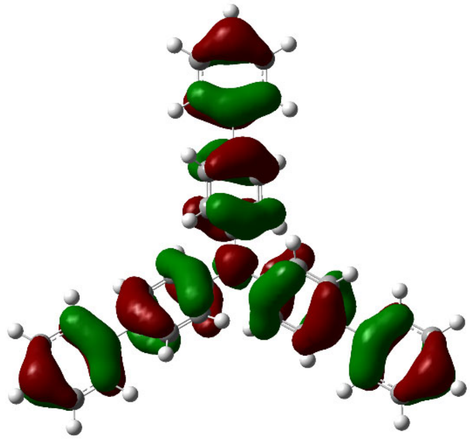
125 (SOMO)

Ground → Excited state 8 (385 nm) MOs:



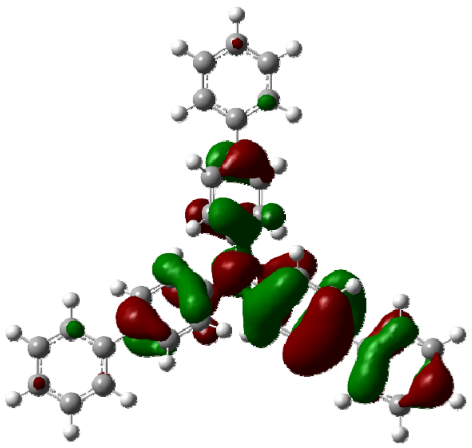
121

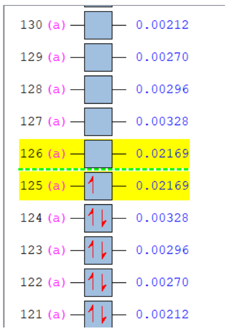
→

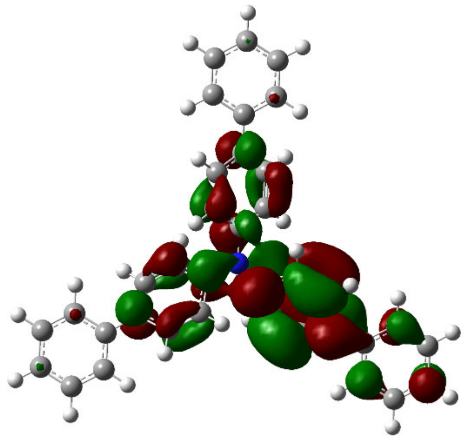


125 (SOMO)

Ground → Excited state 1 NTOs:

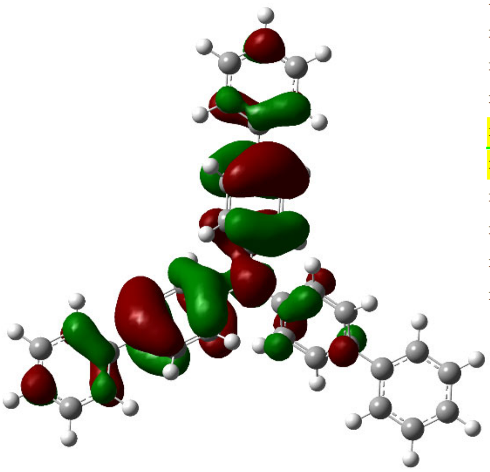


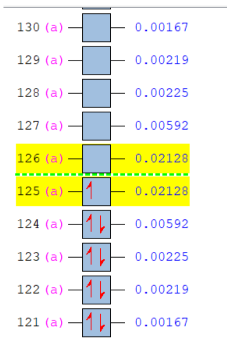


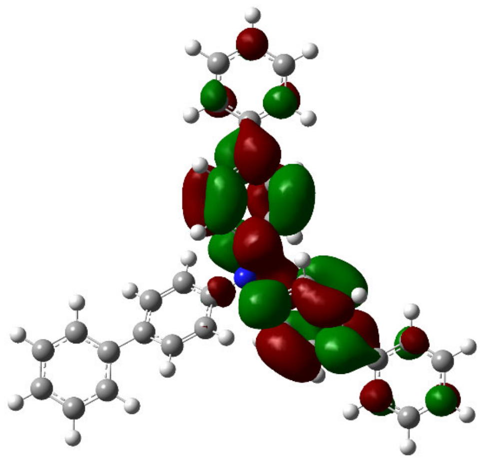


125 (NTO) → 126 (NTO)

Ground → Excited state 2 NTOs:

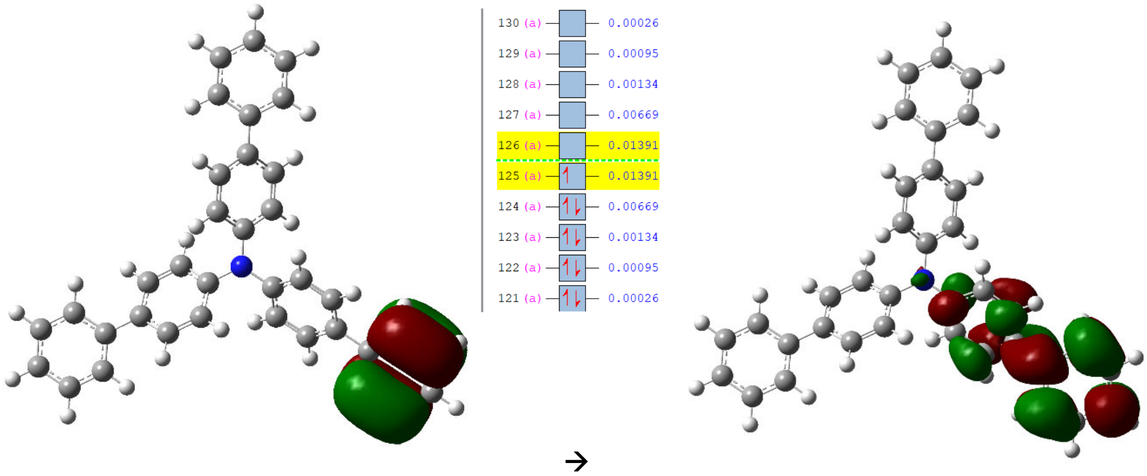






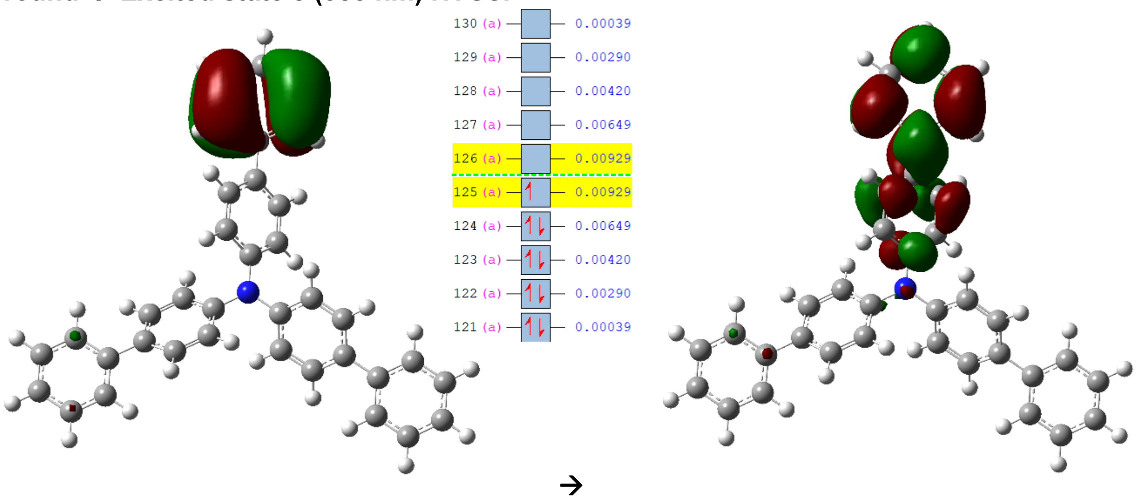
125 (NTO) → 126 (NTO)

Ground → Excited state 7 (385 nm) NTOs:



125 (NTO) 126 (NTO)

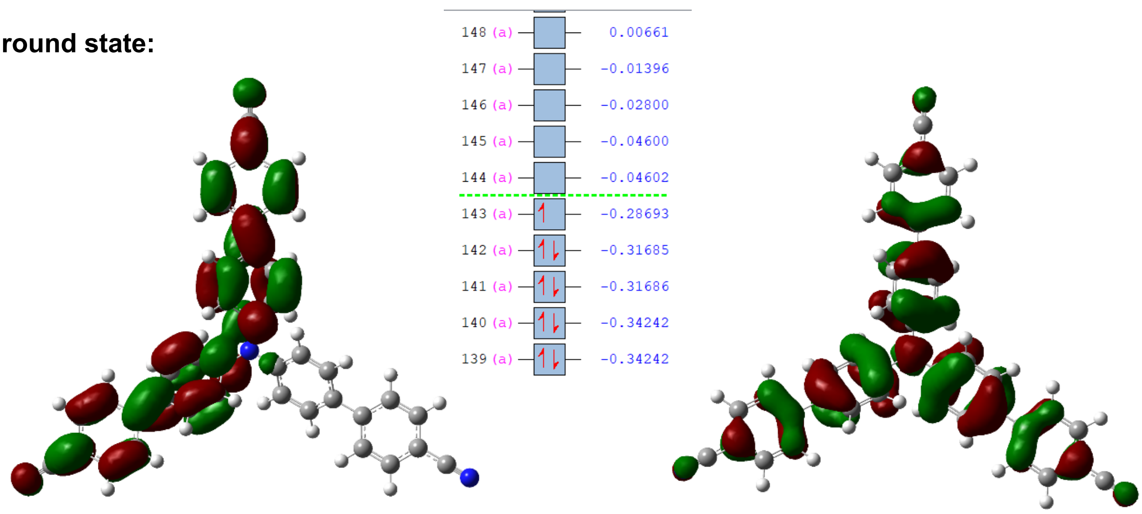
Ground → Excited state 8 (385 nm) NTOs:



125 (NTO) 126 (NTO)

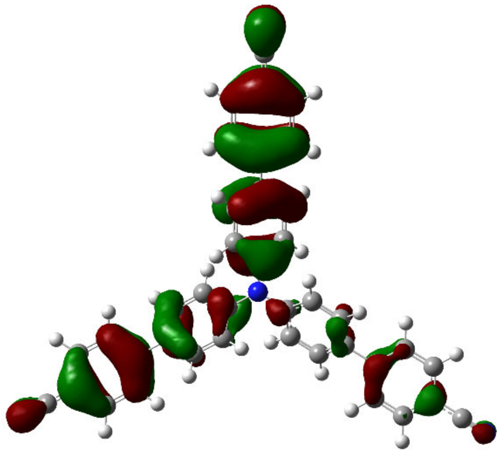
TCBPA$^{\cdot+}$ in DCM, CAM-B3LYP/6-31G(d,p)

Ground state:



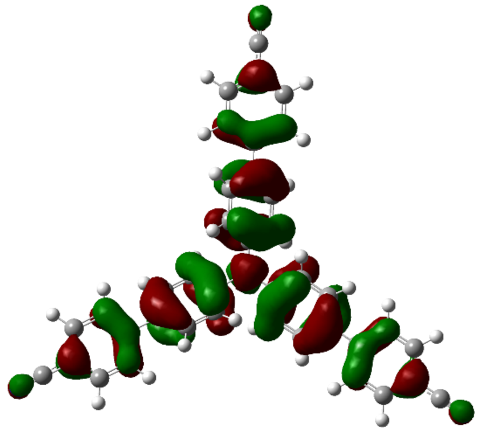
144 (LUMO) 143 (SOMO)

Ground → Excited state 1 MOs:



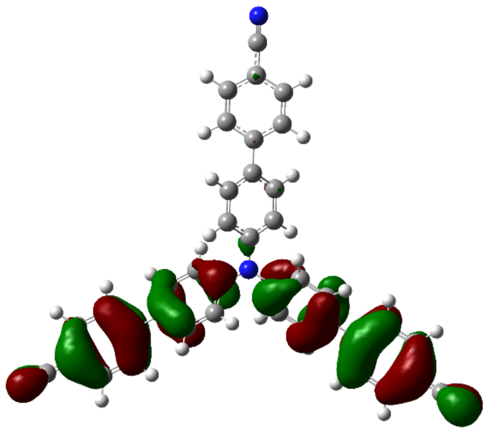
142 (HOMO)

→



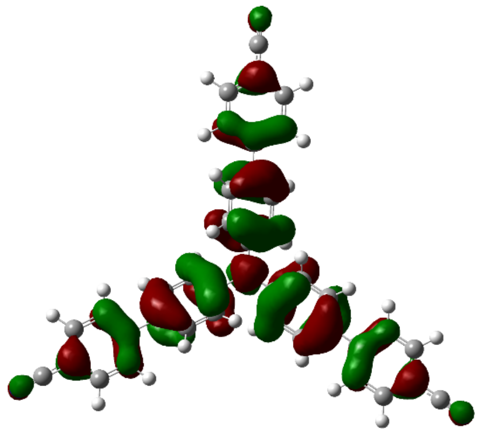
143 (SOMO)

Ground → Excited state 2 MOs:



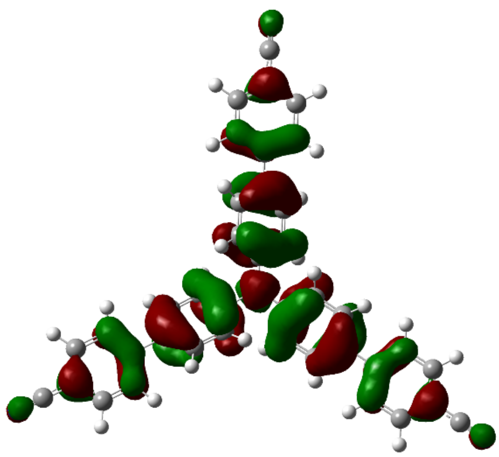
141 (HOMO-1)

→



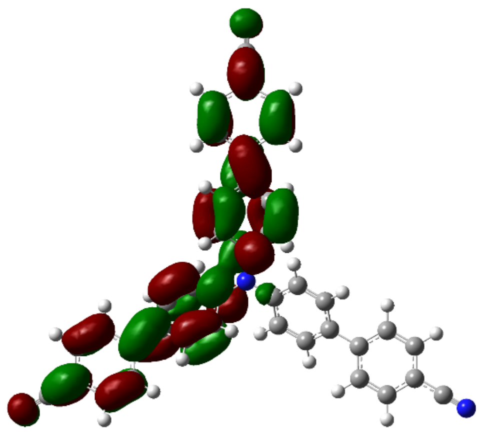
143 (SOMO)

Ground → Excited state 7 (401 nm) MOs:



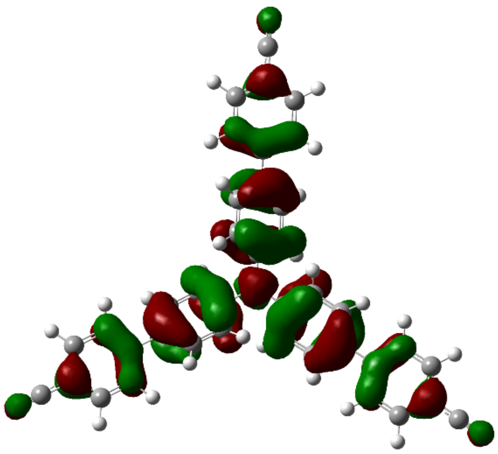
143 (SOMO)

→

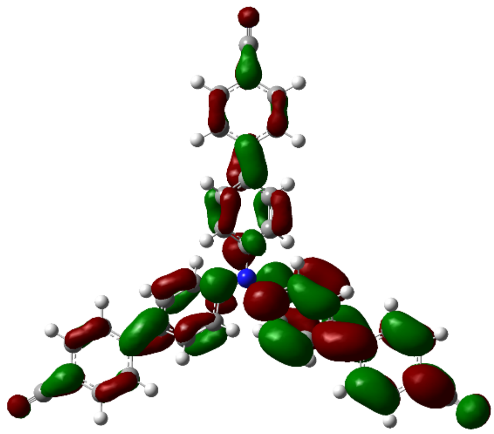


144 (LUMO)

Ground → Excited state 8 (401 nm) MOs:

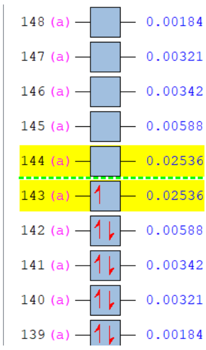


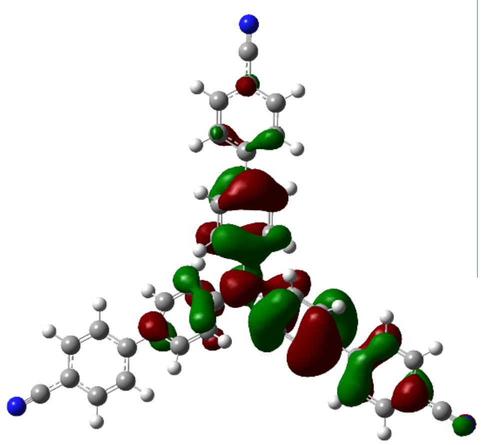
→



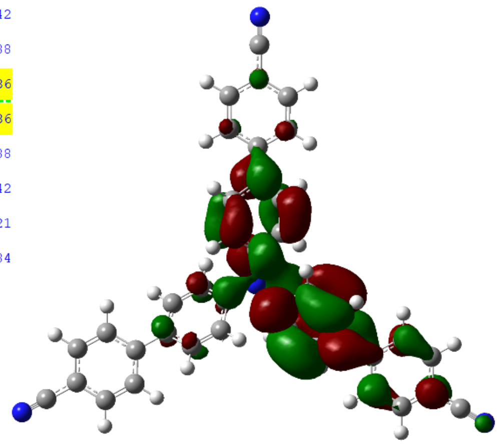
143 (SOMO) 144 (LUMO+1)

Ground → Excited state 1 NTOs:



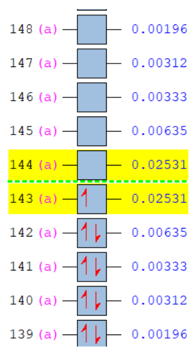


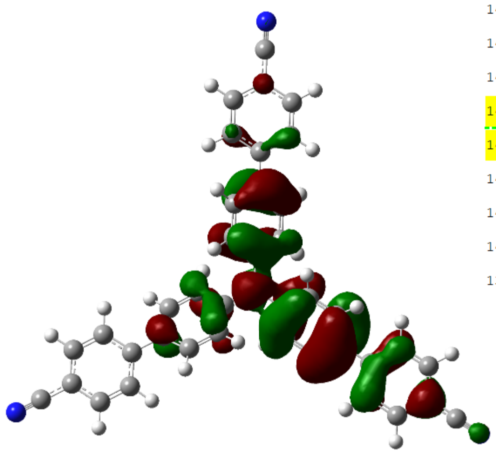
→



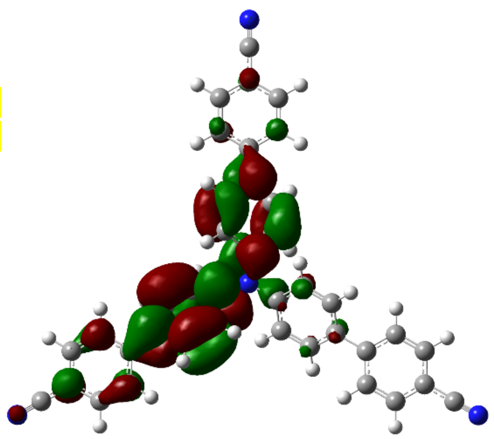
143 (NTO) 144 (NTO)

Ground → Excited state 2 NTOs:



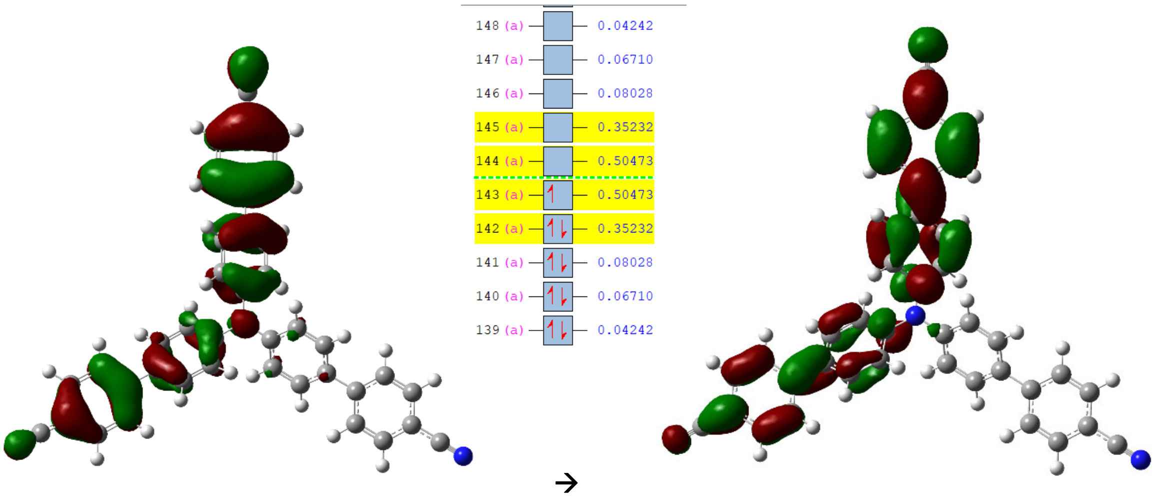


→



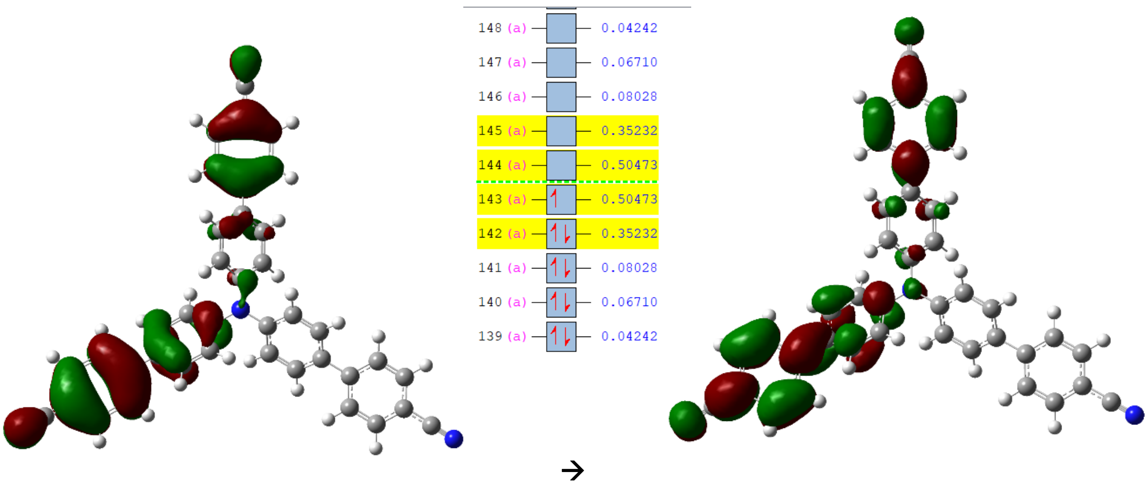
143 (NTO) 144 (NTO)

Ground → Excited state 7 (401 nm) NTOs:



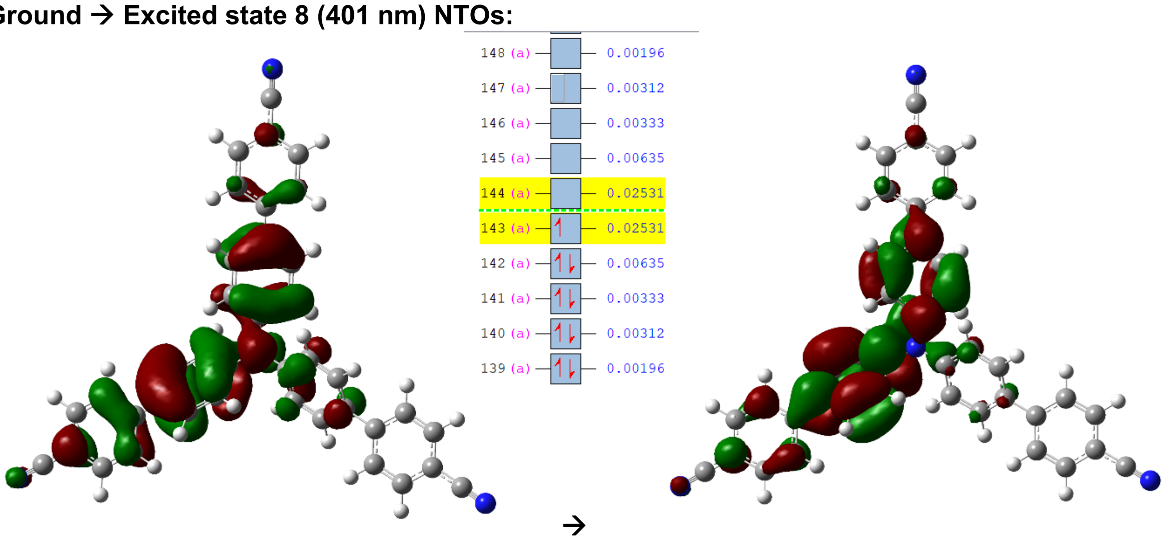
143 (NTO) 144 (NTO)

and



142 (NTO) 145 (NTO)

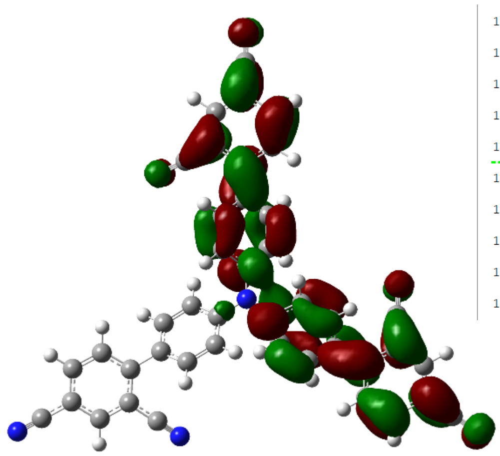
Ground → Excited state 8 (401 nm) NTOs:

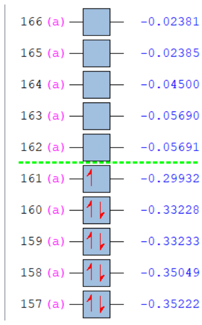


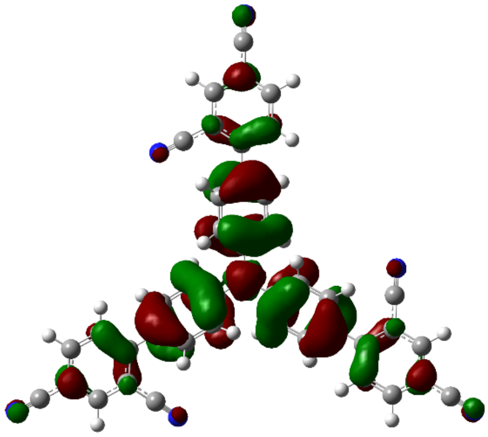
143 (NTO) 144 (NTO)

TdCBPA$^{\cdot+}$ in DCM, CAM-B3LYP/6-31G(d,p)

Ground state:

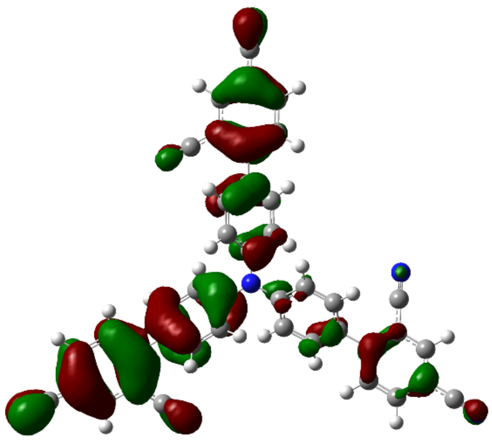


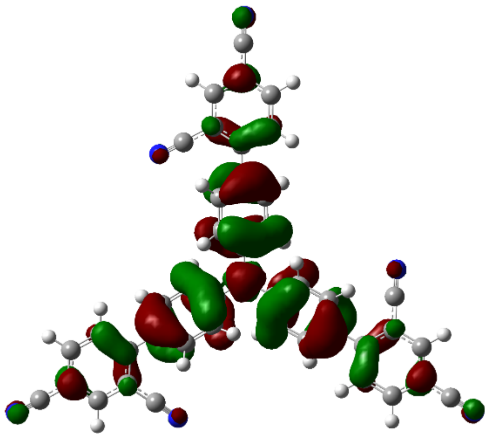




162 (LUMO) → 161 (SOMO)

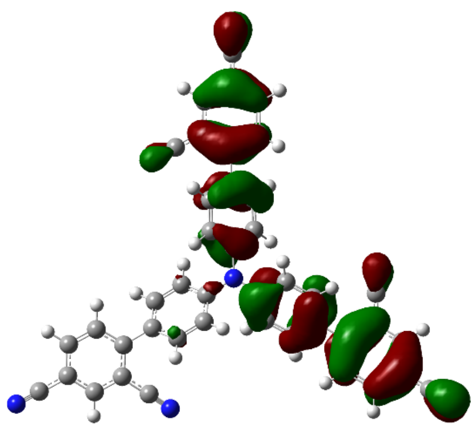
Ground → Excited state 1 MOs:

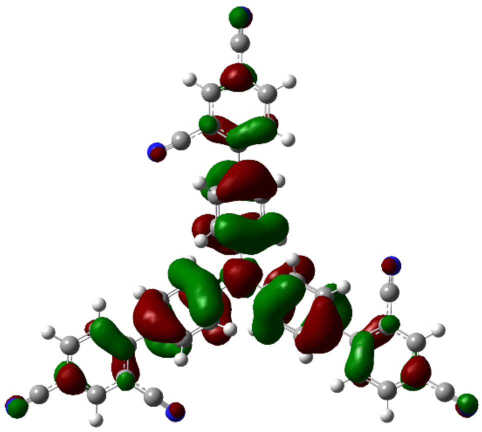




160 (HOMO) → 161 (SOMO)

Ground → Excited state 2 MOs:

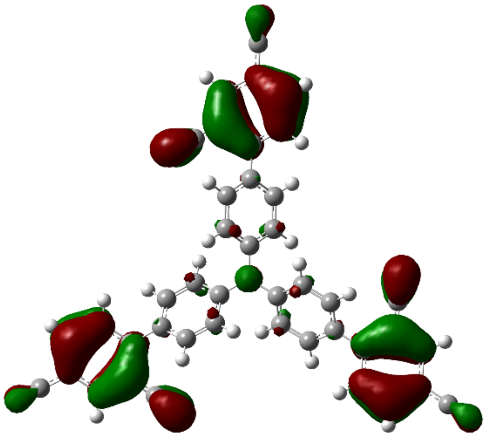




159 (HOMO-1) → 161 (SOMO)

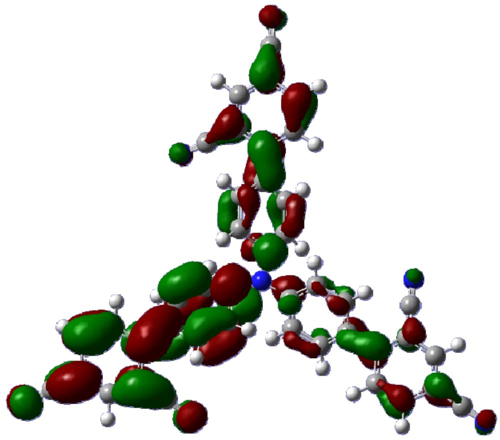
182

Ground → Excited state 7 (410 nm) MOs:



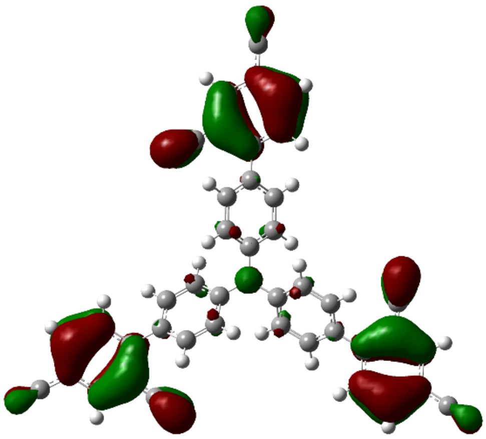
158 (HOMO-2)

→



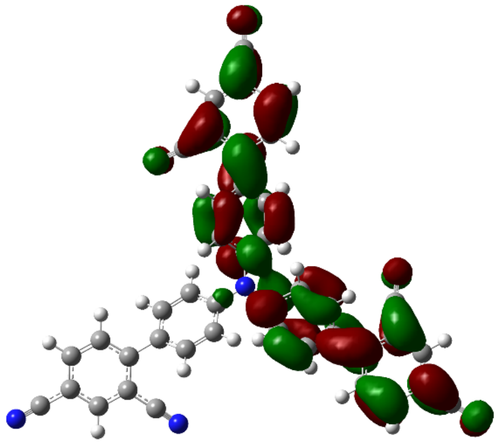
163 (LUMO+1)

Ground → Excited state 8 (410 nm) MOs:



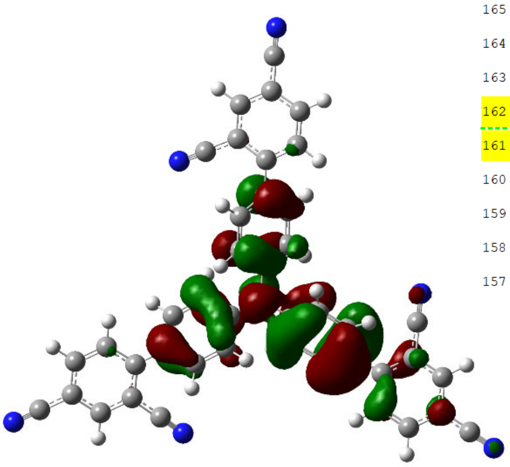
158 (HOMO-2)

→

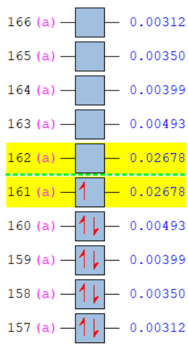


163 (LUMO)

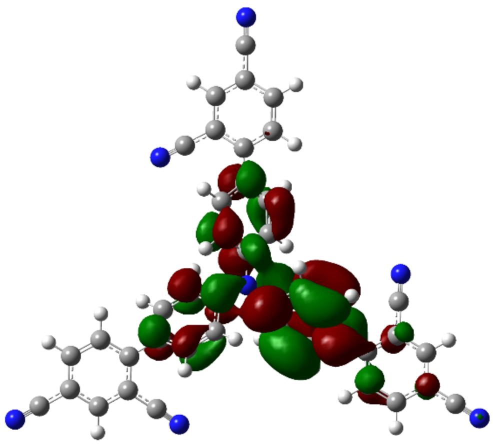
Ground → Excited state 1 NTOs:



161 (NTO)

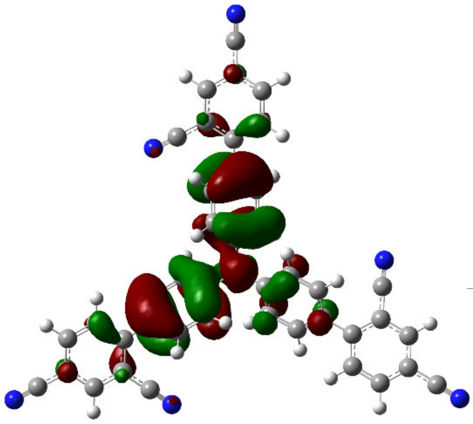


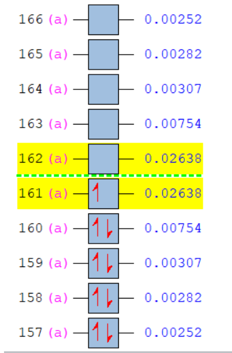
→

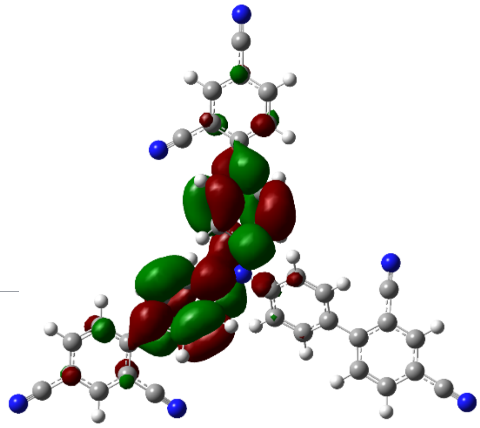


162 (NTO)

Ground → Excited state 2 NTOs:

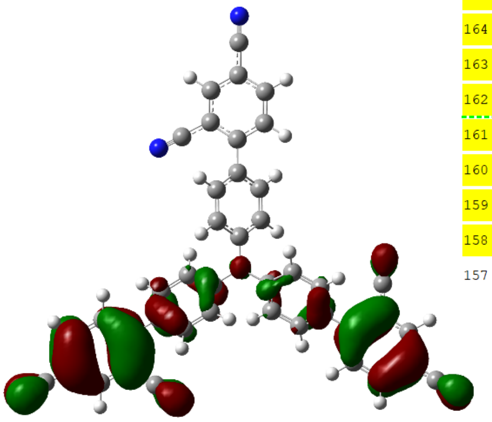


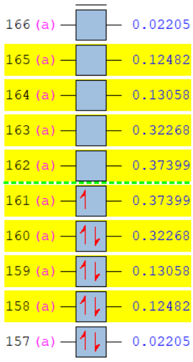


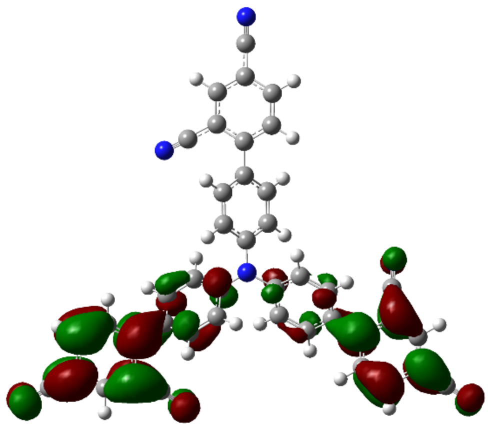


161 (NTO) → 162 (NTO)

Ground → Excited state 7 NTOs:

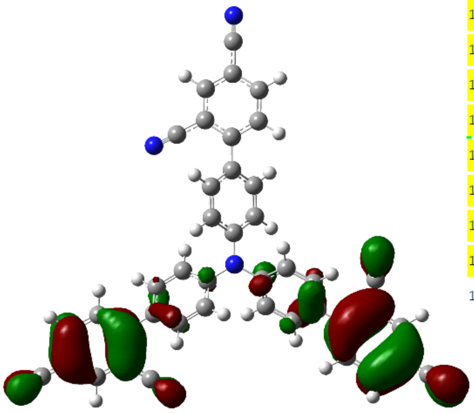


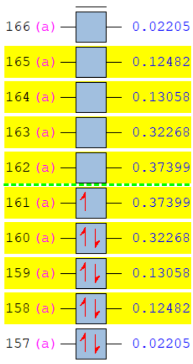


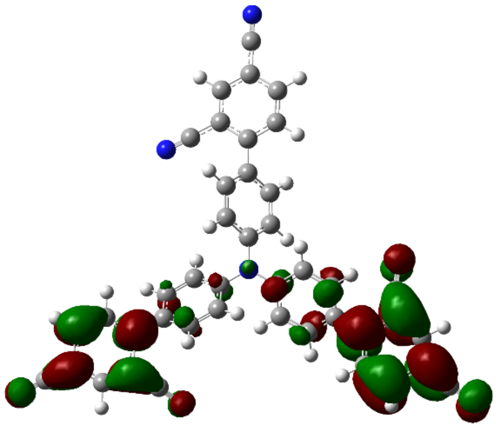


161 (NTO) → 162 (NTO)

and

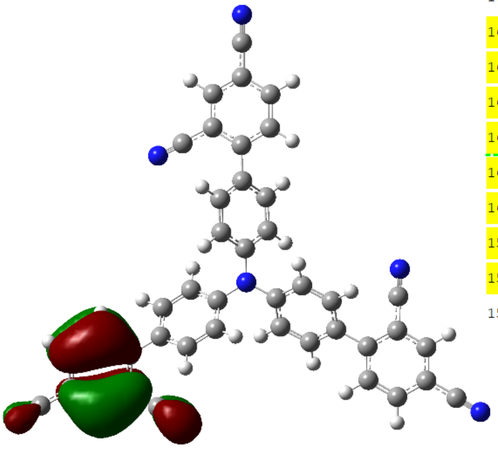


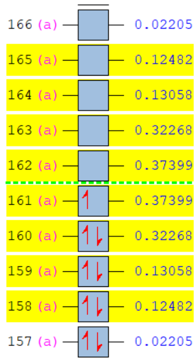


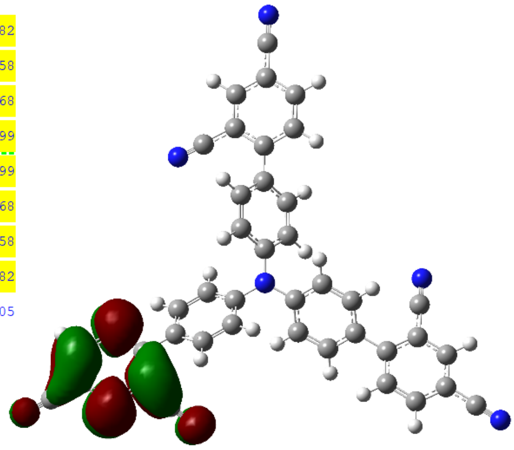


160 (NTO) → 163 (NTO)

and

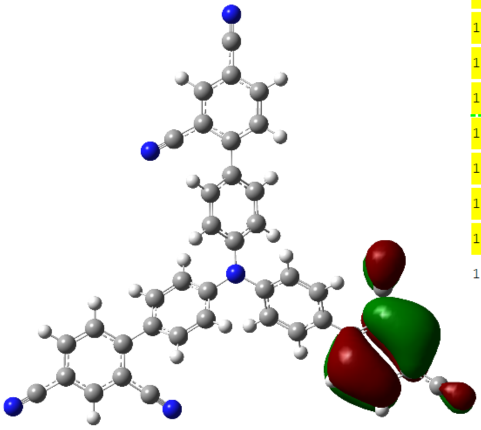


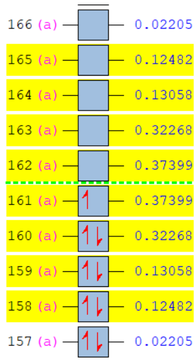


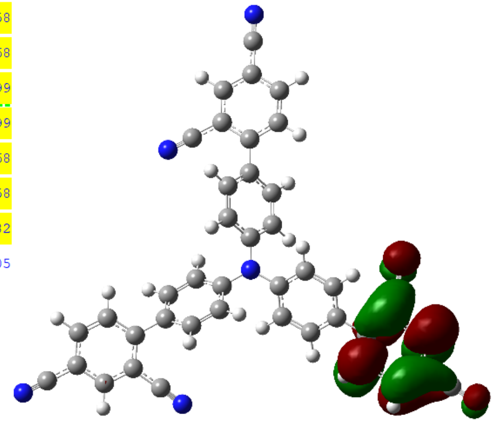


159 (NTO) → 164 (NTO)

and

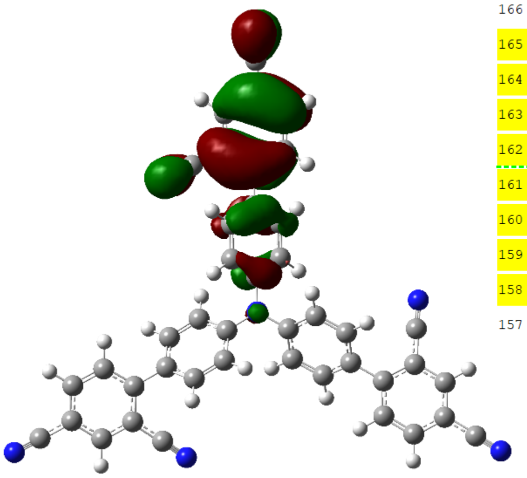


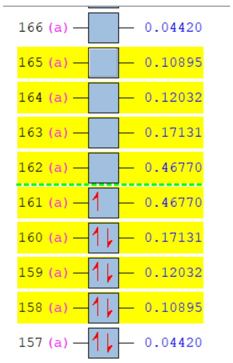


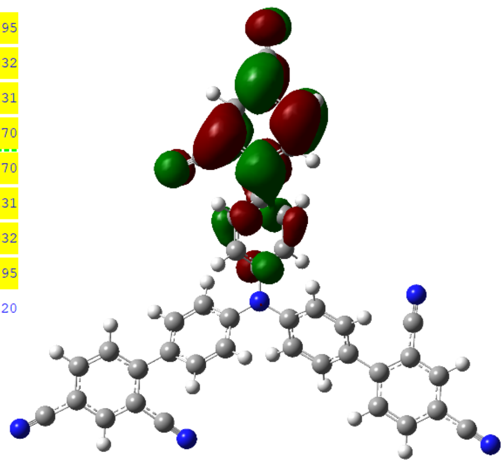


158 (NTO) → 165 (NTO)

Ground → Excited state 8 NTOs:

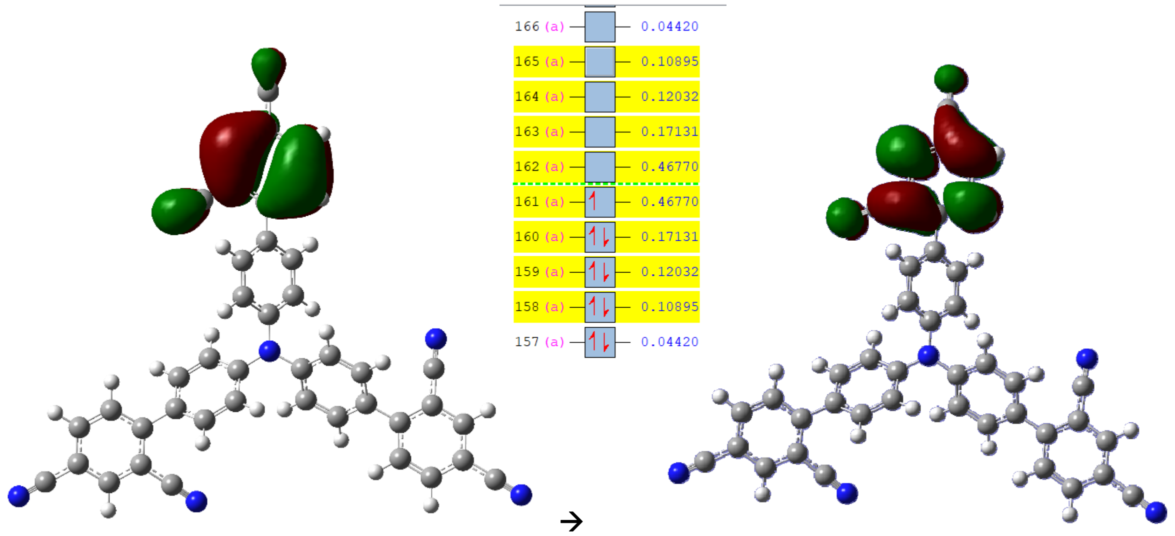






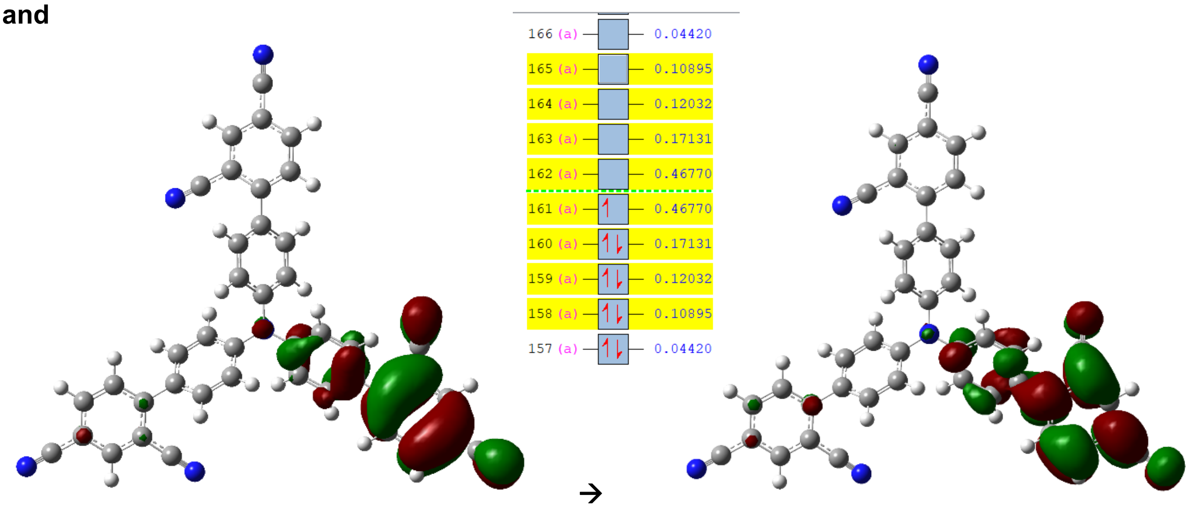
161 (NTO) → 162 (NTO)

and



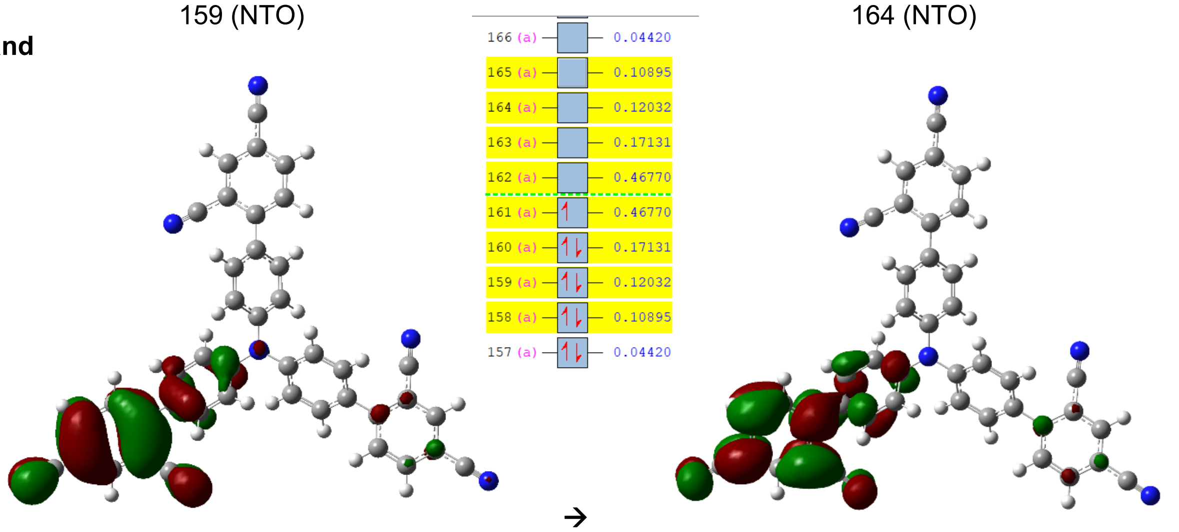
160 (NTO) 163 (NTO)

and



159 (NTO) 164 (NTO)

and



158 (NTO) 165 (NTO)

15. X-RAY CRYSTALLOGRAPHY

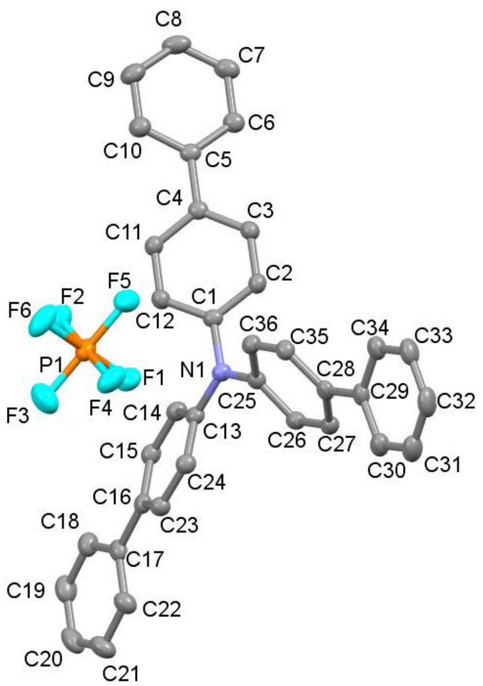
Single crystal x-ray diffraction data were recorded on Agilent Technologies Supernova (for [**T*p*BPA**$^{\cdot+}$]PF_6), Xcalibur Gemini Ultra (for [**TCBPA**$^{\cdot+}$]PF_6·MeCN) or GV1000 (for **TCBPA**) TitanS2 diffractometers with Cu-K_a radiation (l= 1.54184 Å). Empirical multi-scan[47] and analytical absorption corrections[48] were applied to the data. Structures were solved using SHELXT[49] using dual methods and Olex2 as the graphical interface,[50] and least-squares refinements on F^2 were carried out using SHELXL.[49,51] Hydrogen atoms were located in idealized positions and refined isotropically with a riding model.

