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Electronic Supplementary Information

For

Bi-Blatter diradicals: Convenient access to regioisomers with tunable electronic and magnetic properties

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1. Additional synthetic details

1-Fluoro-4-iodo-2-nitrobenzene (4a).[1,2] Following a modified procedure,[1] to a solution of 1-fluoro-2-nitrobenzene (3.000 g, 21.26 mmol, 1 equiv.) in triflic acid (9.4 mL, 106.48 mmol, 5 equiv.) *N*-iodosuccinimide (5.760 g, 25.66 mmol, 1.2 equiv.) was added portionwise at 0 °C and the mixture was stirred at rt for 2 h. The mixture was quenched by the addition of water (250 mL) and extracted with diethyl ether (3×150 mL). The combined organic layers were washed with water, aqueous $Na_2S_2O_3$, brine and dried (Na_2SO_4). The solvent was evaporated and the crude residue was purified by passing through a short silica plug (pet. ether/AcOEt, 9:1) to afford pure product **4a** as a pale yellow oil (5.415 g, 20.28 mmol, 99% yield; 95–99% in several runs): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (dd, J_1 = 6.9 Hz, J_2 =2.3 Hz, 1H), 7.93 (ddd, J_1 = 8.8 Hz, J_2 =4.2 Hz, J_3 = 2.2 Hz, 1H), 7.07 (dd, J_1 = 10.5 Hz, J_2 =8.7 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 155.6 (d, $^1J_{F\text{-}C}$ = 266.5 Hz), 144.5 (d, $^2J_{F\text{-}C}$ = 8.2 Hz), 138.1, 134.7 (d, $^3J_{F\text{-}C}$ = 2.9 Hz), 120.5 (d, $^2J_{F\text{-}C}$ = 21.5 Hz), 86.2 (d, $^3J_{F\text{-}C}$ = 4.7 Hz). ^{19}F NMR ($CDCl_3$, 377 MHz) δ -118.4. ASAP(+)–MS, *m/z* 267 (100, $[M + H]^+$). HRMS (ASAP+–TOF) *m/z* $[M + H]^+$ calcd for $C_6H_3FINO_2$: 266.9192, found: 266.9202.

2-Fluoro-4-iodo-1-nitrobenzene (4b).[3,4] Following a general procedure,[5] $NaNO_2$ (1.313 g, 19.03 mmol, 1.1 equiv.) in water (4.3 mL, 4.6 M) was added to a solution of 3-fluoro-4-nitroaniline (**14**, 2.870 g, 18.64 mmol, 1 equiv.) in 32% aq. H_2SO_4 (10 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 1 h. A solution of KI (4.846 g, 29.19 mmol, 1.5 equiv.) in water (6 mL, 4.6 mL) was added at 0 °C, and the resulting mixture was stirred at 0 °C for 1h. The aqueous solution was extracted with AcOEt (2×50 mL) and the combined organic layers were washed with aqueous $Na_2S_2O_3$ and dried (Na_2SO_4). The solvent was evaporated and the crude residue was purified by column chromatography (pet. ether/AcOEt, 9:1) to afford the pure product **4b** as a pale yellow solid. Analytically pure product (4.025 g, 15.08 mmol, 82% yield; 75–85% in several runs) was obtained by recrystallization from EtOH to give pale yellow crystals: mp 116–118 °C (EtOH, lit.[4] mp

118–118.5 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.78 (t, J = 8.1 Hz, 1H), 7.74–7.64 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) δ 154.9 (d, $^1J_{\text{F-C}}$ = 270.7 Hz), 137.2, 134.2 (d, $^3J_{\text{F-C}}$ = 4.4 Hz), 128.0 (d, $^2J_{\text{F-C}}$ = 22.9 Hz, 127.1 (d, $^3J_{\text{F-C}}$ = 2.7 Hz), 101.5 (d, $^2J_{\text{F-C}}$ = 7.5 Hz). ^{19}F NMR (CDCl$_3$, 377 MHz) δ -114.6. ASAP(+)–MS, *m/z* 268 (100, [M + H]$^+$). HRMS (ASAP+ – TOF) *m/z* [M + H]$^+$ calcd for $C_6H_4FINO_2$: 267.9271, found: 267.9288. Anal. Calcd for $C_6H_3FINO_2$: C, 26.99; H, 1.13; N, 5.25. Found: C, 26.87; H, 1.19; N, 5.49.