CCDC 2035879 ([**T*p*BPA**$^{\cdot+}$]PF_6), 2035880 ([**TCBPA**$^{\cdot+}$]PF_6·MeCN) and 2038665 (**TCBPA**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Table S16. Crystallographic data and structure refinement for compounds [**T*p*BPA**$^{\cdot+}$]PF_6, [**TCBPA**$^{\cdot+}$]PF_6·MeCN and **TCBPA**.

Compound	[**T*p*BPA**$^{\cdot+}$]PF_6	[**TCBPA**$^{\cdot+}$]PF_6·MeCN	**TCBPA**
Empirical formula	$C_{36}H_{27}F_6NP$	$C_{41}H_{27}F_6N_5P$	$C_{39}H_{24}N_4$
ρ_{calc}**/(g/cm³)**	1.396	1.427	1.311
***μ*/mm⁻¹**	1.400	1.338	0.607
Formula weight	618.55	734.64	548.62 g mol^{-1}
Crystal colour	dark purple	dark blue	clear yellow
Crystal shape	block	plate	prism
Crystal size/mm³	0.373 × 0.171 × 0.109	0.605 × 0.266 × 0.065	0.16 × 0.10 × 0.06
Temperature/K	123.00(10)	123	122.97(10)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
***a*/Å**	9.9242(2)	10.0127(2)	9.7013(2)
***b*/Å**	24.0647(4)	27.7882(5)	25.4439(5)
***c*/Å**	12.6848(2)	12.2929(3)	11.5990(3)
***α*/°**	90	90	90
***β*/°**	103.769(2)	90.730(2)	103.924(2)
***γ*/°**	90	90	90
Volume/Å³	2942.36(9)	3420.04(12)	2778.95(11)
Z	4	4	4
Z'	1	1	1

Wavelength/ Å	1.54184	1.54184	1.54184
Radiation	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$
Θ_{min}/°	7.346	7.864	3.474
Θ_{max}/°	131.8	144.51	73.756
Reflections collected	15020	12436	16698
Independent reflections	4989	6419	5374
Reflections I≥2 σ(I)	4989	6419	4455
R$_{int}$	0.0164	0.0278	0.0322
Parameters	397	479	388
Restraints	0	0	0
Largest peak	0.53	0.47	0.168
Deepest hole	-0.46	-0.34	-0.238
GooF	1.031	1.043	1.060
***wR$_2$* (all data)**	0.1051	0.1322	0.1115
wR$_2$	0.1029	0.1255	0.1054
***R$_1$* (all data)**	0.0401	0.0610	0.0576
R$_1$	0.0374	0.0493	0.0451



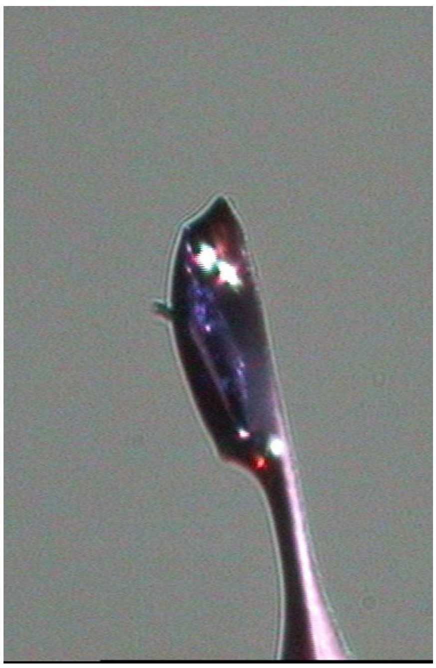


Figure S83 Solid-state molecular structure of [**T*p*BPA$^{\cdot+}$**]PF$_6$ (right) Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. C atoms shown in grey, F atoms in cyan, N atom in blue, and P atom in orange. Picture of the [**T*p*BPA$^{\cdot+}$**]PF$_6$ crystal in the diffractometer (right).

Table S17. Bond lengths for [**T*p*BPA**$^{\cdot+}$]PF_6.

Atom	Atom	Length/Å
P1	F2	1.5959(12)
P1	F1	1.5855(11)
P1	F4	1.6044(12)
P1	F6	1.5971(12)
P1	F5	1.5922(13)
P1	F3	1.5772(13)
N1	C1	1.419(2)
N1	C13	1.386(2)
N1	C25	1.423(2)
C1	C12	1.397(2)
C1	C2	1.394(2)
C4	C11	1.404(2)
C4	C5	1.484(2)
C4	C3	1.401(2)
C13	C24	1.407(2)
C13	C14	1.408(2)
C11	C12	1.382(2)
C5	C6	1.401(2)
C5	C10	1.399(2)
C24	C23	1.371(2)
C27	C26	1.382(2)
C27	C28	1.405(2)
C25	C26	1.395(2)
C25	C36	1.395(2)
C23	C16	1.410(2)
C35	C28	1.402(2)
C35	C36	1.377(2)
C16	C17	1.473(2)
C16	C15	1.409(2)
C28	C29	1.477(2)
C3	C2	1.377(2)
C17	C18	1.401(3)
C17	C22	1.401(3)
C15	C14	1.371(2)
C6	C7	1.388(2)
C29	C34	1.398(3)
C29	C30	1.396(2)
C10	C9	1.387(3)
C34	C33	1.383(3)
C9	C8	1.387(3)
C18	C19	1.387(3)
C22	C21	1.381(3)

Atom	Atom	Length/Å
C7	C8	1.382(3)
C30	C31	1.388(3)
C33	C32	1.384(3)
C21	C20	1.385(3)
C31	C32	1.384(3)
C19	C20	1.380(3)

Table S18. Bond angles for [**T*p*BPA**$^{\cdot+}$]PF_6.

Atom	Atom	Atom	Angle/˚
F2	P1	F4	178.62(7)
F2	P1	F6	89.99(6)
F1	P1	F2	90.50(6)
F1	P1	F4	89.90(6)
F1	P1	F6	179.49(7)
F1	P1	F5	90.41(7)
F6	P1	F4	89.61(6)
F5	P1	F2	89.57(7)
F5	P1	F4	89.10(7)
F5	P1	F6	89.75(8)
F3	P1	F2	91.06(7)
F3	P1	F1	90.26(7)
F3	P1	F4	90.26(7)
F3	P1	F6	89.58(8)
F3	P1	F5	179.07(8)
C1	N1	C25	116.47(13)
C13	N1	C1	121.52(13)
C13	N1	C25	121.96(13)
C12	C1	N1	120.95(15)
C2	C1	N1	118.95(14)
C2	C1	C12	120.09(15)
C11	C4	C5	121.46(15)
C3	C4	C11	117.70(15)
C3	C4	C5	120.84(15)
N1	C13	C24	120.73(14)
N1	C13	C14	120.48(15)
C24	C13	C14	118.78(15)
C12	C11	C4	121.61(15)
C6	C5	C4	120.46(15)
C10	C5	C4	121.65(15)
C10	C5	C6	117.88(15)
C23	C24	C13	120.12(15)
C26	C27	C28	121.19(15)
C11	C12	C1	119.29(15)
C26	C25	N1	121.45(14)
C26	C25	C36	120.41(15)
C36	C25	N1	118.13(14)
C24	C23	C16	121.97(16)

Atom	Atom	Atom	Angle/°
C27	C26	C25	119.52(15)
C36	C35	C28	121.67(16)
C23	C16	C17	121.66(15)
C15	C16	C23	117.00(15)
C15	C16	C17	121.31(15)
C27	C28	C29	122.34(15)
C35	C28	C27	117.85(15)
C35	C28	C29	119.81(15)
C2	C3	C4	121.38(16)
C18	C17	C16	121.53(16)
C22	C17	C16	120.71(16)
C22	C17	C18	117.75(16)
C14	C15	C16	121.77(15)
C7	C6	C5	120.80(17)
C3	C2	C1	119.92(15)
C35	C36	C25	119.36(15)
C34	C29	C28	120.52(16)
C30	C29	C28	120.91(16)
C30	C29	C34	118.56(16)
C15	C14	C13	120.31(15)
C9	C10	C5	121.15(17)
C33	C34	C29	120.78(18)
C8	C9	C10	120.07(18)
C19	C18	C17	120.80(18)
C21	C22	C17	121.03(18)
C8	C7	C6	120.45(17)
C31	C30	C29	120.55(18)
C7	C8	C9	119.64(17)
C34	C33	C32	119.95(18)
C22	C21	C20	120.45(19)
C32	C31	C30	120.02(18)
C31	C32	C33	120.13(17)
C20	C19	C18	120.49(19)
C19	C20	C21	119.47(18)

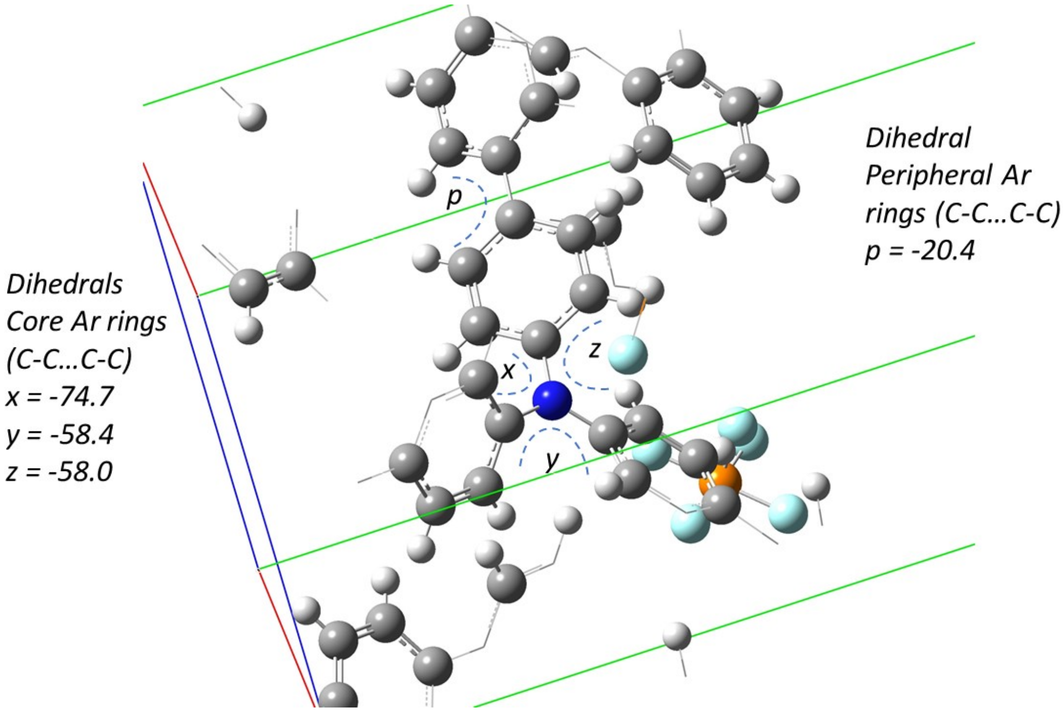


Figure S84. Dihedrals of [**T*p*BPA$^{\cdot+}$**]PF_6 visualized in GaussView 5.0.9.

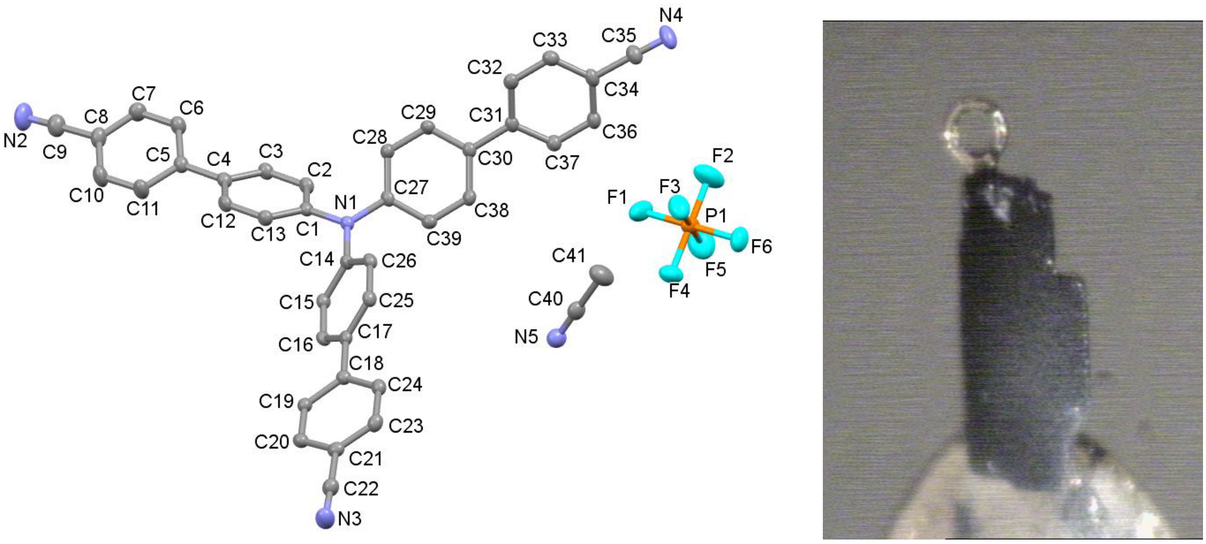


Figure S85. Solid-state molecular structure of [**TCBPA$^{\cdot+}$**]PF_6·MeCN, including atom numbering scheme. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. C atoms shown in grey, F atoms in cyan, N atoms in blue, and P atom in orange. Picture of the [**TCBPA$^{\cdot+}$**]PF_6 crystal in the diffractometer (right).

Table S19. Bond lengths for [**TCBPA**$^{\cdot+}$]PF_6·MeCN.

Atom	Atom	Length/Å
P1	F6	1.5832(15)
P1	F4	1.5904(17)
P1	F3	1.5907(18)
P1	F1	1.5937(16)
P1	F2	1.5923(19)
P1	F5	1.595(2)
N1	C1	1.412(3)
N1	C14	1.419(3)
N1	C27	1.408(3)
N3	C22	1.145(3)
N5	C40	1.134(3)
N4	C35	1.141(3)
C1	C2	1.397(3)
C1	C13	1.402(3)
C18	C17	1.481(3)
C18	C24	1.403(3)
C18	C19	1.405(3)
C14	C15	1.401(3)
C14	C26	1.402(3)
C29	C30	1.407(3)
C29	C28	1.384(3)
C27	C39	1.405(3)
C27	C28	1.397(3)
C39	C38	1.380(3)
C30	C31	1.486(3)
C30	C38	1.400(3)
C31	C37	1.400(3)
C31	C32	1.395(3)
C17	C16	1.403(3)
C17	C25	1.403(3)
C2	C3	1.383(3)
C15	C16	1.376(3)
C13	C12	1.381(3)
C4	C12	1.396(3)
C4	C5	1.481(3)
C4	C3	1.399(3)
C24	C23	1.386(3)
C26	C25	1.380(3)
C23	C21	1.395(3)
C37	C36	1.384(3)
C32	C33	1.386(3)
C5	C6	1.389(3)
C5	C11	1.403(3)
C34	C33	1.388(3)
C34	C36	1.391(3)
C34	C35	1.448(3)
C19	C20	1.374(3)
C21	C20	1.399(3)
C21	C22	1.442(3)
C6	C7	1.388(3)

Atom	Atom	Length/Å
N2	C9	1.148(3)
C40	C41	1.455(4)
C8	C7	1.392(3)
C8	C10	1.383(4)
C8	C9	1.446(3)
C11	C10	1.384(3)

Table S20. Bond angles for [**TCBPA**$^{\cdot+}$]PF_6·MeCN.

Atom	Atom	Atom	Angle/˚
F6	P1	F4	90.80(9)
F6	P1	F3	89.45(9)
F6	P1	F1	179.74(12)
F6	P1	F2	89.80(10)
F6	P1	F5	90.73(10)
F4	P1	F3	90.42(10)
F4	P1	F1	89.21(10)
F4	P1	F2	179.40(11)
F4	P1	F5	89.47(11)
F3	P1	F1	90.30(11)
F3	P1	F2	89.52(11)
F3	P1	F5	179.80(11)
F1	P1	F5	89.53(11)
F2	P1	F1	90.19(11)
F2	P1	F5	90.58(12)
C1	N1	C14	119.31(16)
C27	N1	C1	122.05(17)
C27	N1	C14	118.47(16)
C2	C1	N1	121.17(18)
C2	C1	C13	120.00(19)
C13	C1	N1	118.81(18)
C24	C18	C17	121.72(18)
C24	C18	C19	118.17(19)
C19	C18	C17	120.06(18)
C15	C14	N1	120.23(18)
C15	C14	C26	120.13(19)
C26	C14	N1	119.64(18)
C28	C29	C30	120.70(19)
C39	C27	N1	118.69(19)
C28	C27	N1	121.49(18)
C28	C27	C39	119.73(18)
C38	C39	C27	119.81(19)
C29	C30	C31	120.85(19)
C38	C30	C29	118.60(18)
C38	C30	C31	120.46(18)
C37	C31	C30	120.78(19)
C32	C31	C30	120.35(18)
C32	C31	C37	118.77(18)
C29	C28	C27	119.93(19)
C16	C17	C18	120.94(18)

Atom	Atom	Atom	Angle/°
C25	C17	C18	120.89(18)
C25	C17	C16	118.16(19)
C3	C2	C1	119.60(19)
C16	C15	C14	119.39(18)
C12	C13	C1	119.19(19)
C12	C4	C5	120.64(19)
C12	C4	C3	117.89(19)
C3	C4	C5	121.47(19)
C23	C24	C18	120.97(19)
C25	C26	C14	119.60(19)
C24	C23	C21	119.69(19)
C36	C37	C31	120.8(2)
C33	C32	C31	121.0(2)
C15	C16	C17	121.56(19)
C13	C12	C4	121.88(19)
C6	C5	C4	121.93(19)
C6	C5	C11	118.1(2)
C11	C5	C4	119.9(2)
C33	C34	C36	120.93(19)
C33	C34	C35	120.6(2)
C36	C34	C35	118.5(2)
C26	C25	C17	121.15(19)
C20	C19	C18	121.33(19)
C39	C38	C30	120.95(19)
C23	C21	C20	120.1(2)
C23	C21	C22	121.9(2)
C20	C21	C22	118.1(2)
C32	C33	C34	119.2(2)
C2	C3	C4	121.4(2)
C19	C20	C21	119.8(2)
C37	C36	C34	119.3(2)
N3	C22	C21	176.2(3)
N4	C35	C34	178.7(3)
C7	C6	C5	121.3(2)
N5	C40	C41	179.2(3)
C7	C8	C9	120.4(2)
C10	C8	C7	120.0(2)
C10	C8	C9	119.5(2)
C10	C11	C5	120.9(2)
C6	C7	C8	119.6(2)
C8	C10	C11	120.0(2)
N2	C9	C8	177.8(3)

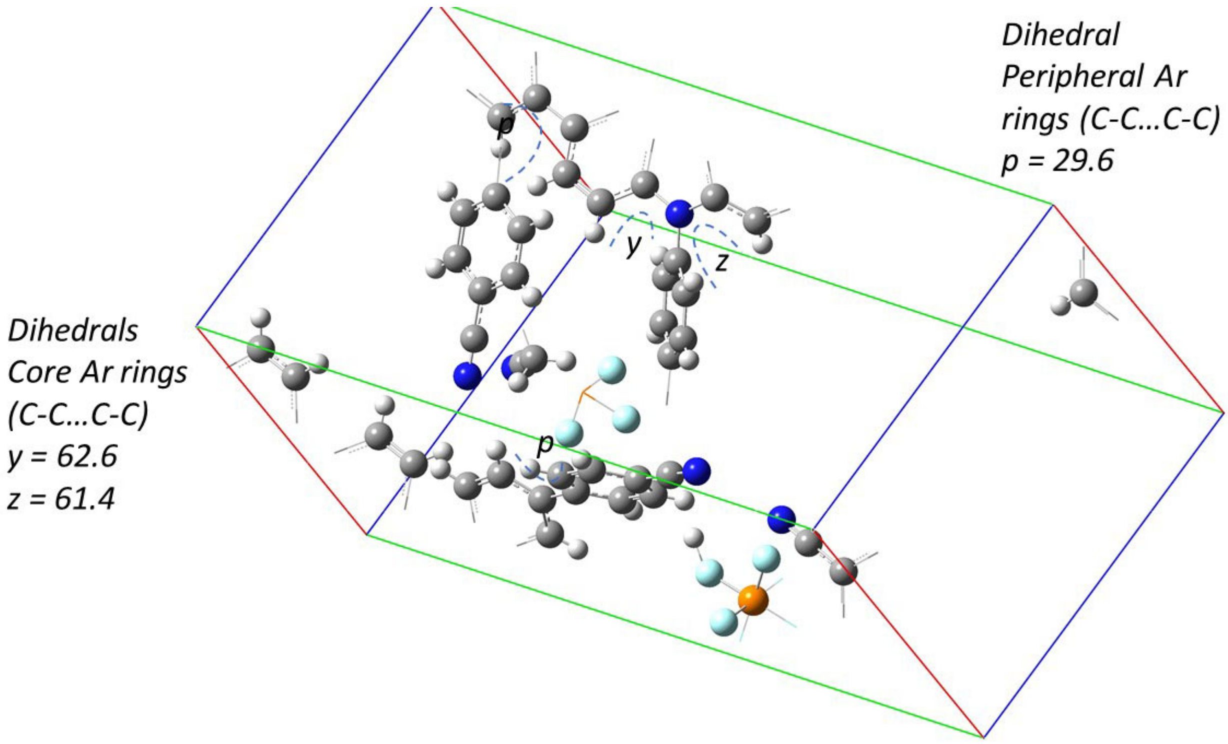


Figure S86. Dihedrals of [**TCBPA**$^{\cdot+}$]PF_6·MeCN visualized in GaussView 5.0.9.

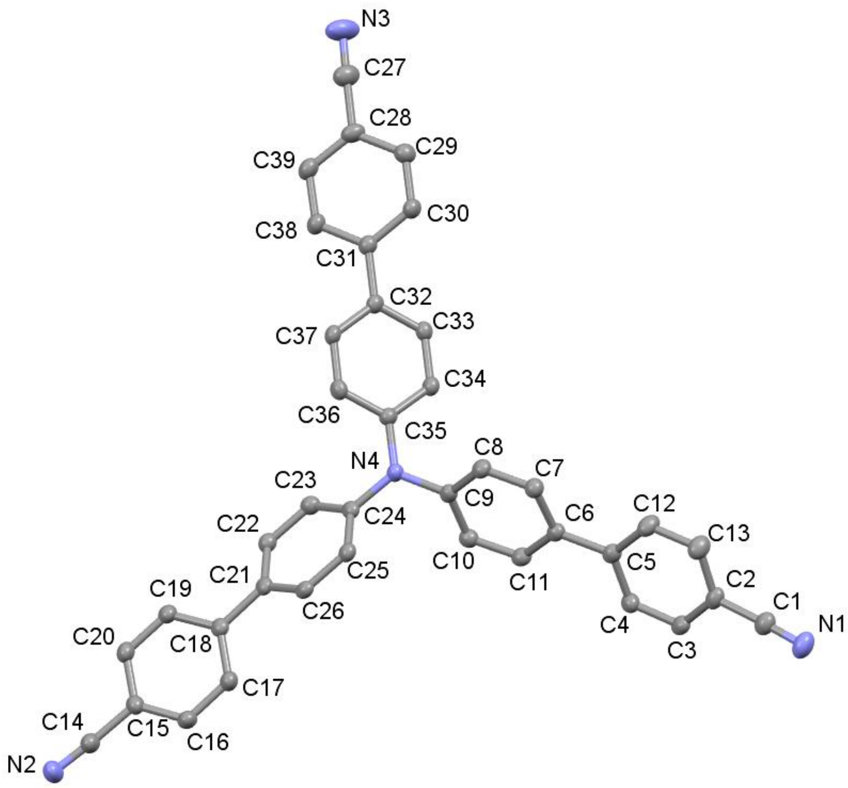


Figure S87. Solid-state molecular structure of **TCBPA**, including atom numbering scheme. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. C atoms shown in grey and N atoms in blue.

Table S21. Bond lengths for **TCBPA**.

Atom	Atom	Length/Å
N4	C24	1.417(2)
N4	C35	1.408(2)
N4	C9	1.428(2)
N1	C1	1.148(2)
C29	C28	1.396(3)
C29	C30	1.382(2)
C4	C3	1.388(2)
C4	C5	1.403(2)
C8	C7	1.387(2)
C8	C9	1.389(2)
C7	C6	1.405(2)
C10	C11	1.384(2)
C10	C9	1.395(2)
C6	C11	1.398(2)
C6	C5	1.490(2)
C12	C13	1.387(3)
C12	C5	1.398(2)
C32	C31	1.476(2)
C32	C33	1.397(2)
C32	C37	1.401(2)
C34	C33	1.384(2)
C34	C35	1.399(2)
C19	C18	1.397(2)
C19	C20	1.385(2)
C31	C38	1.398(2)
C31	C30	1.398(2)
C18	C21	1.479(2)
C18	C17	1.402(2)
C36	C37	1.376(2)
C36	C35	1.401(2)
C16	C17	1.384(2)
C16	C15	1.388(2)
C2	C1	1.445(2)
C2	C3	1.389(2)
C2	C13	1.393(2)
C28	C39	1.394(3)
C28	C27	1.441(3)
C21	C22	1.400(2)
C21	C26	1.402(2)
C25	C24	1.396(2)
C25	C26	1.384(2)
C14	C15	1.443(2)
C14	N2	1.143(2)
C20	C15	1.389(2)
C24	C23	1.394(2)
C22	C23	1.389(2)
C38	C39	1.381(2)
N3	C27	1.147(3)

Table S22. Bond angles for **TCBPA**.

Atom	Atom	Atom	Angle/°
C24	N4	C9	118.88(13)
C35	N4	C24	121.40(13)

Atom	Atom	Atom	Angle/°
C35	N4	C9	119.60(13)
C30	C29	C28	119.90(16)
C3	C4	C5	121.49(16)
C7	C8	C9	119.99(15)
C8	C7	C6	121.67(15)
C11	C10	C9	120.17(15)
C7	C6	C5	121.15(15)
C11	C6	C7	117.09(15)
C11	C6	C5	121.68(14)
C13	C12	C5	121.96(16)
C33	C32	C31	121.75(14)
C33	C32	C37	117.09(15)
C37	C32	C31	121.16(14)
C33	C34	C35	120.74(15)
C20	C19	C18	120.68(16)
C38	C31	C32	120.65(14)
C30	C31	C32	121.42(15)
C30	C31	C38	117.93(15)
C19	C18	C21	121.51(15)
C19	C18	C17	117.84(15)
C17	C18	C21	120.64(15)
C10	C11	C6	121.71(15)
C37	C36	C35	120.48(14)
C34	C33	C32	121.57(14)
C17	C16	C15	119.48(16)
C3	C2	C1	120.59(16)
C3	C2	C13	119.39(16)
C13	C2	C1	119.96(16)
C29	C28	C27	119.45(16)
C39	C28	C29	119.63(16)
C39	C28	C27	120.89(17)
C22	C21	C18	122.04(15)
C22	C21	C26	117.70(14)
C26	C21	C18	120.26(14)
C26	C25	C24	120.31(15)
N2	C14	C15	177.2(2)
N1	C1	C2	176.49(18)
C4	C3	C2	120.18(15)
C16	C17	C18	121.62(16)
C19	C20	C15	120.49(16)
C25	C24	N4	119.42(15)
C23	C24	N4	121.72(14)
C23	C24	C25	118.86(14)
C36	C37	C32	121.99(14)
C23	C22	C21	120.97(15)
C39	C38	C31	121.43(16)
C16	C15	C14	120.90(16)
C16	C15	C20	119.79(15)
C20	C15	C14	119.31(15)
C22	C23	C24	120.67(15)
C12	C13	C2	119.78(16)
C38	C39	C28	119.83(16)
C4	C5	C6	121.28(15)
C12	C5	C4	116.98(15)
C12	C5	C6	121.74(15)
C34	C35	N4	120.62(14)
C34	C35	C36	118.14(14)
C36	C35	N4	121.24(14)
C29	C30	C31	121.28(16)

Atom	Atom	Atom	Angle/˚
C8	C9	N4	120.65(14)
C8	C9	C10	119.33(15)
C10	C9	N4	120.01(15)
C25	C26	C21	121.48(15)
N3	C27	C28	177.7(2)

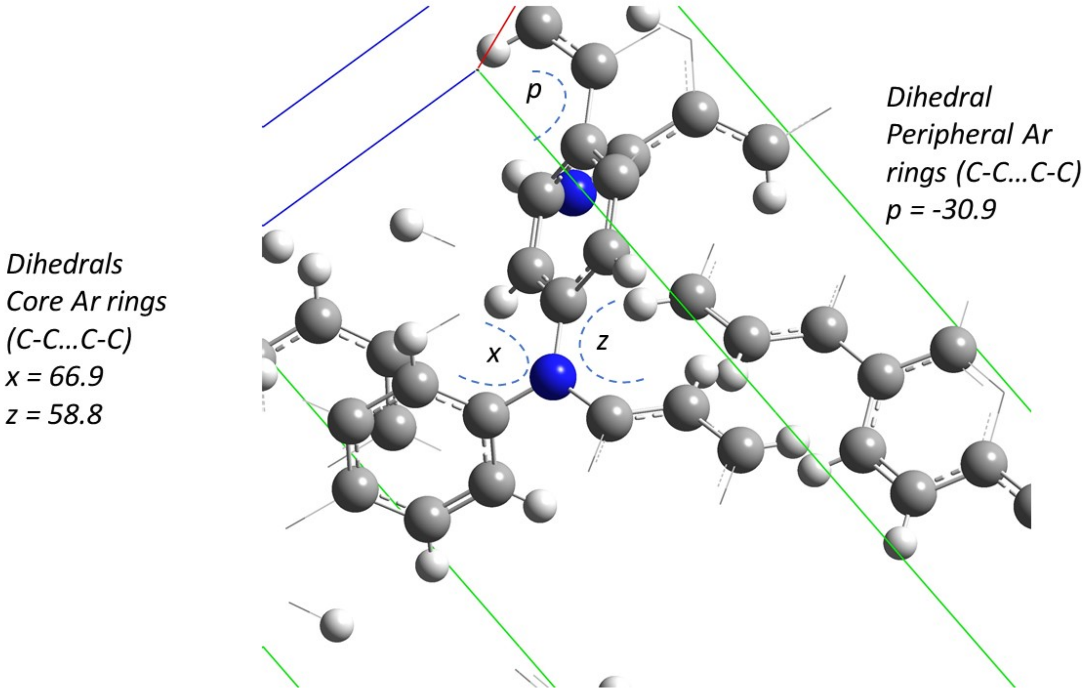
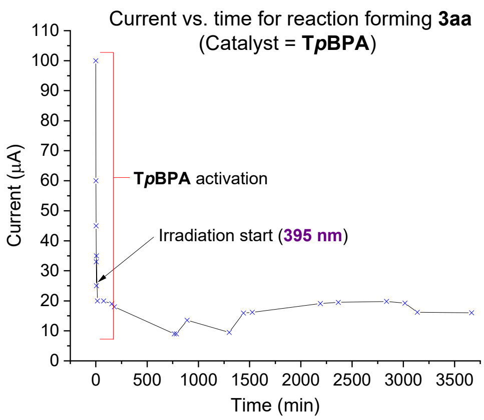


Figure S88. Dihedrals of **TCBPA** visualized in GaussView 5.0.9.

16. Current vs. Time Profile for Representative Reactions



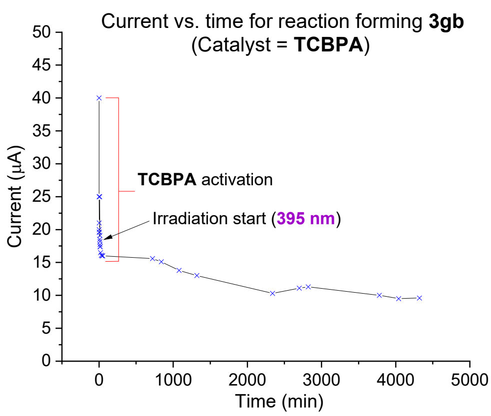
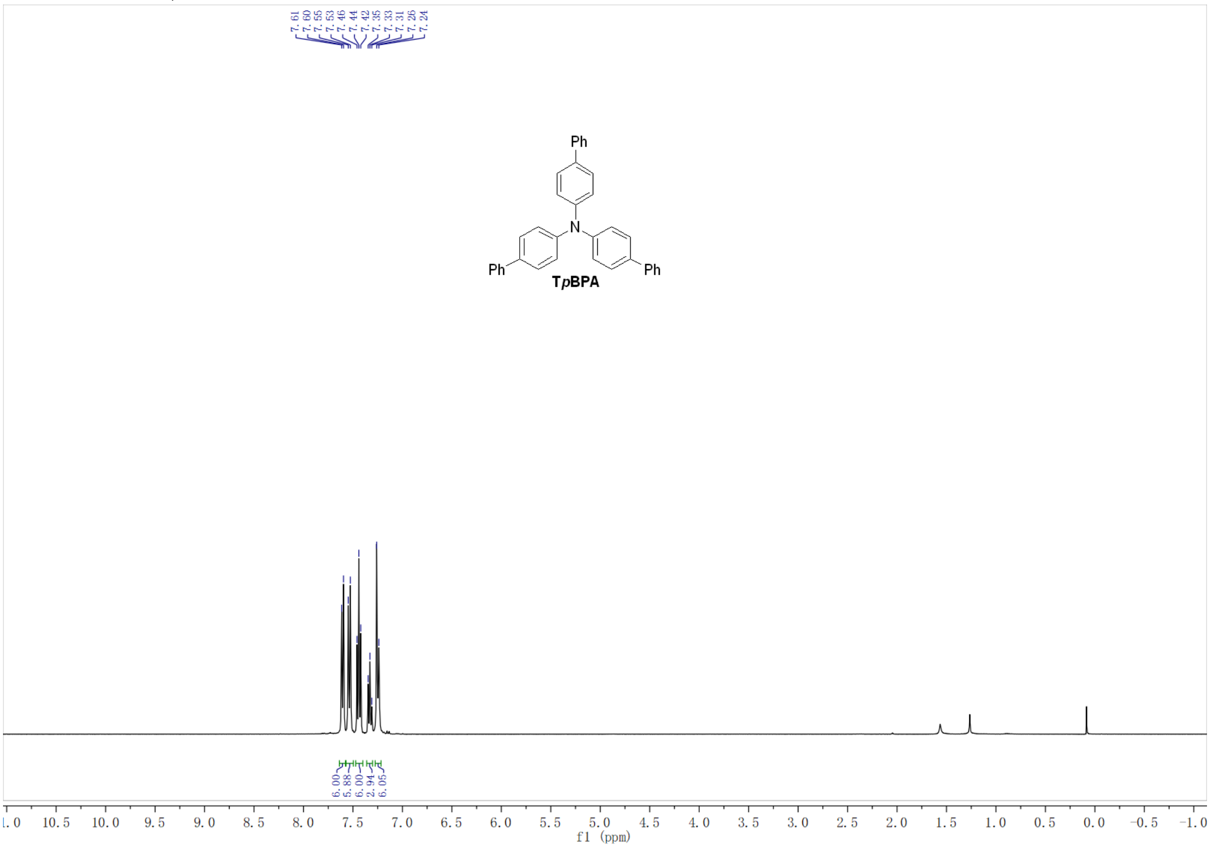
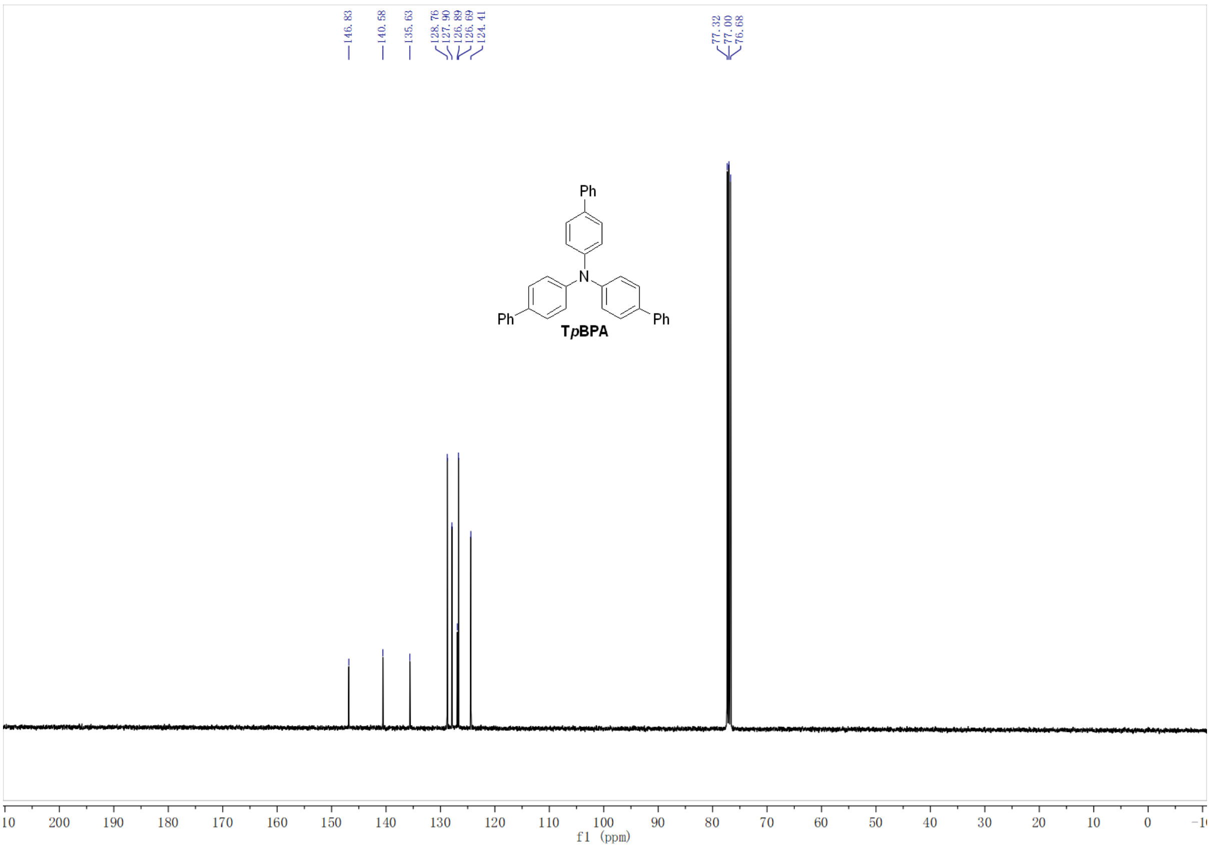


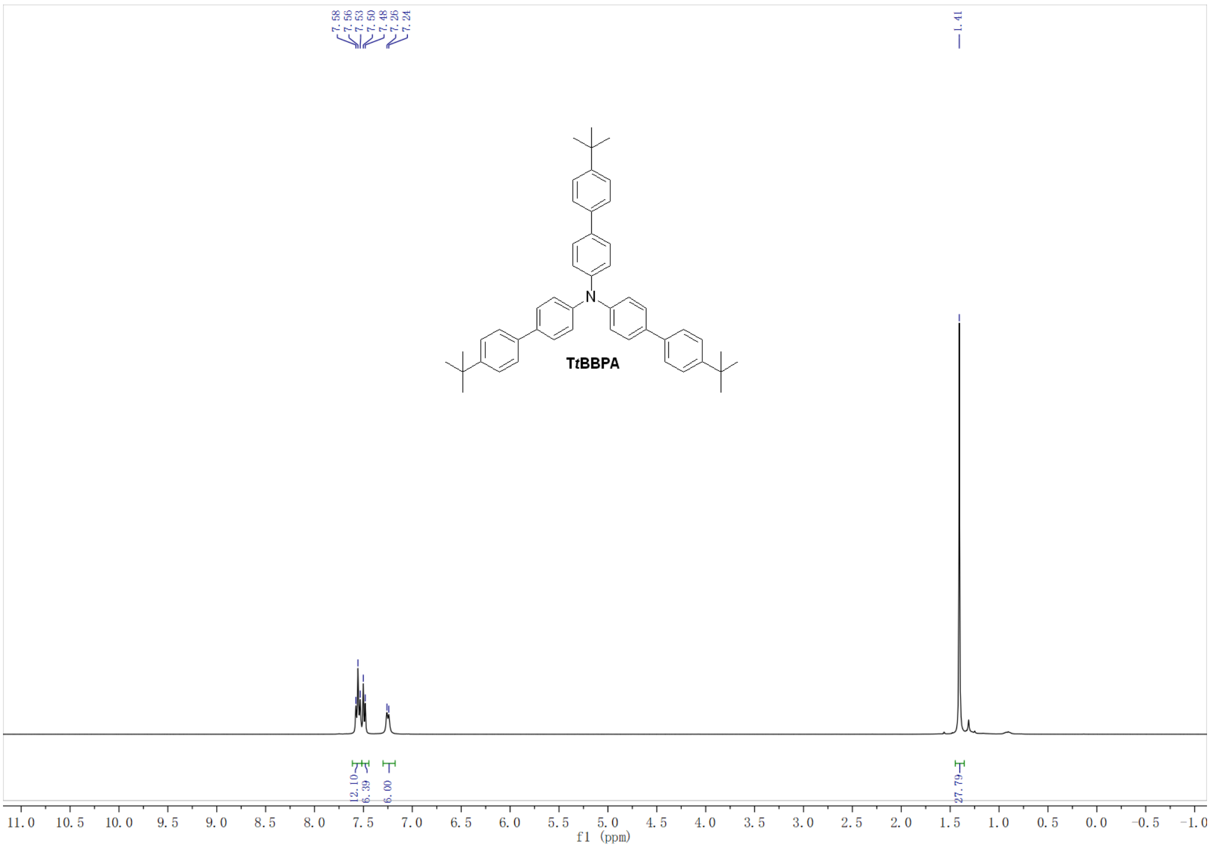
Figure S89. Current vs. time profiles for reactions forming **3aa** and **3gb**.

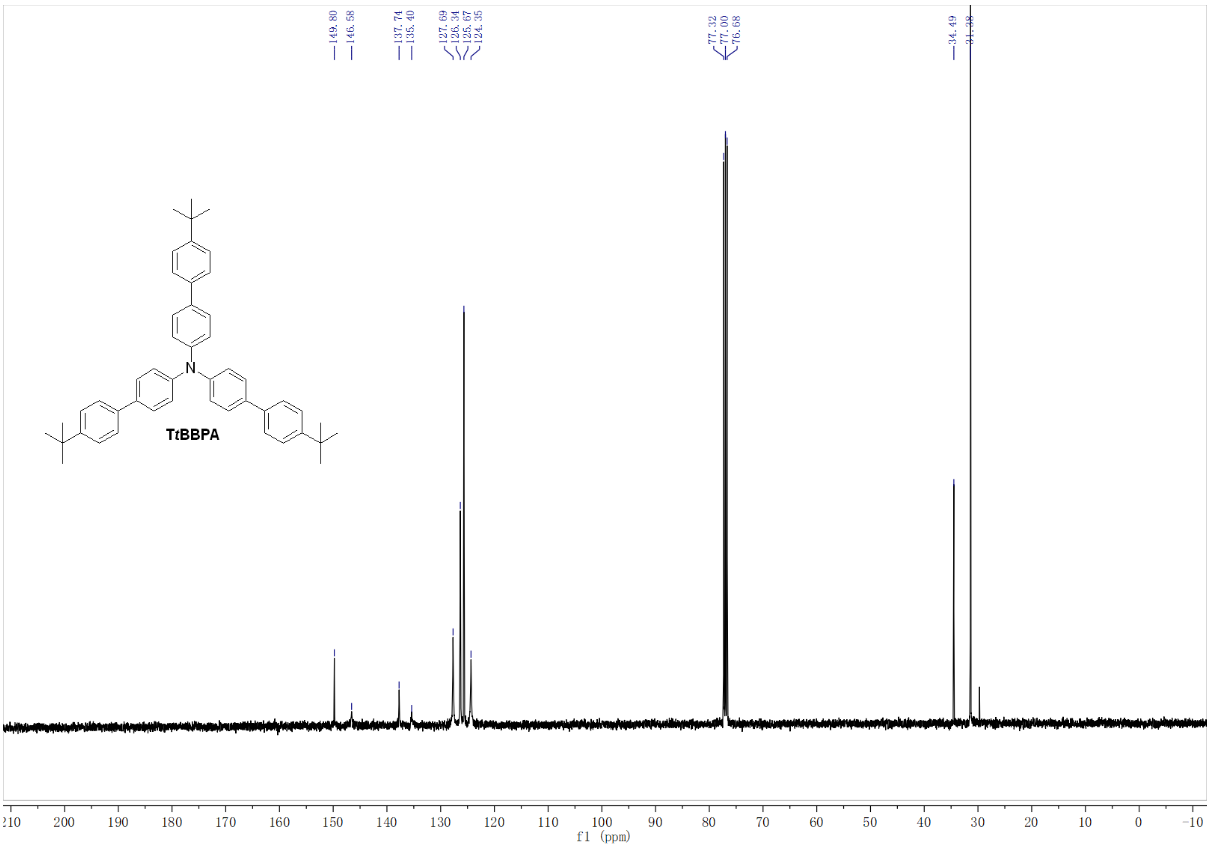
Current vs. time profiles were measured for the optimal conditions forming **3aa** (Table S9, entry 1) and **3gb** (Table S10, entry 1). Current was measured using a digital multimeter (Reichelt, UT 71D). The data do not provide much insight, aside from showing a steep initial decrease in the measured current which is clearly associated with the development of a coloured species as confirmed by spectroelectrochemistry (Section S8). The decrease in current as the radical cation is formed is unsurprising, no obvious further changes occur over time.

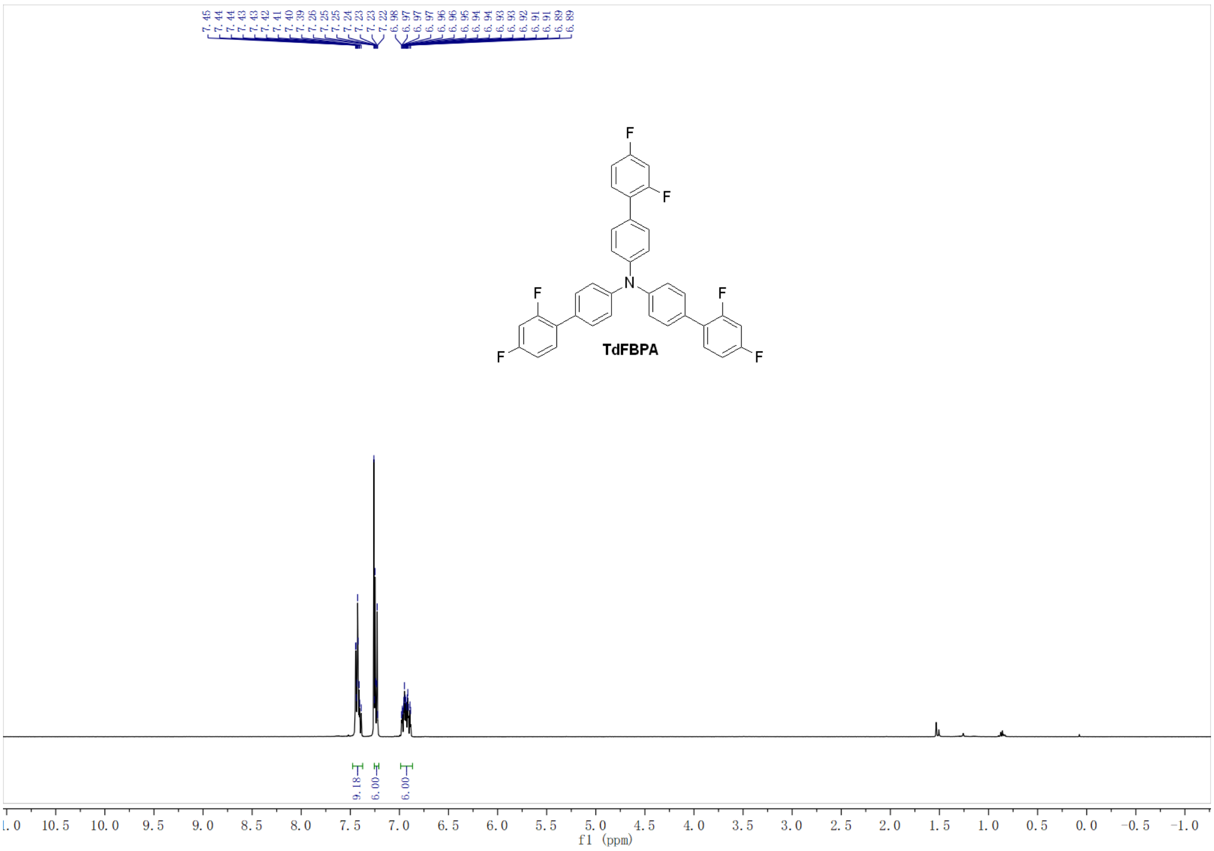
17. ^{1}H NMR, ^{13}C NMR AND ^{19}F NMR SPECTRA OF THE COMPOUNDS PREPARED

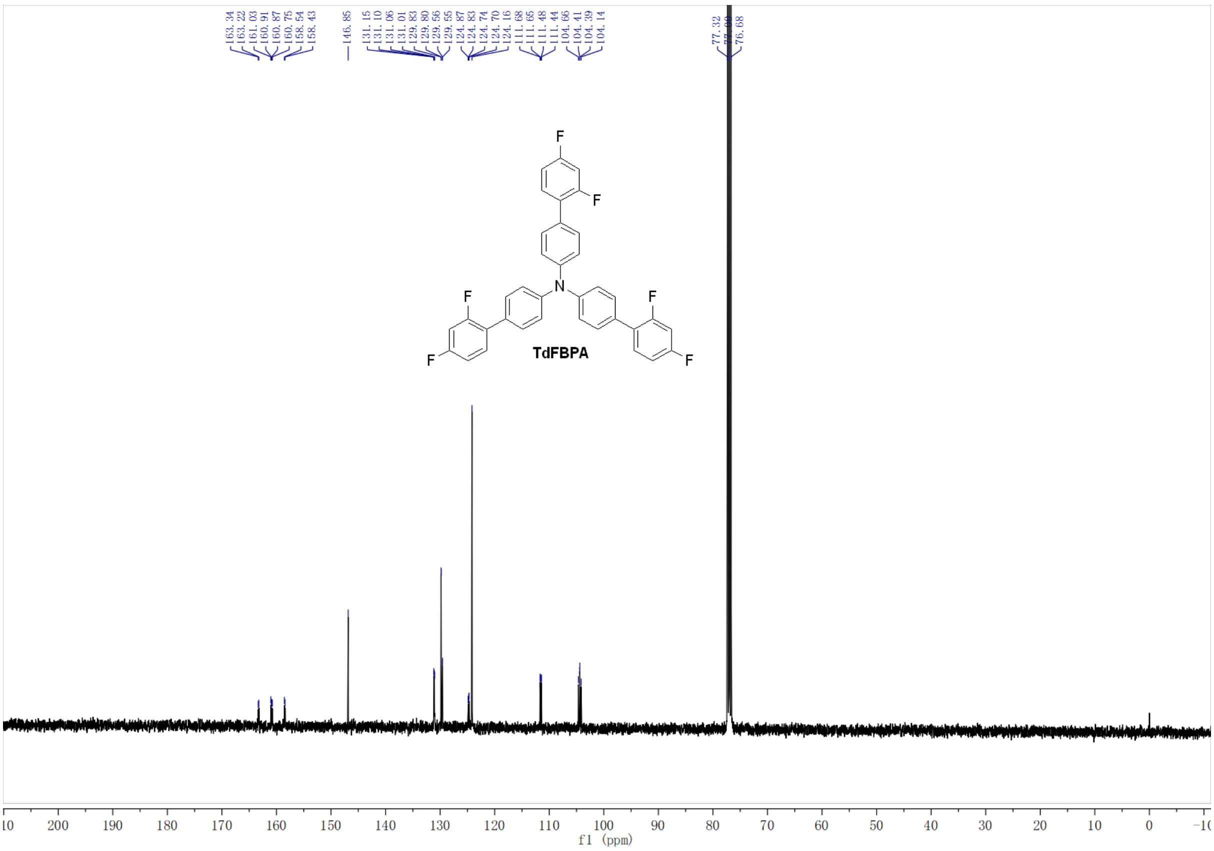





7.58
7.56
7.53
7.50
7.48
7.26
7.24
1.41
TtBBPA
N
12.10
6.39
6.00
27.79
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


149.80
146.58
137.74
135.40
127.69
126.34
125.67
124.35
77.32
77.00
76.68
34.49
31.38
TtBBPA
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


TdFBPA
f1 (ppm)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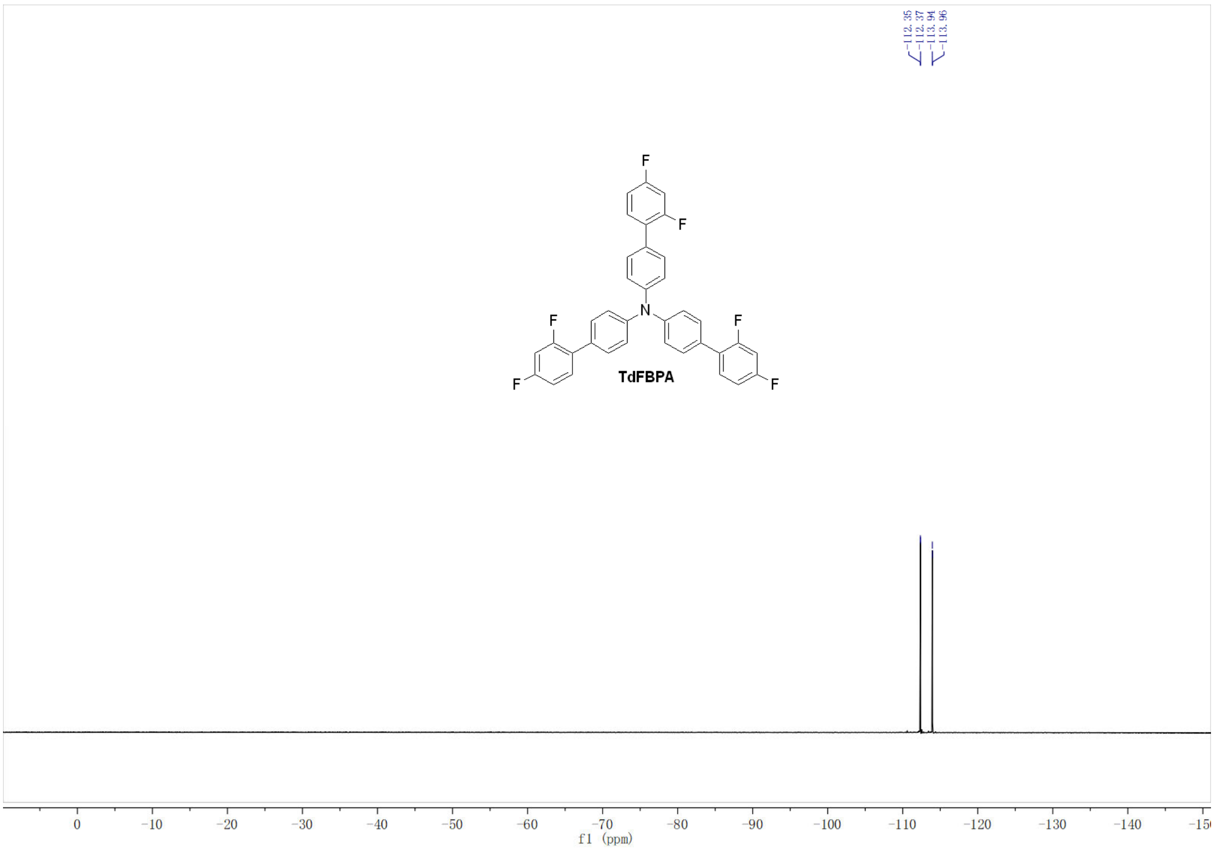

-112.35
-112.37
-113.94
-113.96
TdFBPA
0
-10
-20
-30
-40
-50
-60
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-90
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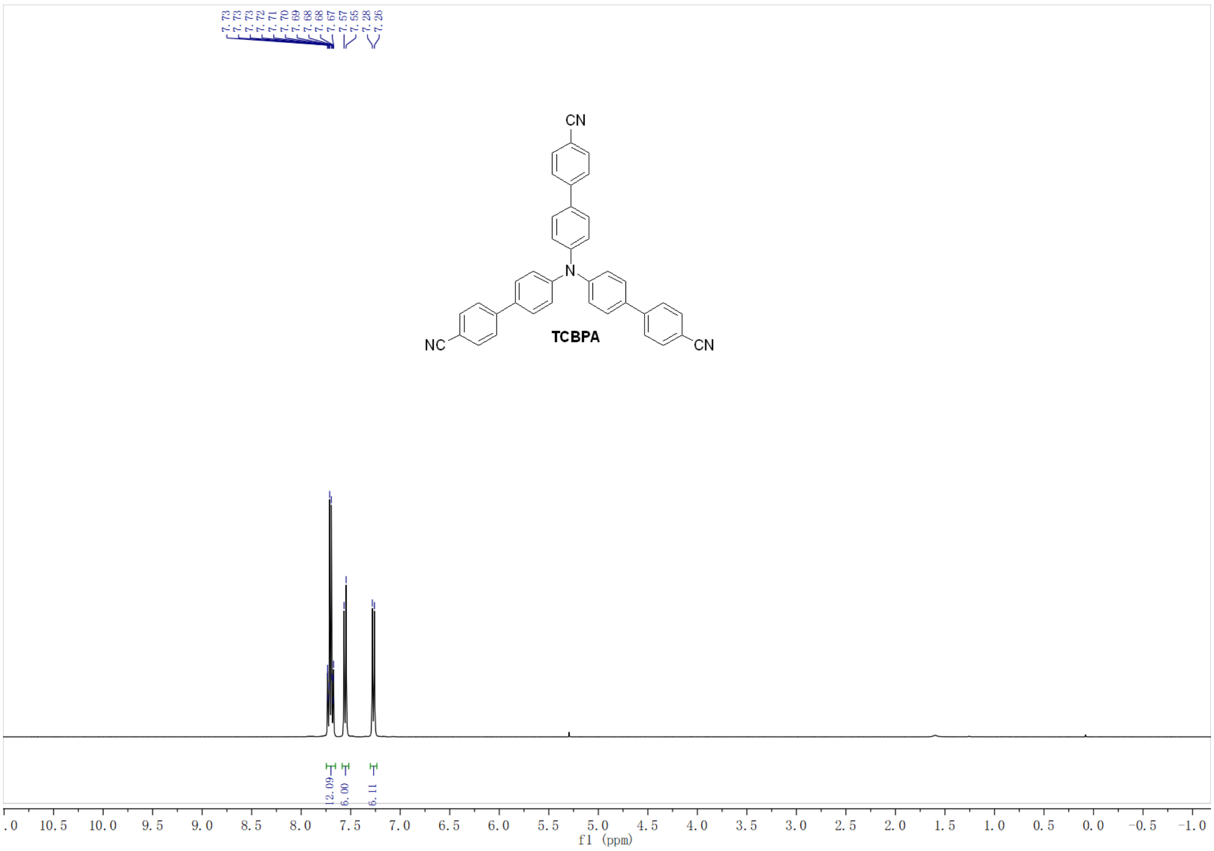
-130
-140
f1 (ppm)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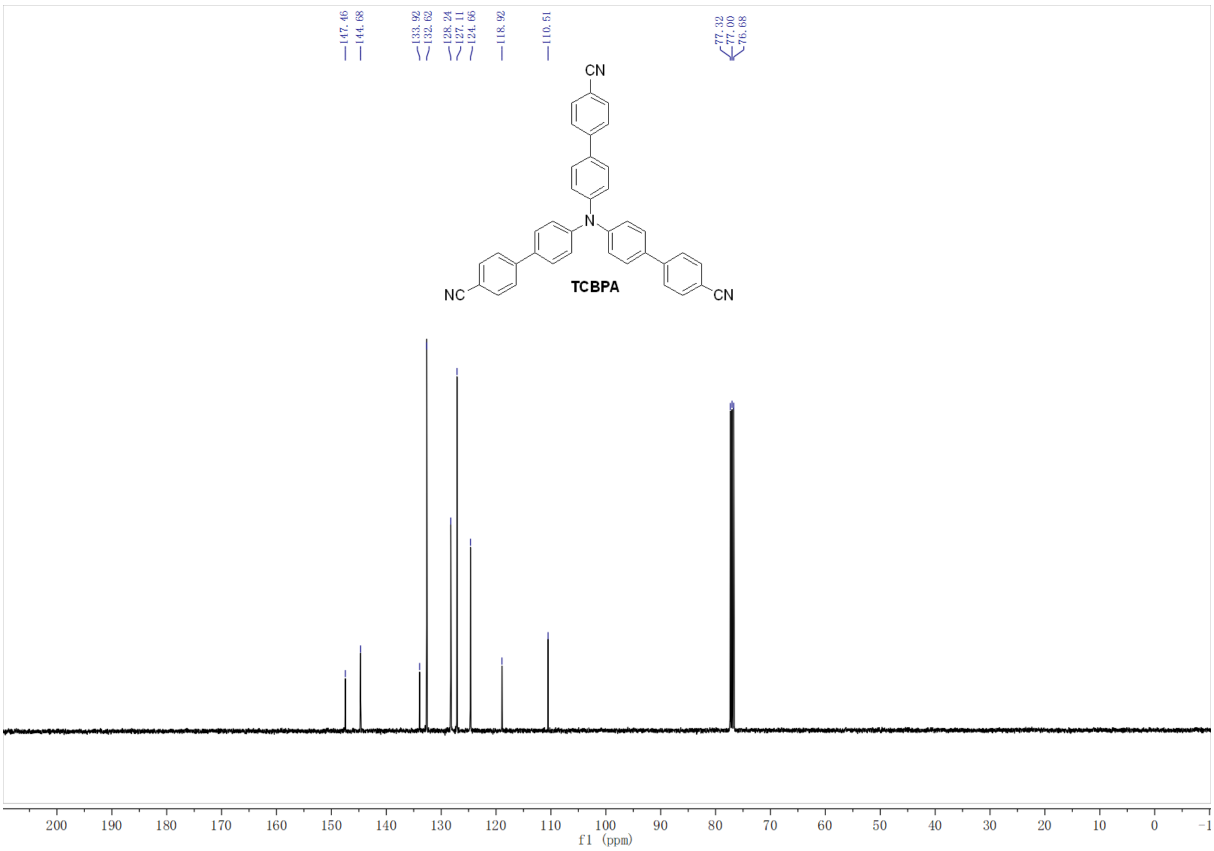
7.73
7.73
7.72
7.71
7.70
7.69
7.68
7.68
7.68
7.67
7.57
7.55
7.28
7.26
CN
N
NC
TCBPA
CN
12.09
6.00
6.11
f1 (ppm)


147.46
144.68
133.92
132.62
128.24
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118.92
110.51
77.32
77.00
76.68
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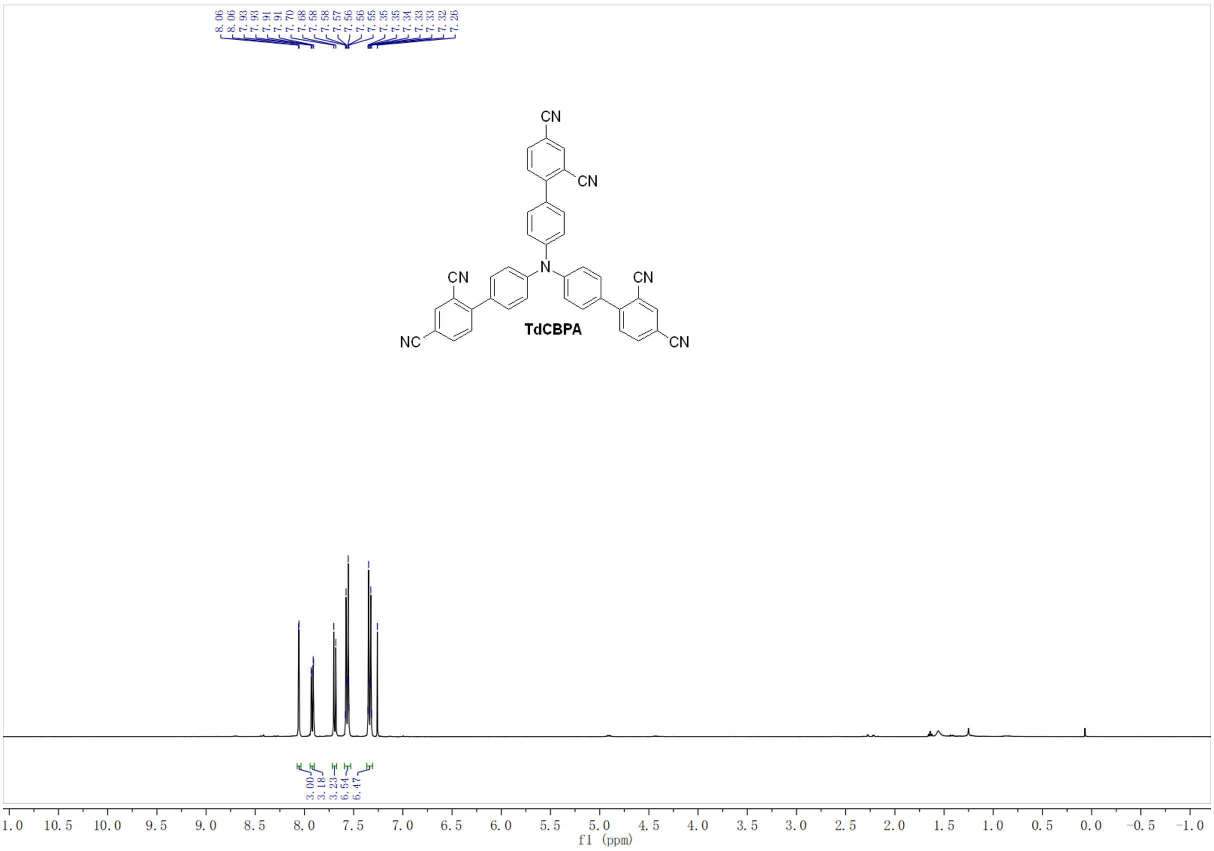
TCBPA
CN
f1 (ppm)


8.06
8.06
7.93
7.93
7.91
7.91
7.70
7.68
7.58
7.58
7.57
7.56
7.56
7.55
7.35
7.35
7.34
7.33
7.32
7.26
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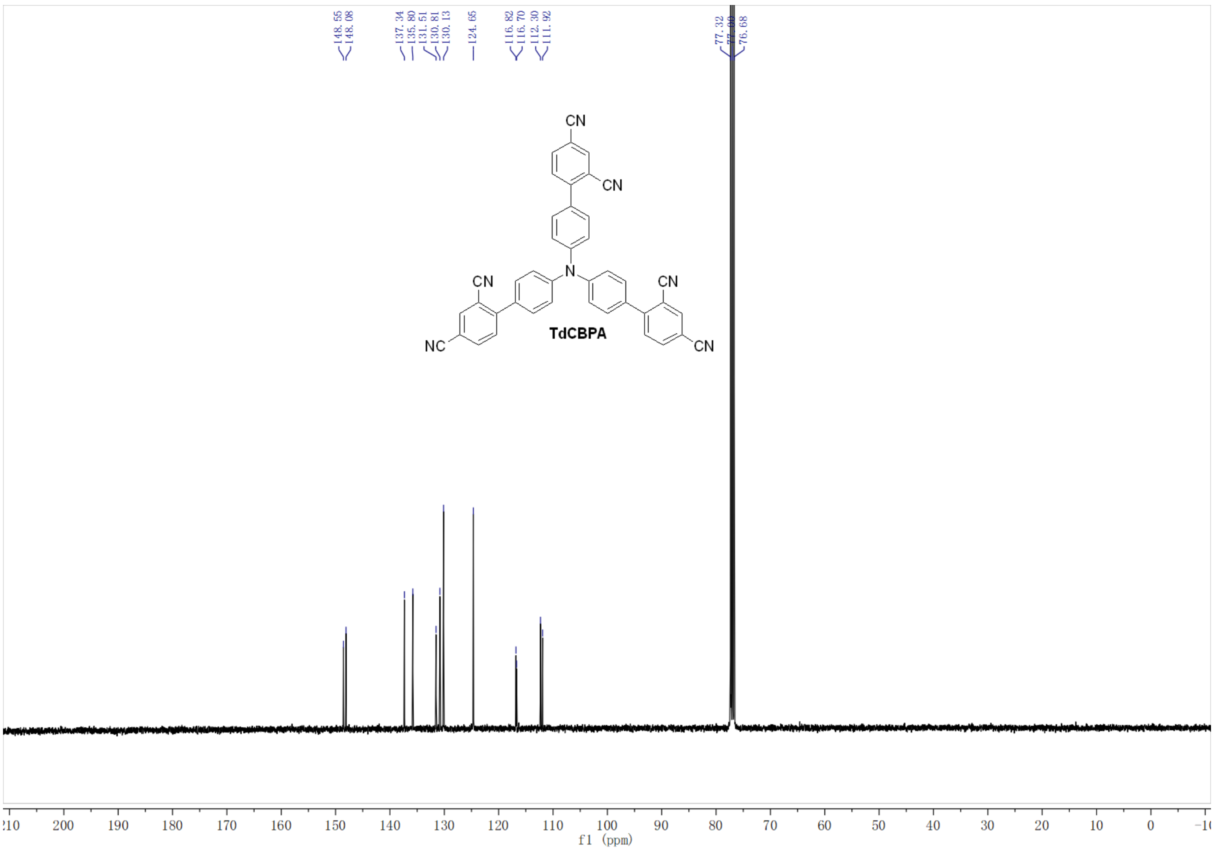
CN
CN
CN
NC
CN
N
TdCBPA
3.00
3.18
3.23
6.54
6.47
f1 (ppm)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148.08
137.34
135.80
131.51
130.81
130.13
124.65
116.82
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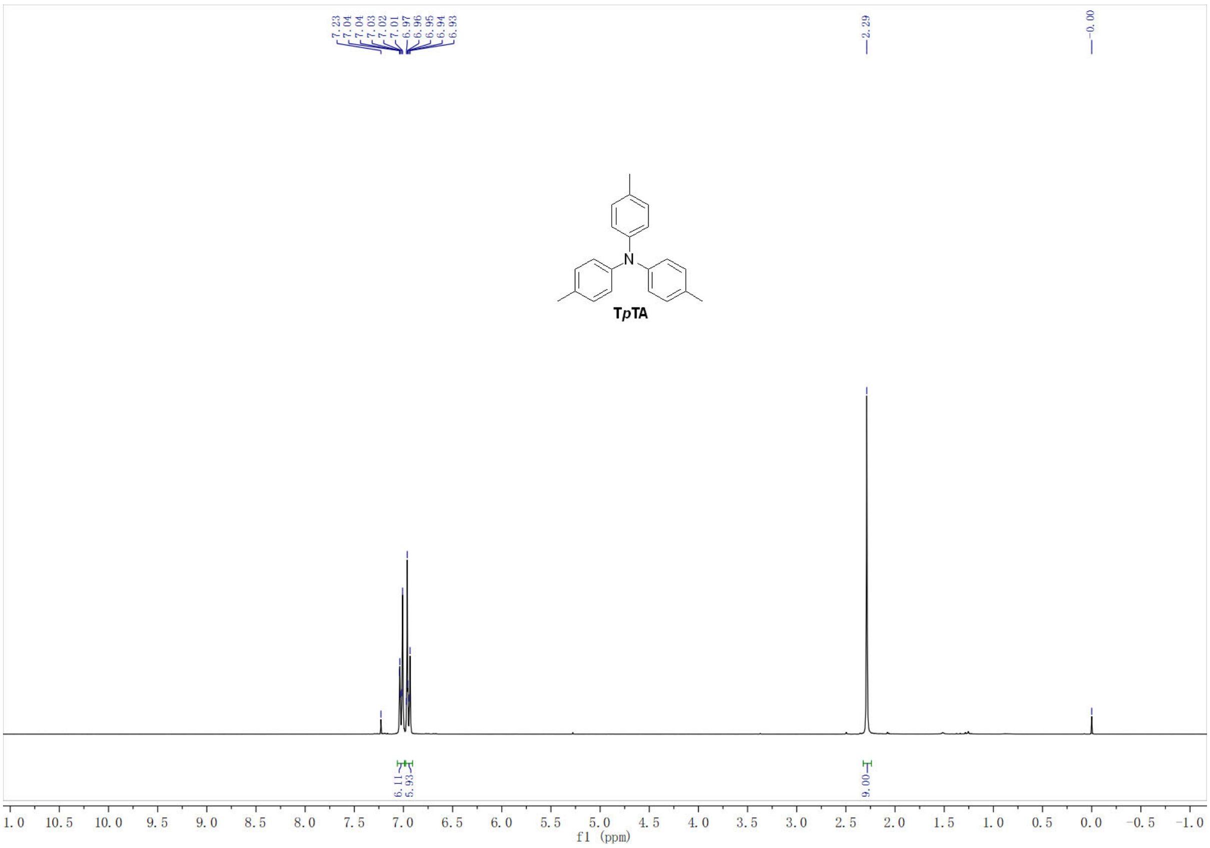
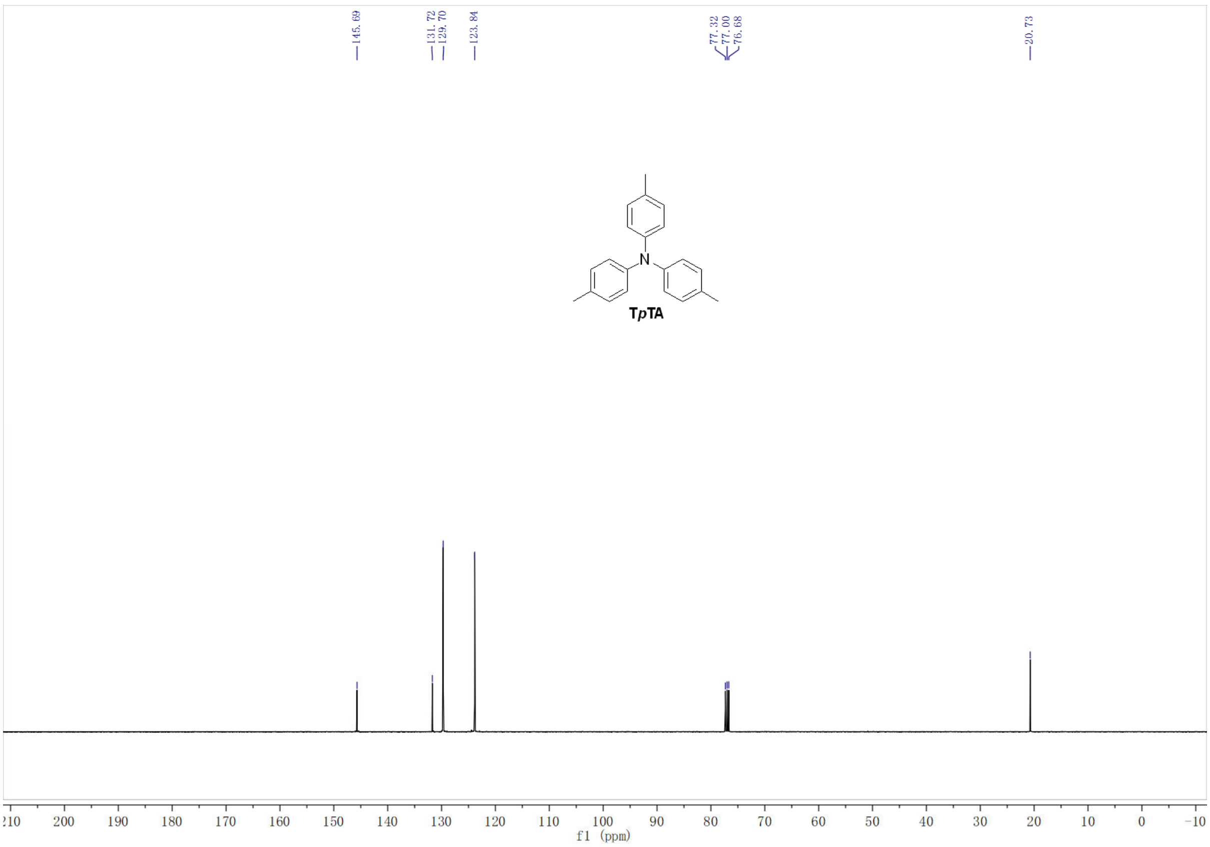
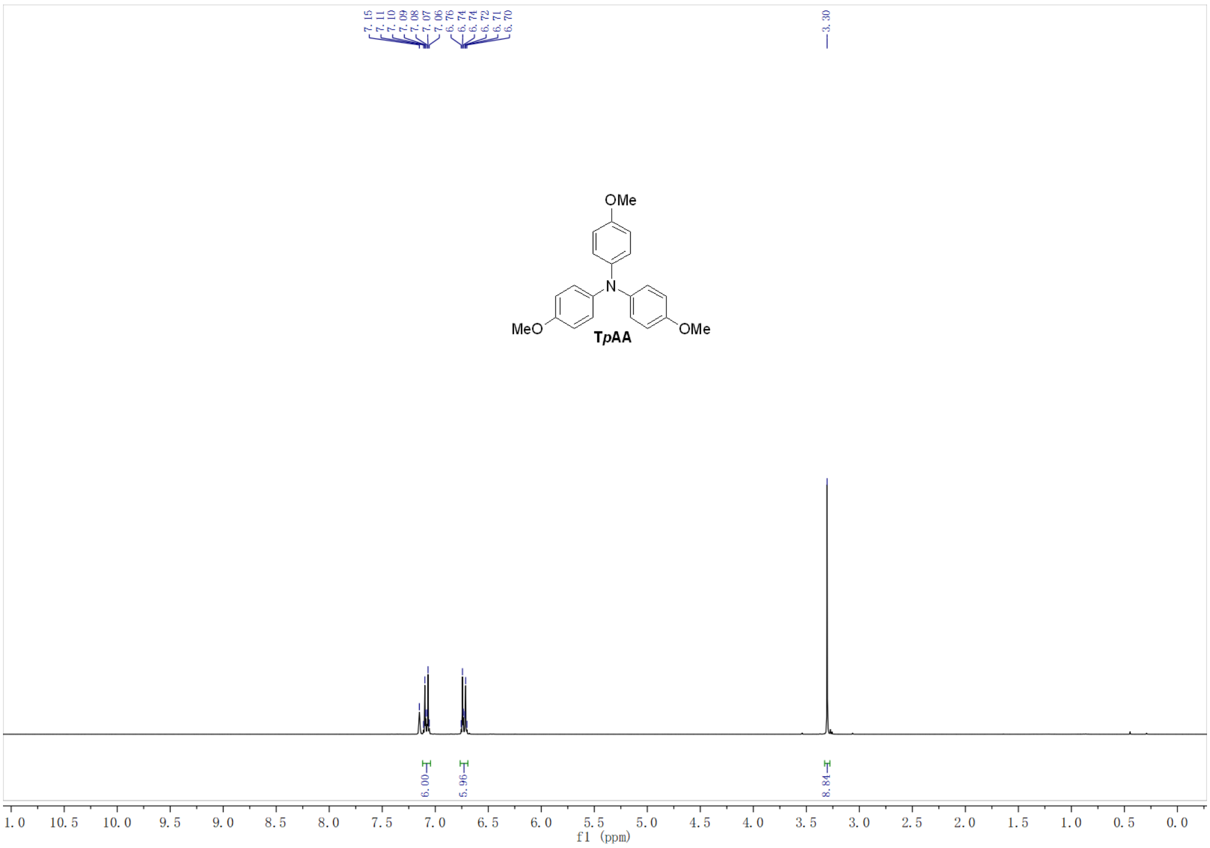
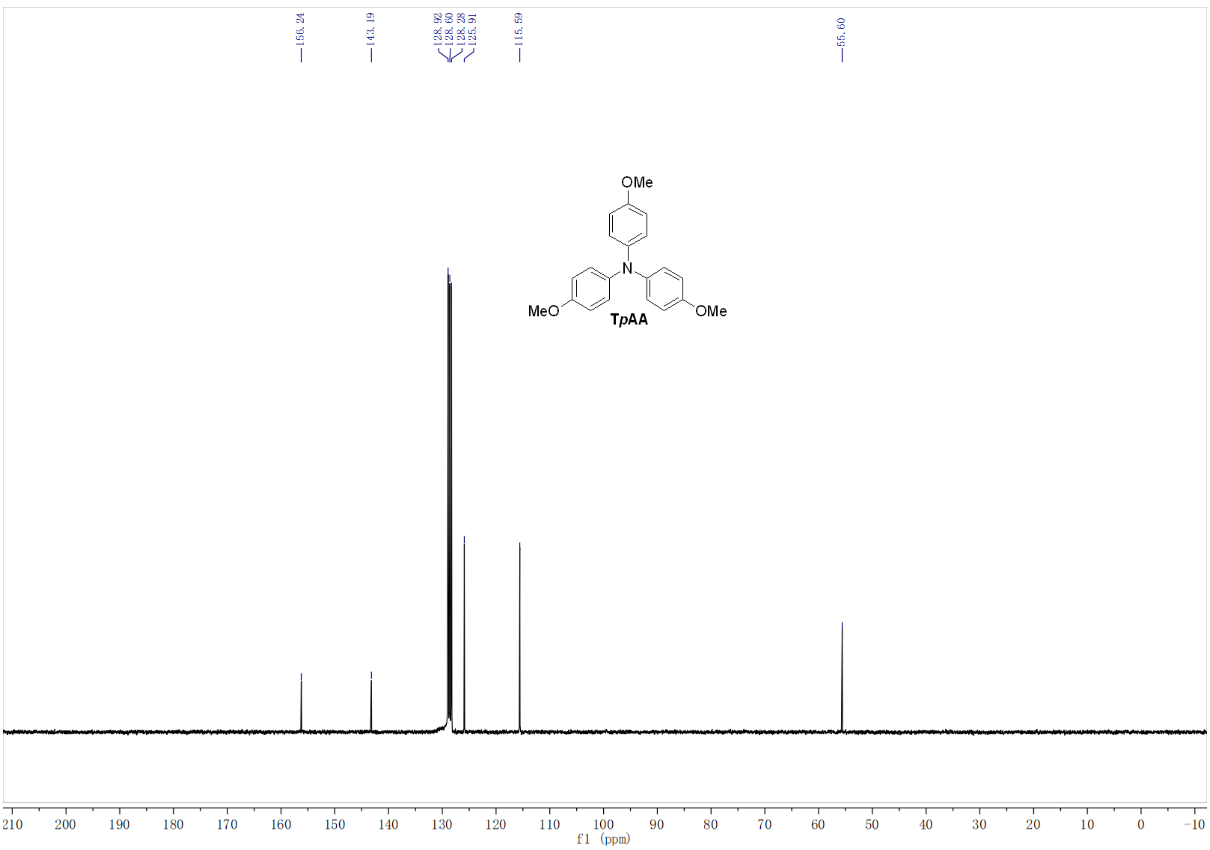
111.92
77.32
76.68
CN
CN
CN
CN
NC
CN
N
TdCBPA
f1 (ppm)


7.23
7.04
7.04
7.03
7.02
7.01
6.97
6.96
6.95
6.94
6.93
2.29
0.00
N
TpTA
6.11
5.93
9.00
f1 (ppm)


145.69
131.72
129.70
123.84
77.32
77.00
76.68
20.73
N
TpTA
f1 (ppm)


7.15
7.11
7.10
7.09
7.08
7.07
7.06
6.76
6.74
6.74
6.72
6.71
6.70
3.30
OMe
N
MeO
OMe
TpAA
6.00
5.96
8.84
f1 (ppm)


156.24
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128.28
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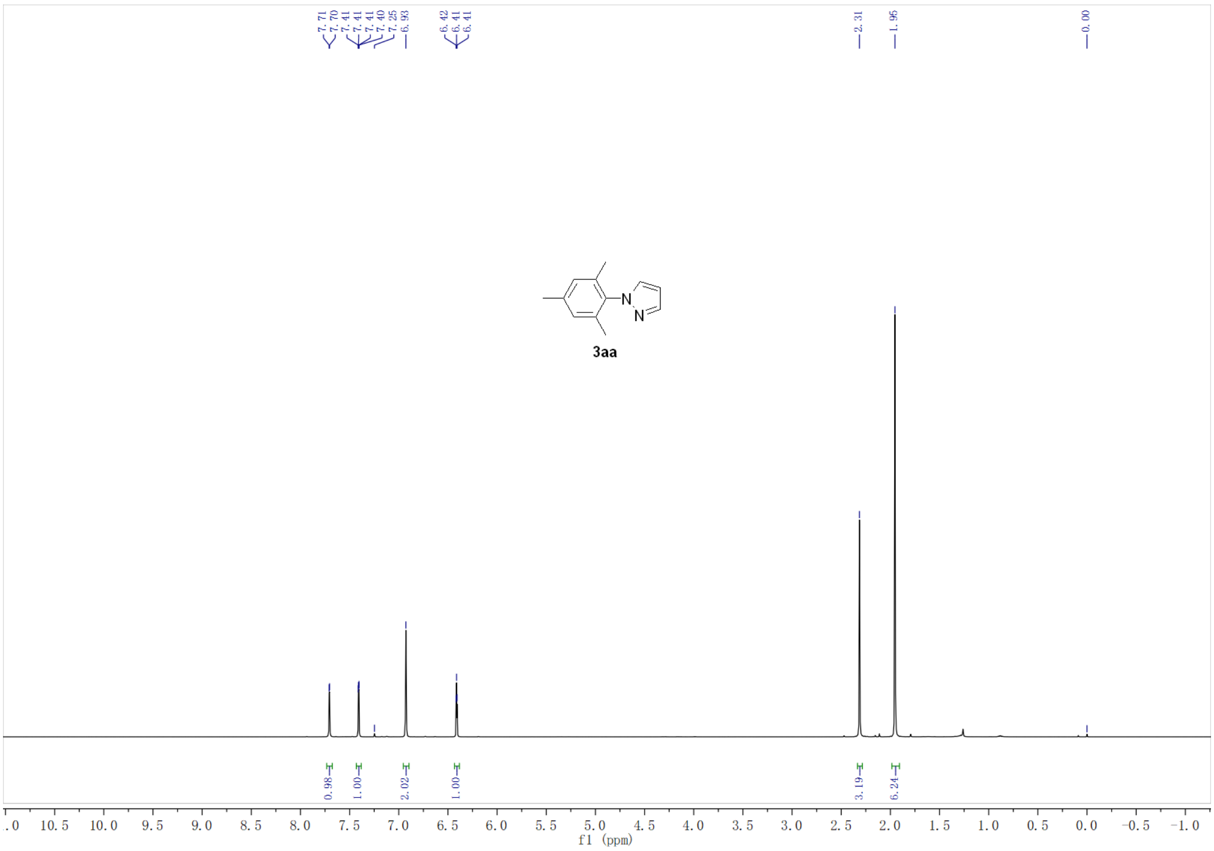
115.59
55.60
OMe
N
MeO
OMe
TpAA
f1 (ppm)


7.71
7.70
7.41
7.41
7.41
7.40
7.25
6.93
6.42
6.41
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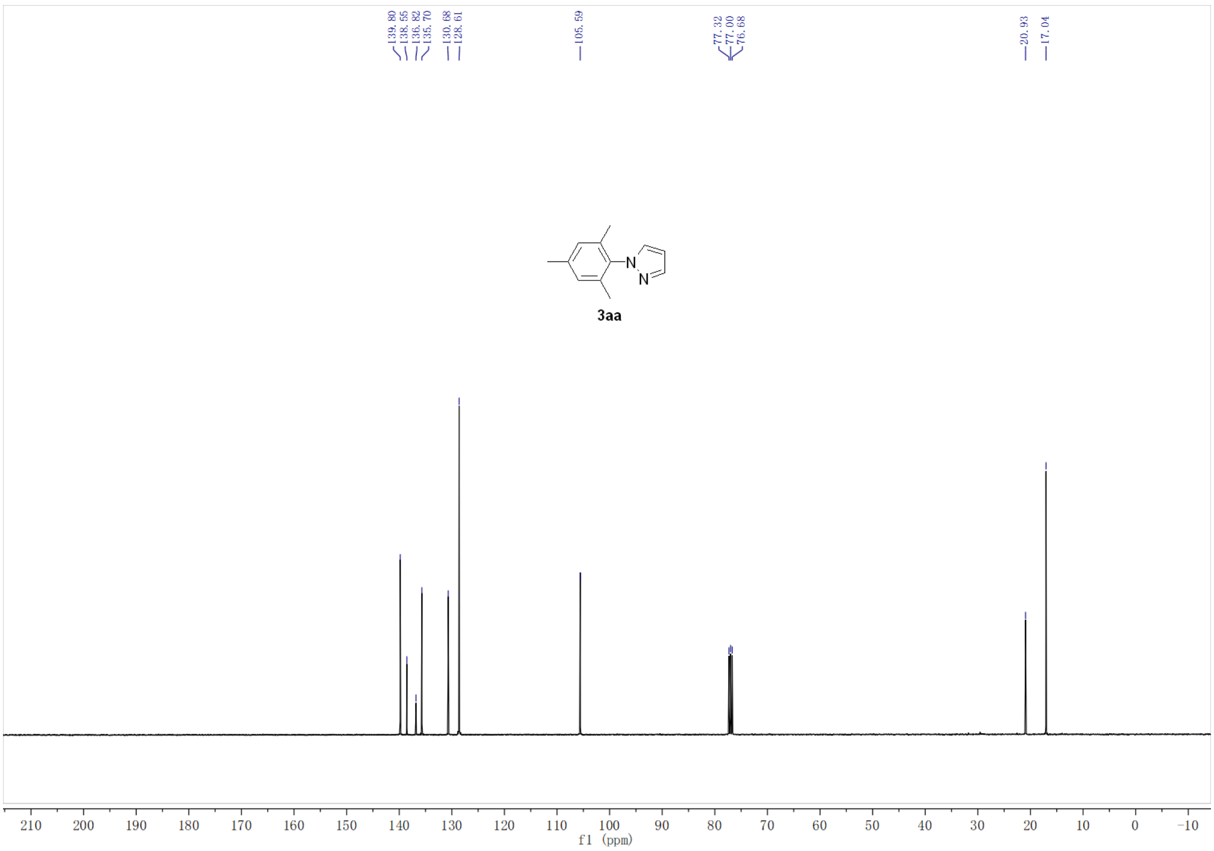
0.00
3aa
0.98
1.00
2.02
1.00
3.19
6.24
f1 (ppm)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138.55
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130.68
128.61
105.59
77.32
77.00
76.68
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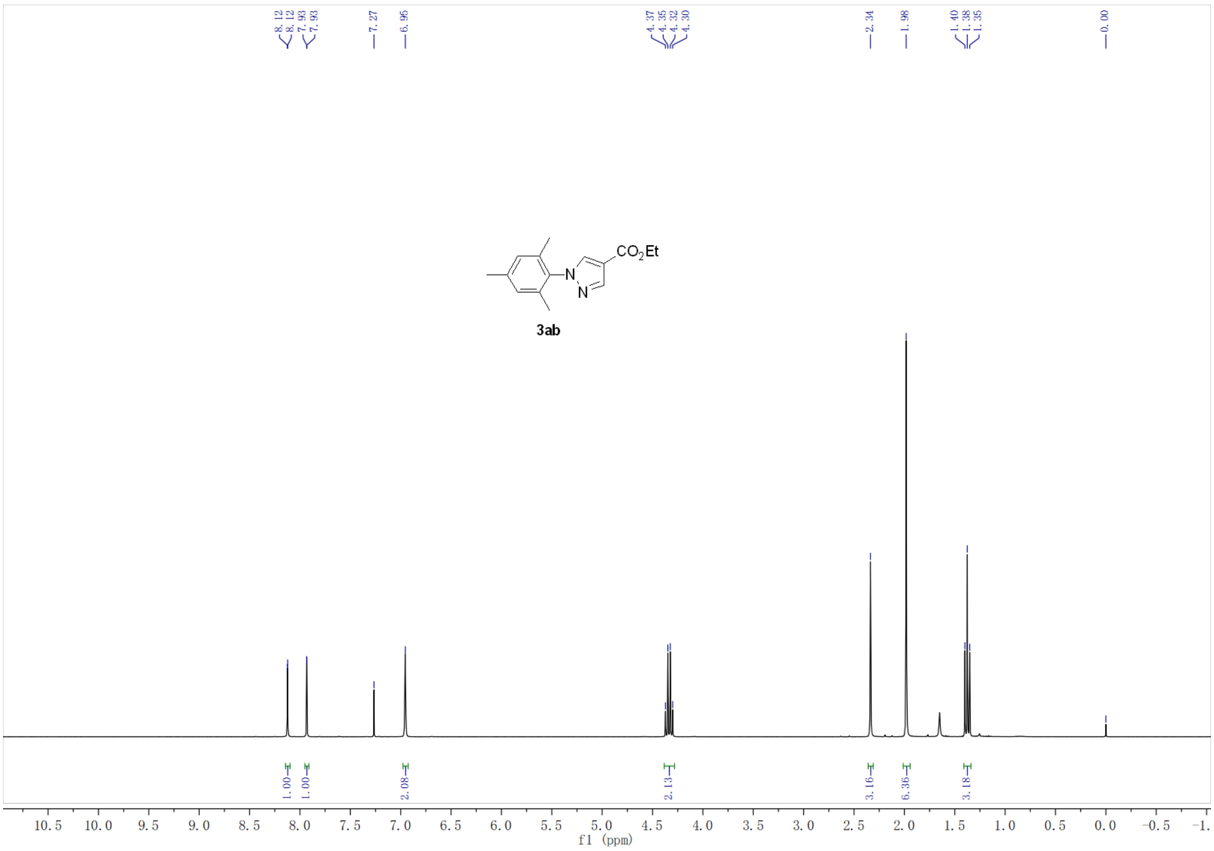
3aa
f1 (ppm)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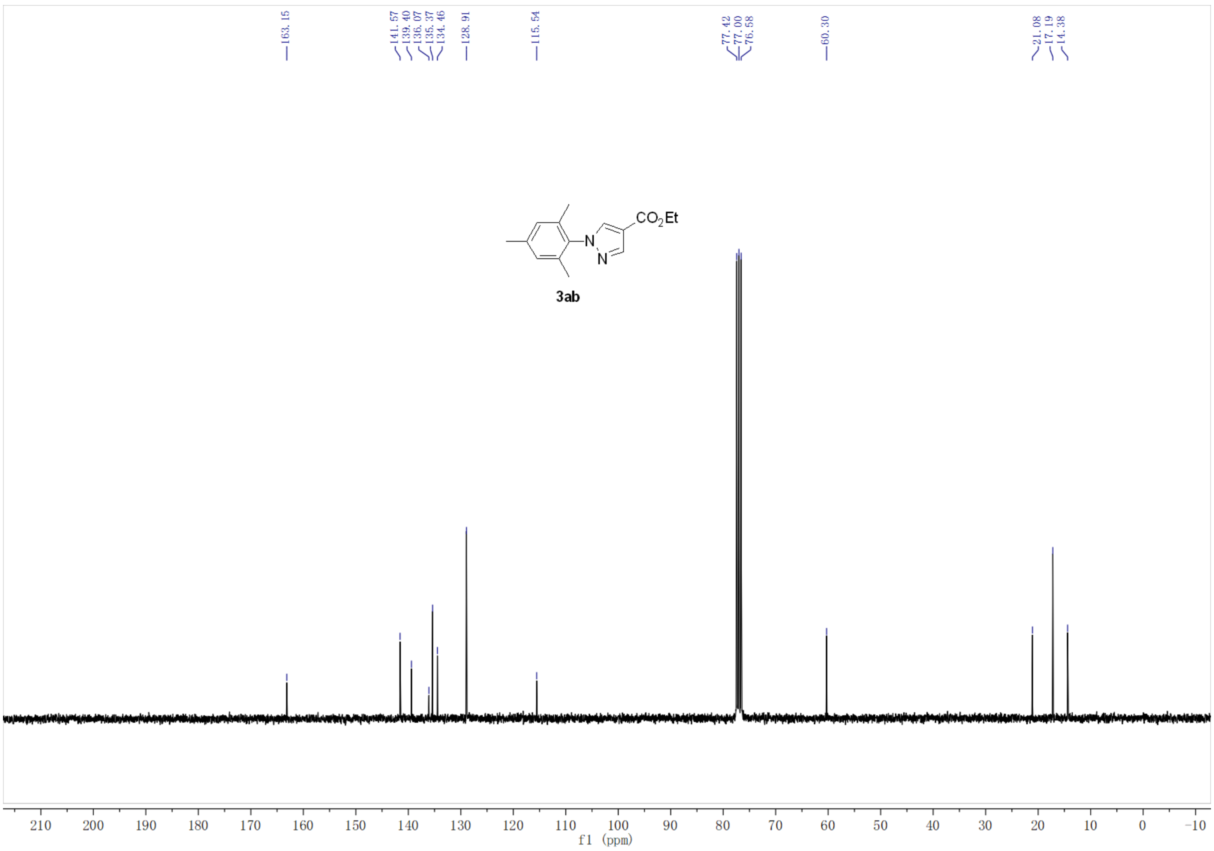
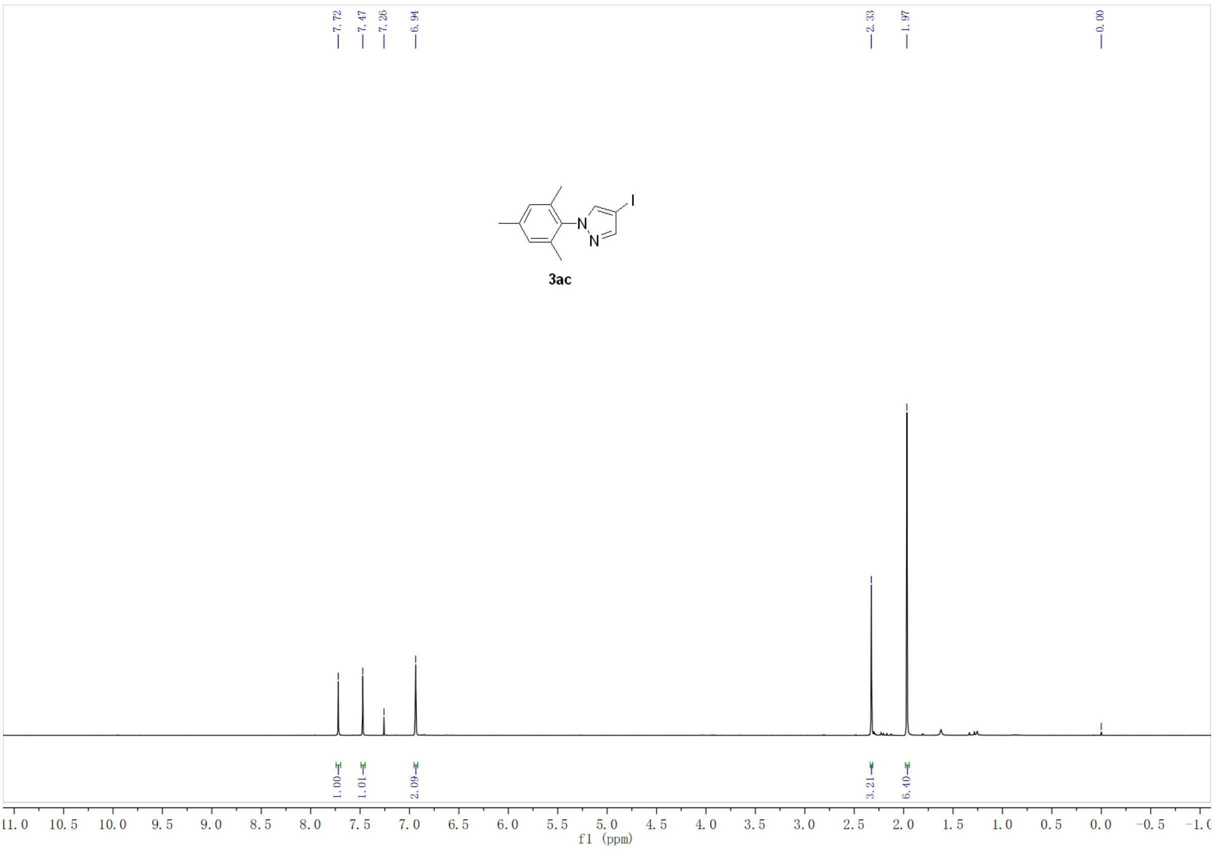
N
N
3ab
f1 (ppm)


CO2Et
N
N
3ab
f1 (ppm)