2-Nitro-4-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)phenol (7).[6] Following an analogous literature procedure,[7] the solution of 4-bromo-2-nitrophenol (1.500 g, 6.88 mmol, 1 equiv.), bis(pinacolato)diboron (2.098 g, 8.26 mmol, 1.2 equiv.) and KOAc (2.026 g, 20.64 mmol, 3 equiv.) in dioxane (10 mL, 0.7 M) was degassed (oil pomp) and purged with N_2 (three times). PdCl$_2$(dppf) (251.7 mg, 0.344 mmol, 0.05 equiv.) was added and the mixture was stirred at 110 °C overnight. After cooling, AcOEt (25 mL) was added and the resulting mixture was passed through a layer of Cellite. Water (25 mL) was added and the organic layer was separated, and the aqueous layer was extracted with AcOEt (2×25 mL). The combined organic extracts were dried (Na_2SO_4), the solvent was evaporated, and the residue was purified by column chromatography (hexane/CH_2Cl_2 3:1 to CH_2Cl_2) to afford pure product **7** as a pale yellow solid. Analytically pure product **7** (1.259 g, 4.75 mmol, 69% yield; 65–72% in several runs) was obtained as pale yellow flake-like crystals by recrystallization from hexane/CH_2Cl_2 mixture: mp 104–105 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 10.78 (s, 1H), 8.55 (s, 1H), 7.96 (dd, J_1 = 8.3 Hz, J_2 = 1.5 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 1.34 (s, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) δ 157.3, 143.5, 133.6, 132.3, 119.5, 84.5, 25.0. ^{11}B{^{1}H} NMR (CDCl$_3$, 128 MHz, ref to BF$_3$•EtO) δ 29.9 (s). ESI(-)–MS, *m/z* 264 (70, [M – H]$^-$), 182 (100); HRMS (ESI- –TOF) *m/z* [M – H]$^-$ calcd for $C_{12}H_{15}BNO_5$: 264.1043, found: 264.1050. Anal. Calcd for $C_{12}H_{16}BNO_5$: C, 54.37; H, 6.08; N, 5.28. Found: C, 54.38; H, 6.09; N, 5.32.

3',4-Dinitrobiphenyl]-3,4'-diol (9[6,7]). **Method A.** The solution of 5-bromo-2-nitrophenol (**8**, 782.6 mg, 3.590 mmol, 1 equiv.), 2-nitro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (**7**, 1.046 g, 3.946 mmol, 1.1 equiv.) and KOAc (1.057 g, 10.770 mmol, 3 equiv.) in dioxane (6 mL, 0.6 M) was degassed (oil pomp) and purged with N_2 (three times).

$PdCl_2$(dppf) (131.7 mg, 0.180 mmol, 0.05 equiv.) was added, and the mixture was stirred at 110 °C overnight. After cooling, AcOEt (15 mL) was added and the resulting mixture was passed through a layer of Cellite. Water (15 mL) was added, the organic layer was separated, and the aqueous layer was extracted with AcOEt (2×15 mL). The combined organic extracts were dried (Na_2SO_4), the solvent was evaporated, and the residue was purified by column chromatography (pet. ether/CH_2Cl_2 3:1) to afford inseparable mixture of the desired product **9[6,7]** and starting borolane **7** in a 2:1 ratio (^{1}H NMR). This mixture was submitted to oxidative hydrolysis reaction according to a general literature procedure:[8] the mixture of **9[6,7]** and **7** (499.4 mg) and $NaIO_4$ (1.970 mg, 7.440 mmol) was stirred in 4:1 THF/H_2O mixture (4 mL) for 30 min and a drop of HCl was added to the suspension. The reaction mixture was stirred for 1 h at rt and the solvent was evaporated. AcOEt (10 mL) followed by H_2O (5 mL) were added. The organic layer was separated, and the aqueous layer was extracted with AcOEt (2×6 mL). The combined organic extracts were dried (Na_2SO_4), the solvent was evaporated, and the crude residue was purified by column chromatography (pet. ether/CH_2Cl_2 3:1) to afford pure product **9[6,7]** as a yellow solid. Analytically pure product was obtained as yellow flake-like crystals by recrystallization from an *n*-heptane/CH_2Cl_2 mixture (148.7 mg, 0.538 mmol, 15% yield; 8–20% in several runs).

3-Fluoro-4-nitroaniline (14).[9] Following a reported procedure,[10] 3-fluoroaniline (5.000 g, 44.96 mmol, 1 equiv.) and benzaldehyde (5.000 g, 47.12 mmol, 4.81 mL, 1.1 equiv.) were heated at 80 °C for 1h. The reaction mixture was cooled in an ice bath, conc. H_2SO_4 (20 mL) was slowly added, and the mixture was stirred at rt until complete dissolution of the resulting solid. The reaction mixture was then cooled to 0 °C with an ice bath and a mixture of conc. HNO_3 (3 mL) and conc. H_2SO_4 (10 mL) was added dropwise, maintaining the temperature at 0 °C. The resulting mixture was stirred at 0°C for 1h and then poured into a saturated solution of K_2CO_3 in water. The aqueous solution was extracted with AcOEt (2×50 mL) and the combined organic layers were collected and dried (Na_2SO_4). The solvent was evaporated and the residue was purified by column chromatography (pet. ether/AcOEt, 3:1) to afford the title product as a yellow solid. The analytically pure product **14** (2.459 g, 15.75 mmol, 35% yield; 32–37% for several runs) was obtained by recrystallization from EtOH as yellow needles: mp 162–164 °C (EtOH lit.[11] 146-148 °C). ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.92 (t, J = 9.0 Hz, 1H), 6.56 (dd, J_1 = 9.1, J_2 = 2.3 Hz, 1H), 6.53 (dd, J_1 = 14.0, J_2 = 2.3 Hz, 1H), 6.31 (bs, 2H). ^{13}C{^{1}H} NMR (acetone-d_6, 100 MHz) δ 159.2 (d, $^1J_{\text{F-C}}$ = 259.4 Hz), 157.4 (d, $^2J_{\text{F-C}}$ = 12.7 Hz), 129.3 (2C), 110.1, 101.1 (d, $^2J_{\text{F-C}}$ = 24.4 Hz). ^{19}F NMR (acetone-d_6, 377 MHz) δ -110.9. ESI(-)–MS, m/z 155 (100, [M – H]$^-$). HRMS (ESI- –TOF) m/z [M – H]$^-$ calcd for $C_6H_4FN_2O_2$: 155.0257, found: 155.0264. Anal. Calcd for $C_6H_5FN_2O_2$: C, 46.16; H, 3.23; N, 17.94. Found: C, 46.22; H, 3.21; N, 18.23.