7.72
7.47
7.26
6.94
2.33
1.97
0.00
N
N
I
3ac
1.00
1.01
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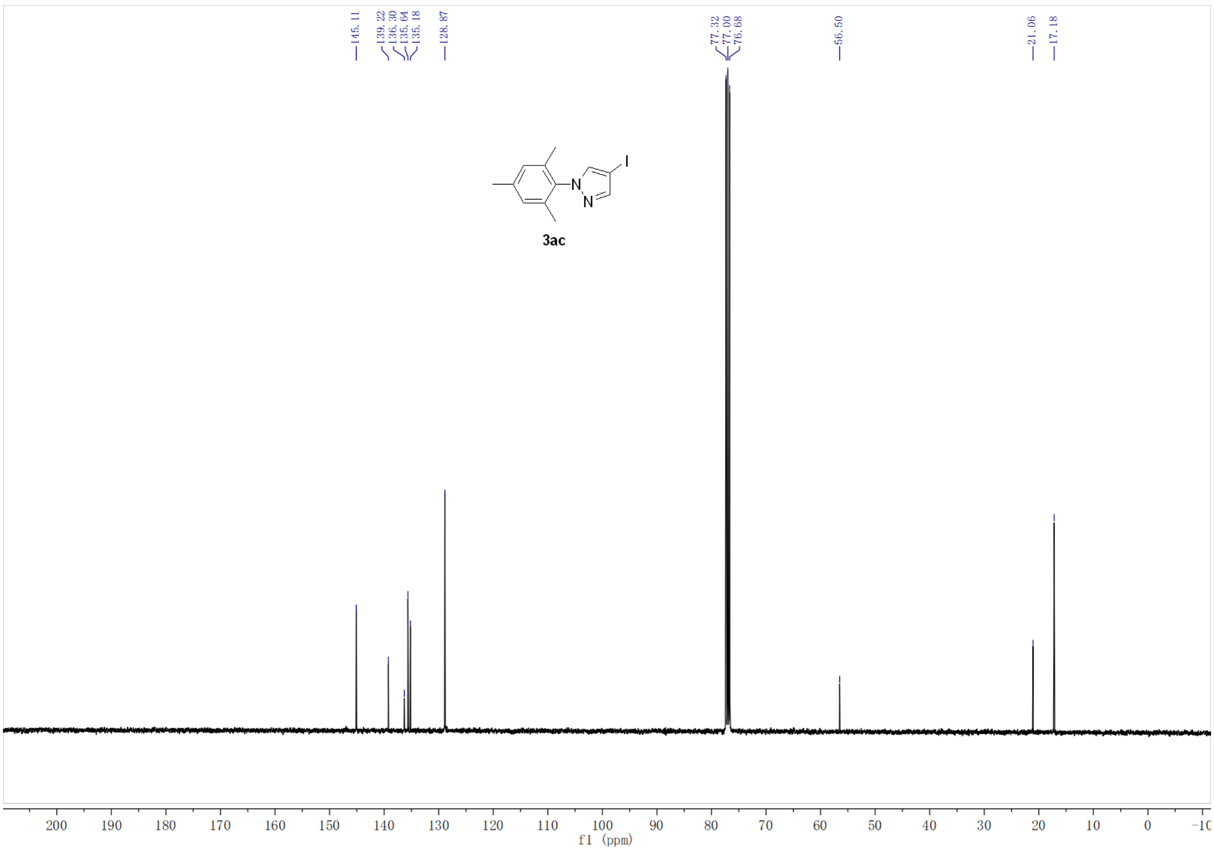
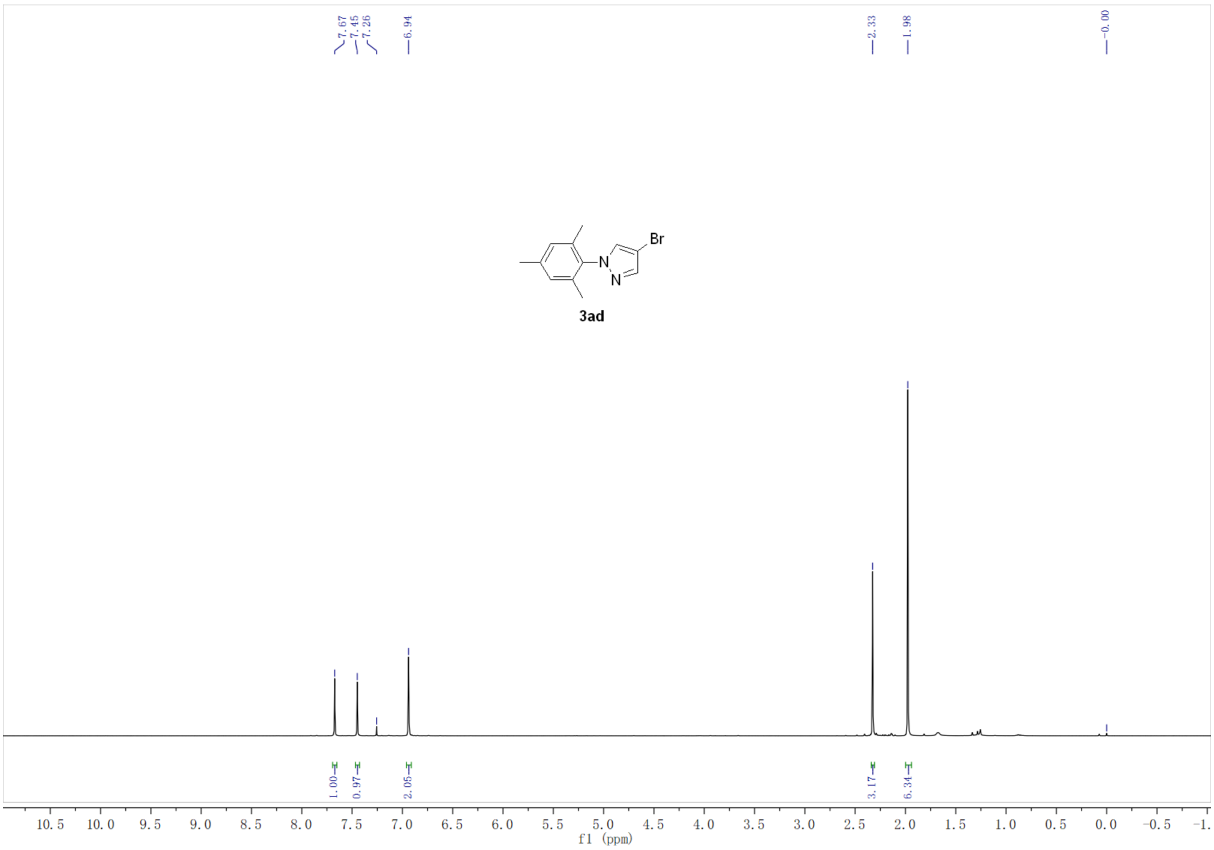
3.21
6.40
f1 (ppm)


145.11
139.22
136.30
135.64
135.18
128.87
77.32
77.00
76.68
56.50
21.06
17.18
N
N
I
3ac
f1 (ppm)


7.67
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7.26
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Br
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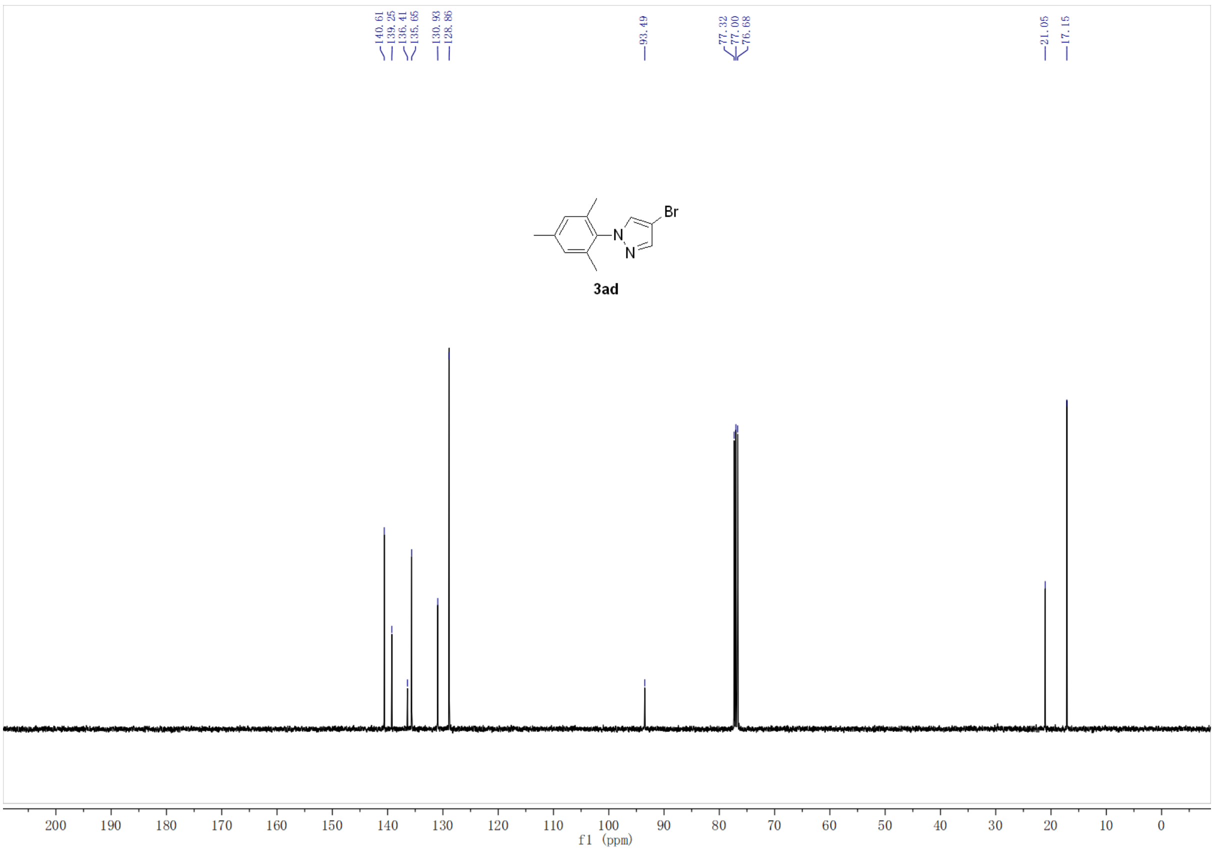
N
3ad
1.00
0.97
2.05
3.17
6.34
f1 (ppm)


140.61
139.25
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135.65
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128.86
93.49
77.32
77.00
76.68
21.05
17.15
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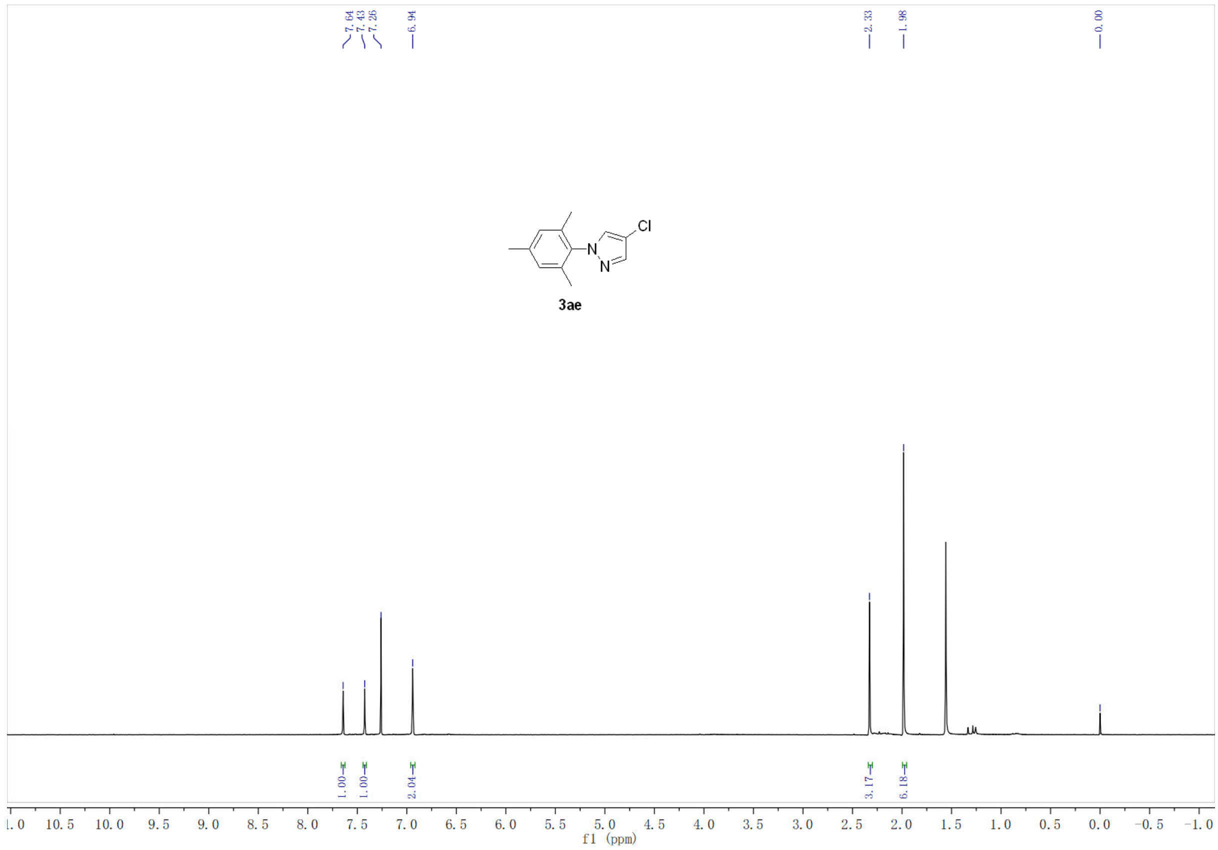
N
N
3ad
f1 (ppm)


7.64
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7.26
6.94
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Cl
N
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3ae
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1.00
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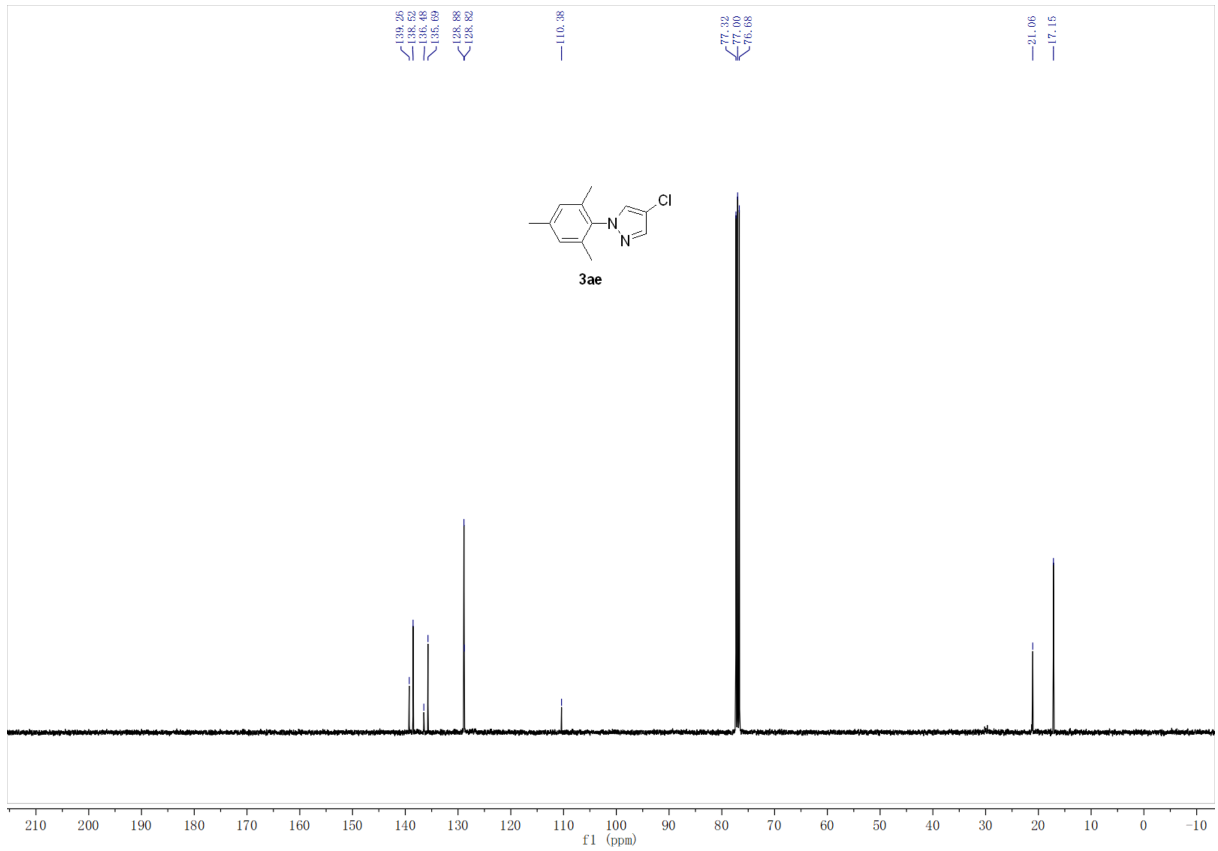
3.17
6.18
f1 (ppm)


139.26
138.52
136.48
135.69
128.88
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110.38
77.32
77.00
76.68
21.06
17.15
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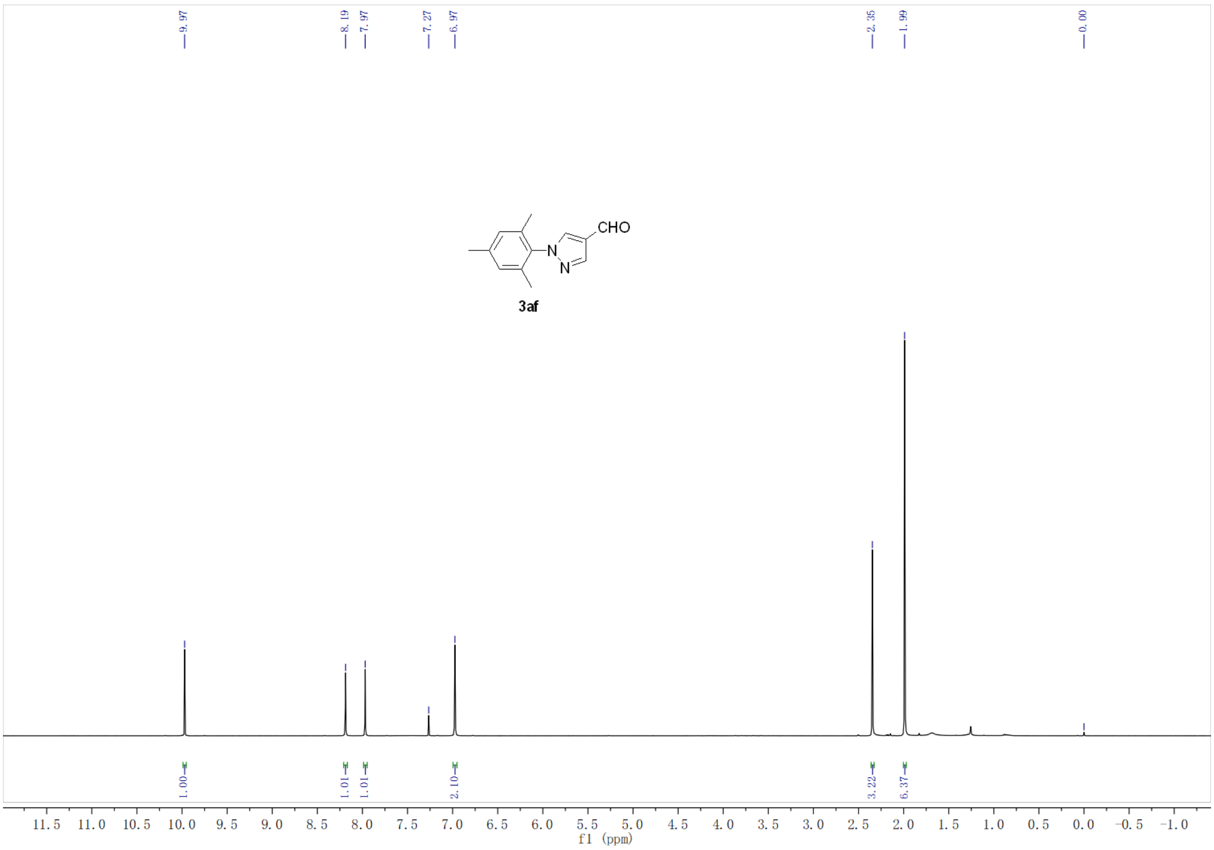
N
N
3ae
f1 (ppm)


9.97
8.19
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7.27
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1.99
0.00
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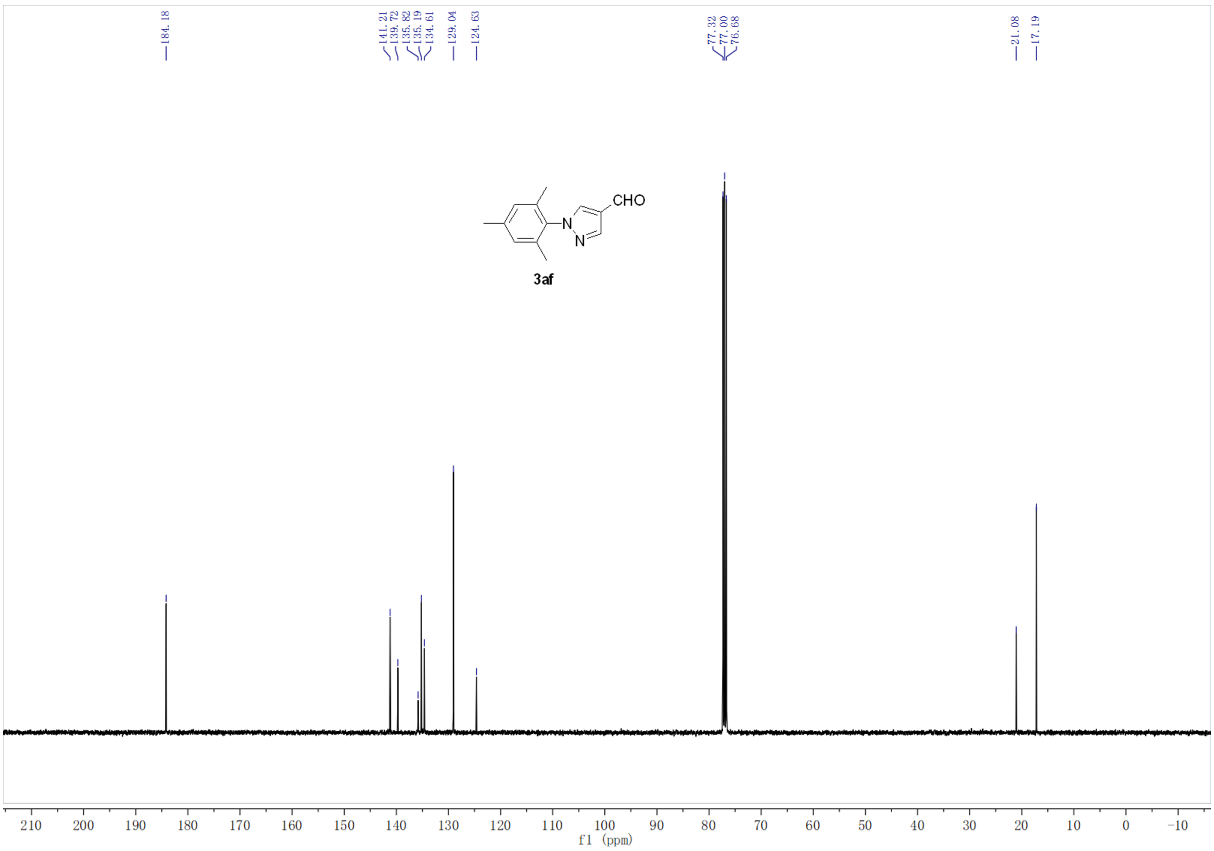
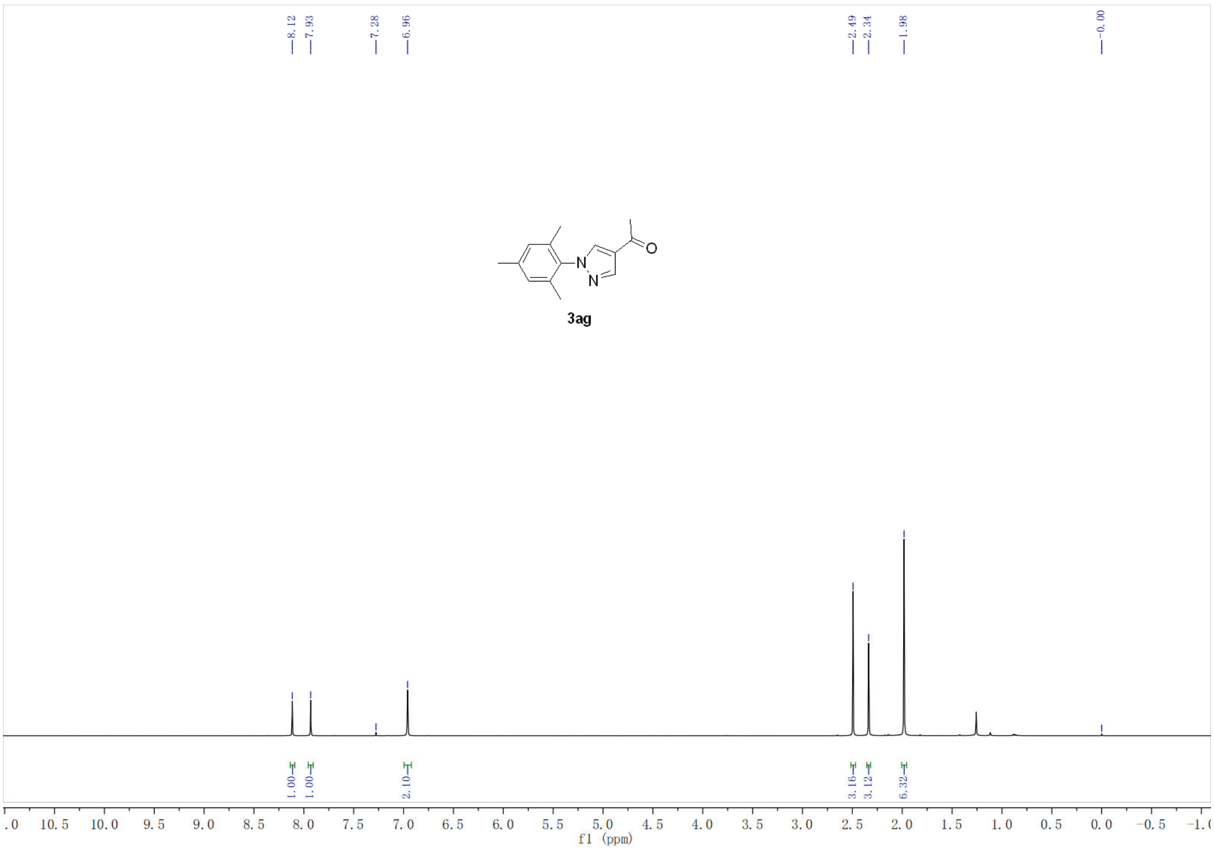
1.00
1.01
1.01
2.10
3.22
6.37
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


184.18
141.21
139.72
135.82
135.19
134.61
129.04
124.63
77.32
77.00
76.68
21.08
17.19
CHO
N
N
3af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.12
7.93
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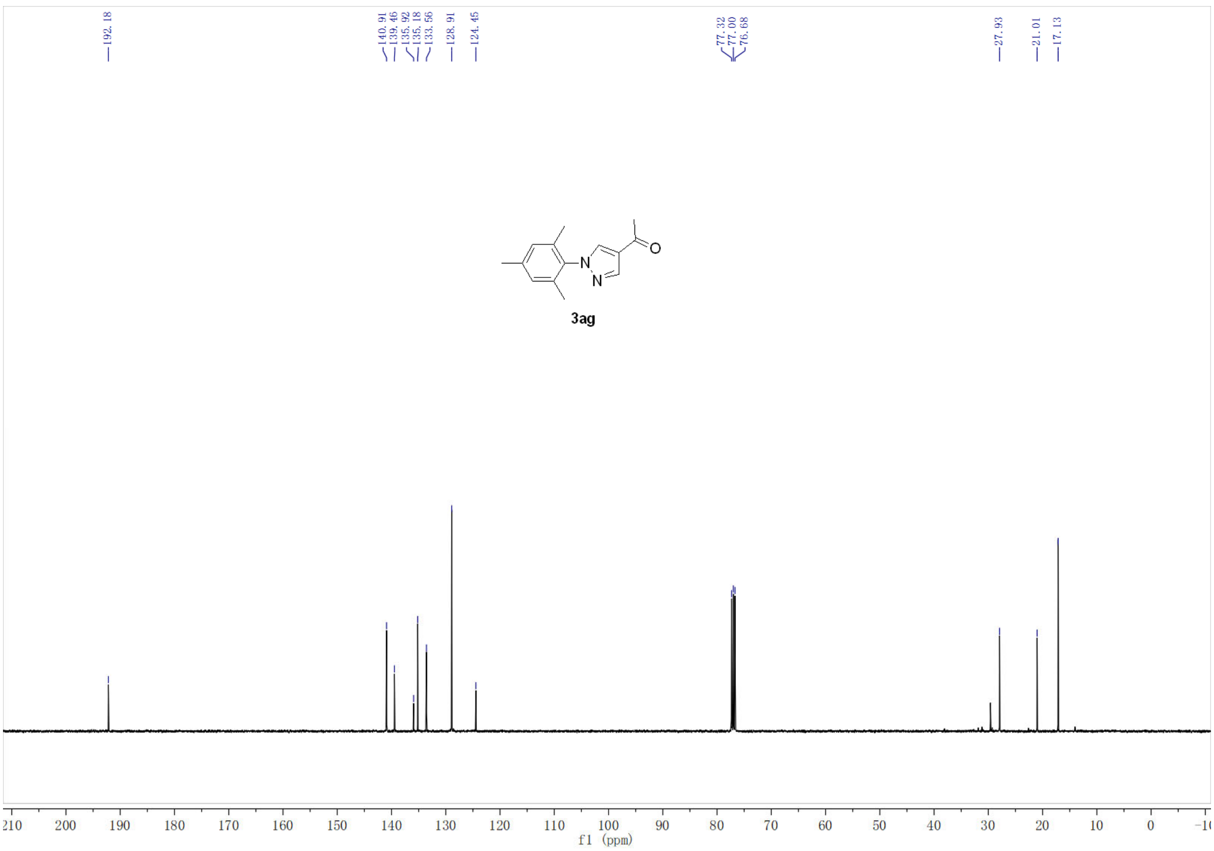
1.00
1.00
2.10
3.16
3.12
6.32
f1 (ppm)


192.18
140.91
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135.92
135.18
133.56
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124.45
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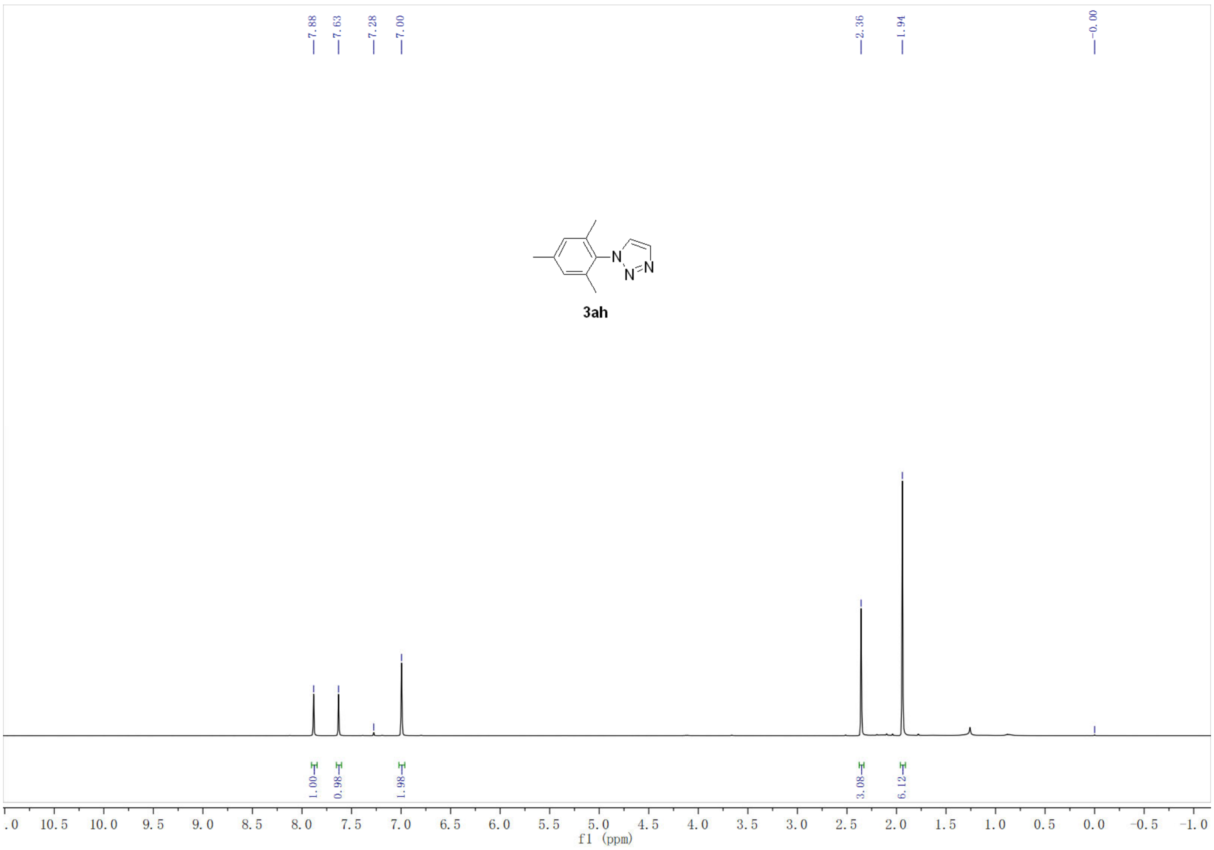
77.00
76.68
27.93
21.01
17.13
3ag
f1 (ppm)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1.98
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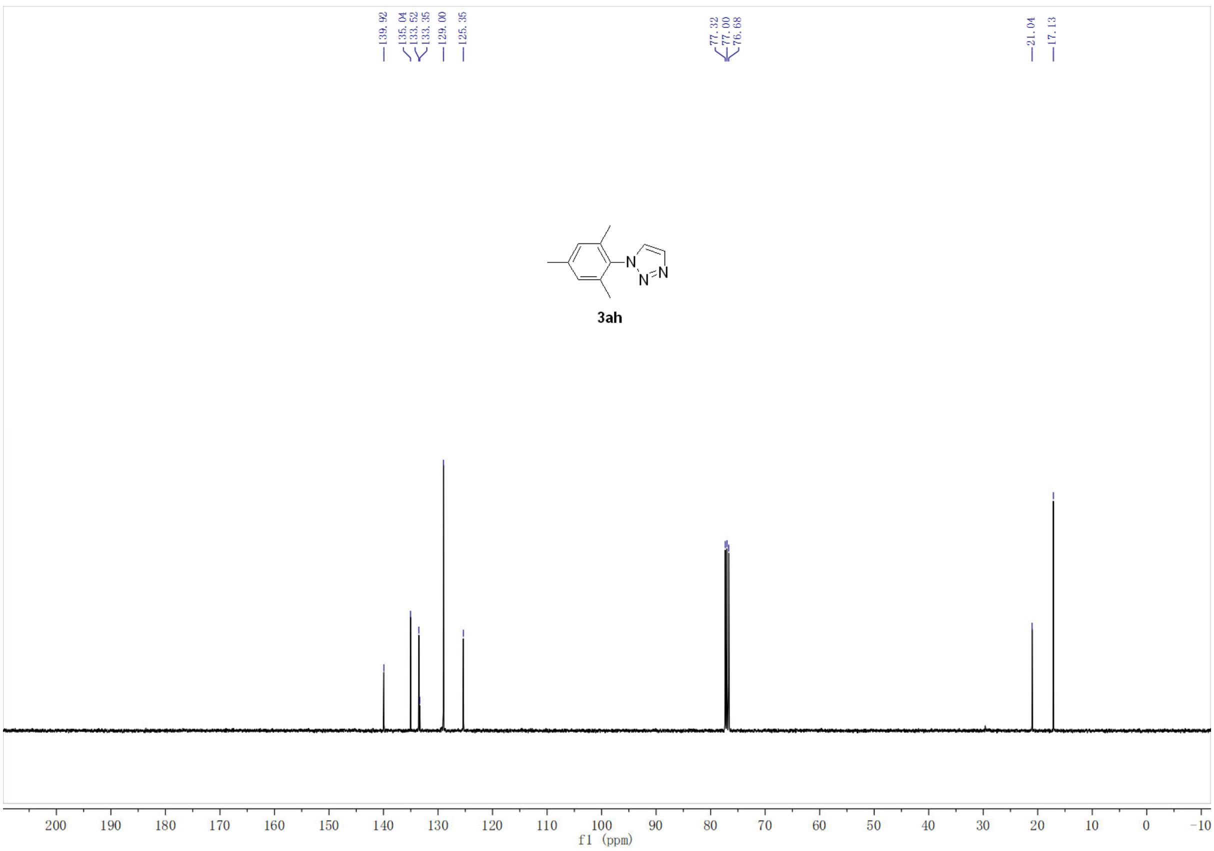
6.12
f1 (ppm)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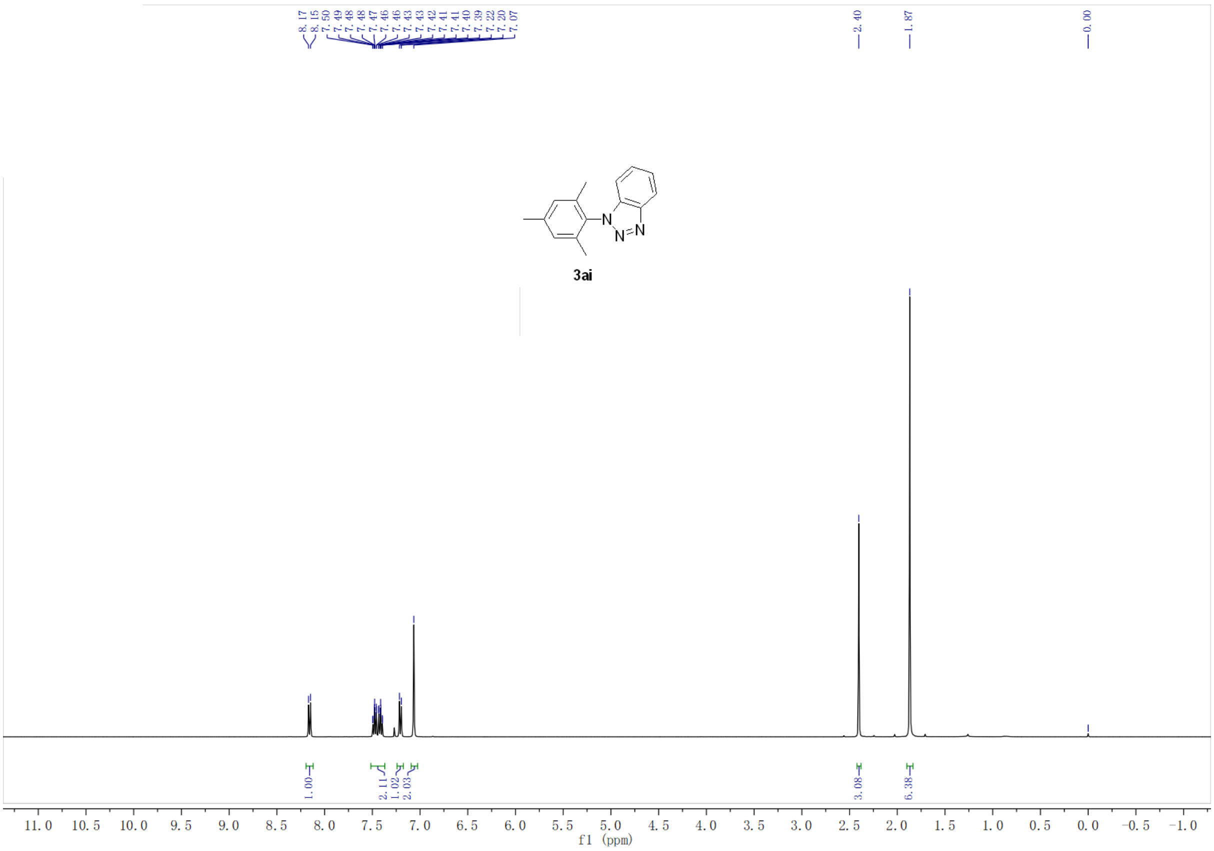
f1 (ppm)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7.46
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7.43
7.42
7.41
7.41
7.40
7.39
7.22
7.20
7.07
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1.00
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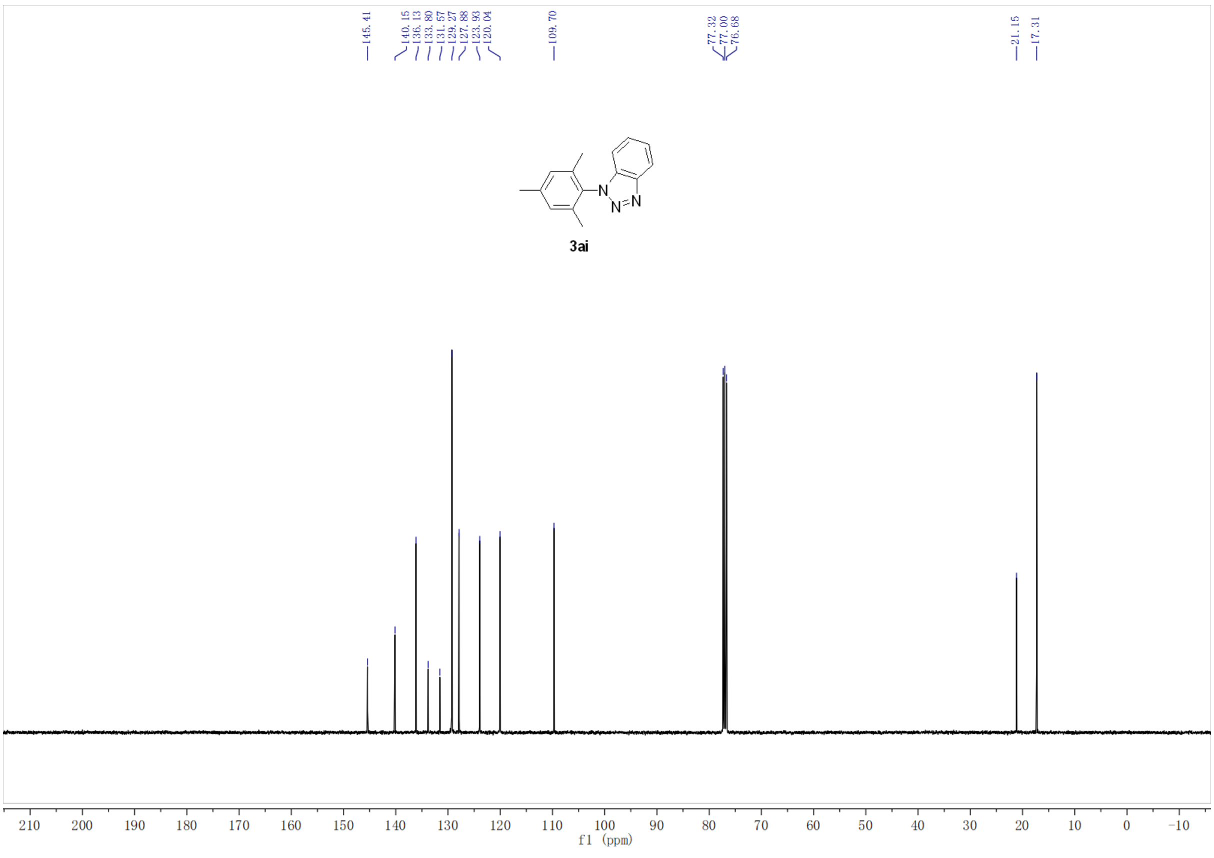
1.02
2.03
3.08
6.38
f1 (ppm)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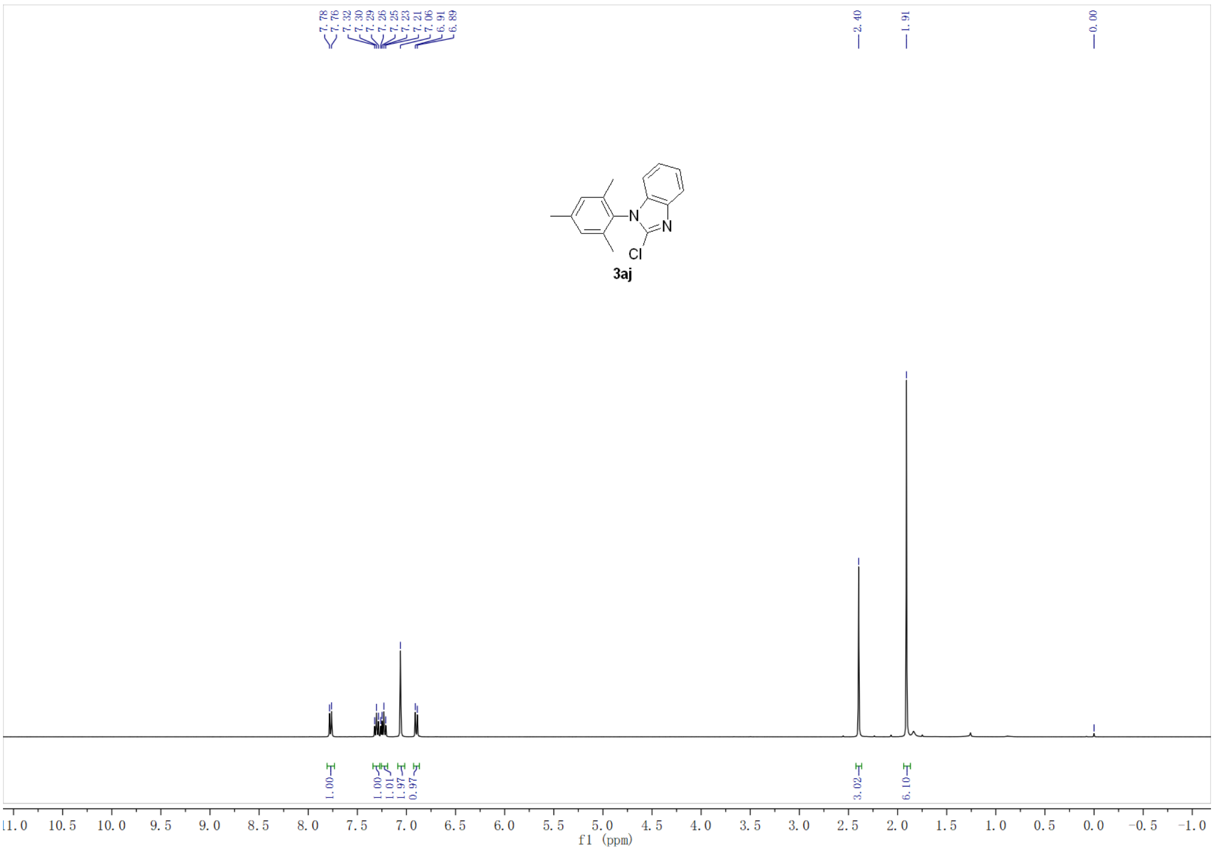
77.32
77.00
76.68
21.15
17.31
3ai
f1 (ppm)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7.32
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7.29
7.26
7.25
7.23
7.21
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6.91
6.89
2.40
1.91
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Cl
3aj
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1.00
1.01
1.97
0.97
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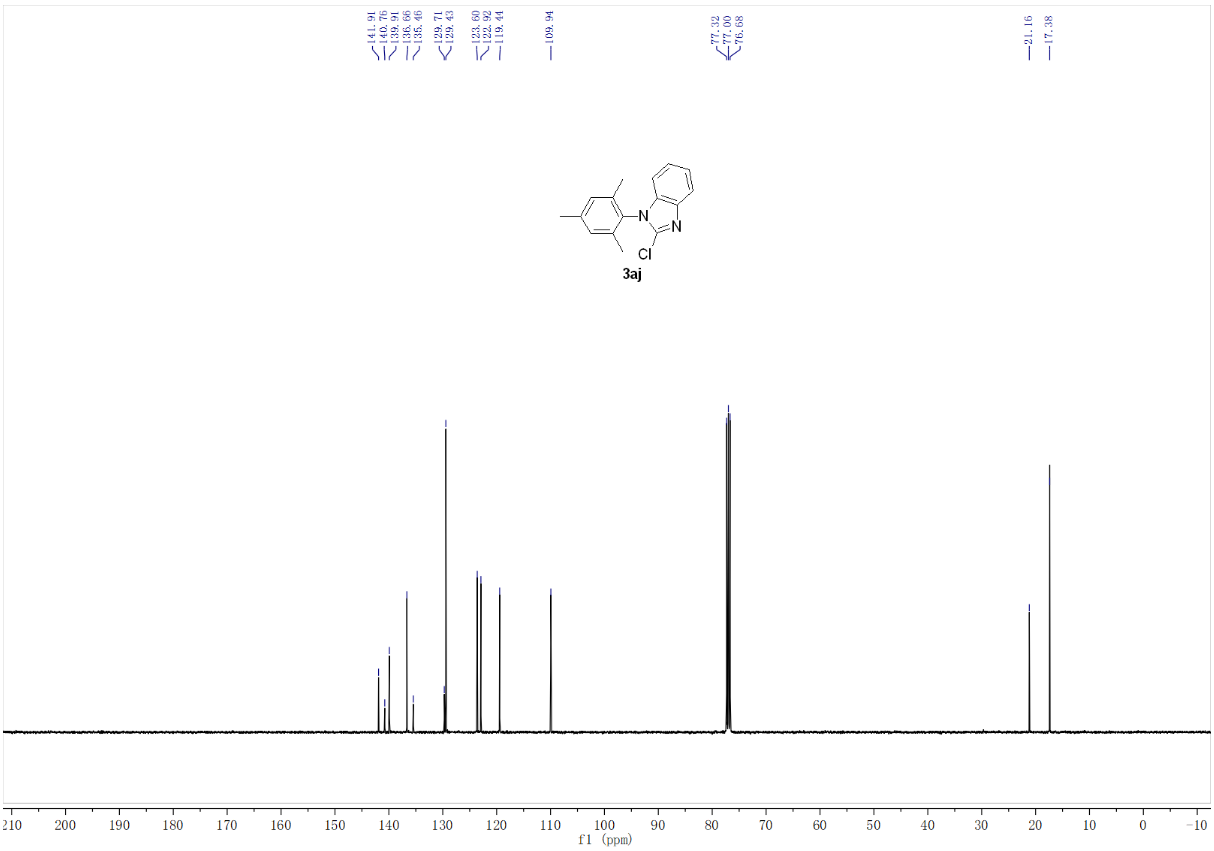
6.10
f1 (ppm)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139.91
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135.46
129.71
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123.60
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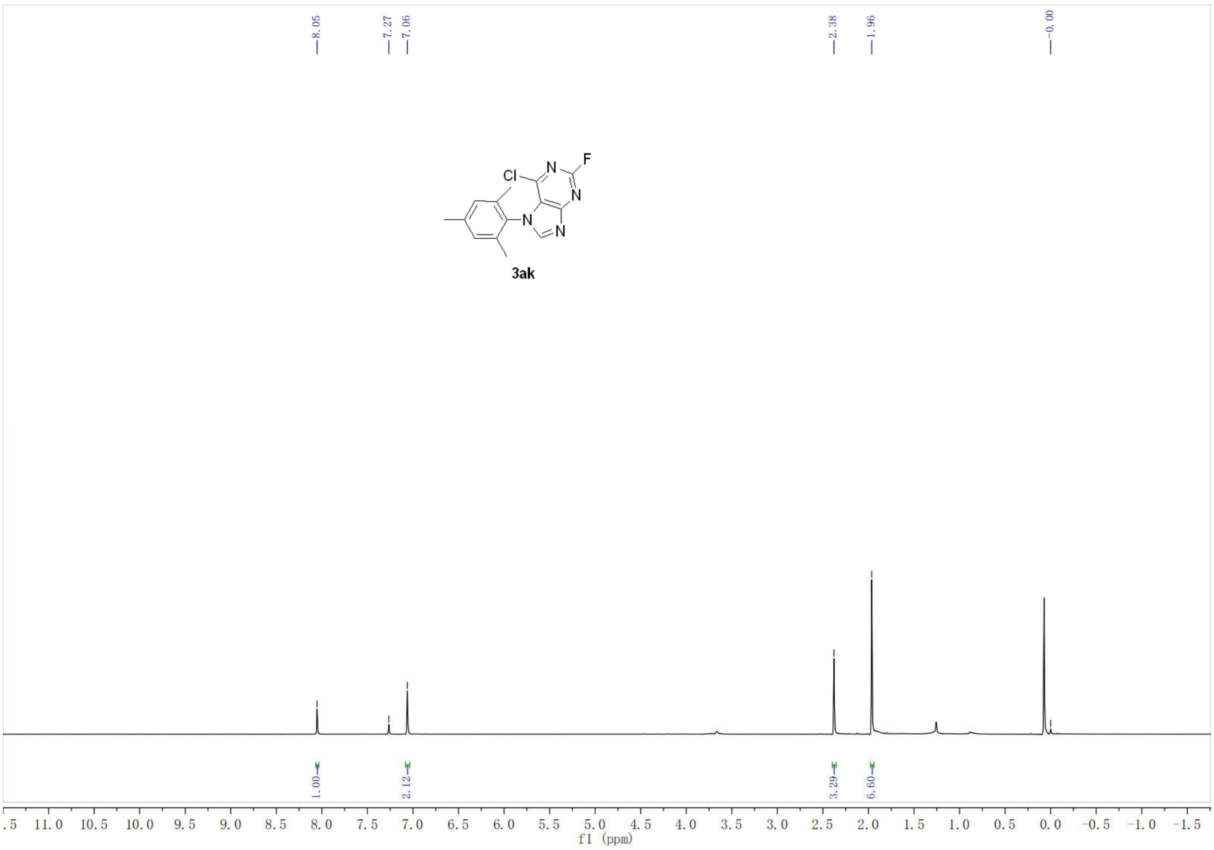
77.00
76.68
21.16
17.38
N
N
Cl
3aj
f1 (ppm)


8.05
7.27
7.06
2.38
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0.00
Cl
N
F
N
N
N
3ak
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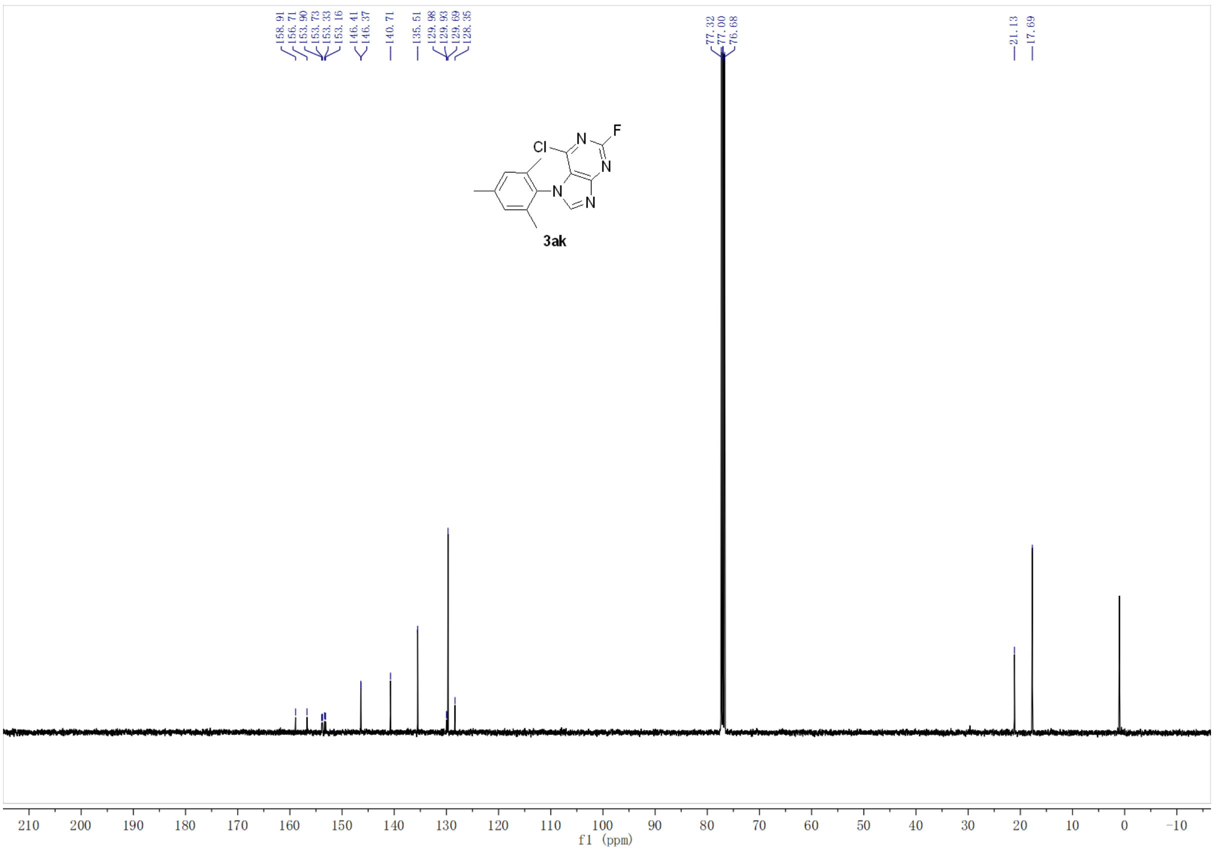
3.29
6.60
f1 (ppm)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153.16
146.41
146.37
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135.51
129.98
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129.69
128.35
77.32
77.00
76.68
21.13
17.69
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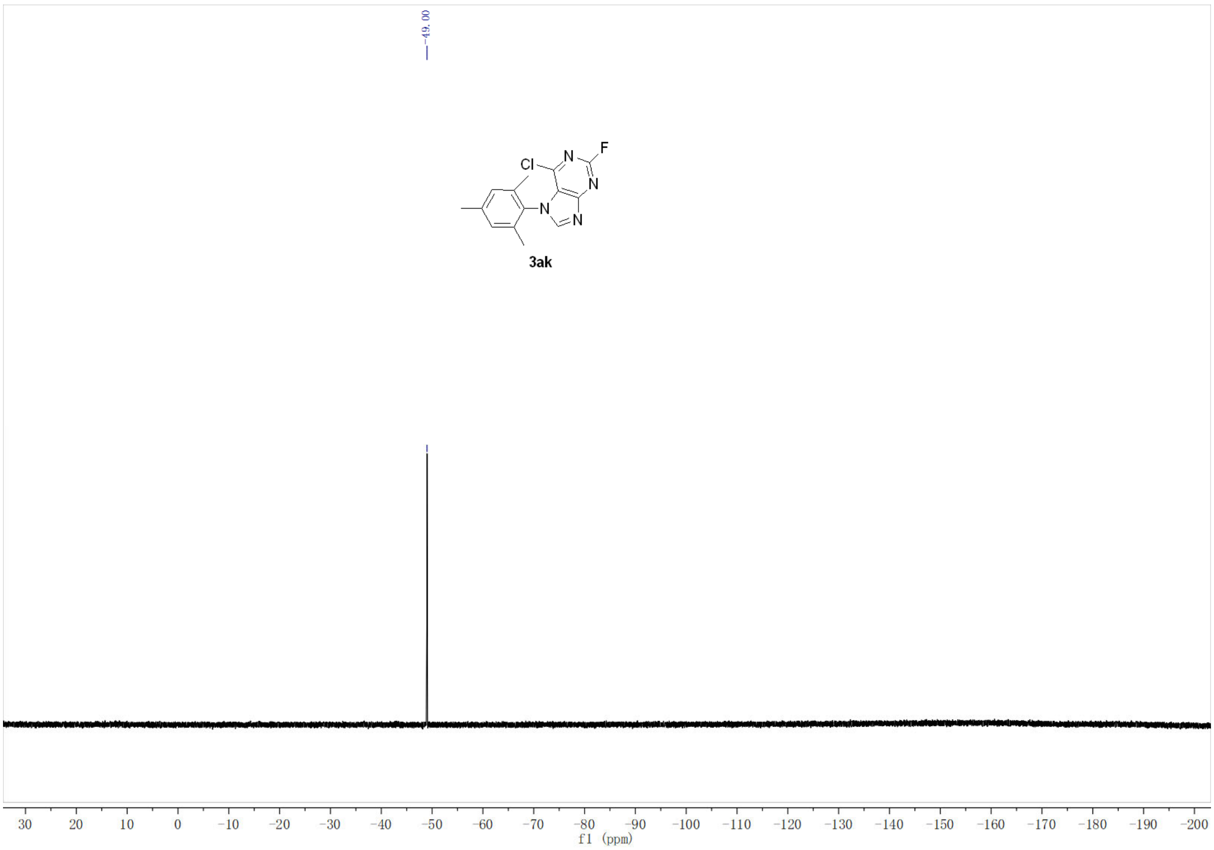
N
F
N
N
N
3ak
f1 (ppm)


-49.00
Cl
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F
N
N
N
3ak
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20
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0
-10
-20
-30
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-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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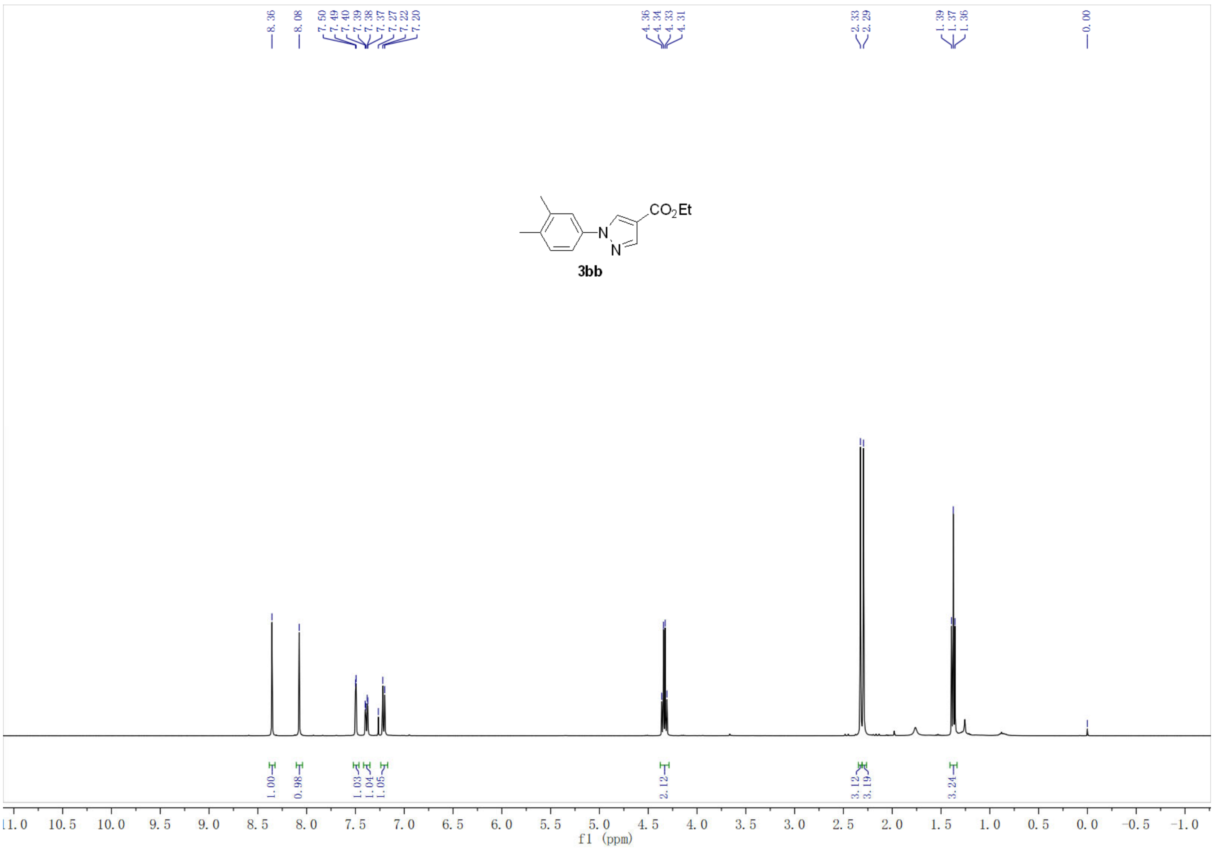
-190
-200
f1 (ppm)



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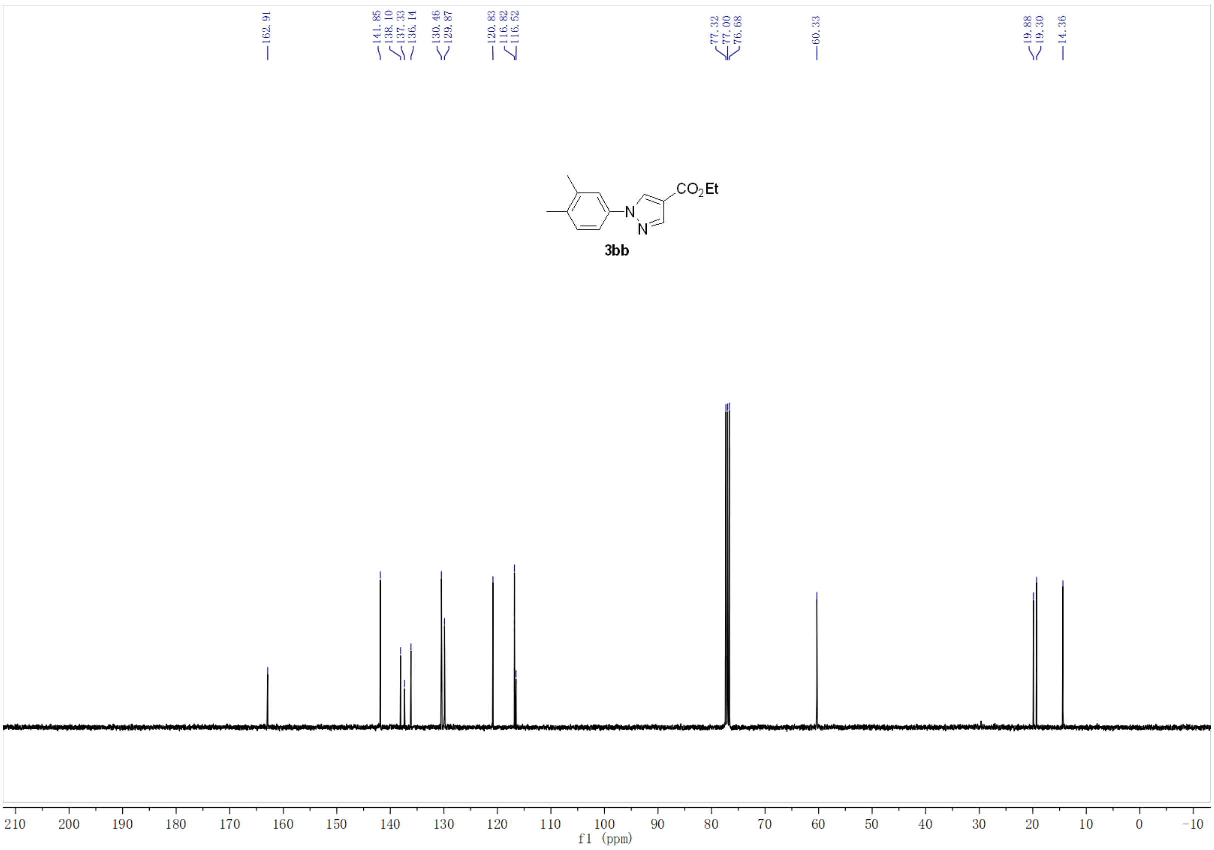
7.40
7.39
7.38
7.37
7.27
7.22
7.20
4.36
4.34
4.33
4.31
2.33
2.29
1.39
1.37
1.36
0.00
CO2Et
N
N
3bb
1.00
0.98
1.03
1.04
1.05
2.12
3.12
3.19
3.24
f1 (ppm)



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130.46
129.87
120.83
116.82
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76.68
60.33
19.88
19.30
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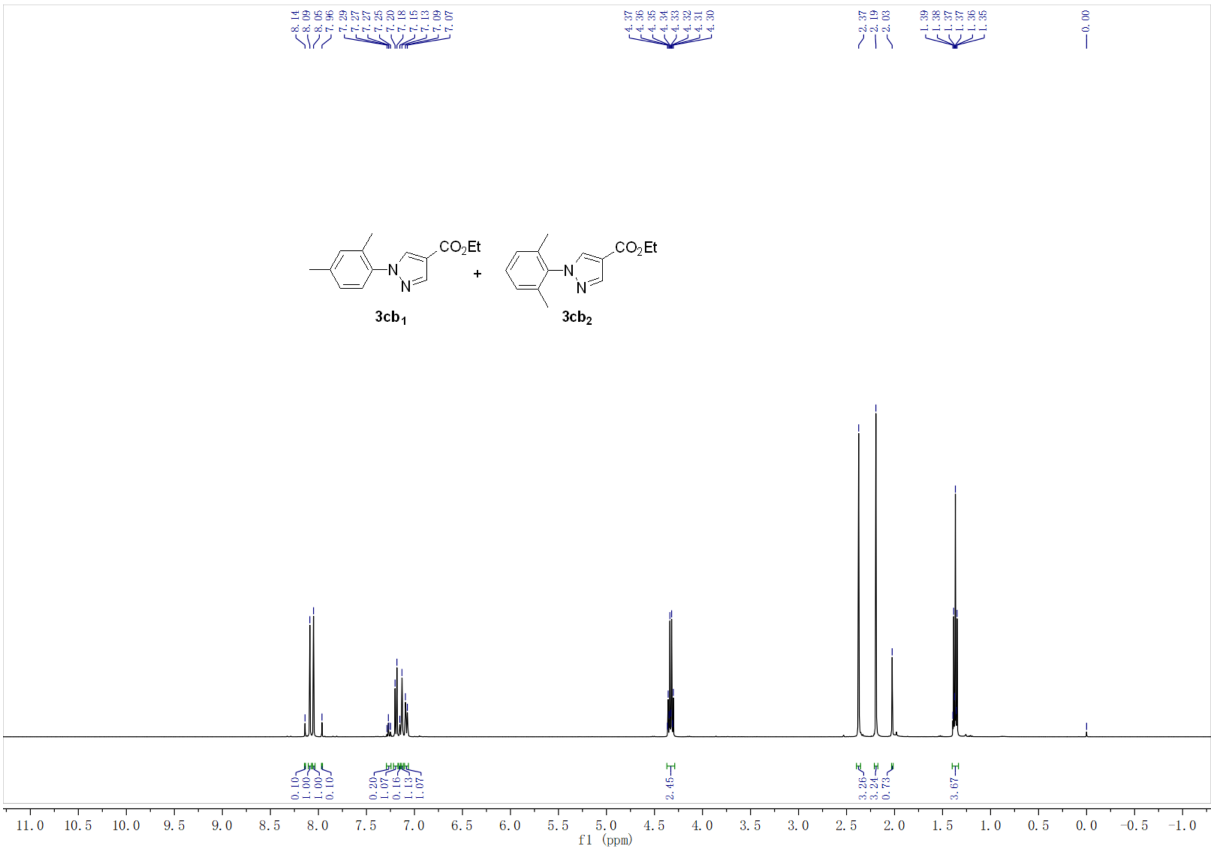
CO2Et
N
N
3bb
f1 (ppm)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8.09
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7.18
7.15
7.13
7.09
7.07
4.37
4.36
4.35
4.34
4.33
4.32
4.31
4.30
2.37
2.19
2.03
1.39
1.38
1.37
1.37
1.36
1.35
0.00
CO2Et
N
N
+
3cb1
3cb2
0.10
1.00
1.00
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0.20
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0.16
1.13
1.07
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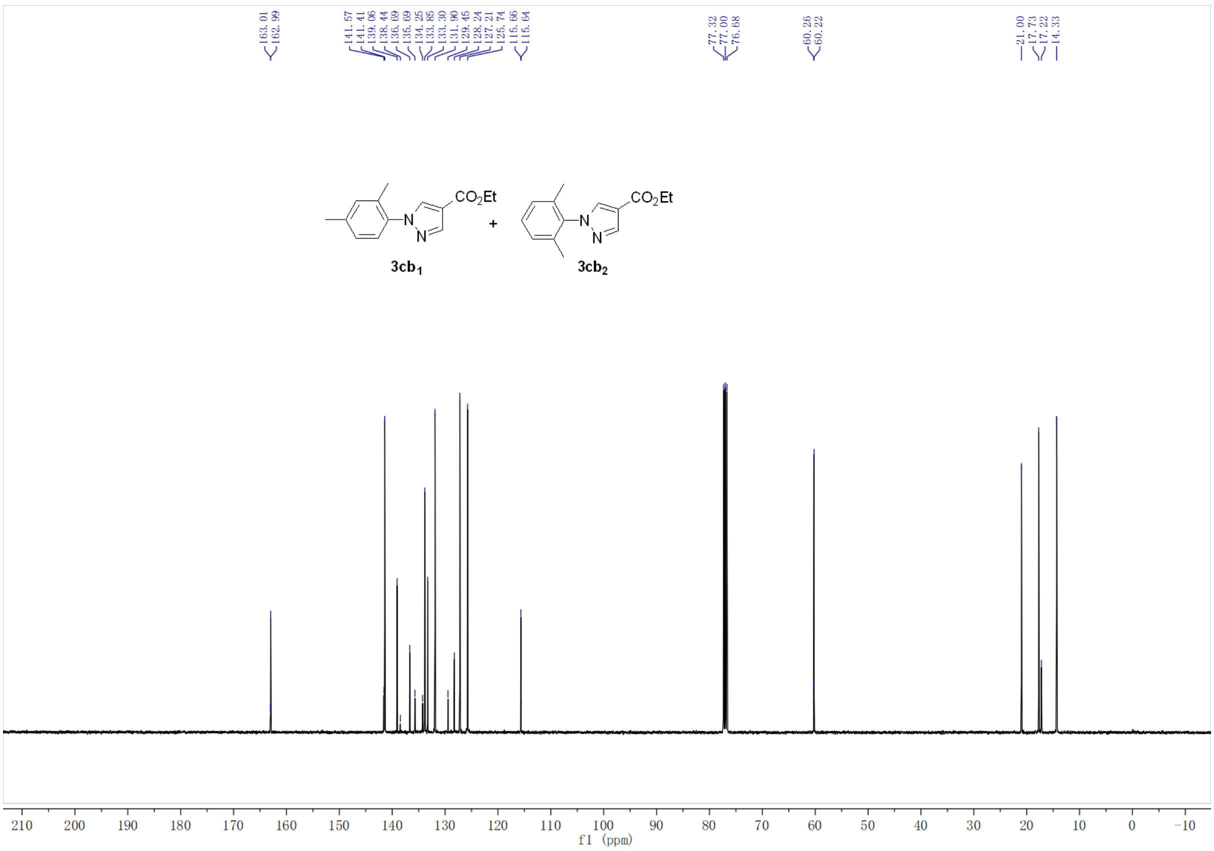
3.24
0.73
3.67
f1 (ppm)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162.99
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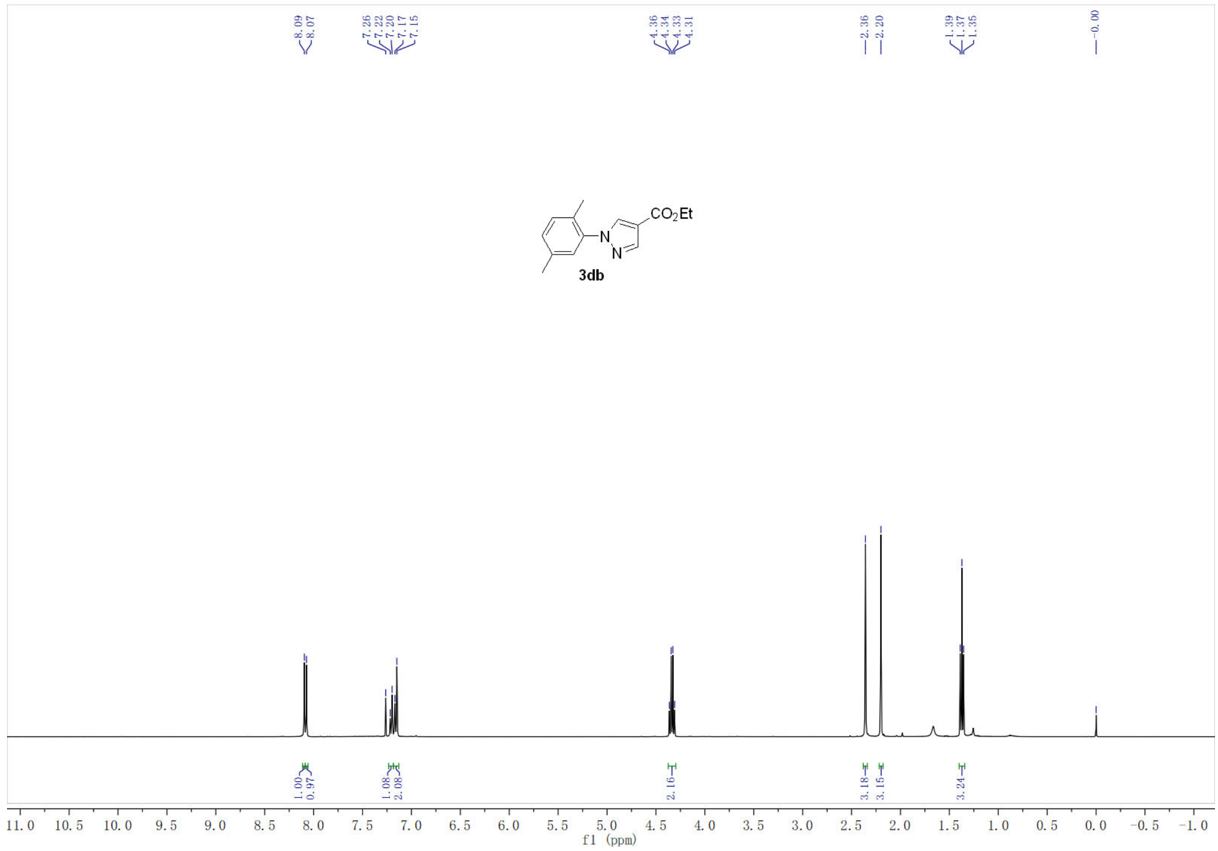
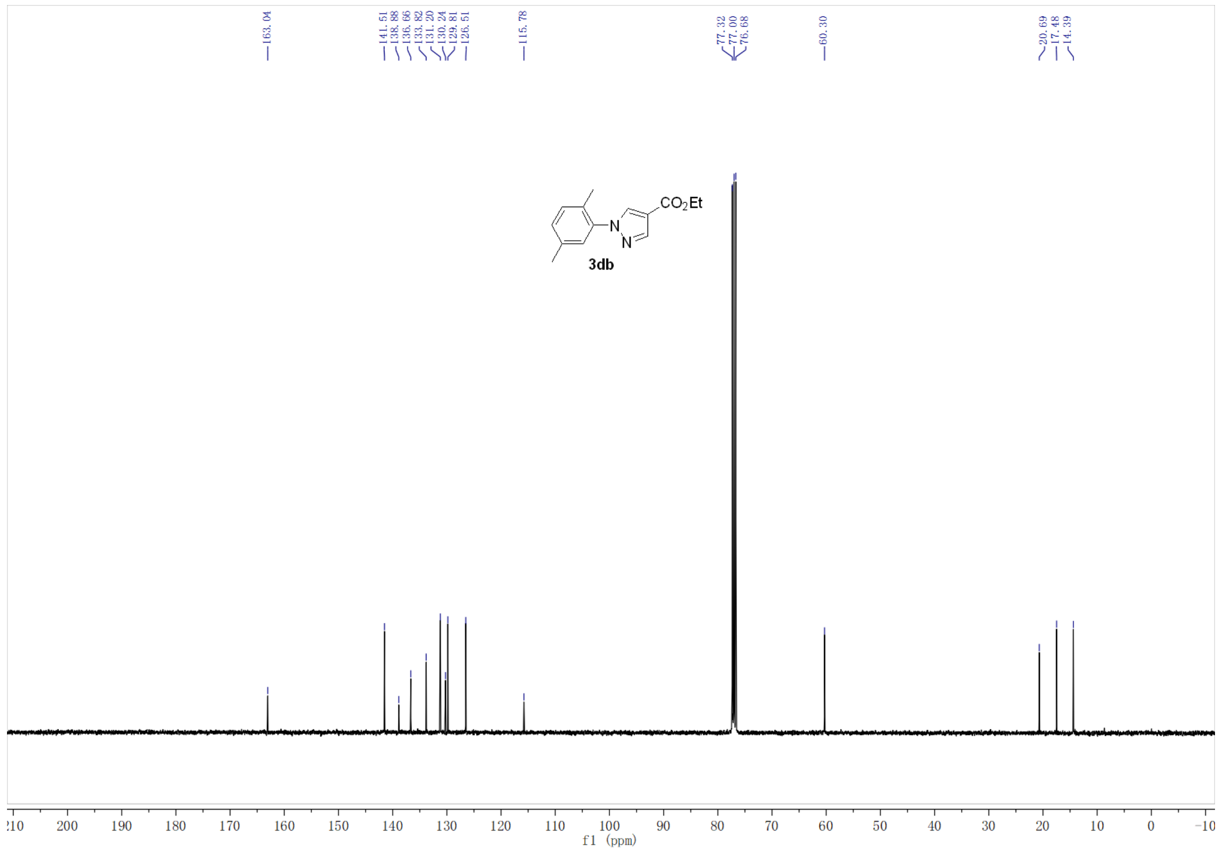
139.06
138.44
136.69
135.69
134.25
133.85
133.30
131.90
129.45
128.24
127.21
125.74
115.66
115.64
77.32
77.00
76.68
60.26
60.22
21.00
17.73
17.22
14.33
CO2Et
N
N
+
3cb1
3cb2
f1 (ppm)


8.09
8.07
7.26
7.22
7.20
7.17
7.15
4.36
4.34
4.33
4.31
2.36
2.20
1.39
1.37
1.35
0.00
CO2Et
N
N
3db
1.00
0.97
1.08
2.08
2.16
3.18
3.15
3.24
f1 (ppm)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141.51
138.88
136.66
133.82
131.20
130.24
129.81
126.51
115.78
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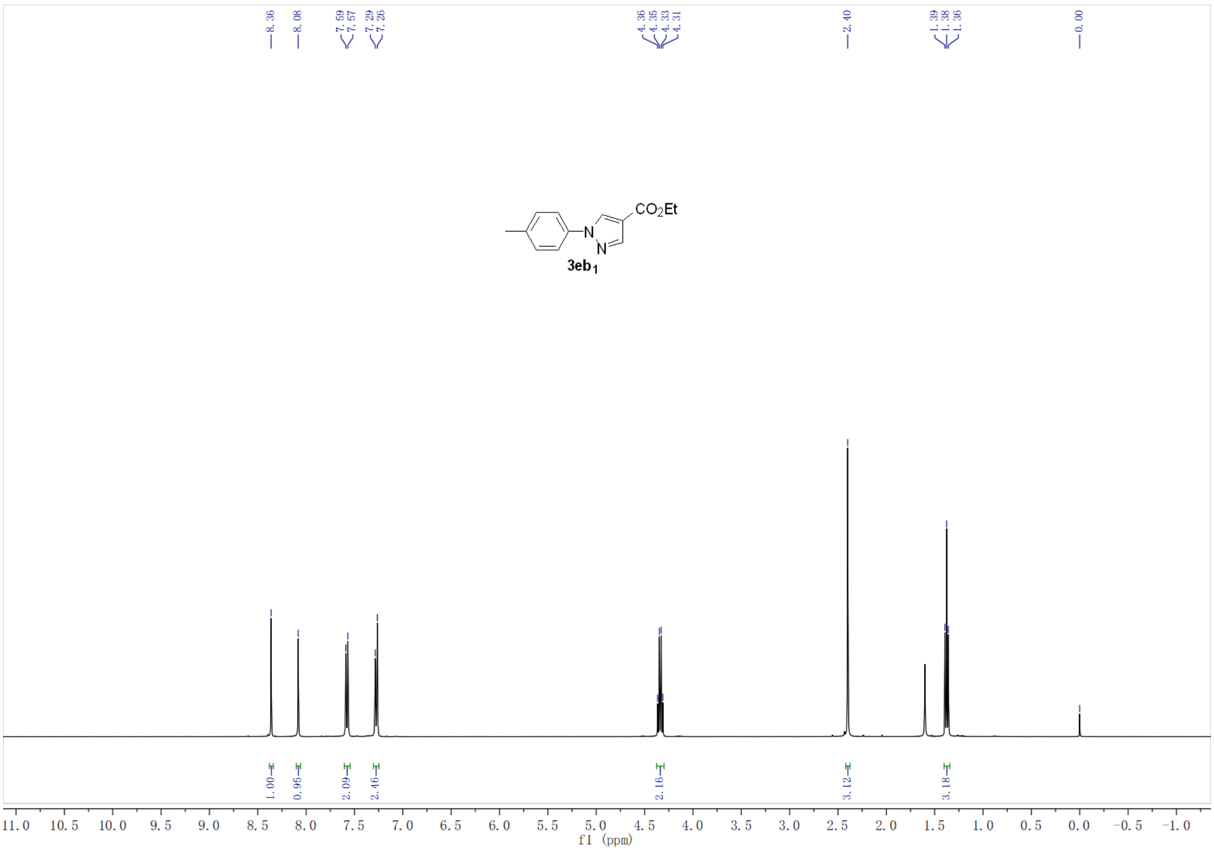
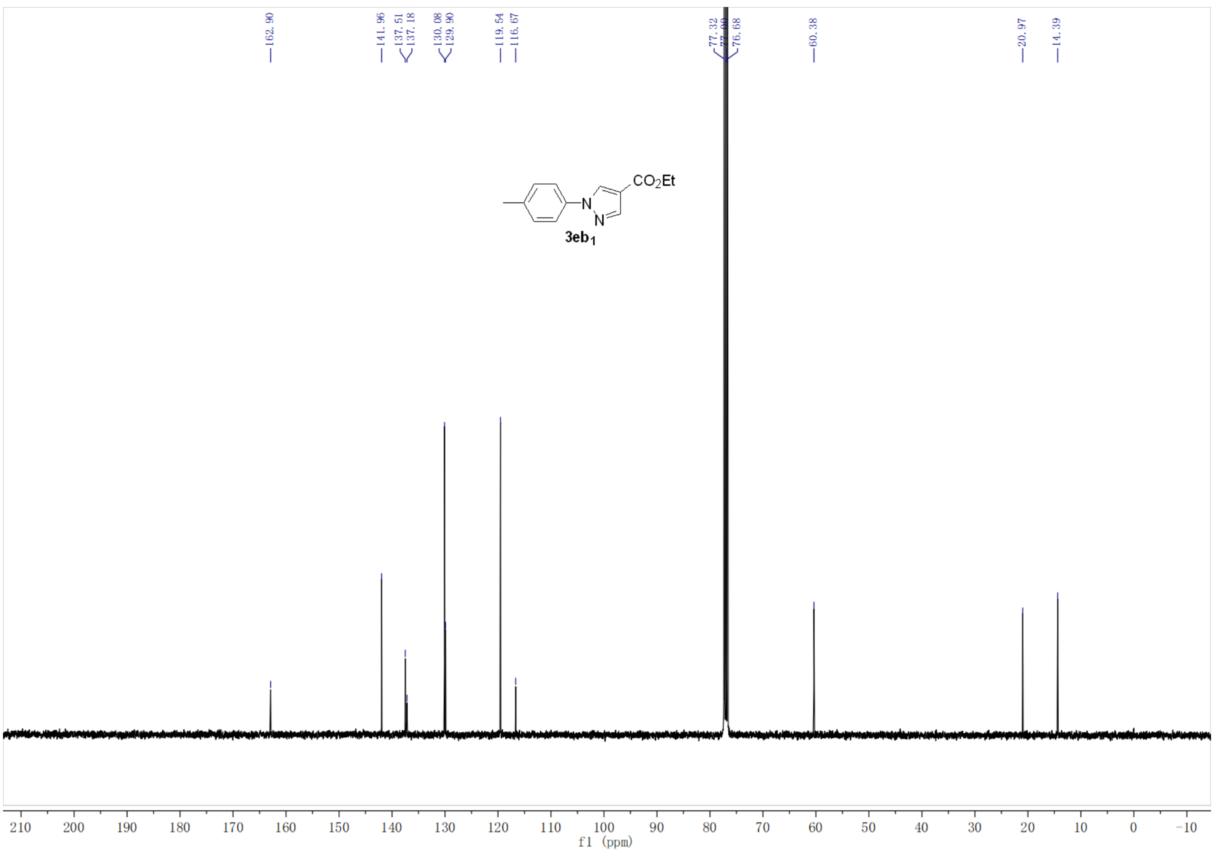
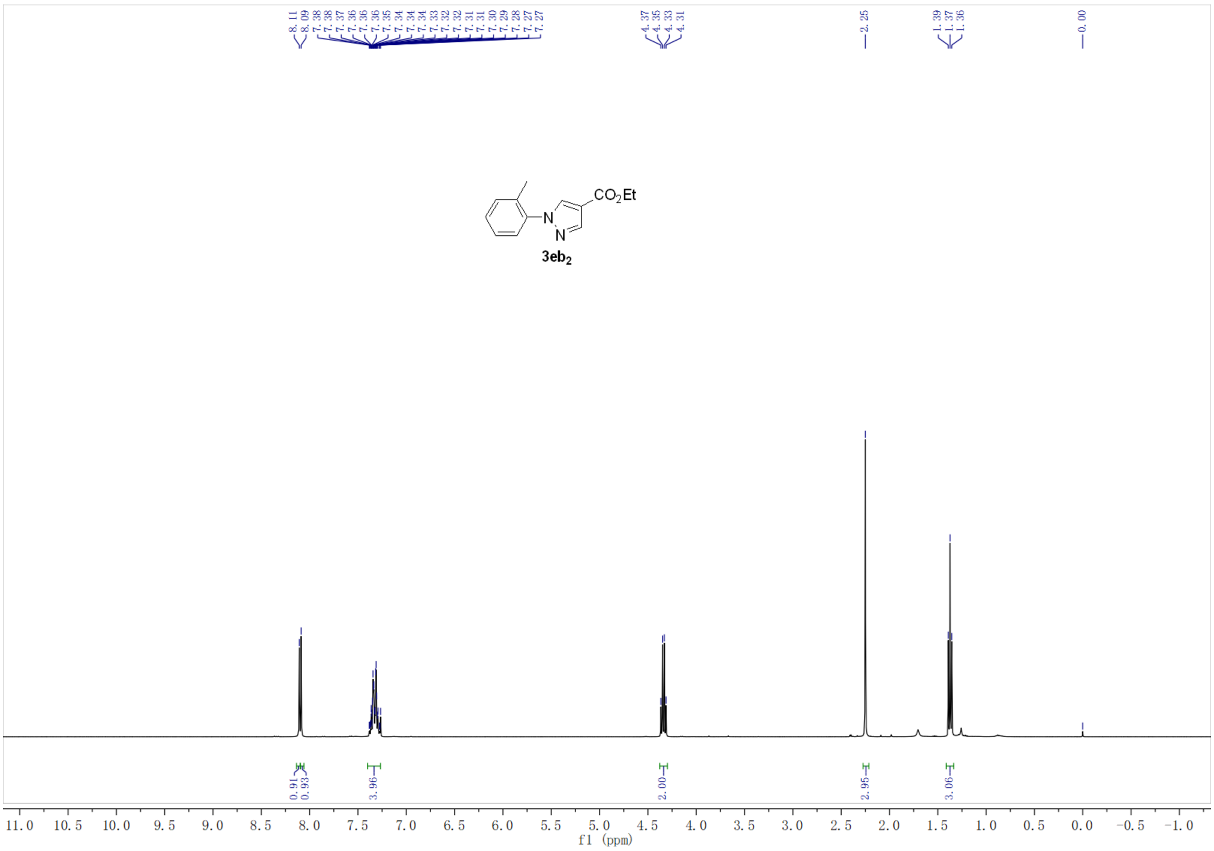
77.00
76.68
60.30
20.69
17.48
14.39
CO2Et
N
N
3db
f1 (ppm)


8.36
8.08
7.59
7.57
7.29
7.26
4.36
4.35
4.33
4.31
2.40
1.39
1.38
1.36
0.00
CO2Et
N
N
3eb1
1.00
0.95
2.09
2.46
2.16
3.12
3.18
f1 (ppm)


162.90
141.96
137.51
137.18
130.08
129.90
119.54
116.67
77.32
76.68
60.38
20.97
14.39
CO2Et
N
N
3eb1
f1 (ppm)



8.11
8.09
4.37
4.35
4.33
4.31
2.25
1.39
1.37
1.36
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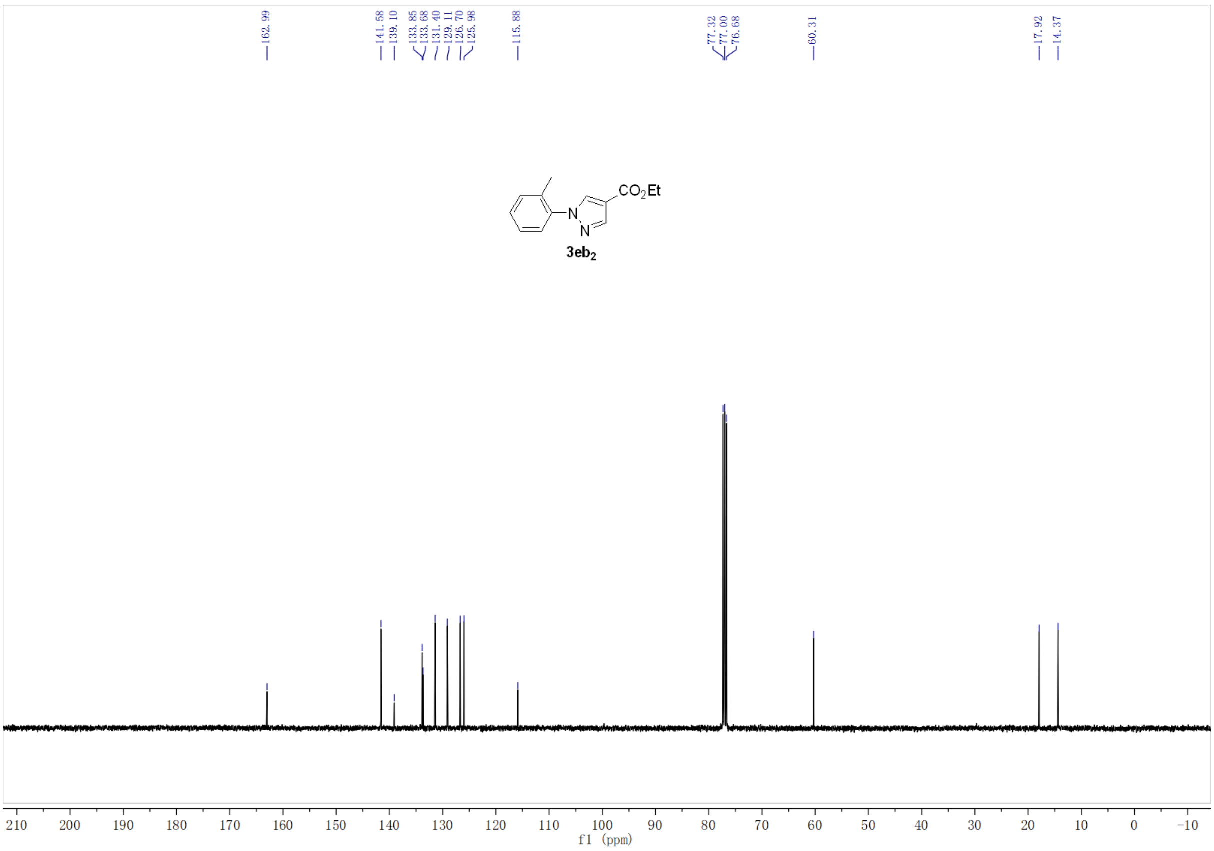
N
N
3eb2
0.91
0.93
3.96
2.00
2.95
3.06
f1 (ppm)



162.99
141.58
139.10
133.85
133.68
131.40
129.11
126.70
125.98
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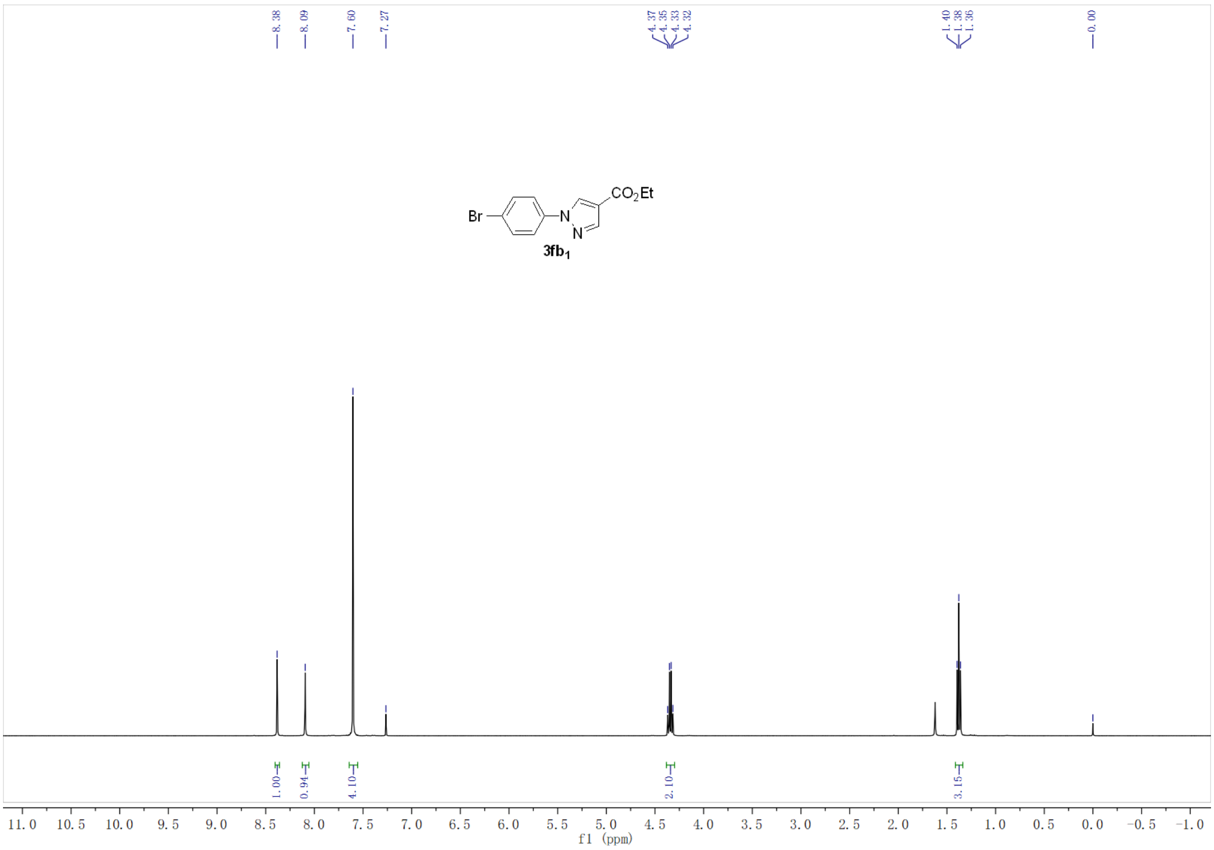
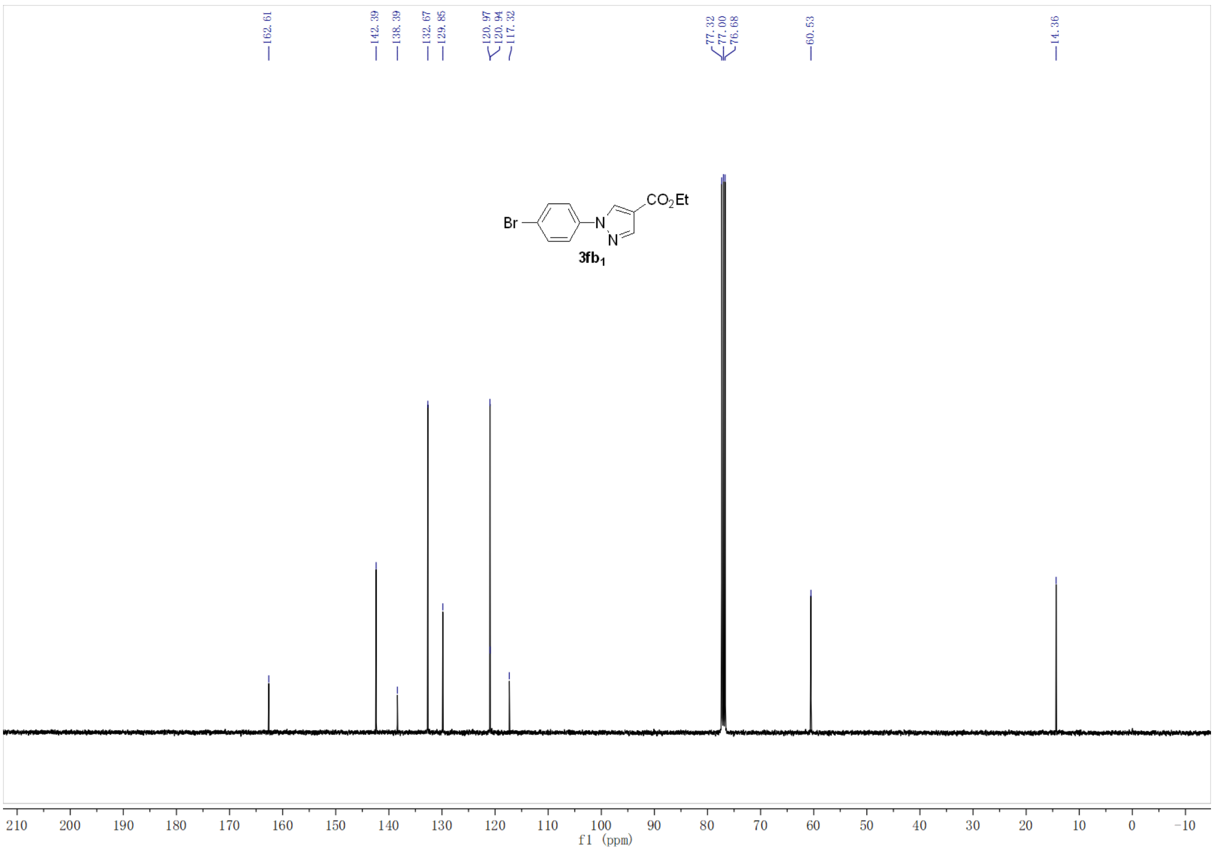
77.00
76.68
60.31
17.92
14.37
CO2Et
N
N
3eb2
f1 (ppm)



8.38
8.09
7.60
7.27
4.37
4.35
4.33
4.32
1.40
1.38
1.36
0.00
Br
N
N
CO2Et
3fb1
1.00
0.94
4.10
2.10
3.15
f1 (ppm)



162.61
142.39
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132.67
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120.97
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77.32
77.00
76.68
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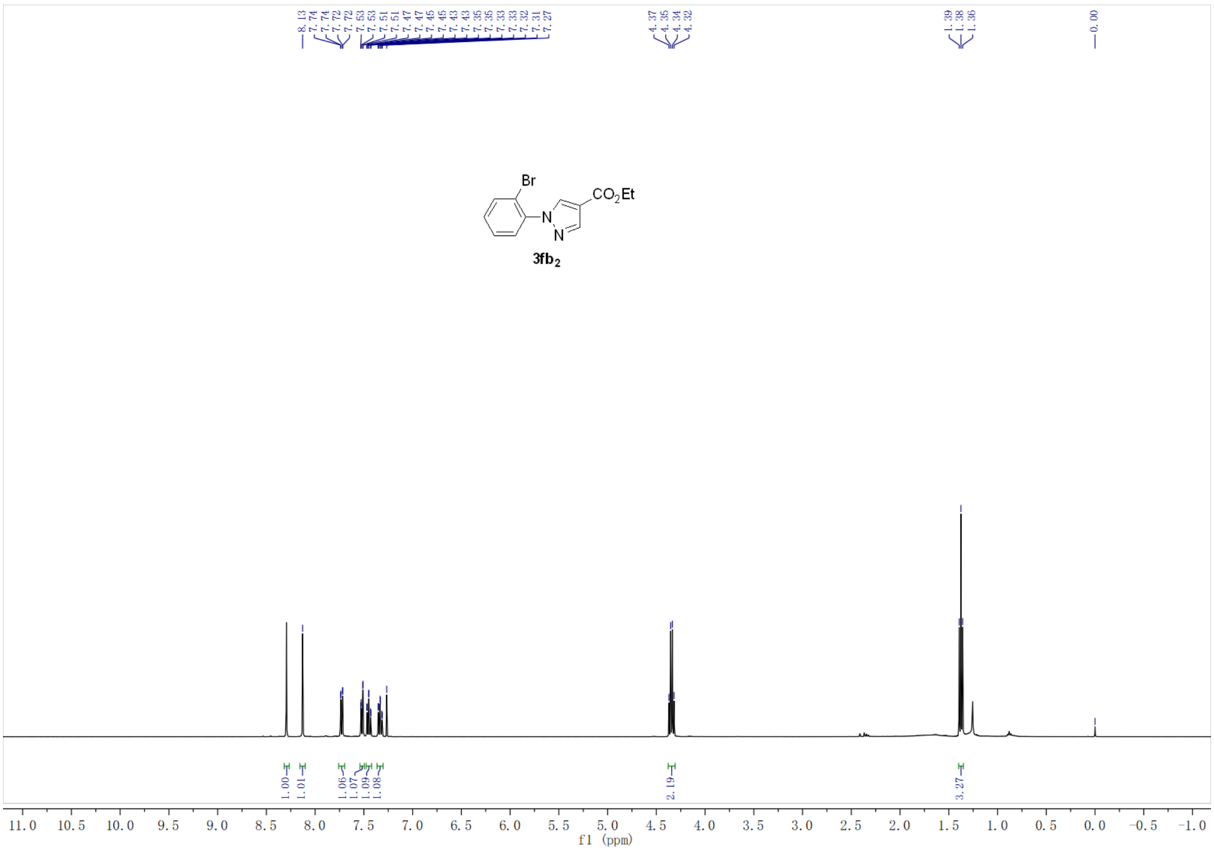
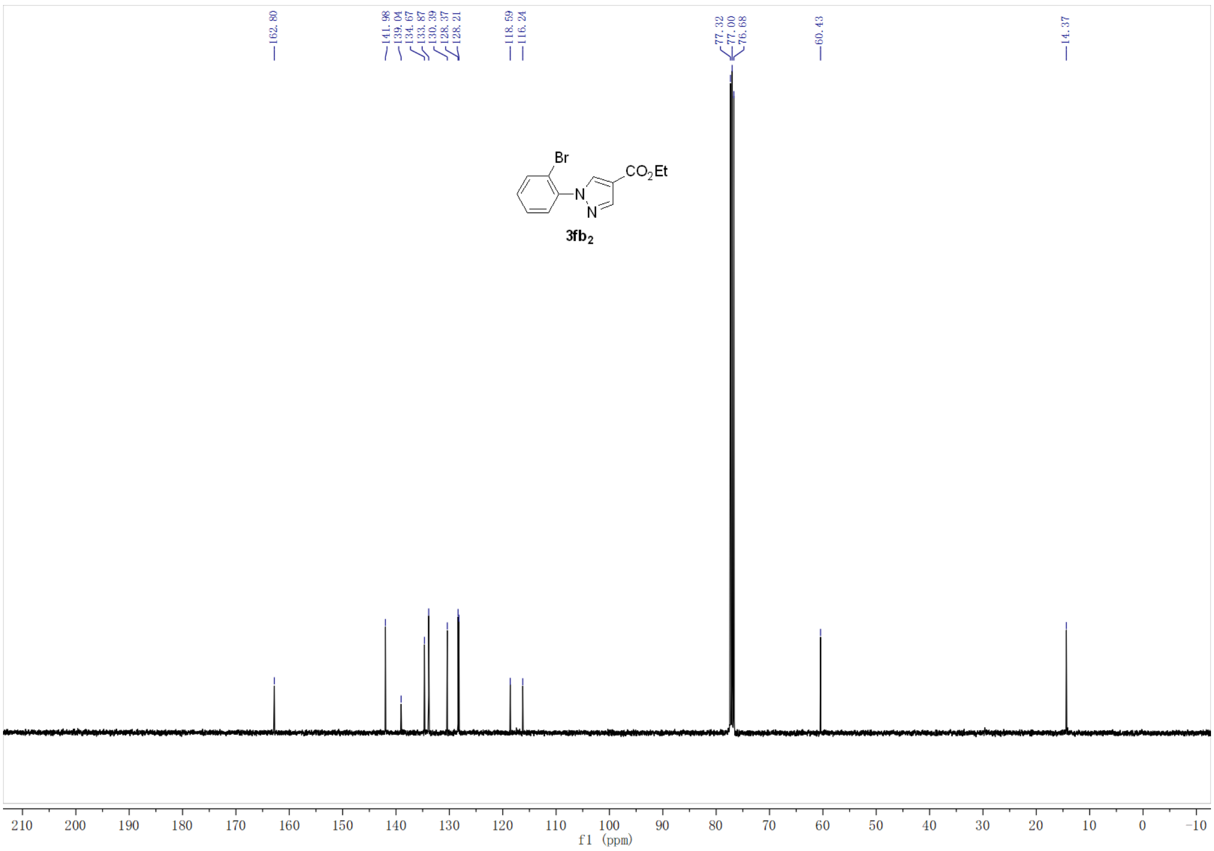
Br
N
N
CO2Et
3fb1
f1 (ppm)


8.13
7.74
7.74
7.72
7.72
7.53
7.53
7.51
7.51
7.47
7.47
7.45
7.45
7.43
7.43
7.35
7.35
7.33
7.33
7.32
7.31
7.27
4.37
4.35
4.34
4.32
1.39
1.38
1.36
0.00
Br
CO2Et
N
N
3fb2
1.00
1.01
1.06
1.07
1.09
1.08
2.19
3.27
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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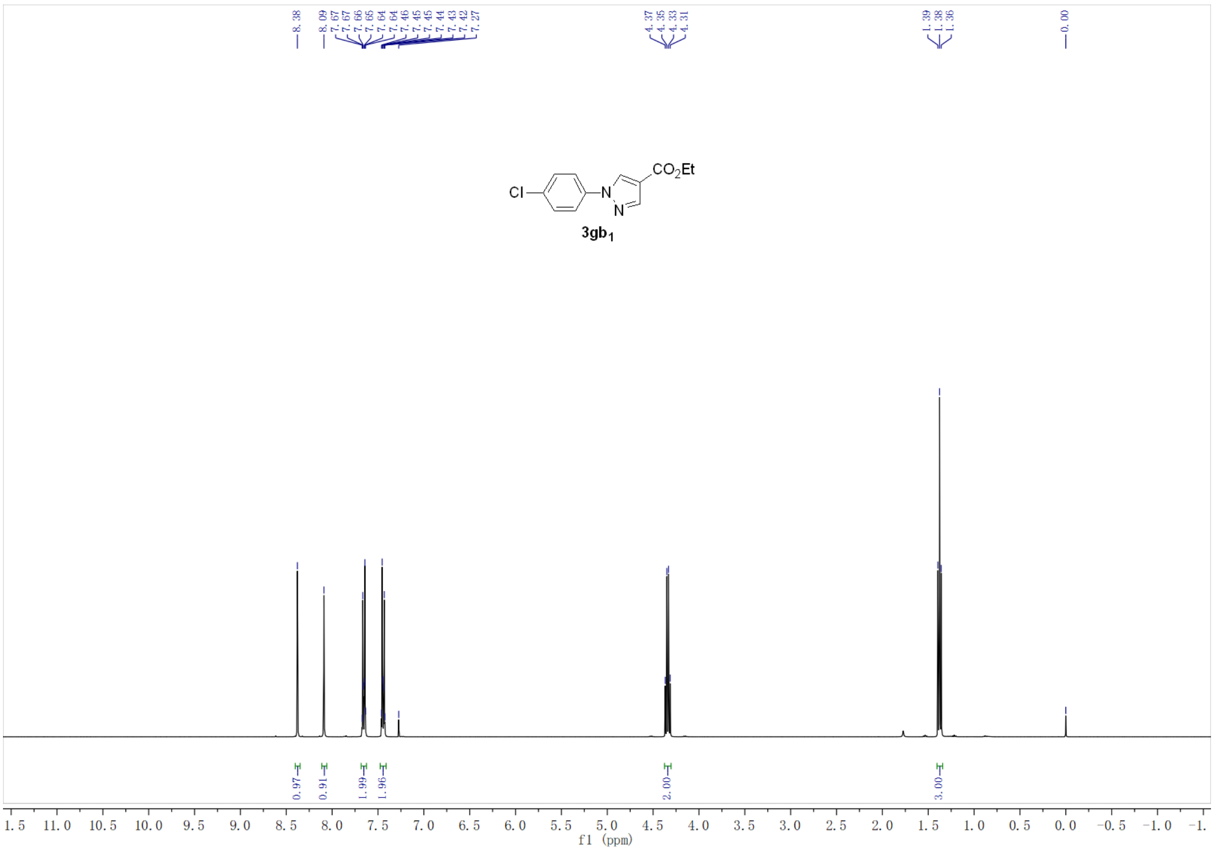
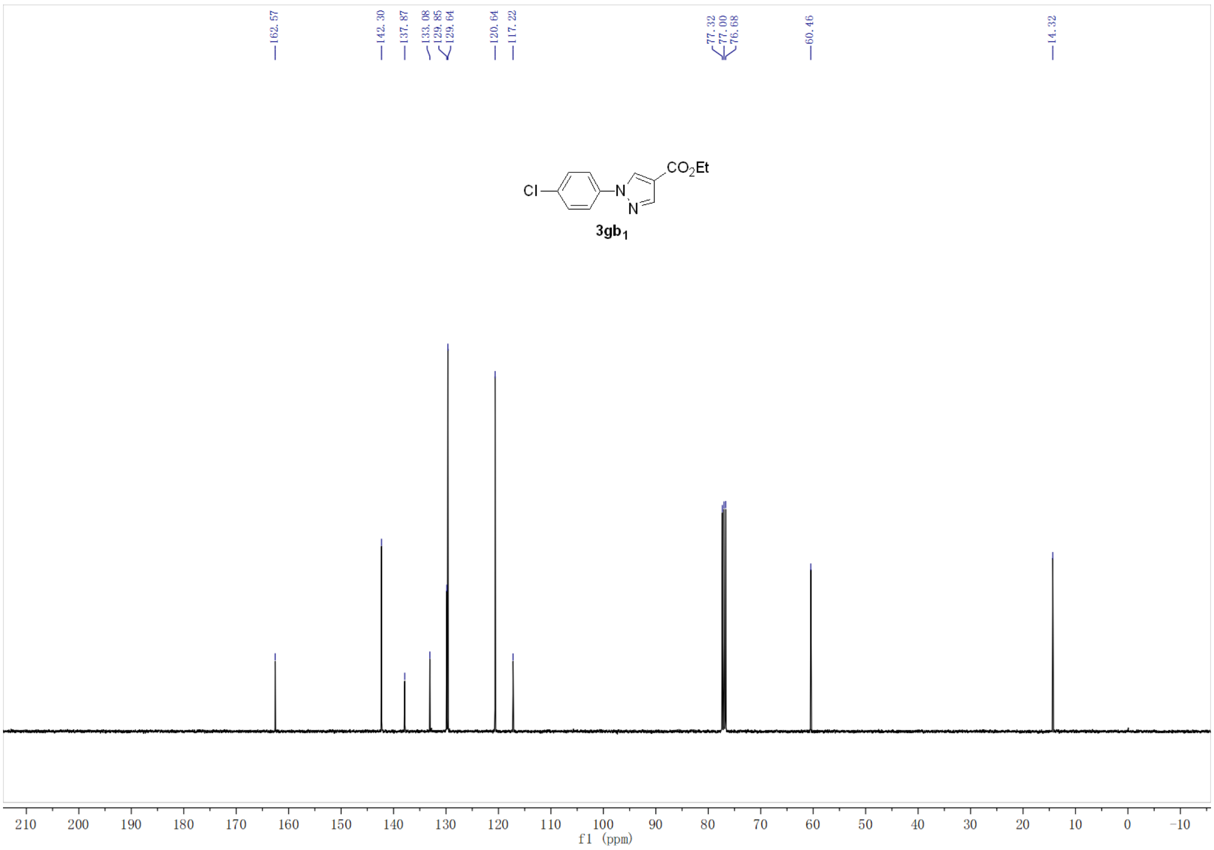
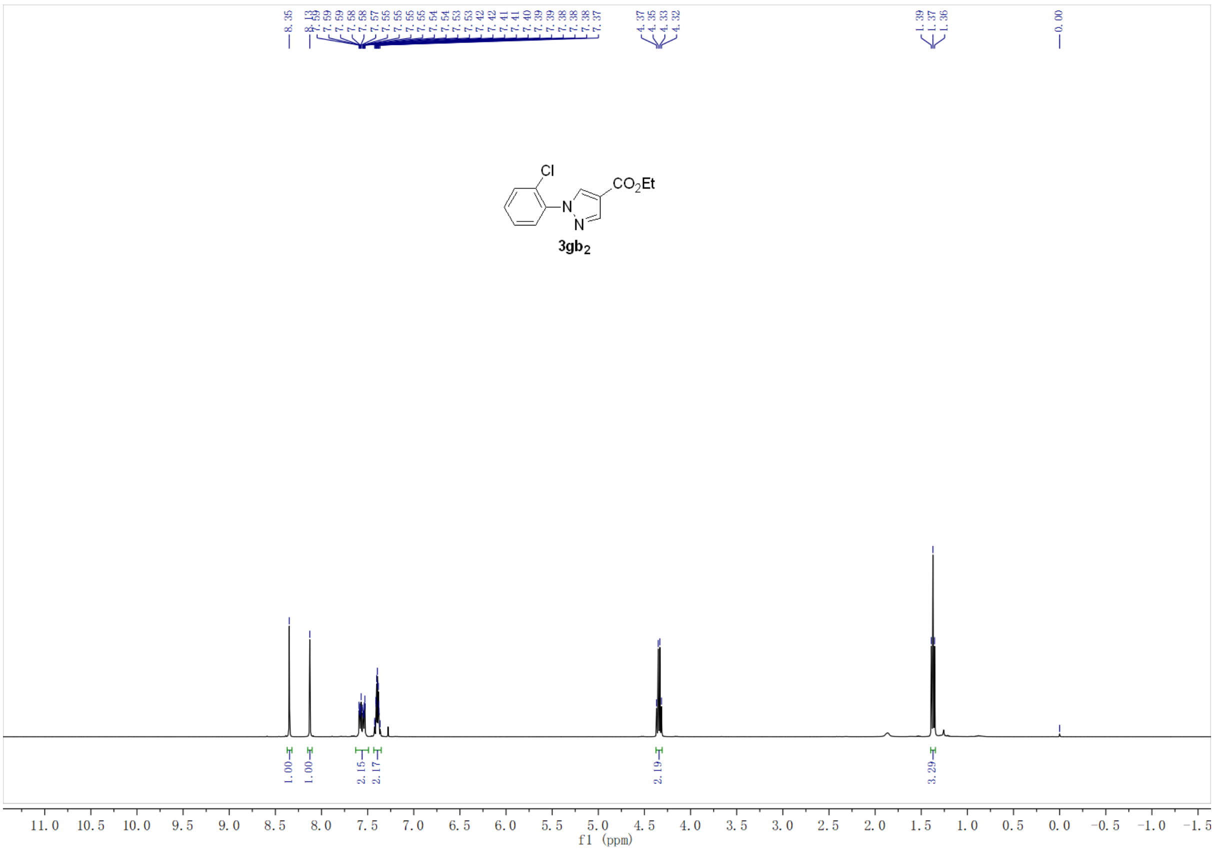
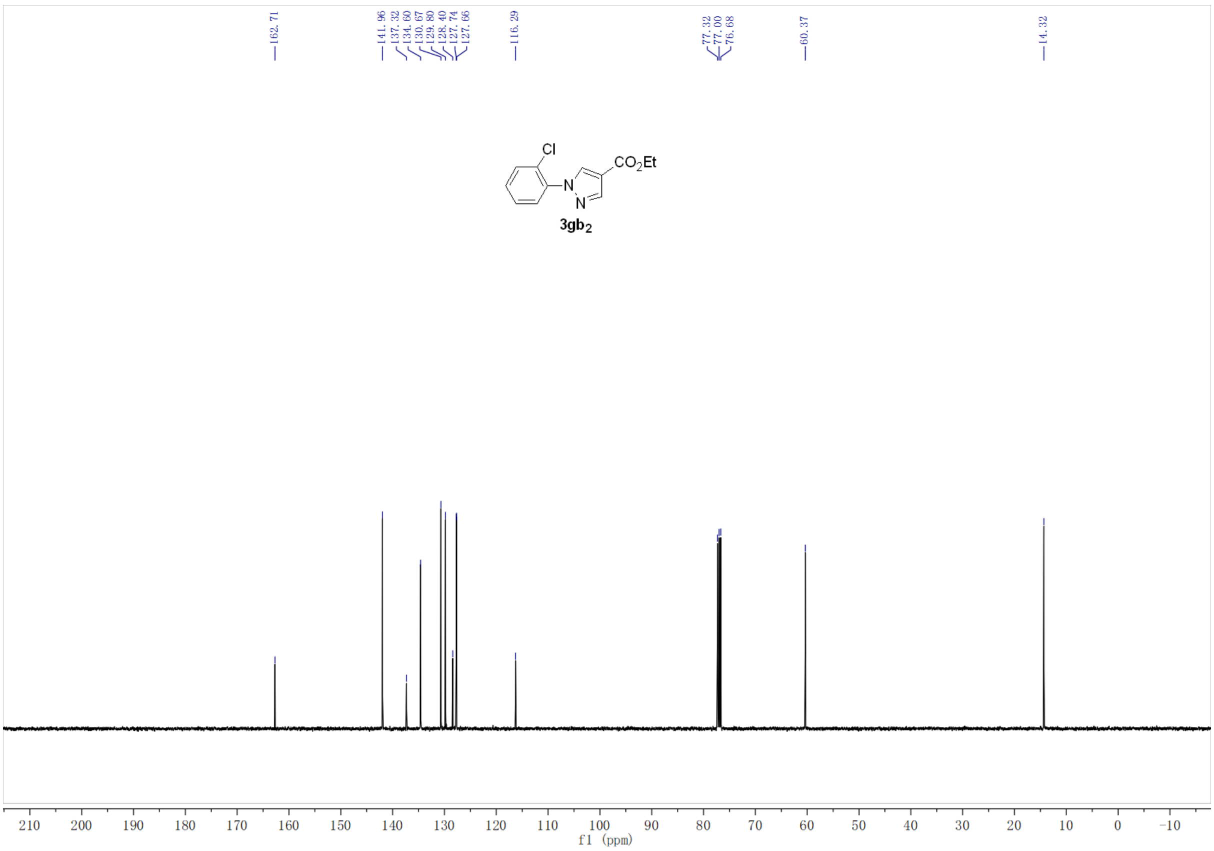
139.04
134.67
133.87
130.39
128.37
128.21
118.59
116.24
77.32
77.00
76.68
60.43
14.37
Br
CO2Et
N
N
3fb2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.38
8.09
7.67
7.67
7.66
7.65
7.64
7.64
7.46
7.45
7.45
7.44
7.43
7.42
7.27
4.37
4.35
4.33
4.31
1.39
1.38
1.36
0.00
Cl
N
N
CO2Et
3gb1
0.97
0.91
1.99
1.96
2.00
3.00
f1 (ppm)

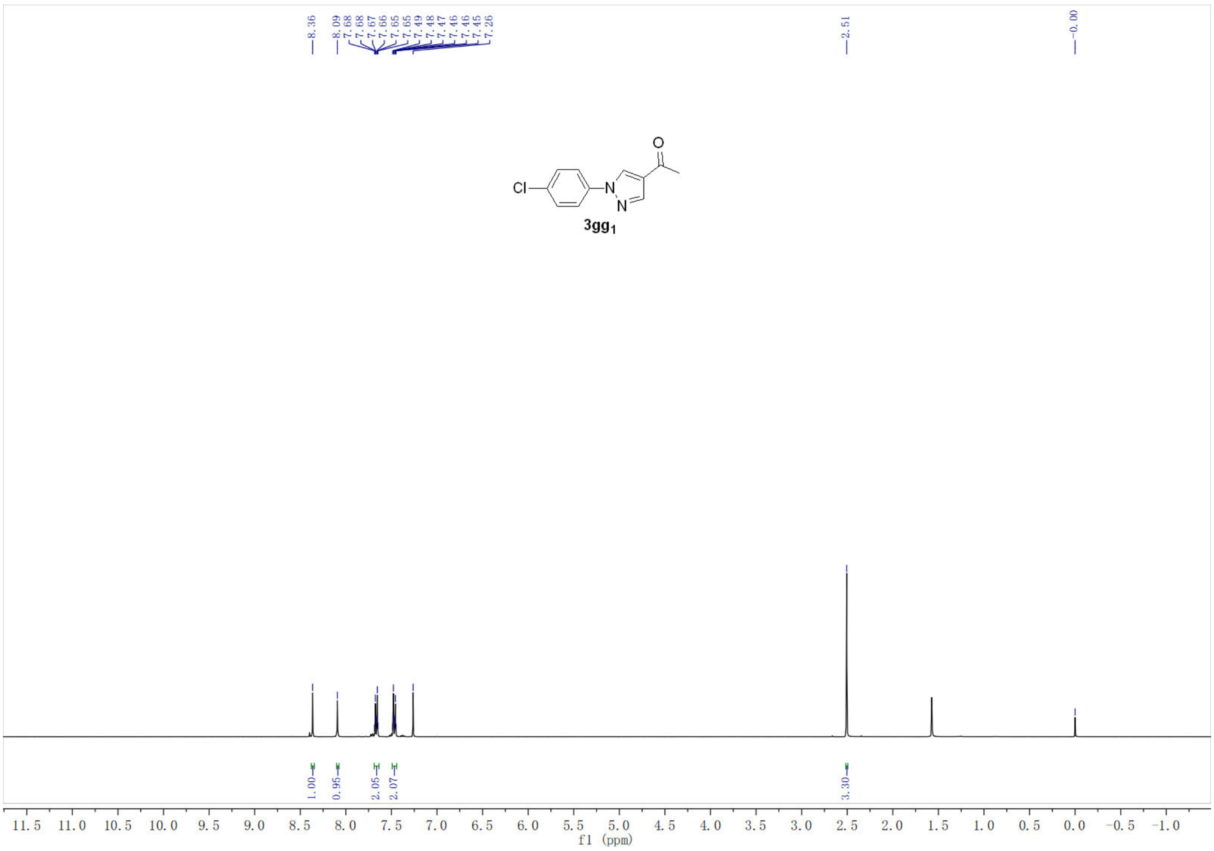

162.57
142.30
137.87
133.08
129.85
129.64
120.64
117.22
77.32
77.00
76.68
60.46
14.32
Cl
N
N
CO2Et
3gb1
f1 (ppm)

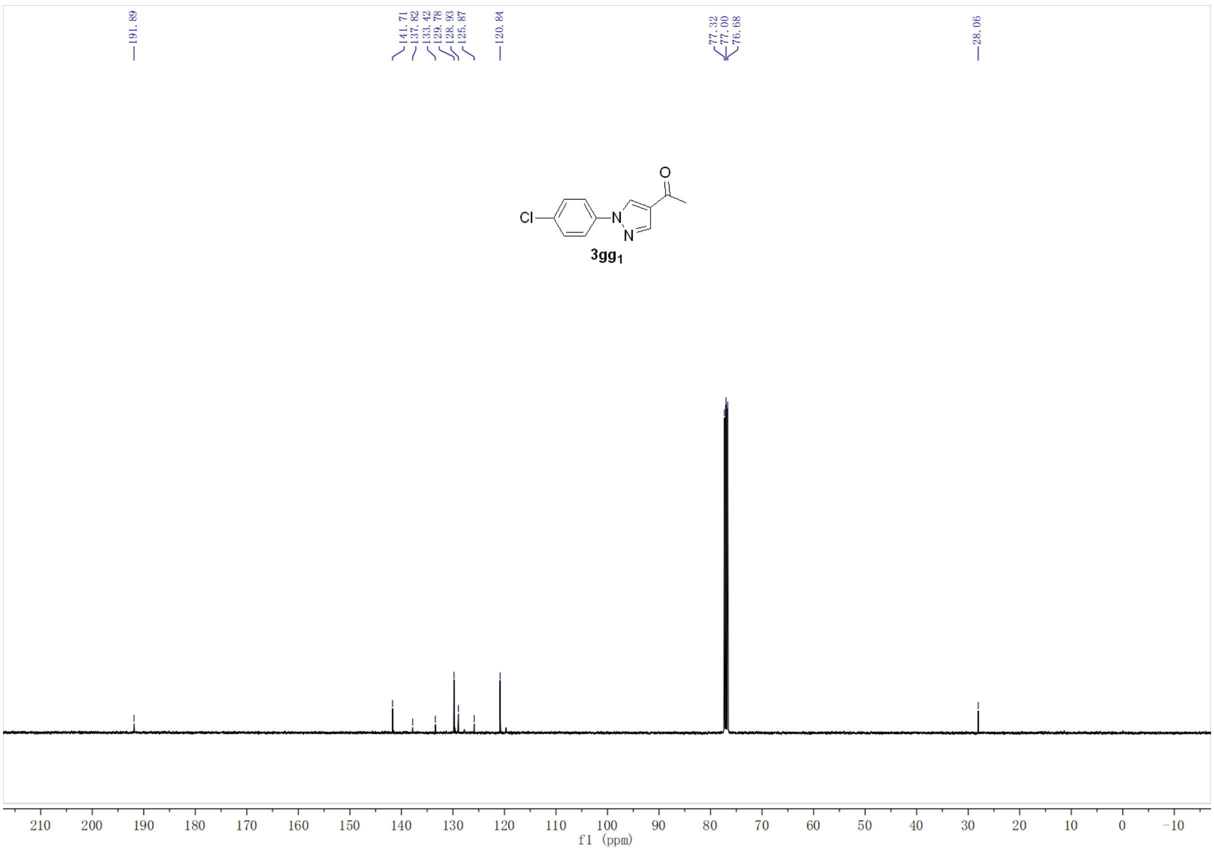


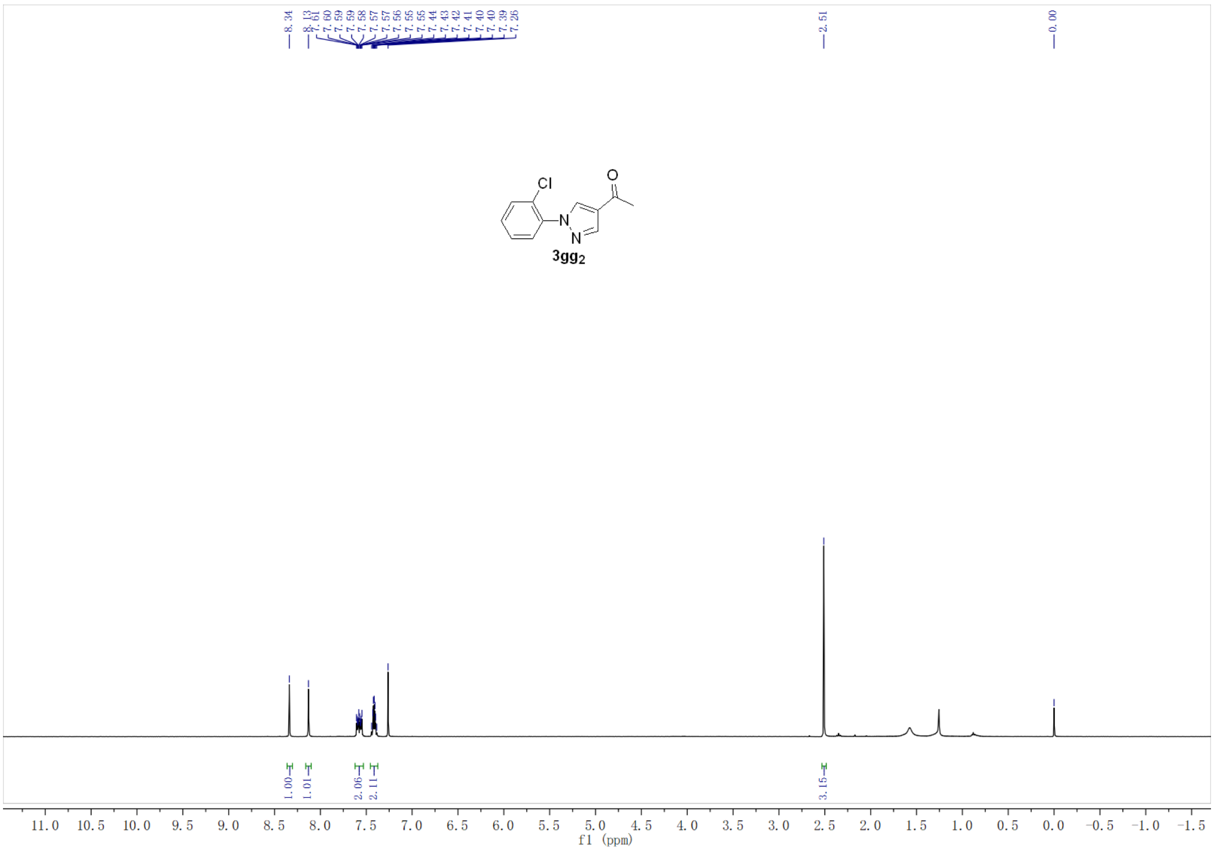
3gb2
f1 (ppm)

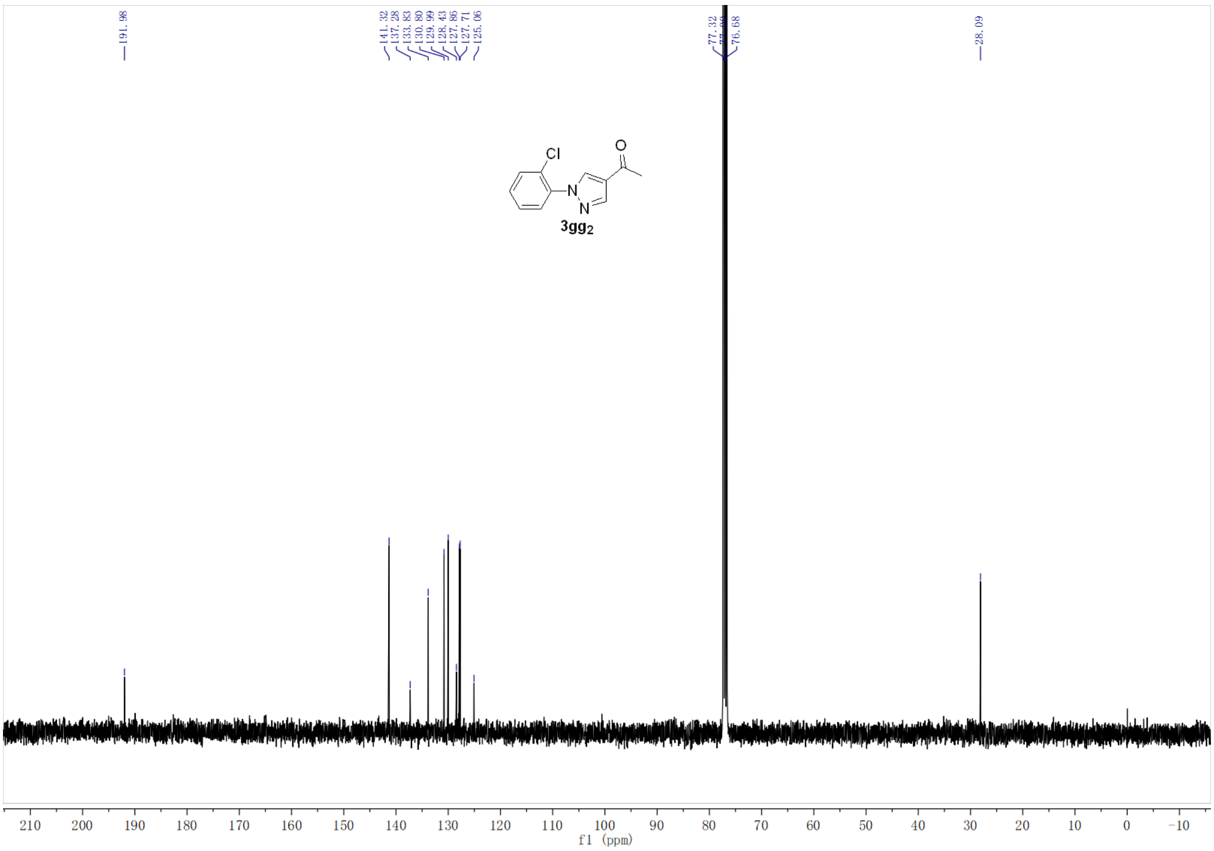


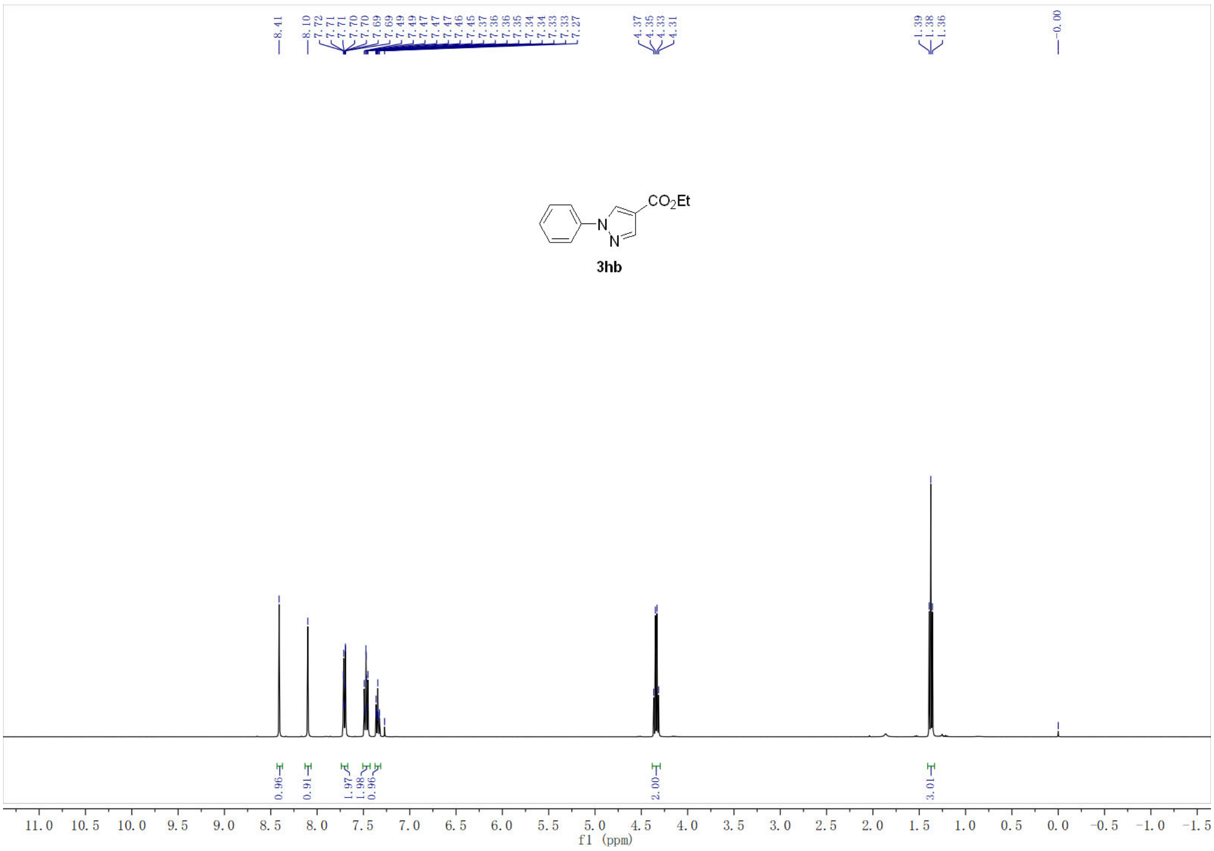
3gb2
f1 (ppm)

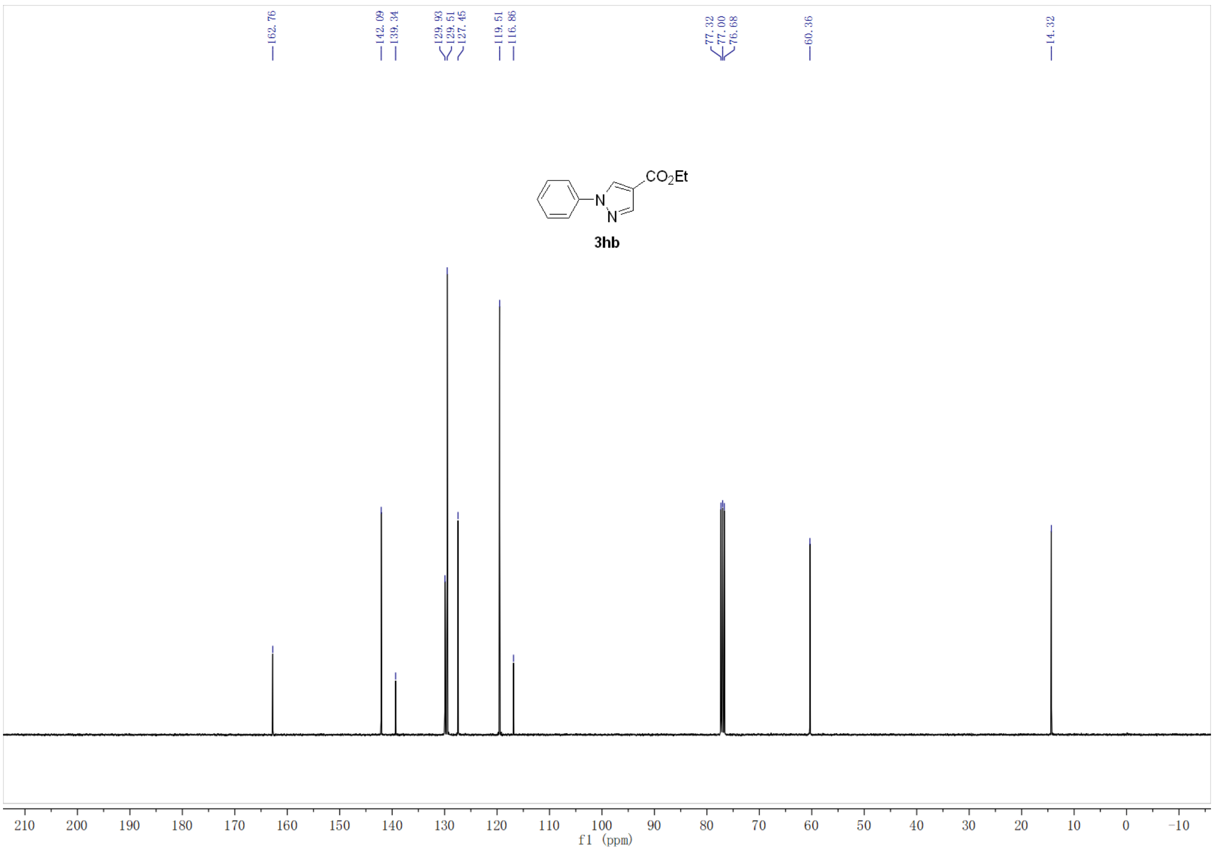

8.36
8.09
7.68
7.68
7.67
7.66
7.65
7.65
7.49
7.48
7.47
7.46
7.46
7.45
7.26
2.51
0.00
Cl
N
N
O
3gg1
1.00
0.95
2.05
2.07
3.30
f1 (ppm)

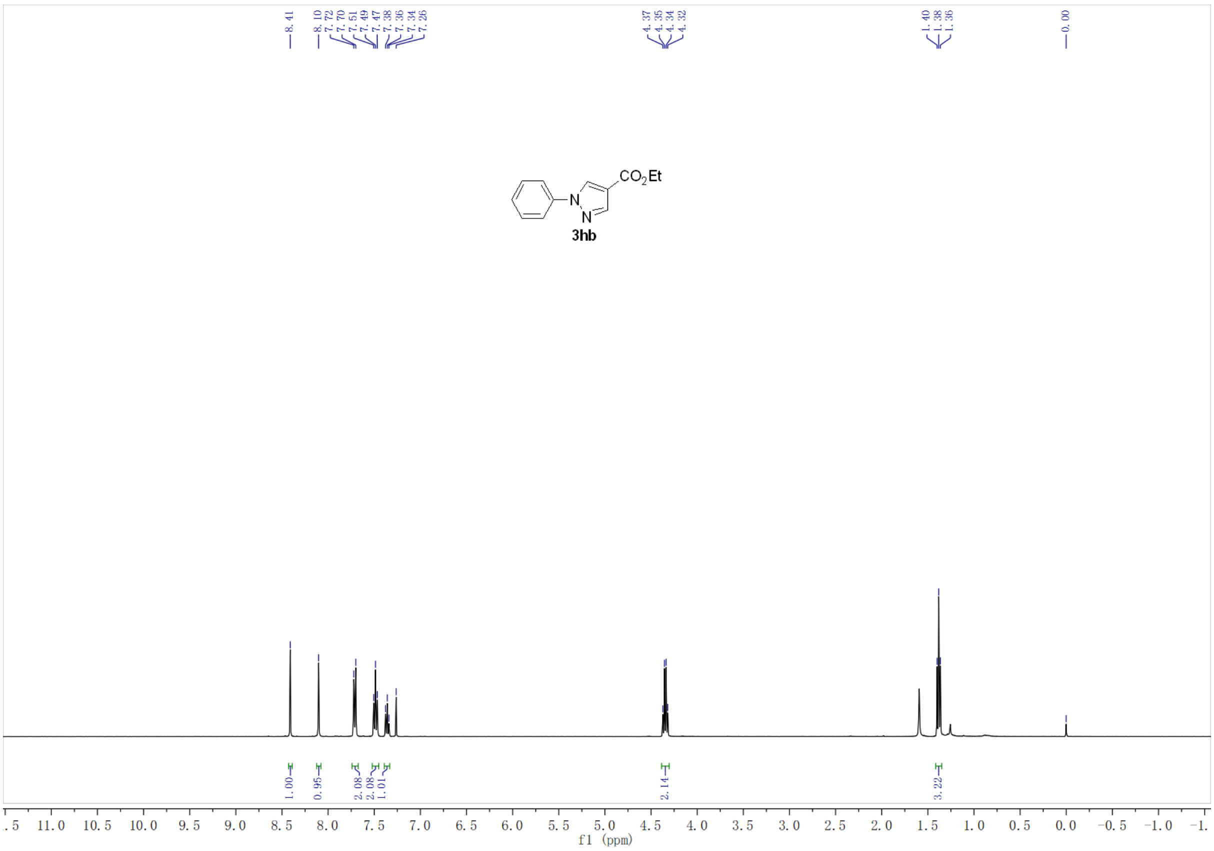

191.89
141.71
137.82
133.42
129.78
128.93
125.87
120.84
77.32
77.00
76.68
28.06
Cl
N
N
O
3gg1
f1 (ppm)


8.34
8.13
7.61
7.60
7.59
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.44
7.43
7.42
7.41
7.40
7.40
7.39
7.26
2.51
0.00
Cl
O
N
N
3gg2
1.00
1.01
2.06
2.11
3.15
f1 (ppm)

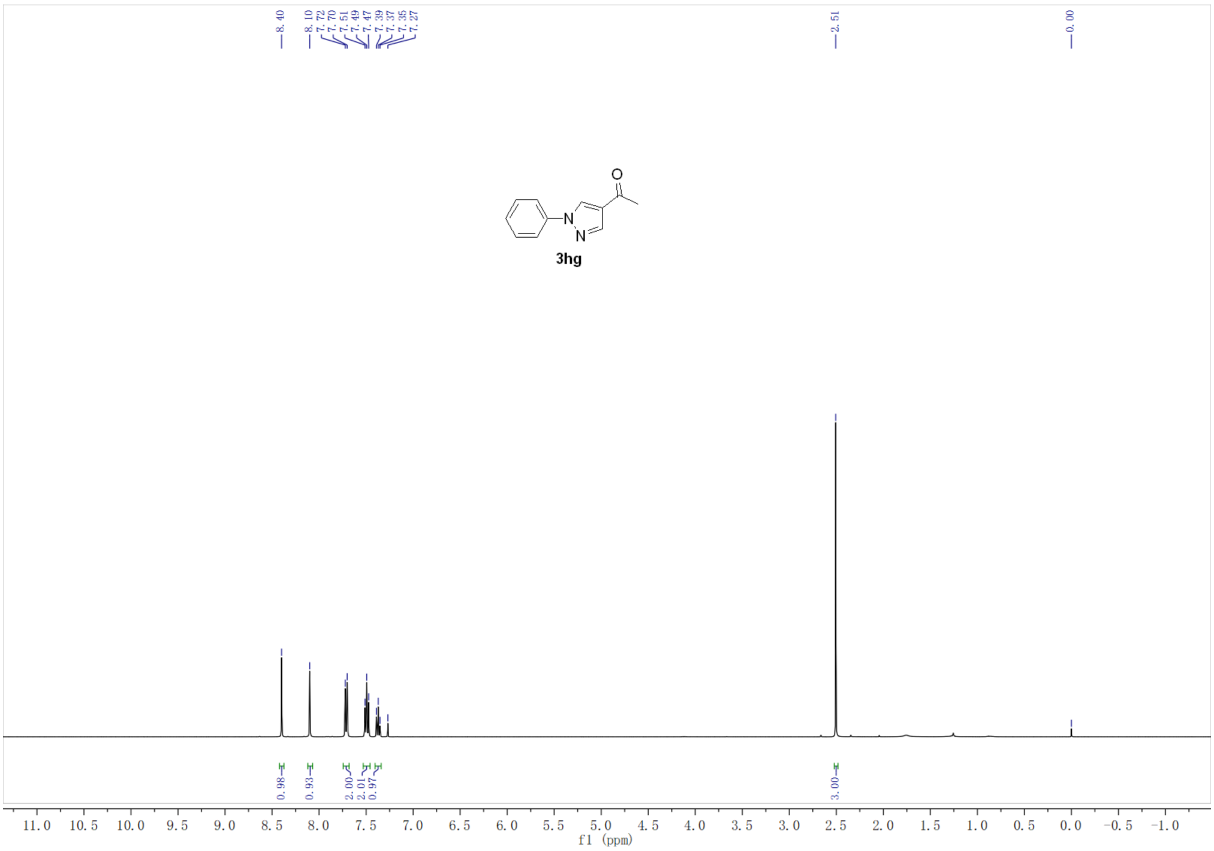

191.98
141.32
137.28
133.83
130.80
129.99
128.43
127.86
127.71
125.06
77.32
76.68
28.09
Cl
O
N
N
3gg2
f1 (ppm)

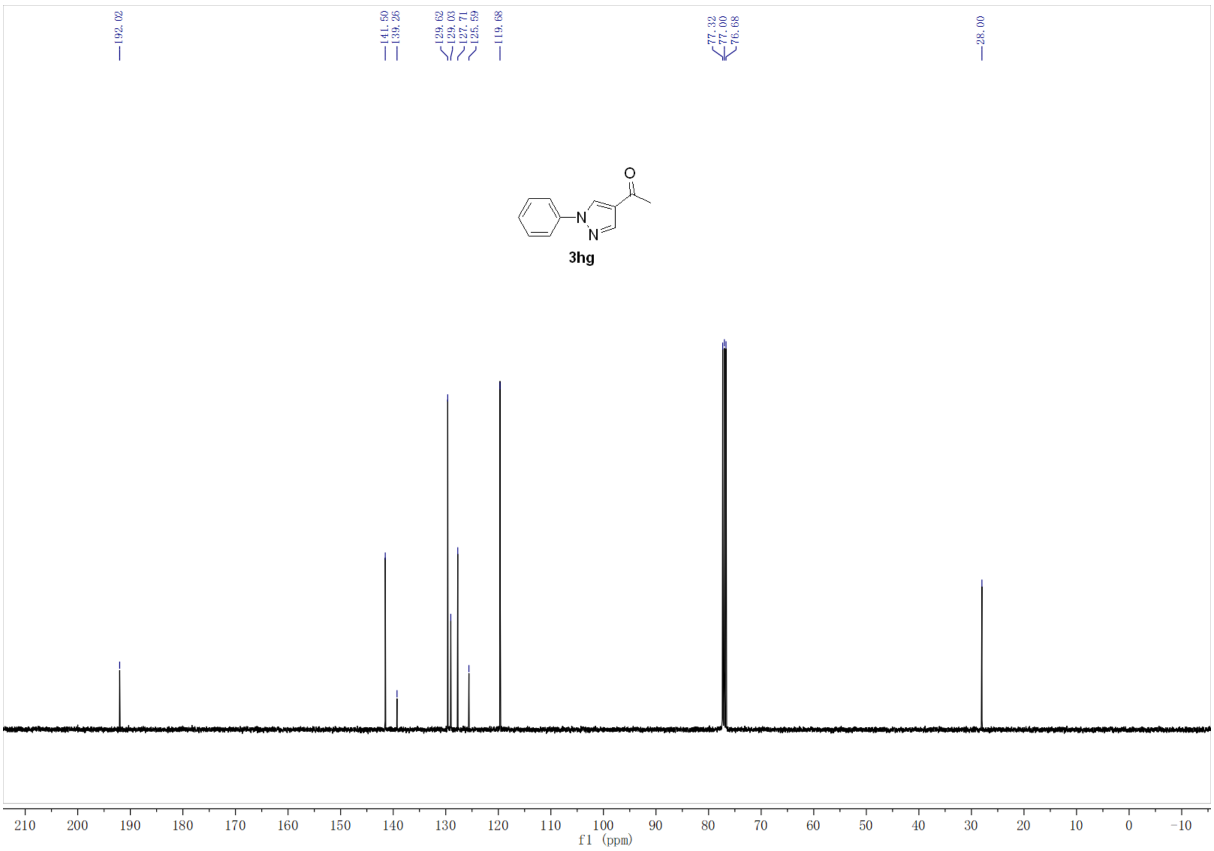

CO2Et
N
N
3hb
f1 (ppm)

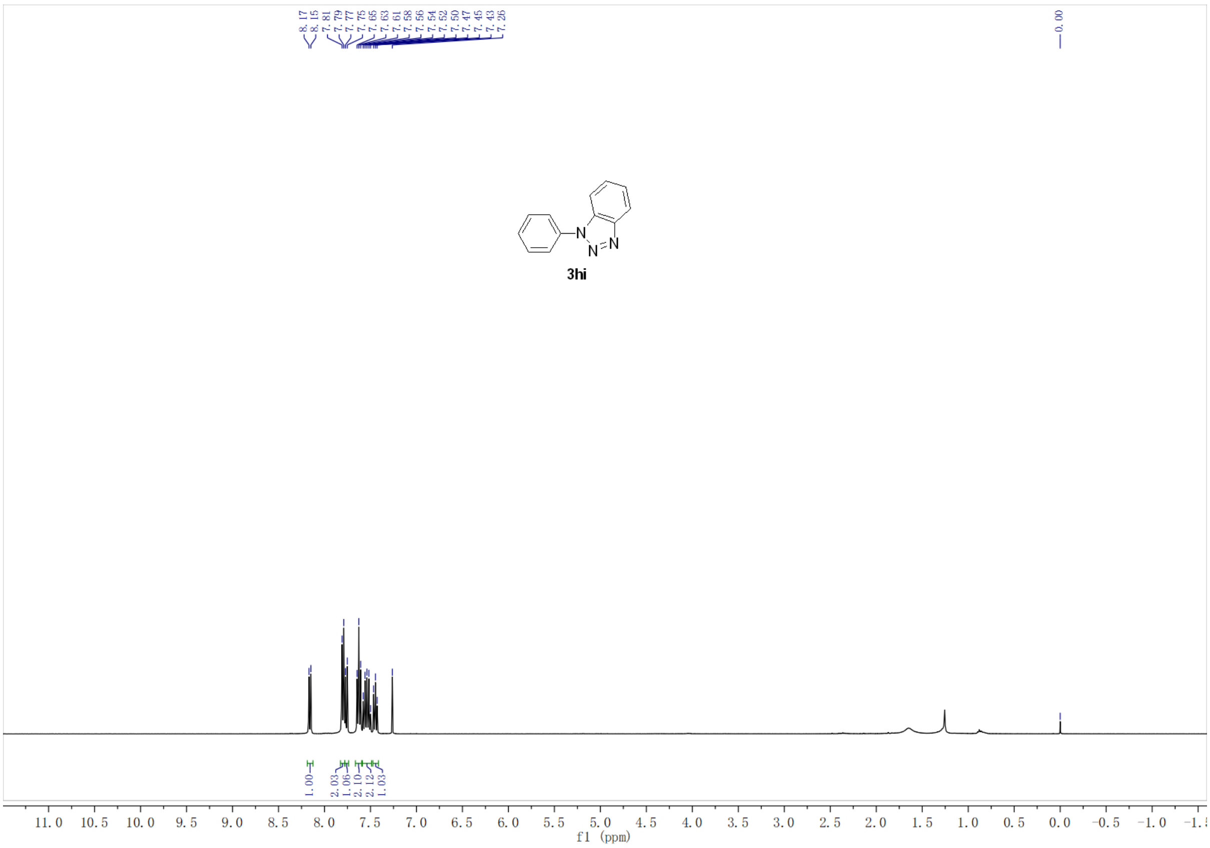

CO2Et
N
N
3hb
f1 (ppm)

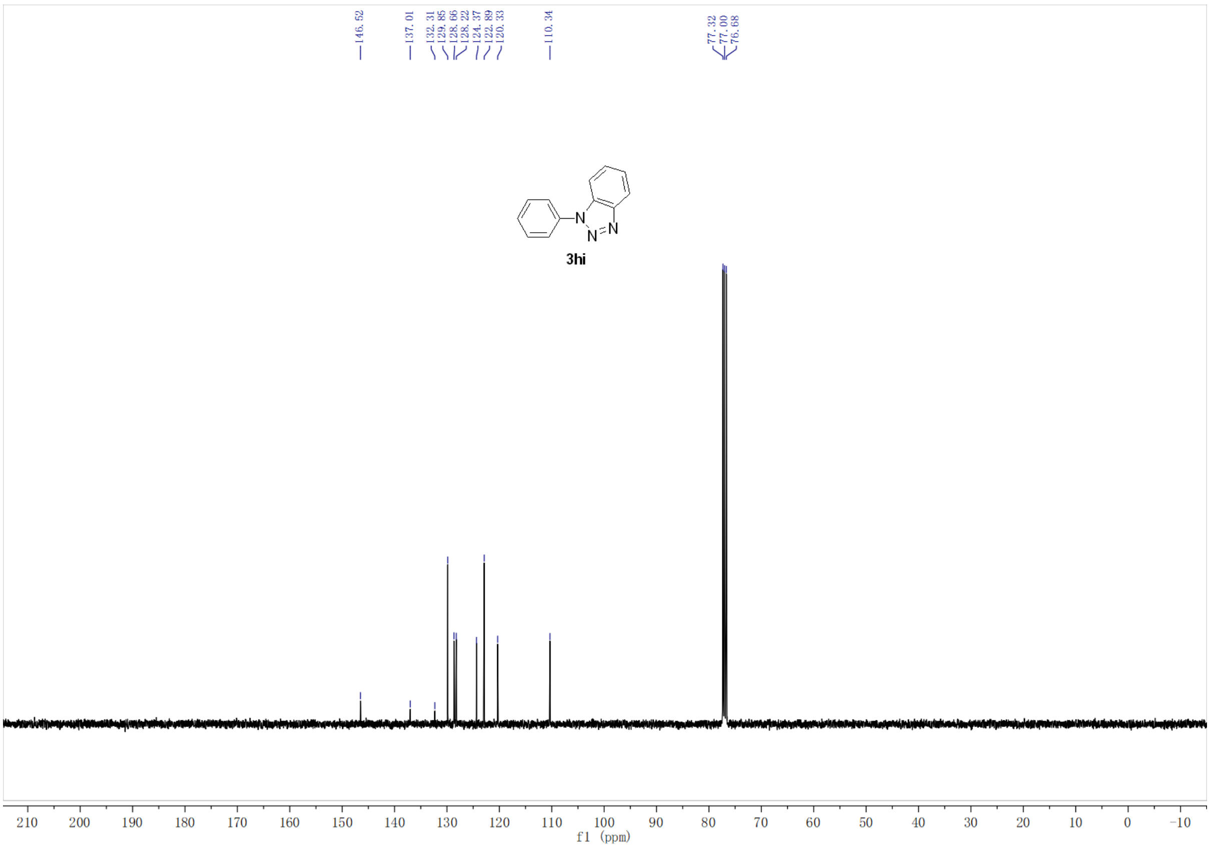


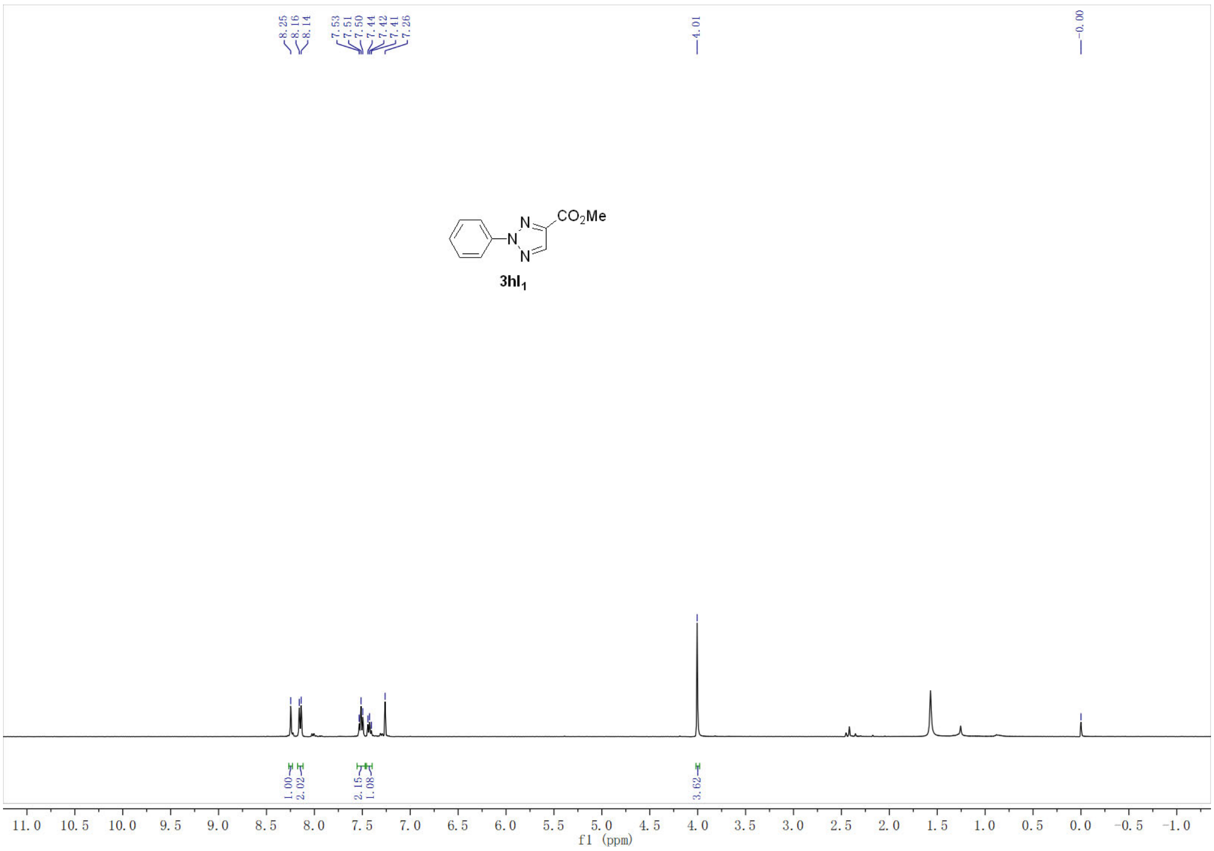
(from trifluorotoluene as strating material)

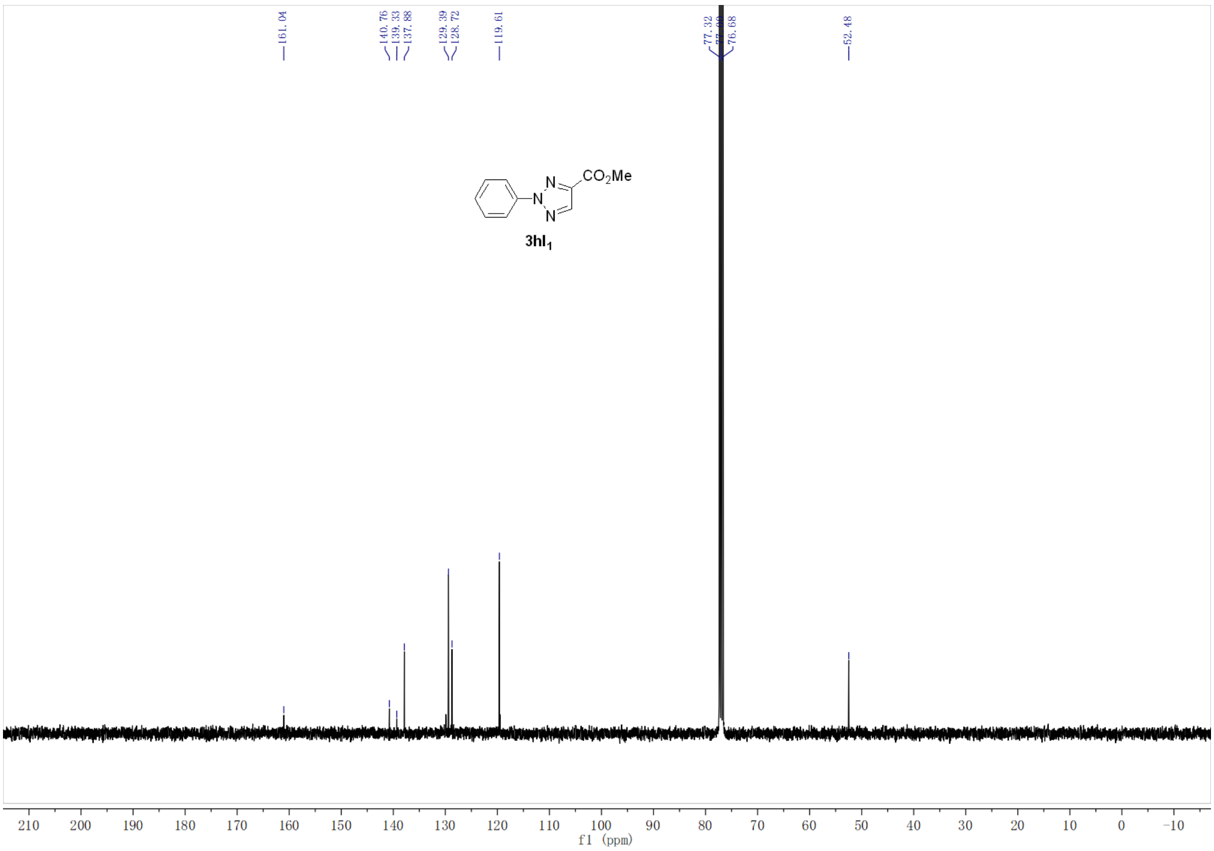

8.40
8.10
7.72
7.70
7.51
7.49
7.47
7.39
7.37
7.35
7.27
2.51
0.00
3hg
0.98
0.93
2.00
2.01
0.97
3.00
f1 (ppm)

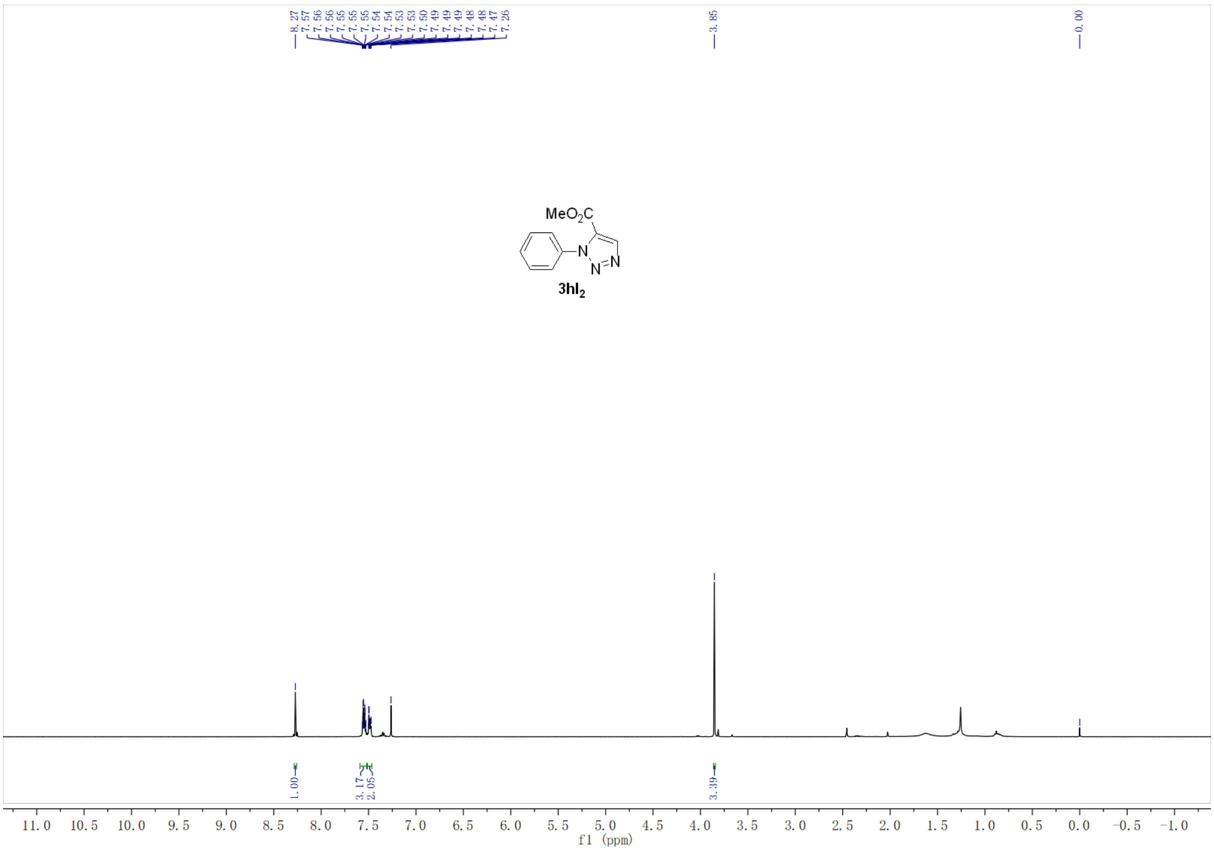

192.02
141.50
139.26
129.62
129.03
127.71
125.59
119.68
77.32
77.00
76.68
28.00
3hg
f1 (ppm)

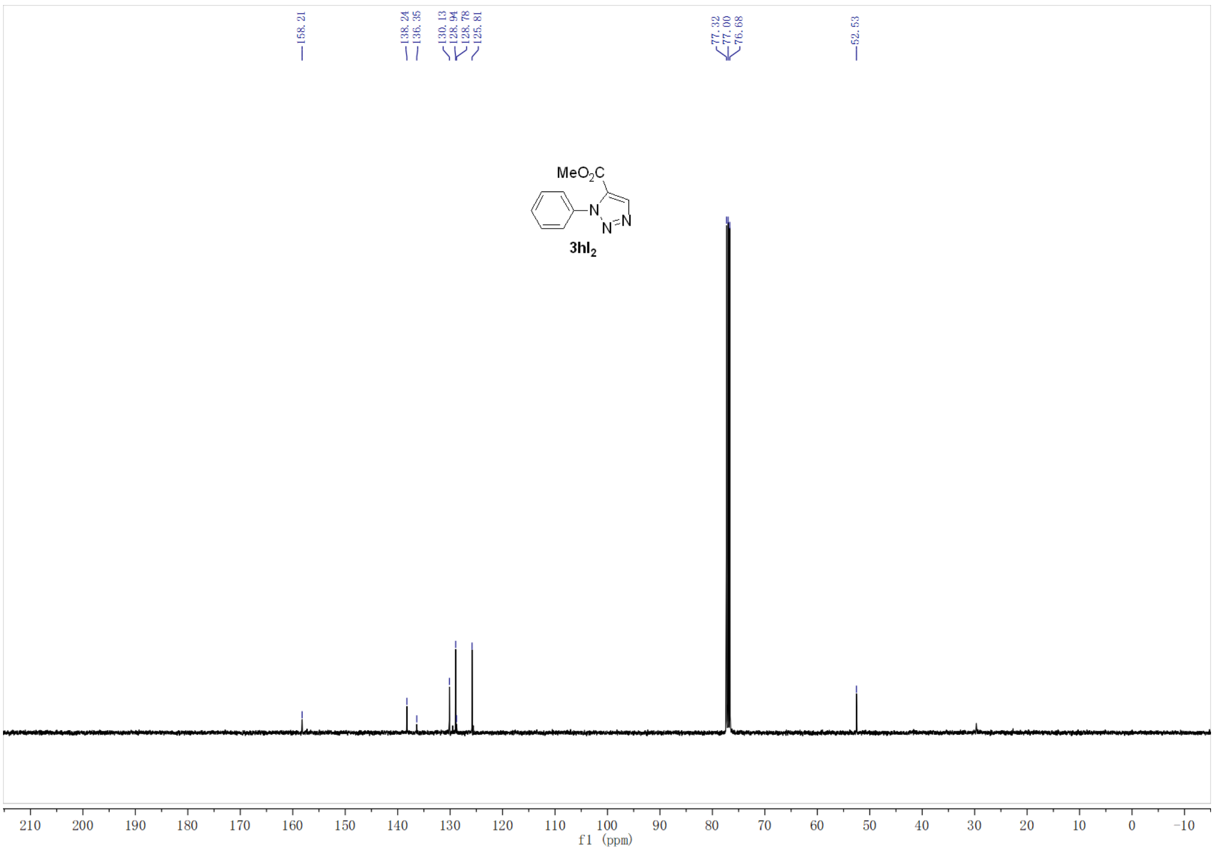


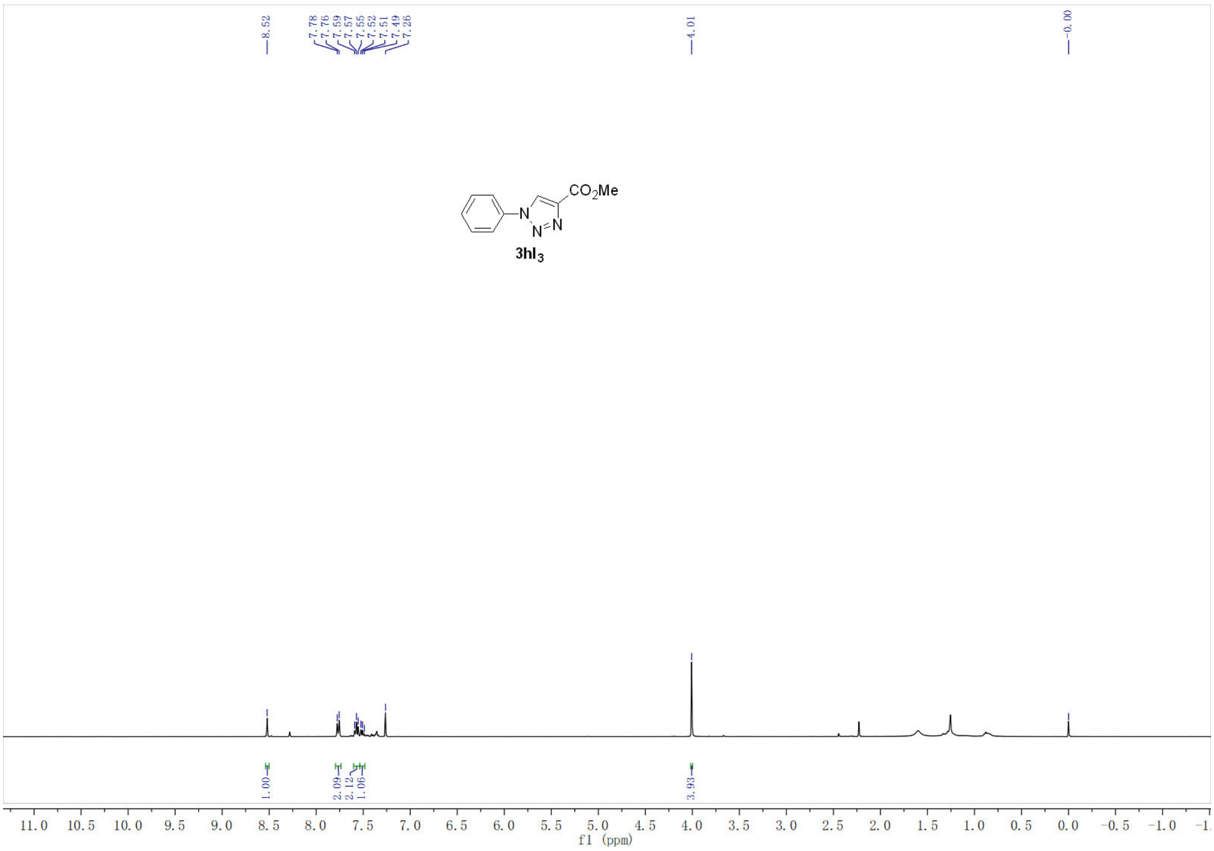


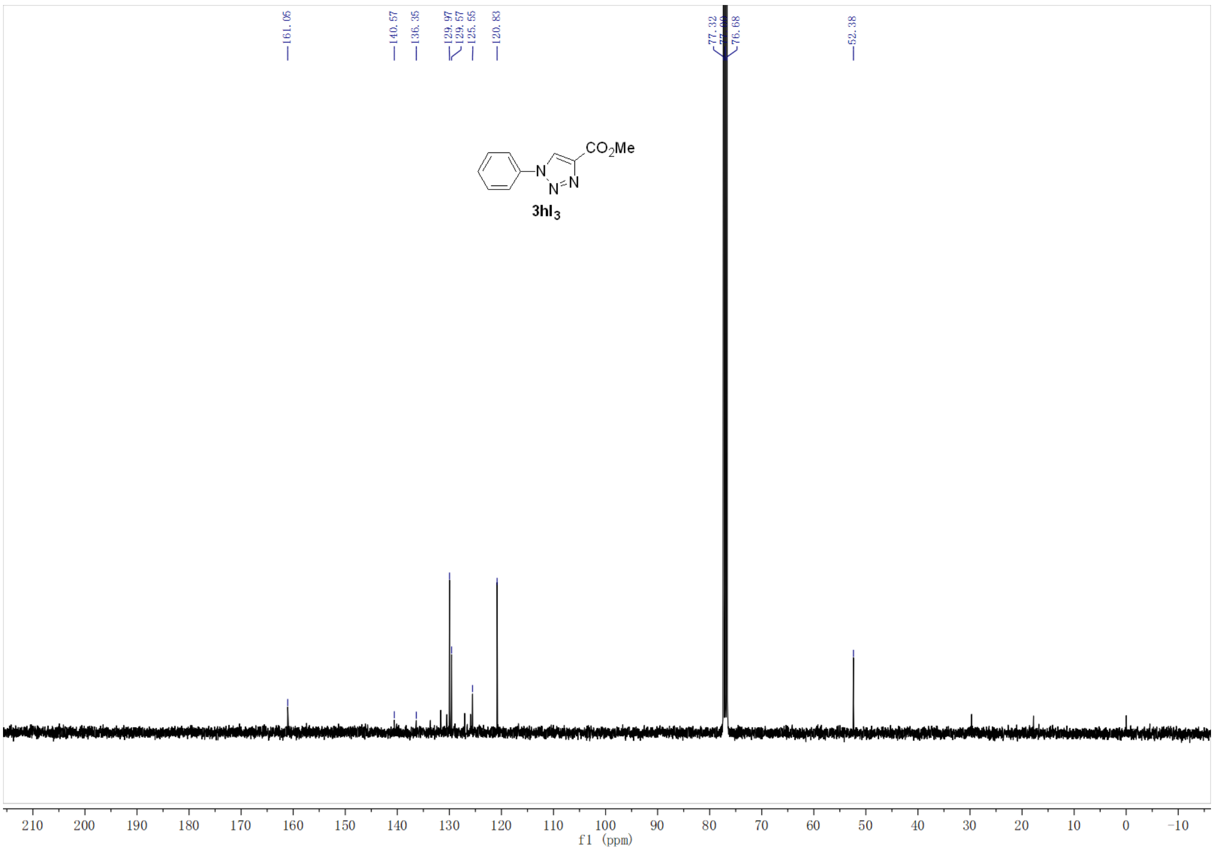

8.25
8.16
8.14
7.53
7.51
7.50
7.44
7.42
7.41
7.26
4.01
0.00
CO2Me
N
N
N
3hl1
1.00
2.02
2.15
1.08
3.62
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


161.04
140.76
139.33
137.88
129.39
128.72
119.61
77.32
76.68
52.48
CO2Me
N
N
N
3hl1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.27
7.57
7.56
7.56
7.55
7.55
7.55
7.54
7.54
7.53
7.53
7.50
7.49
7.49
7.49
7.48
7.48
7.47
7.26
3.85
0.00
MeO2C
N
N
N
3hI2
1.00
3.17
2.05
3.39
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


158.21
138.24
136.35
130.13
128.94
128.78
125.81
77.32
77.00
76.68
52.53
MeO2C
N
N
N
3hI2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.52
7.78
7.76
7.59
7.57
7.55
7.52
7.51
7.49
7.26
4.01
0.00
CO2Me
N
N
N
3hI3
1.00
2.09
2.12
1.06
3.93
f1 (ppm)


161.05
140.57
136.35
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129.57
125.55
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77.32
76.68
52.38
CO2Me
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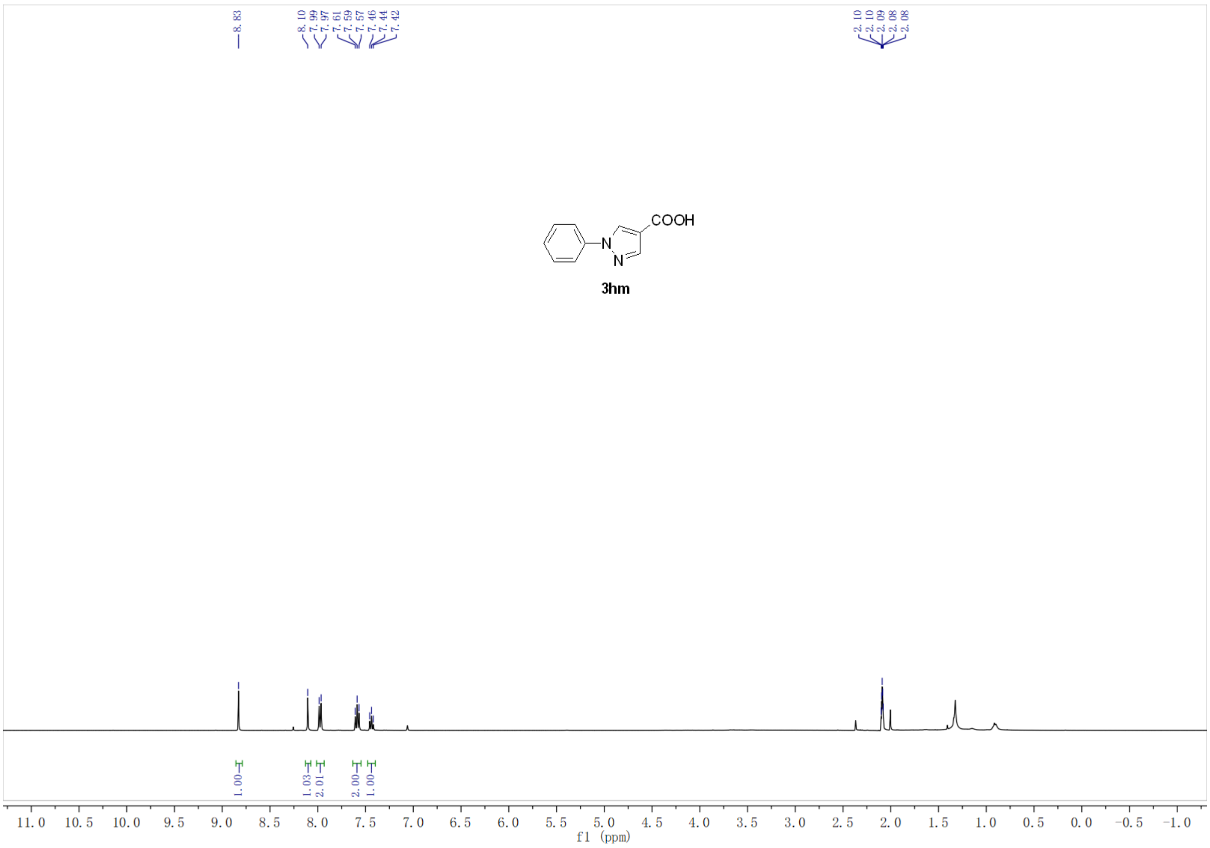
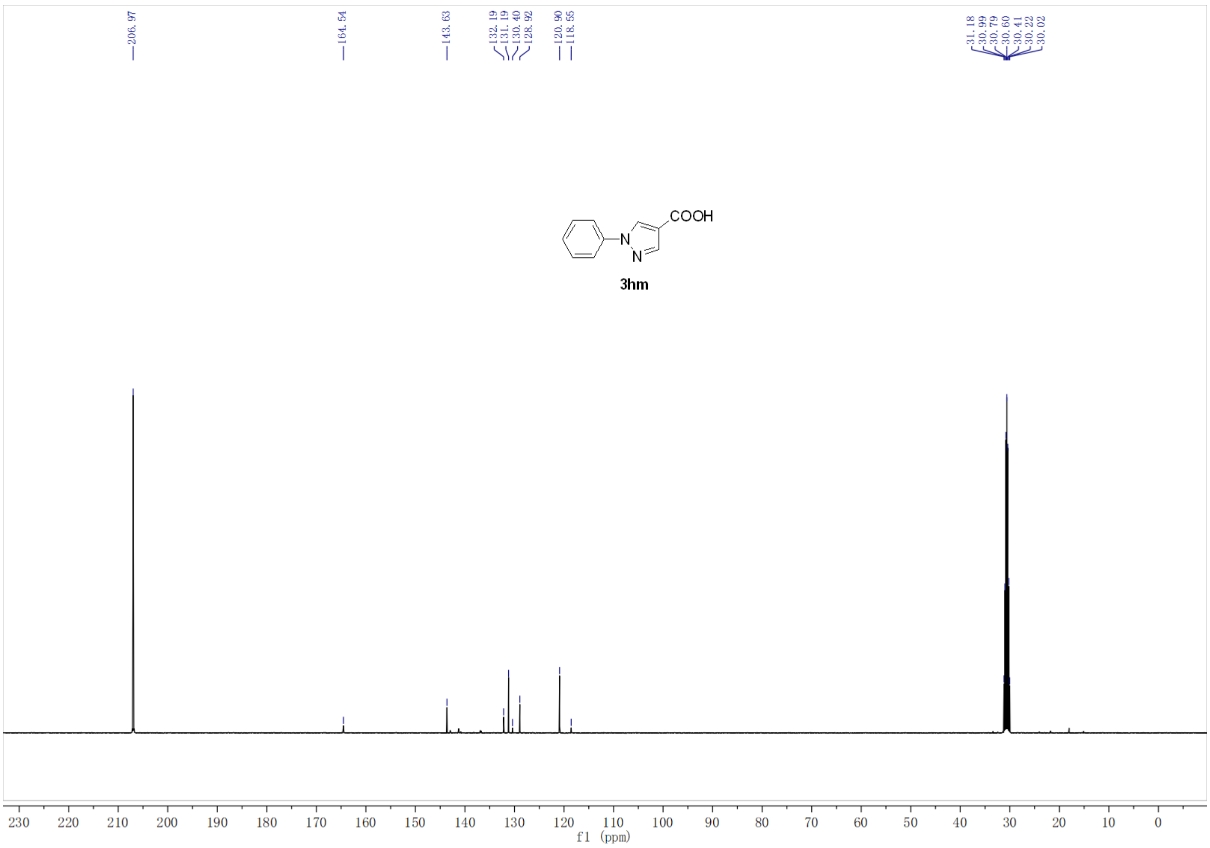
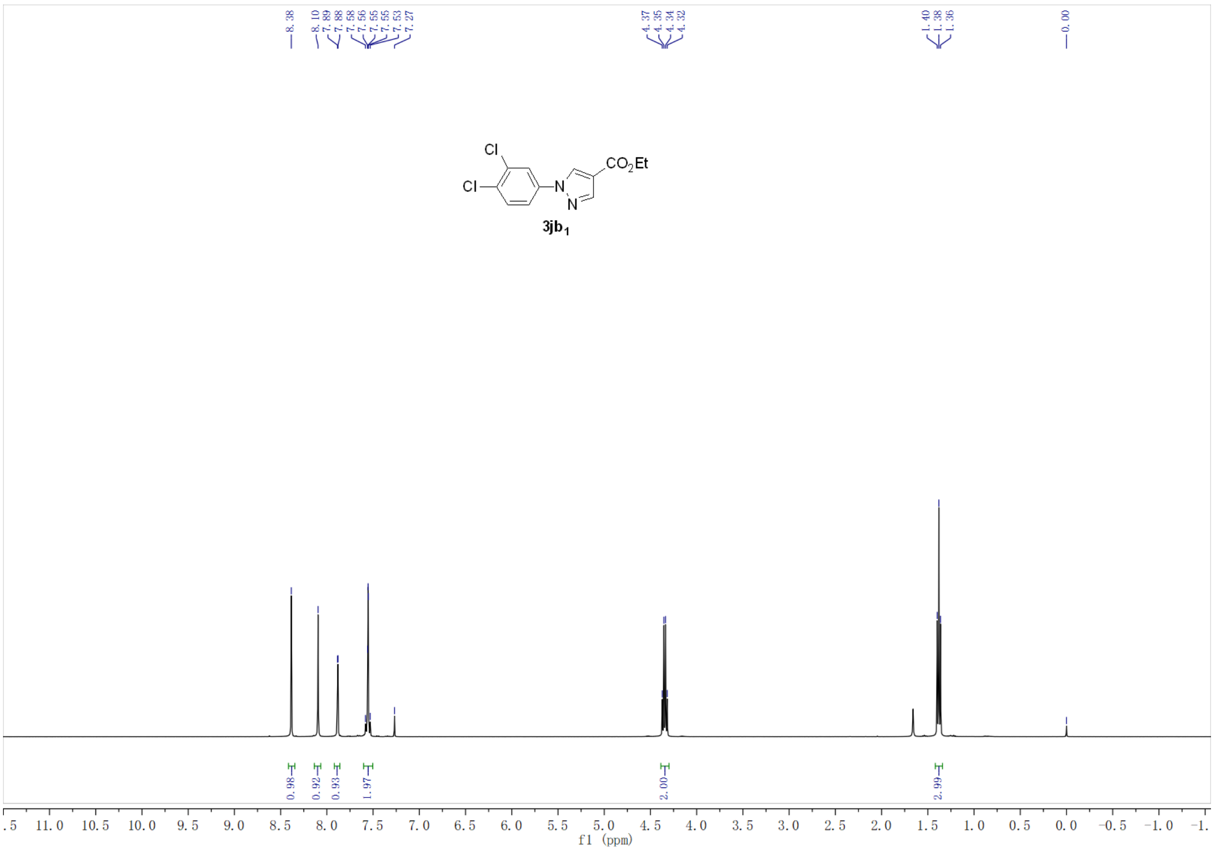
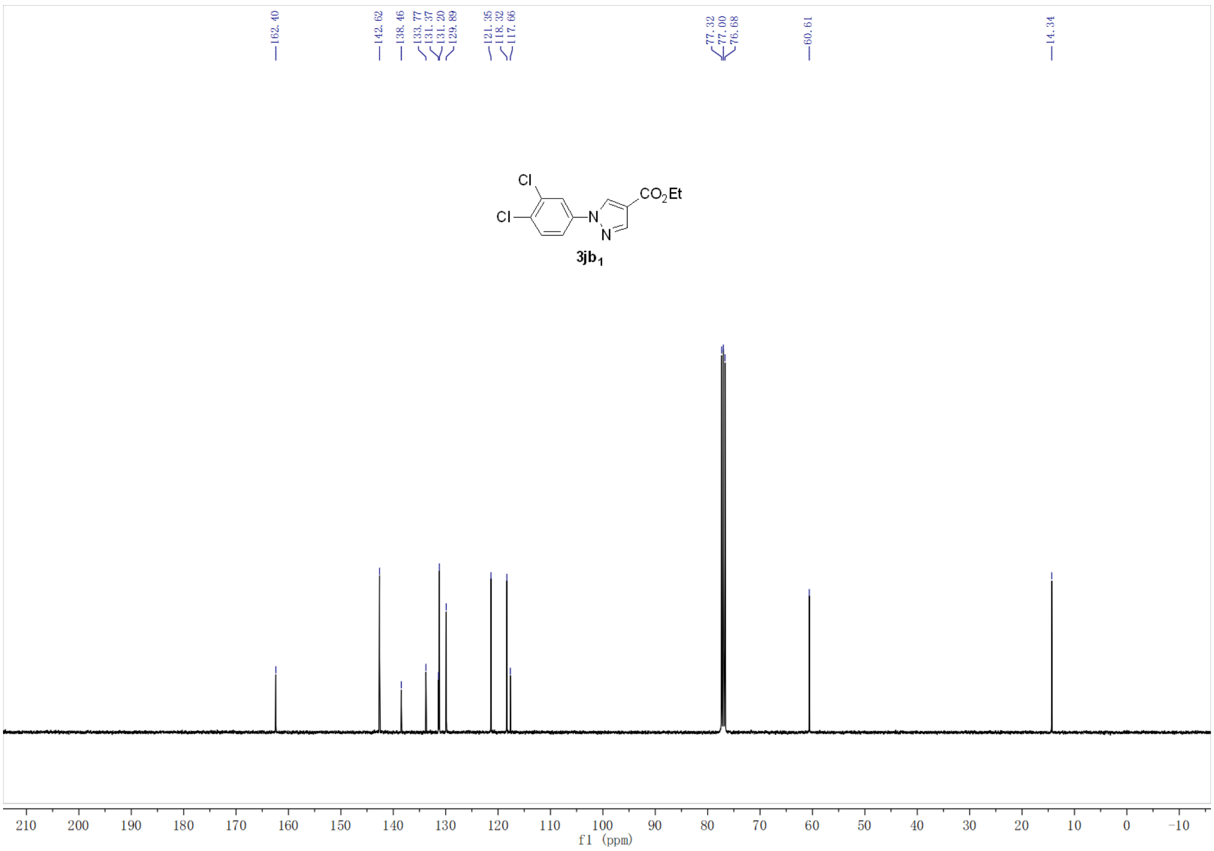
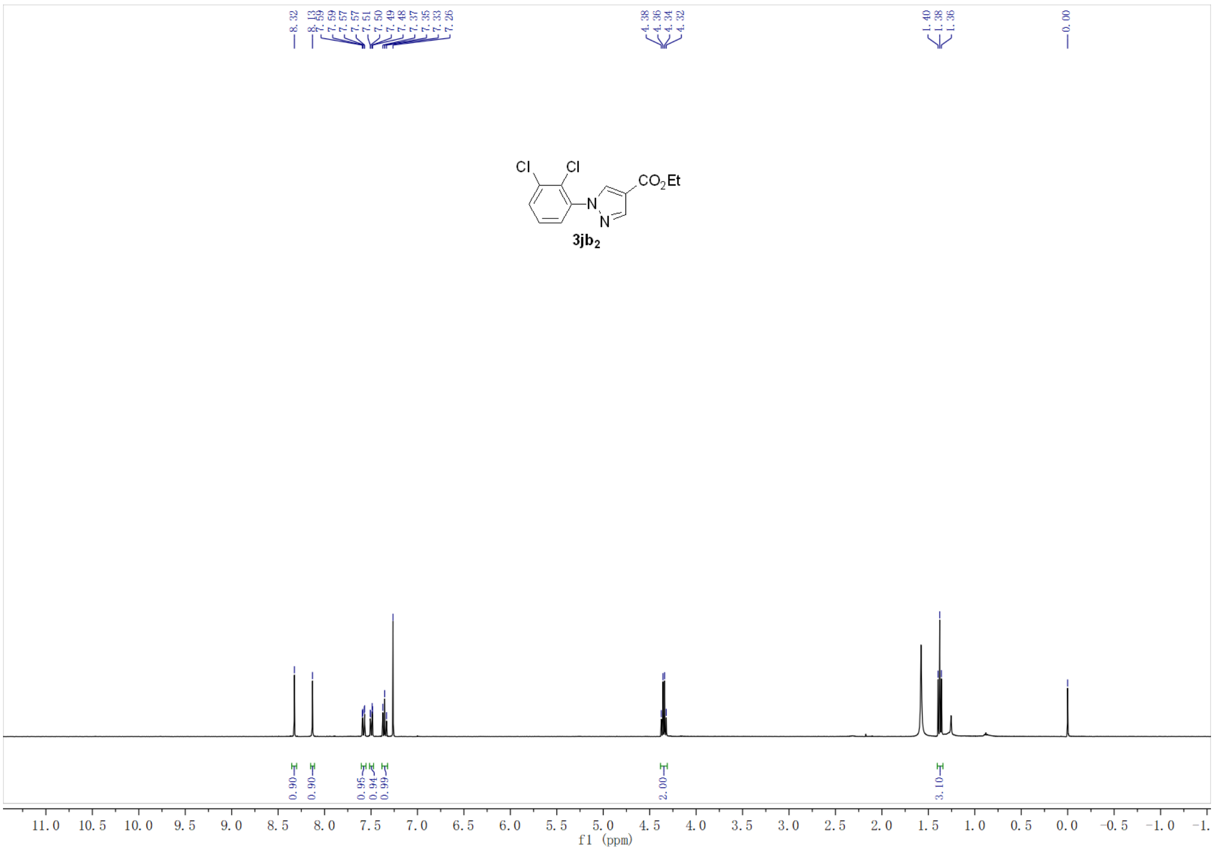
N
N
3hI3
f1 (ppm)


8.83
8.10
7.99
7.97
7.61
7.59
7.57
7.46
7.44
7.42
2.10
2.10
2.09
2.08
2.08
COOH
N
N
3hm
1.00
1.03
2.01
2.00
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


206.97
164.54
143.63
132.19
131.19
130.40
128.92
120.90
118.55
31.18
30.99
30.79
30.60
30.41
30.22
30.02
COOH
N
N
3hm
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.38
8.10
7.89
7.88
7.58
7.56
7.55
7.55
7.53
7.27
4.37
4.35
4.34
4.32
1.40
1.38
1.36
0.00
Cl
Cl
N
N
CO2Et
3jb1
0.98
0.92
0.93
1.97
2.00
2.99
f1 (ppm)


162.40
142.62
138.46
133.77
131.37
131.20
129.89
121.35
118.32
117.66
77.32
77.00
76.68
60.61
14.34
Cl
Cl
N
N
CO2Et
3jb1
f1 (ppm)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8.13
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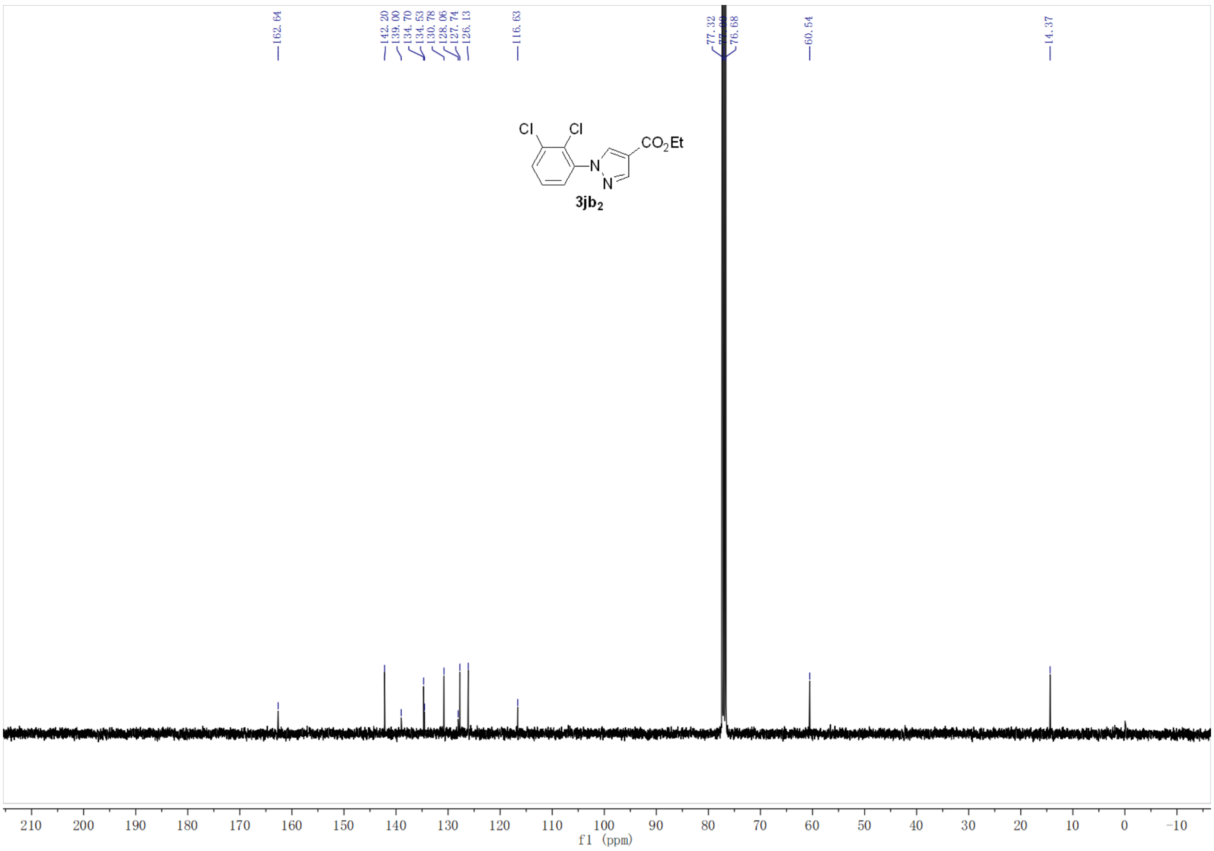
7.57
7.57
7.51
7.50
7.49
7.48
7.37
7.35
7.33
7.26
4.38
4.36
4.34
4.32
1.40
1.38
1.36
0.00
Cl
Cl
CO2Et
N
N
3jb2
0.90
0.90
0.95
0.94
0.99
2.00
3.10
f1 (ppm)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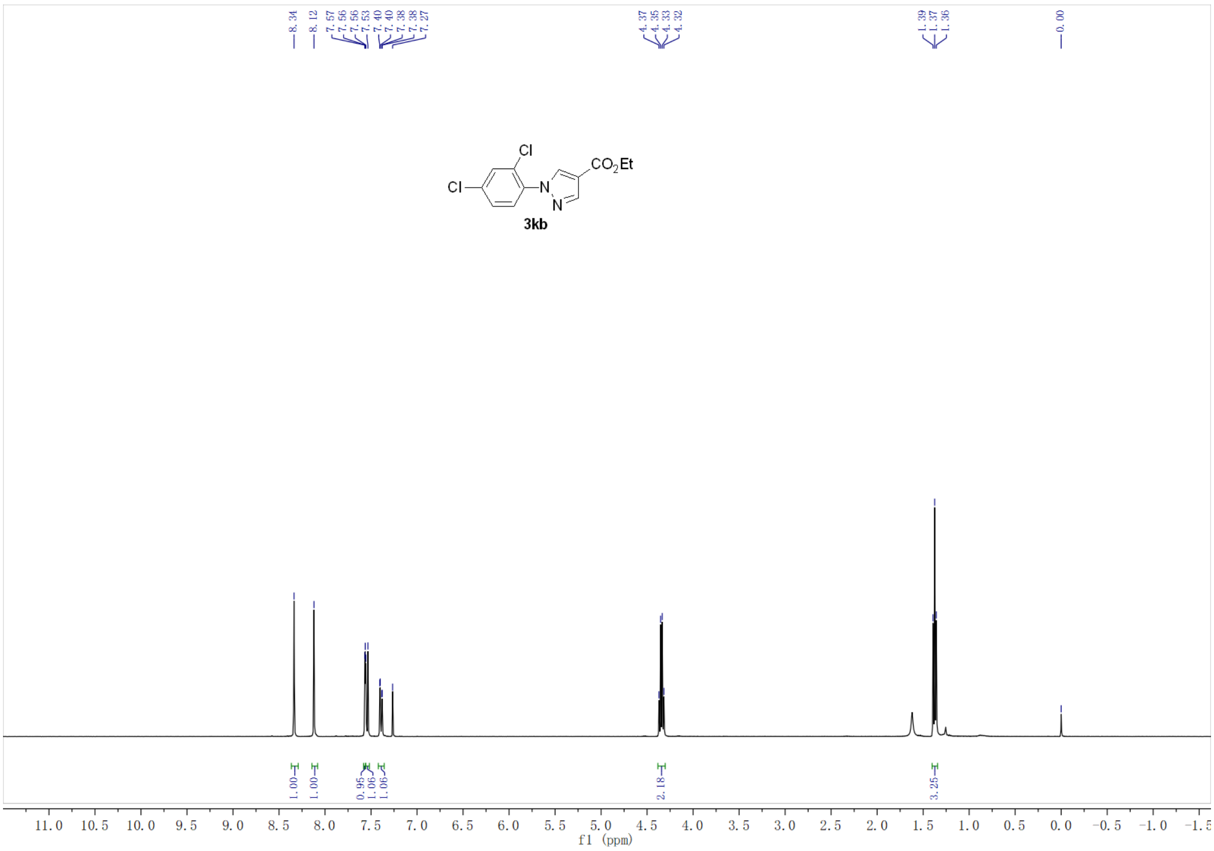
142.20
139.00
134.70
134.53
130.78
128.06
127.74
126.13
116.63
77.32
76.68
60.54
14.37
Cl
Cl
CO2Et
N
N
3jb2
f1 (ppm)


8.34
8.12
7.57
7.56
7.56
7.53
7.40
7.40
7.38
7.38
7.27
4.37
4.35
4.33
4.32
1.39
1.37
1.36
0.00
Cl
CO2Et
Cl
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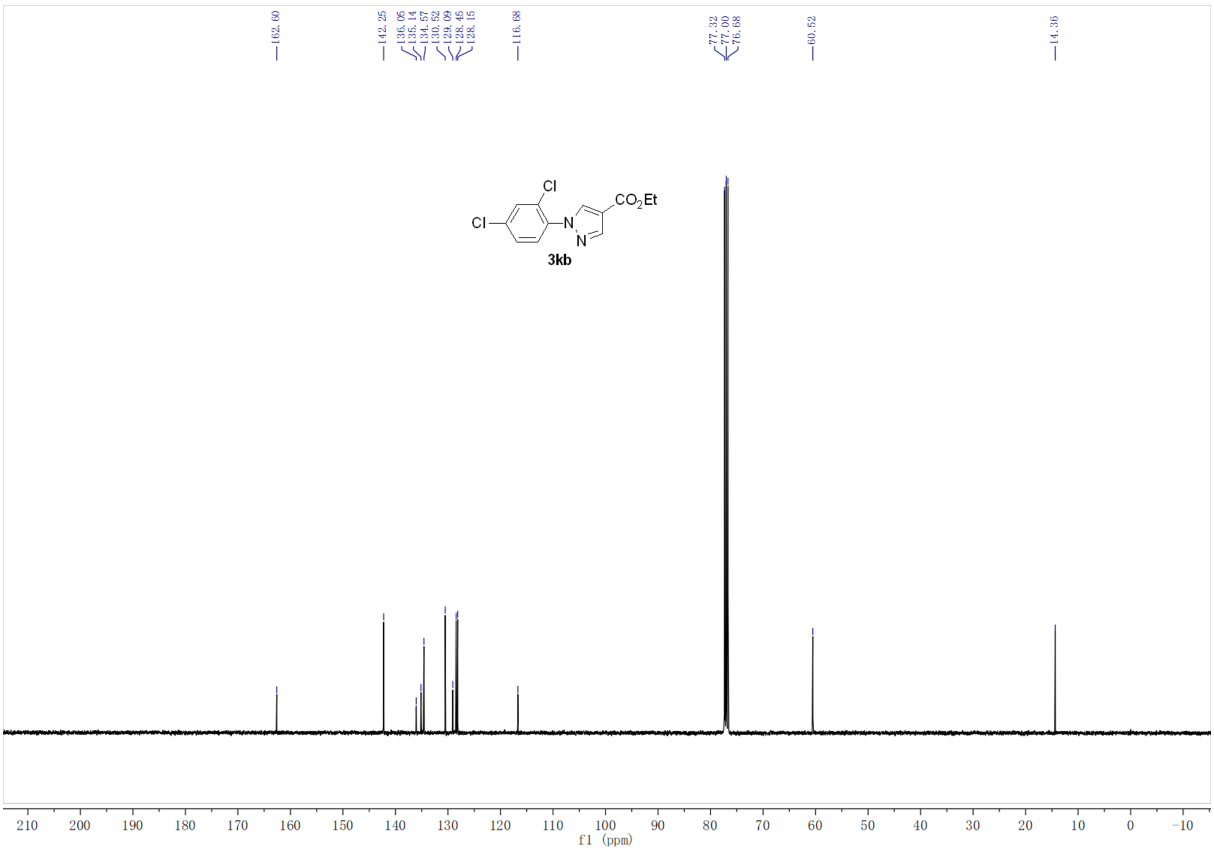
N
3kb
1.00
1.00
0.95
1.06
1.06
2.18
3.25
f1 (ppm)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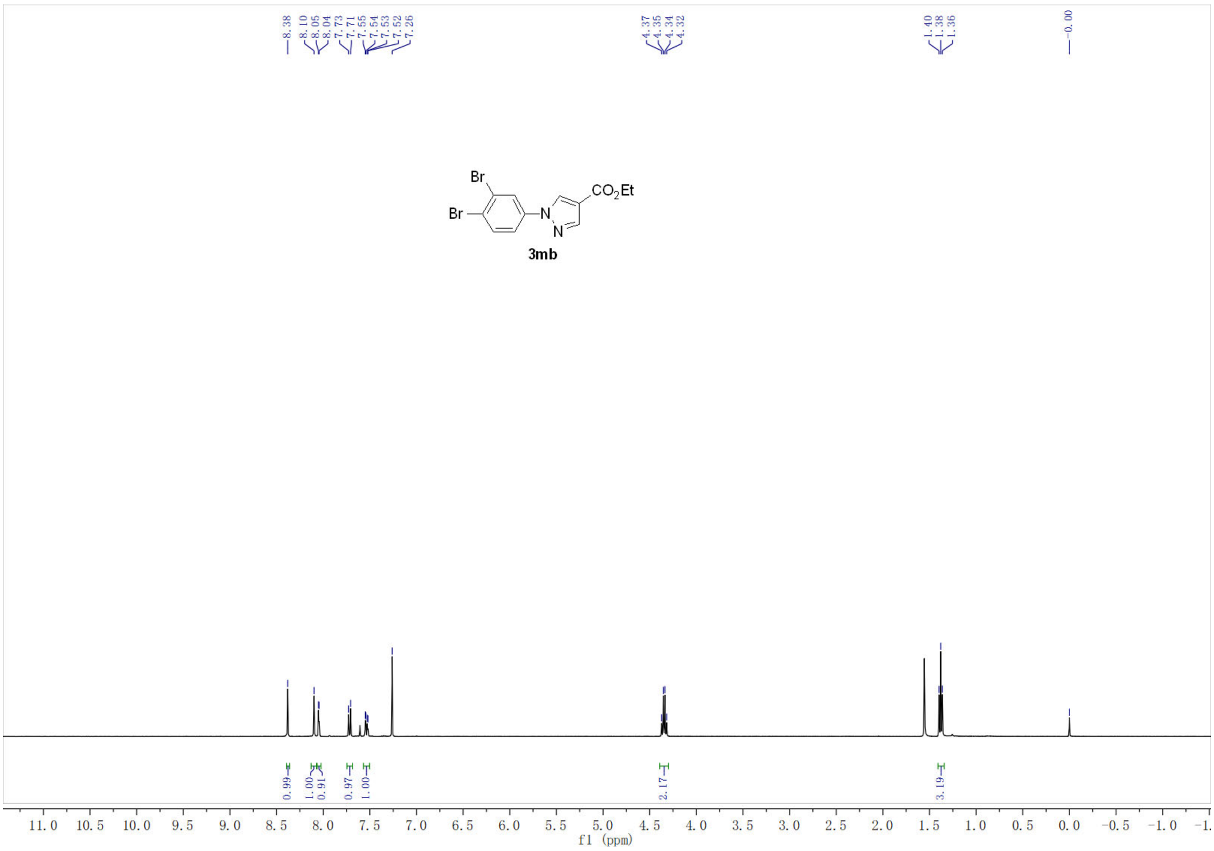
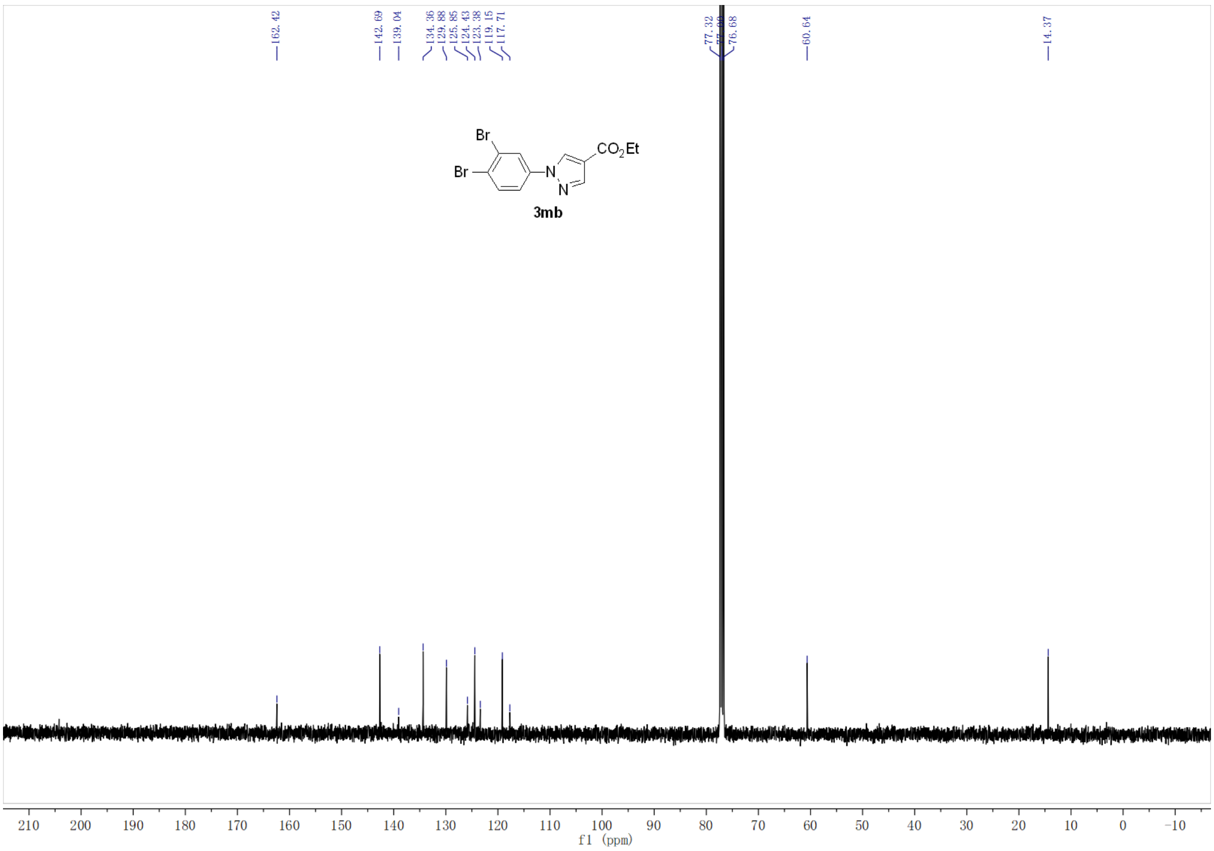
142.25
136.05
135.14
134.57
130.52
129.09
128.45
128.15
116.68
77.32
77.00
76.68
60.52
14.36
Cl
CO2Et
Cl
N
N
3kb
f1 (ppm)


8.38
8.10
8.05
8.04
7.73
7.71
7.55
7.54
7.53
7.52
7.26
4.37
4.35
4.34
4.32
1.40
1.38
1.36
0.00
Br
Br
N
N
CO2Et
3mb
0.99
1.00
0.91
0.97
1.00
2.17
3.19
f1 (ppm)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139.04
134.36
129.88
125.85
124.43
123.38
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77.32
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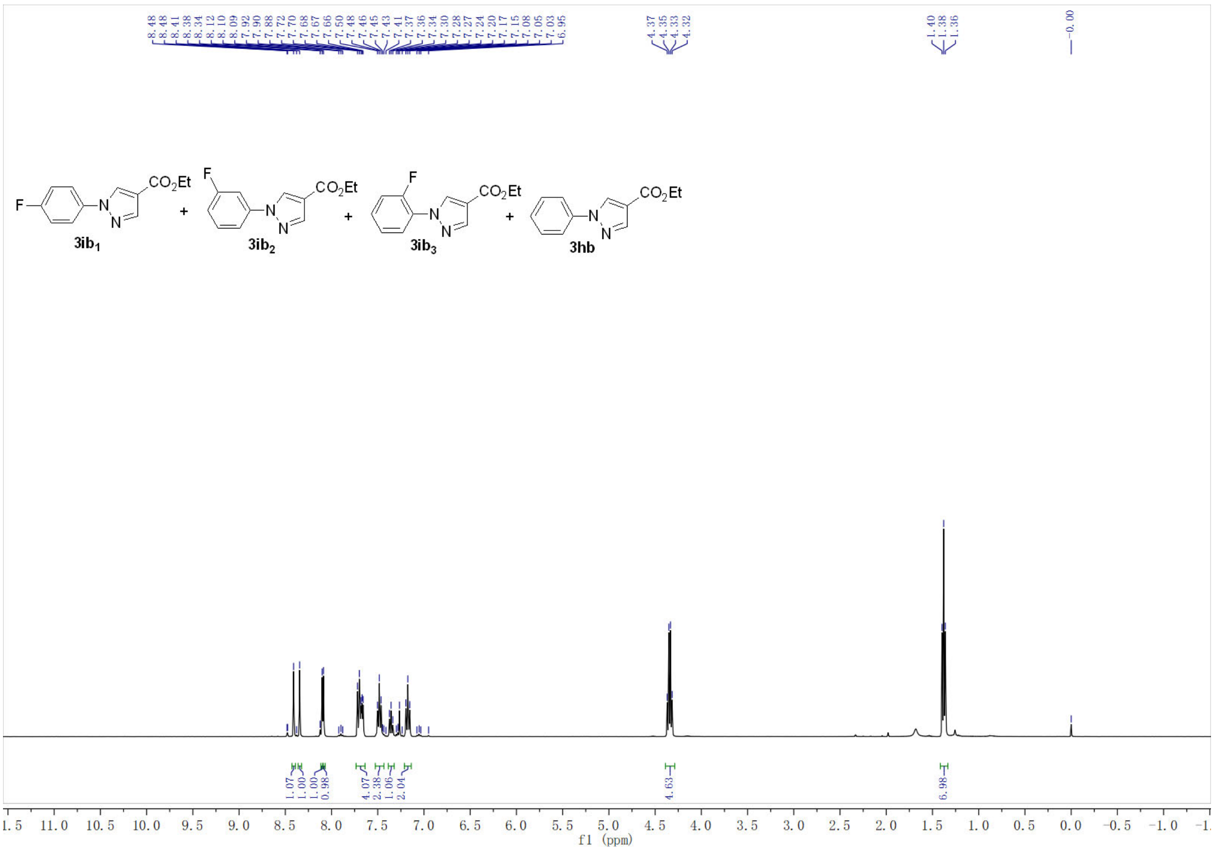
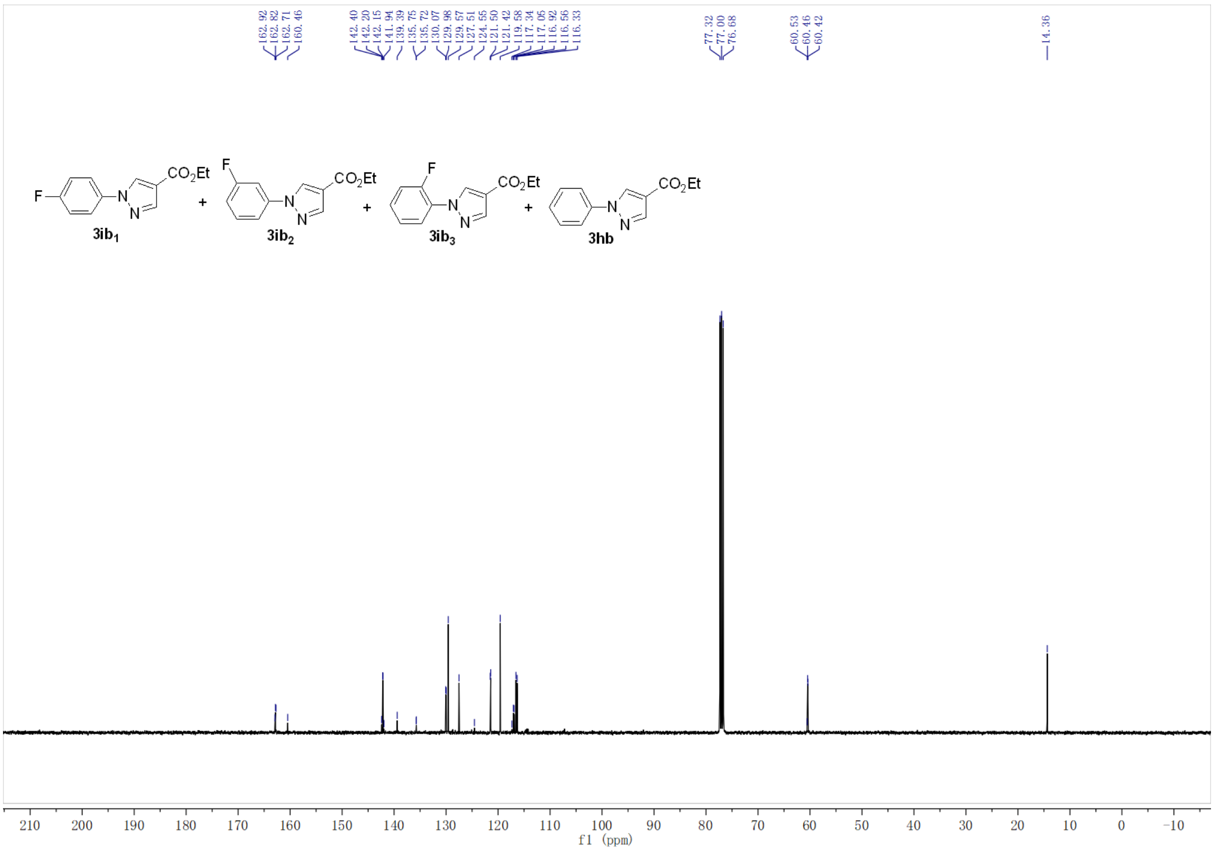
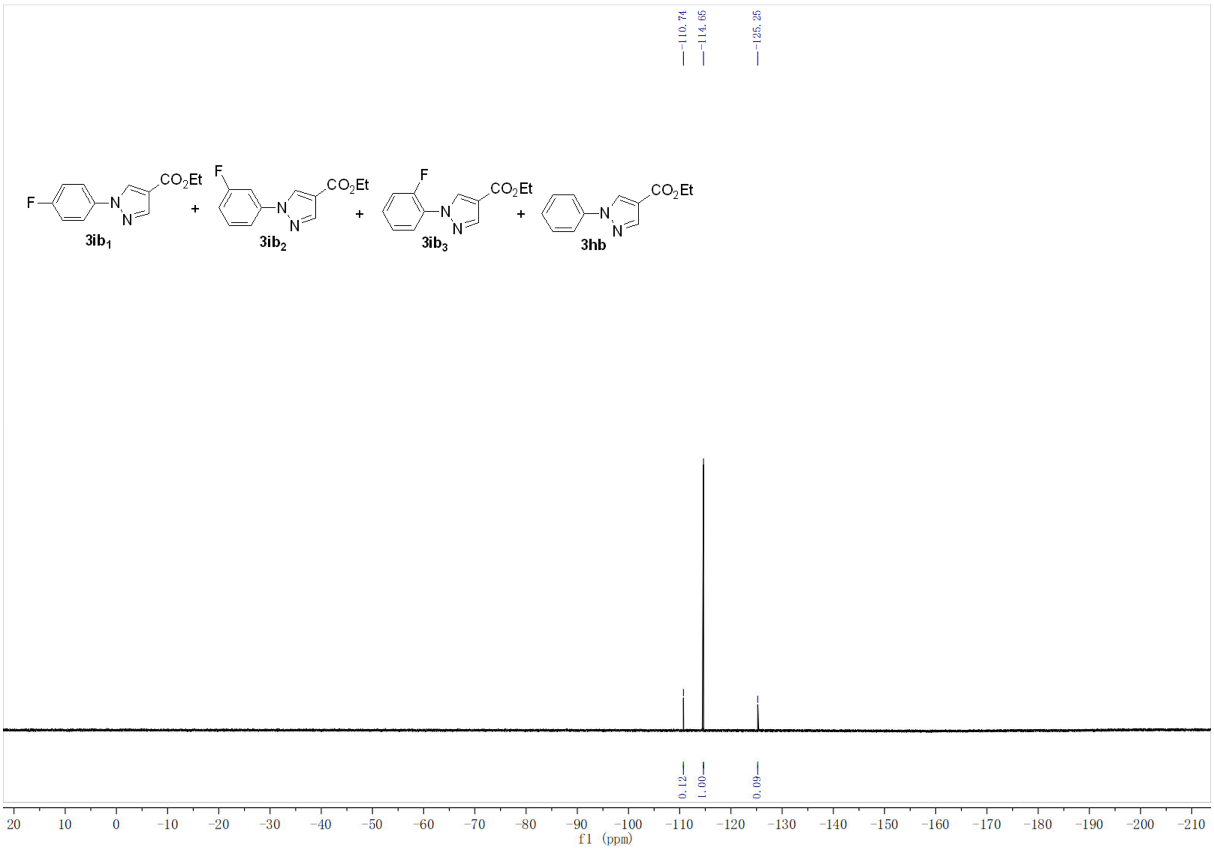
CO2Et
3mb
f1 (ppm)



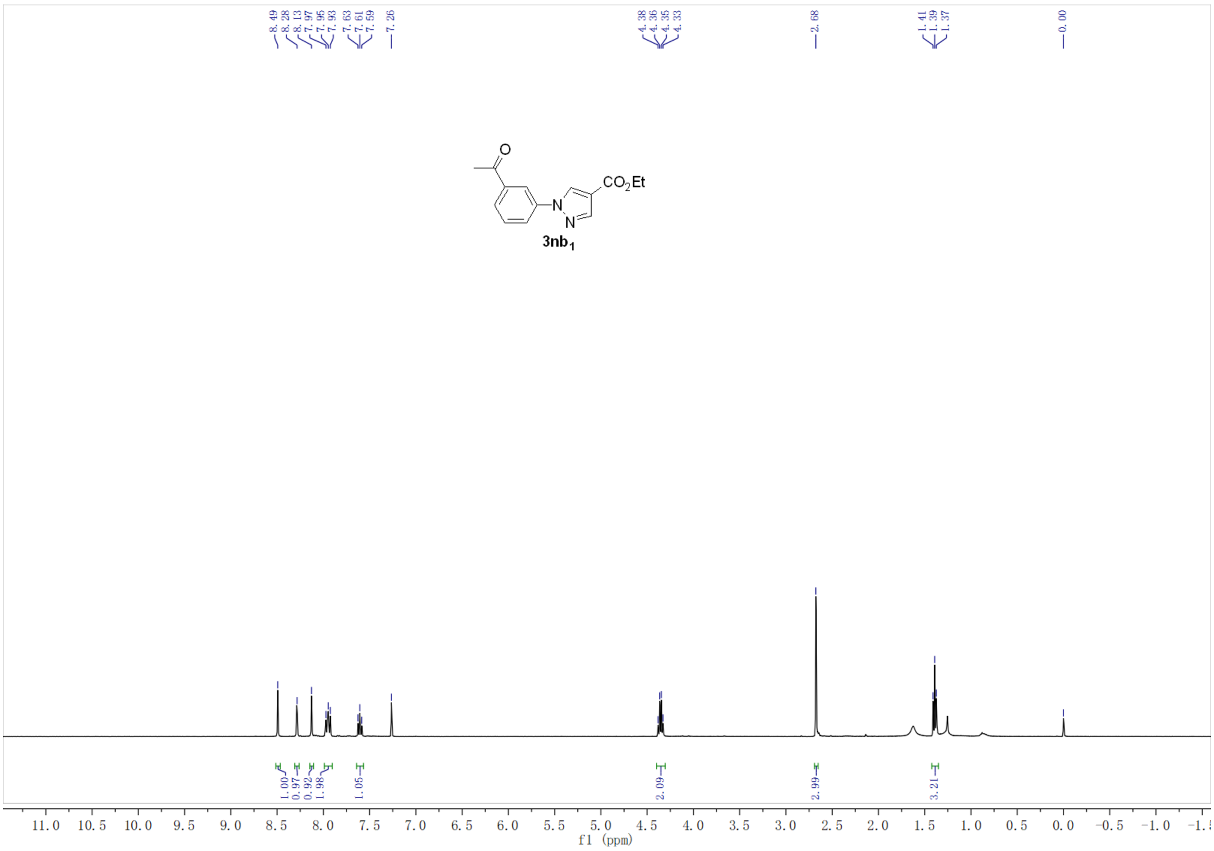
3ib1
3ib2
3ib3
3hb
f1 (ppm)



3ib1
3ib2
3ib3
3hb
f1 (ppm)



-110.74
-114.65
-125.25
F
CO2Et
N
N
+
3ib1
3ib2
3ib3
3hb
0.12
1.00
0.09
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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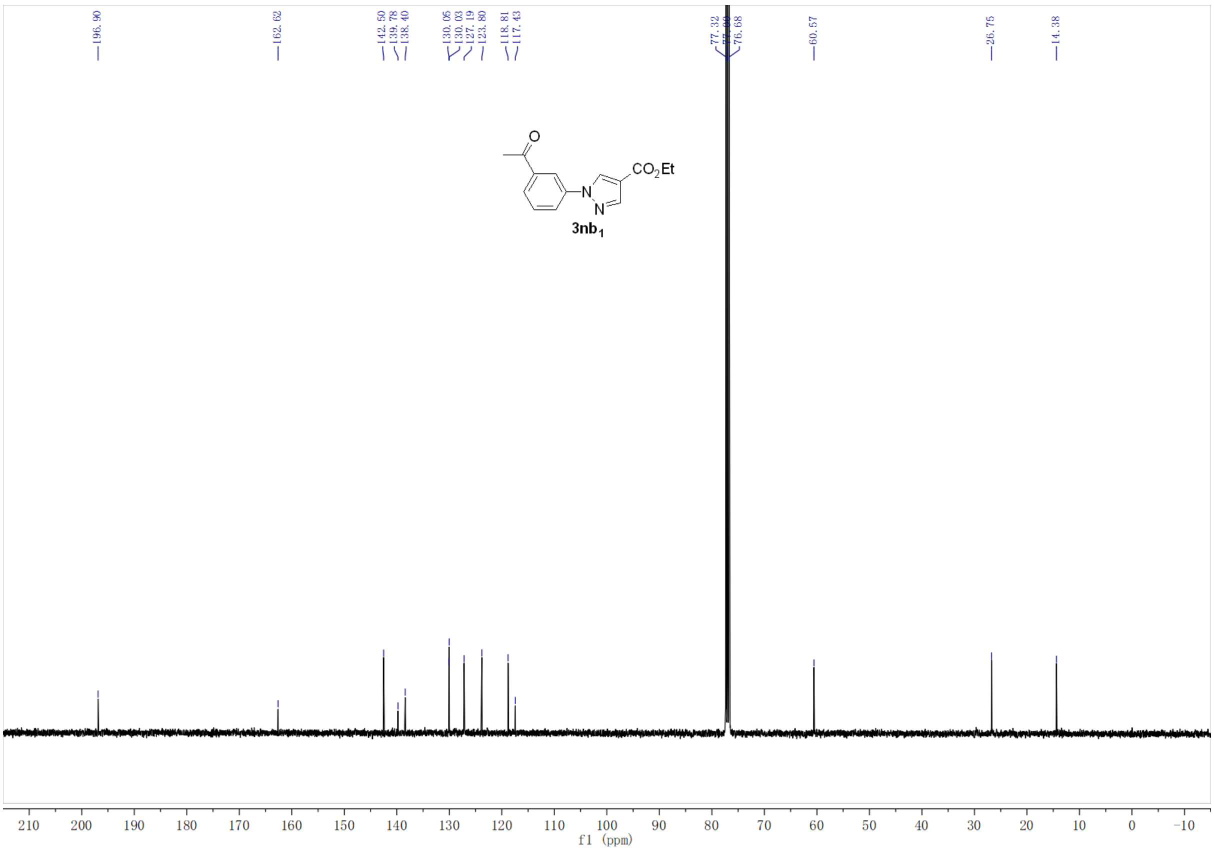
8.28
8.13
7.97
7.96
7.93
7.63
7.61
7.59
7.26
4.38
4.36
4.35
4.33
2.68
1.41
1.39
1.37
0.00
O
CO2Et
N
N
3nb1
1.00
0.97
0.92
1.98
1.05
2.09
2.99
3.21
f1 (ppm)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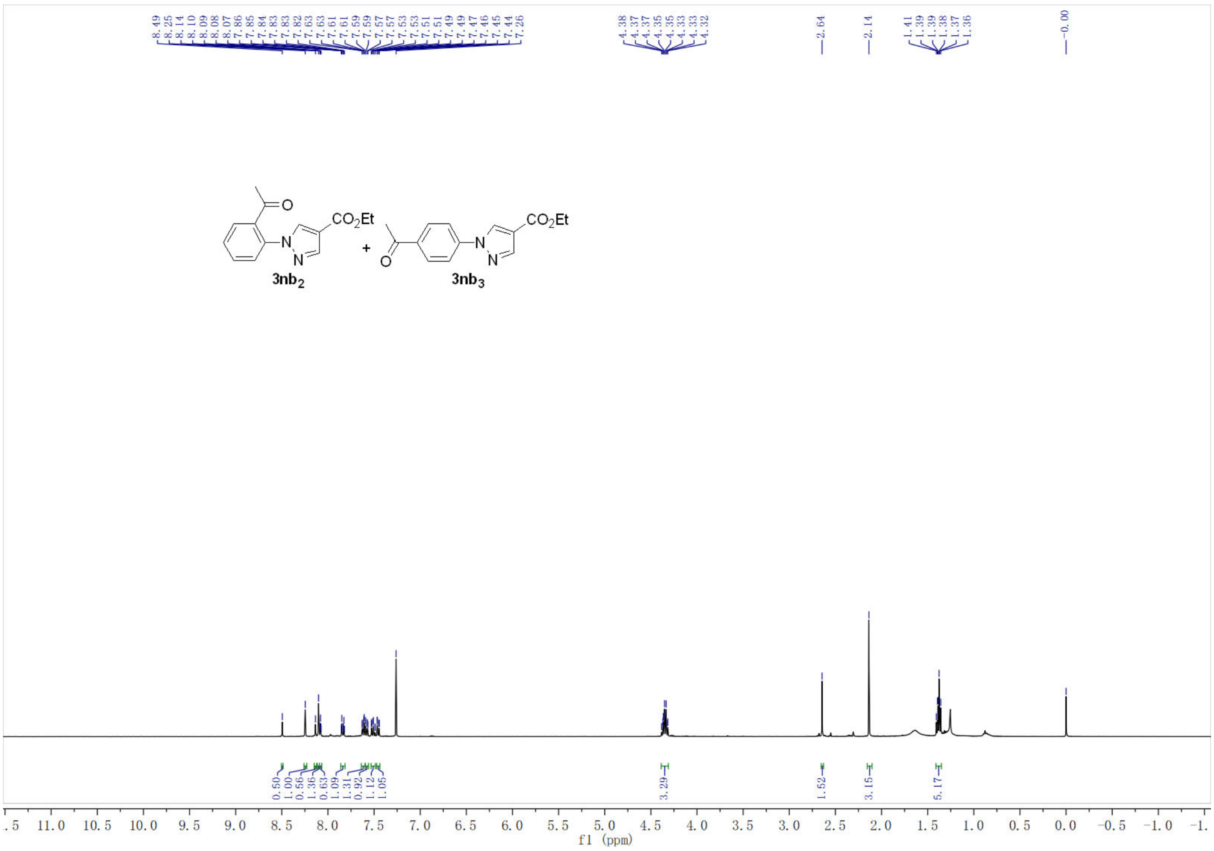
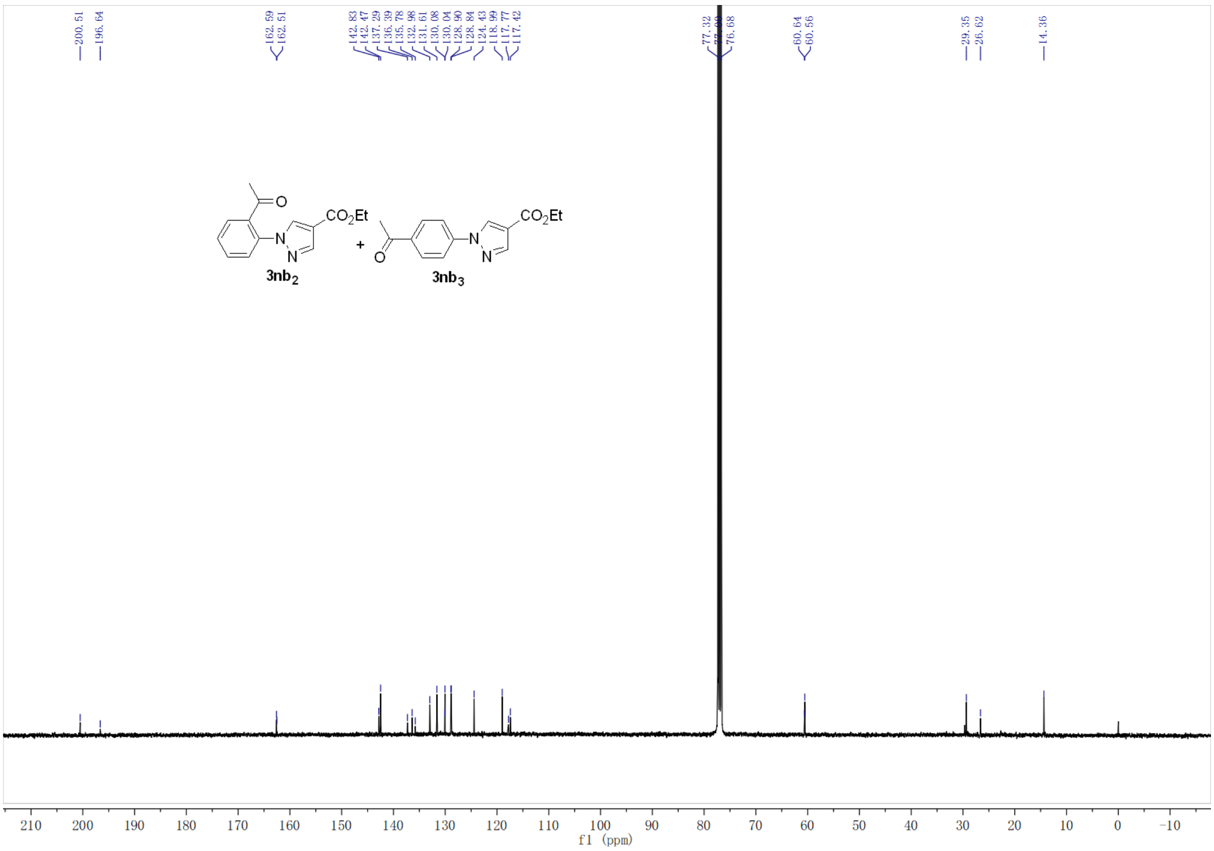
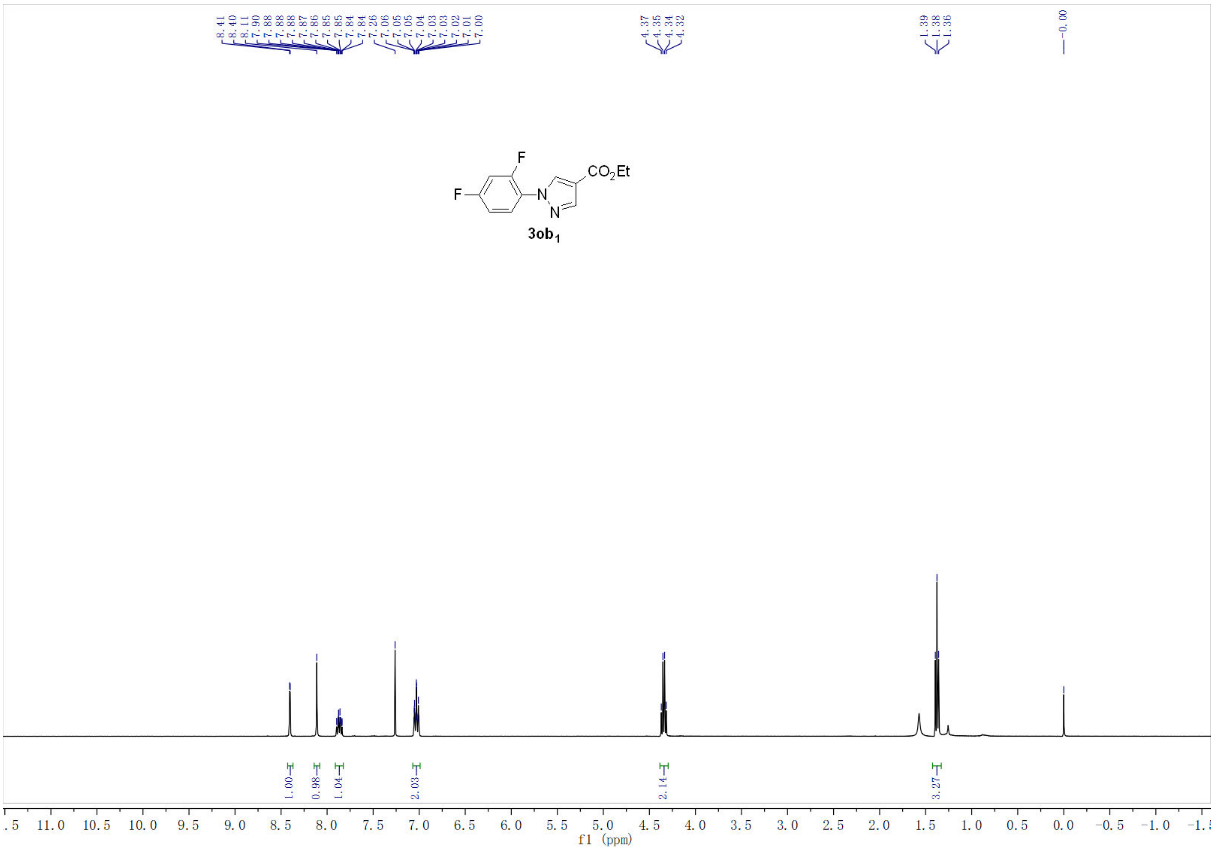
138.40
130.05
130.03
127.19
123.80
118.81
117.43
77.32
76.68
60.57
26.75
14.38
O
CO2Et
N
N
3nb1
f1 (ppm)

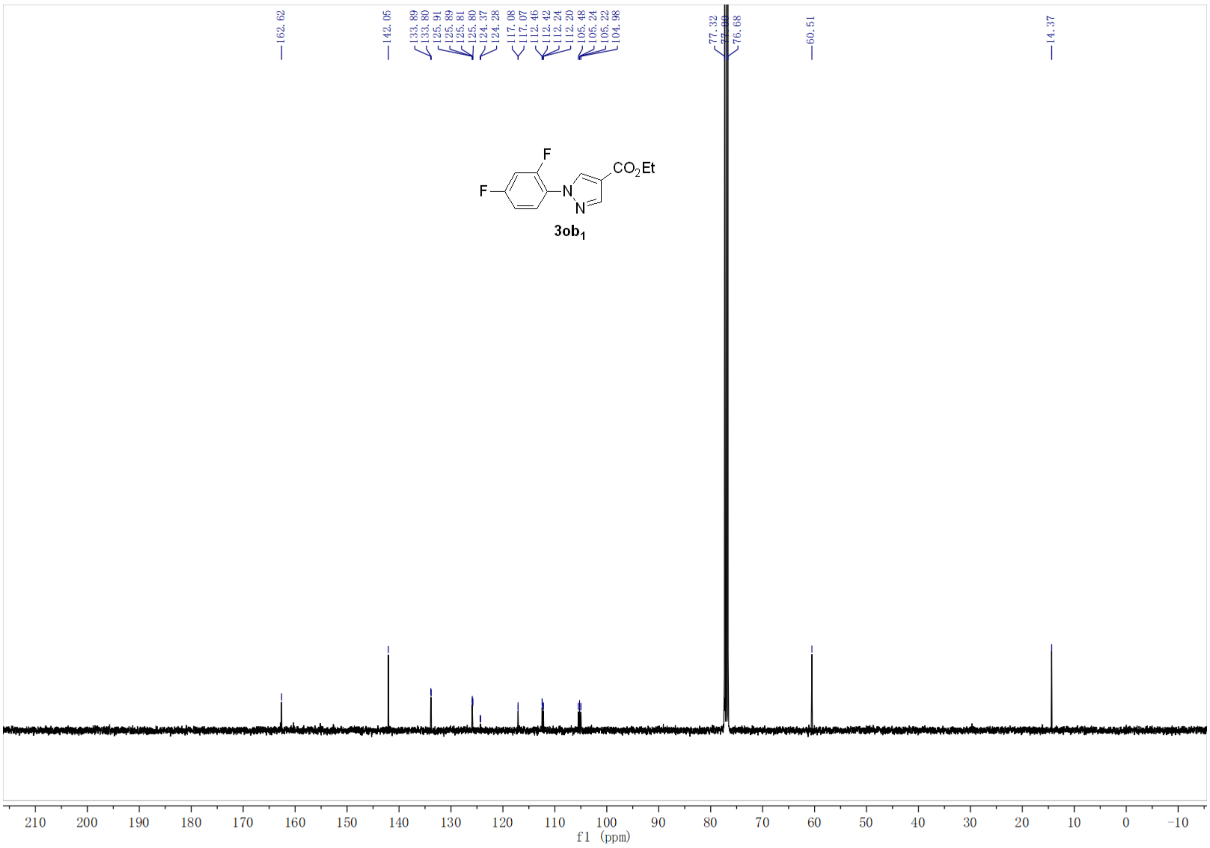


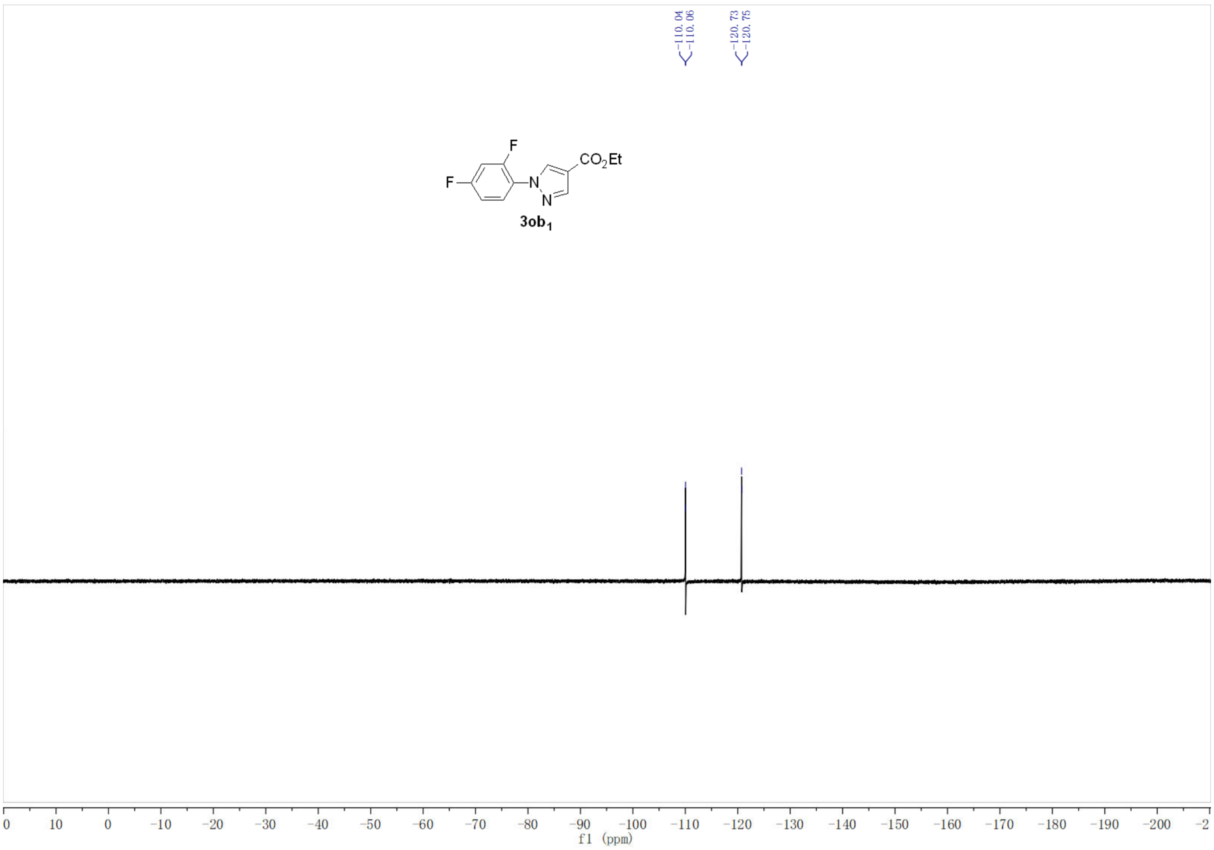
8.49 8.25 8.14 8.10 8.09 8.08 8.07 7.86 7.85 7.84 7.83 7.82 7.63 7.63 7.61 7.61 7.59 7.59 7.57 7.57 7.53 7.53 7.51 7.51 7.49 7.47 7.46 7.45 7.44 7.26
4.38 4.37 4.37 4.35 4.35 4.33 4.33 4.32
2.64
2.14
1.41 1.39 1.39 1.38 1.37 1.36
0.00
CO2Et
3nb2
+
3nb3
0.50 1.00 0.56 1.36 0.63 1.09 1.31 0.92 1.12 1.05
3.29
1.52
3.15
5.17
f1 (ppm)

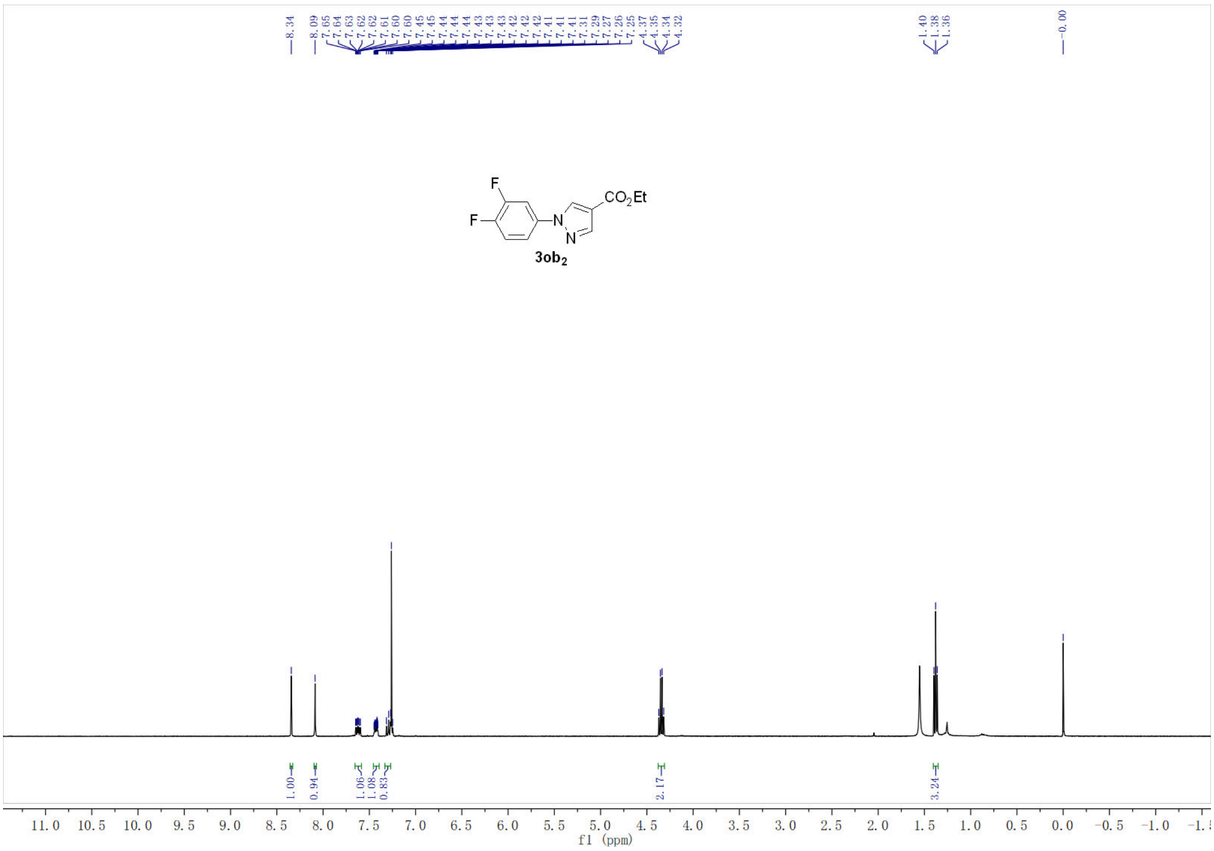


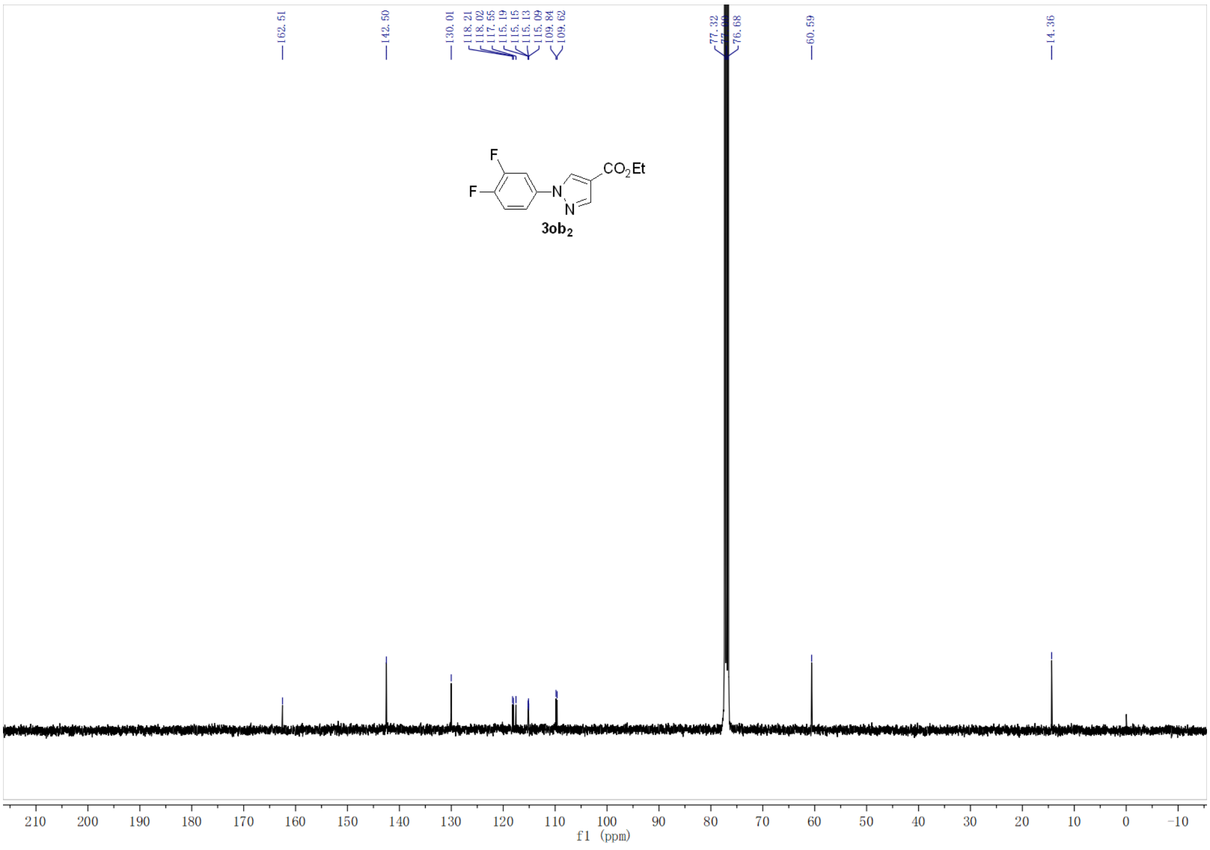
200.51 196.64
162.59 162.51
142.83 142.47 137.29 136.39 135.78 132.98 131.61 130.08 130.04 128.90 128.84 124.43 118.99 117.77 117.42
77.32 76.68
60.64 60.56
29.35 26.62
14.36
CO2Et
3nb2
+
3nb3
f1 (ppm)

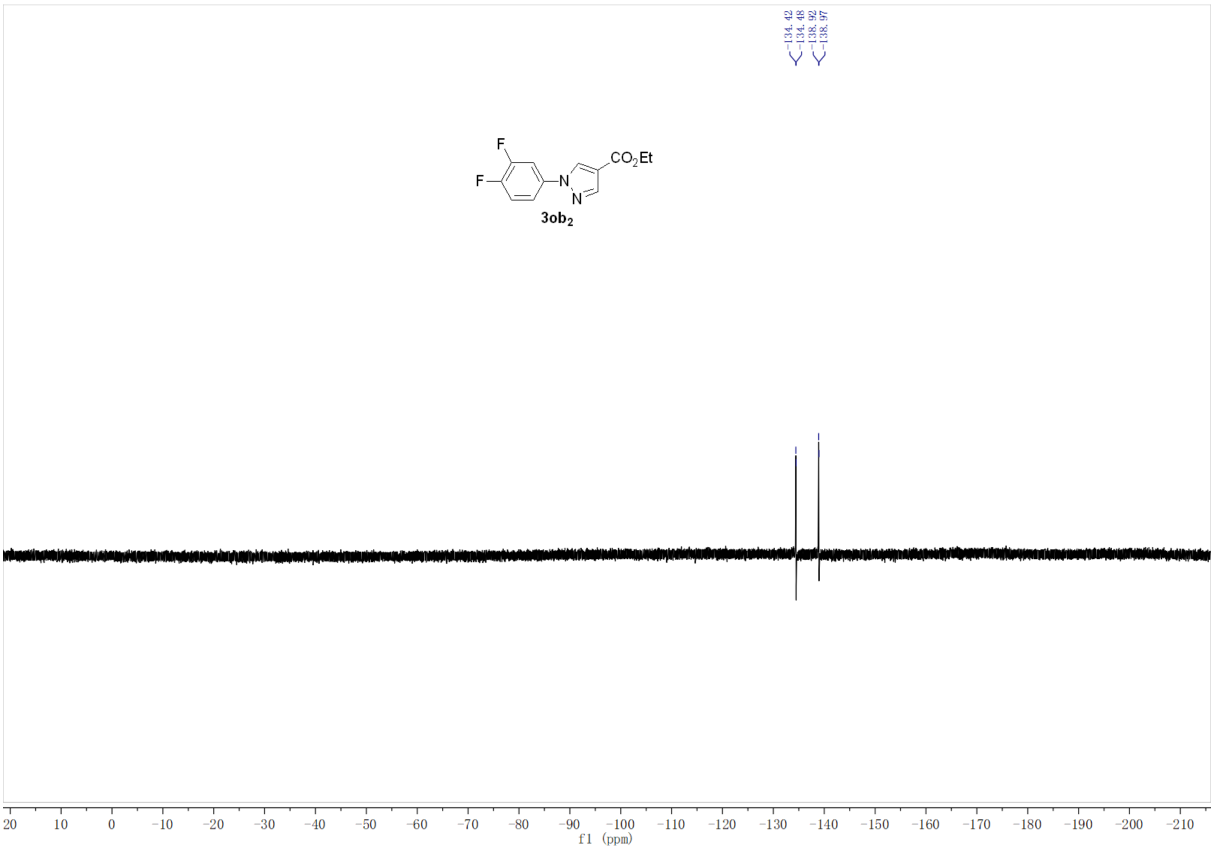





-110.04
-110.06
-120.73
-120.75
F
F
N
N
CO2Et
3ob1
f1 (ppm)






-134.42
-134.48
-138.92
-138.97
F
F
N
N
CO2Et
3ob2
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

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