2. NMR spectra

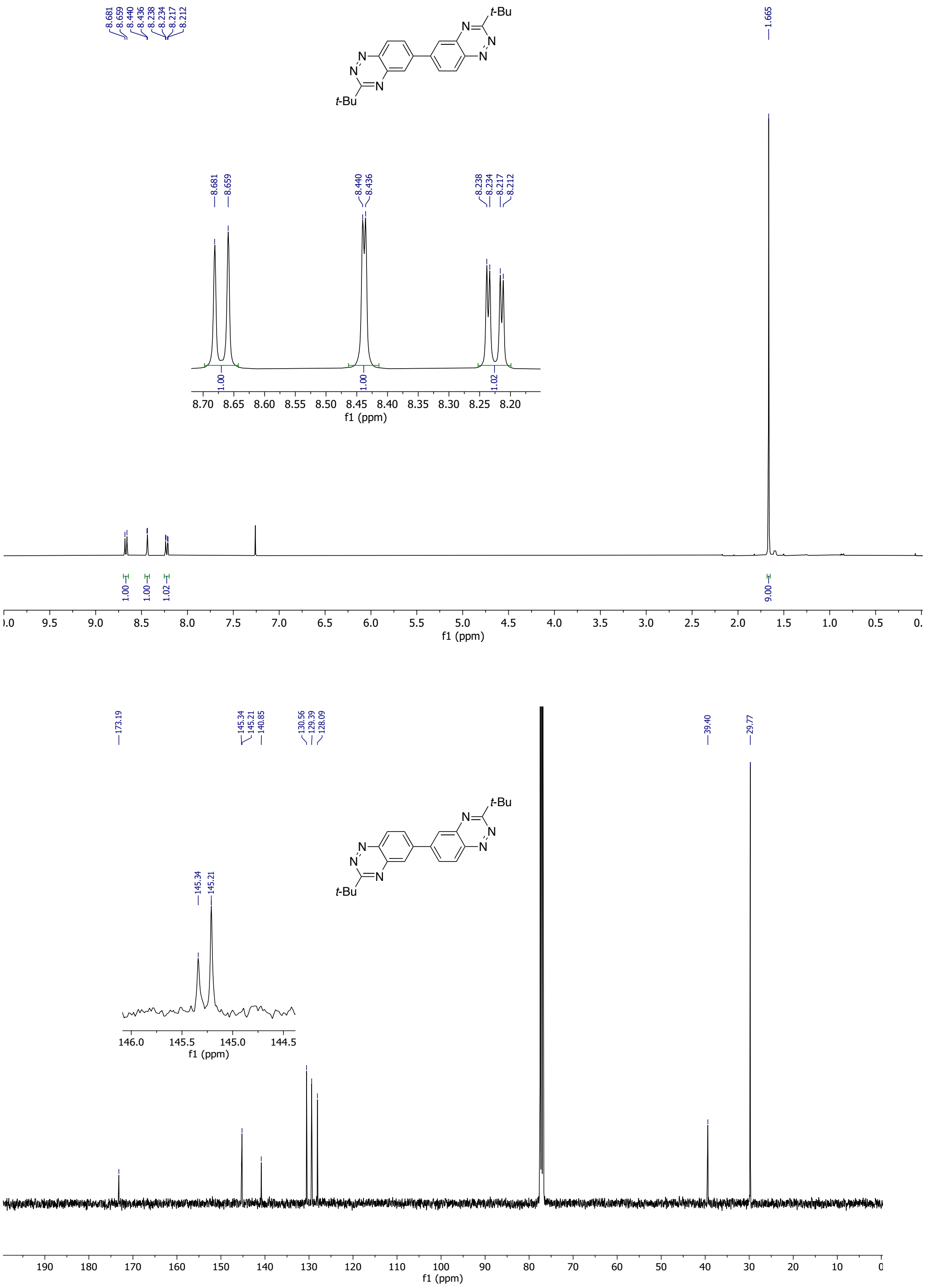


Figure S1. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3[6,6]** (CDCl$_3$).

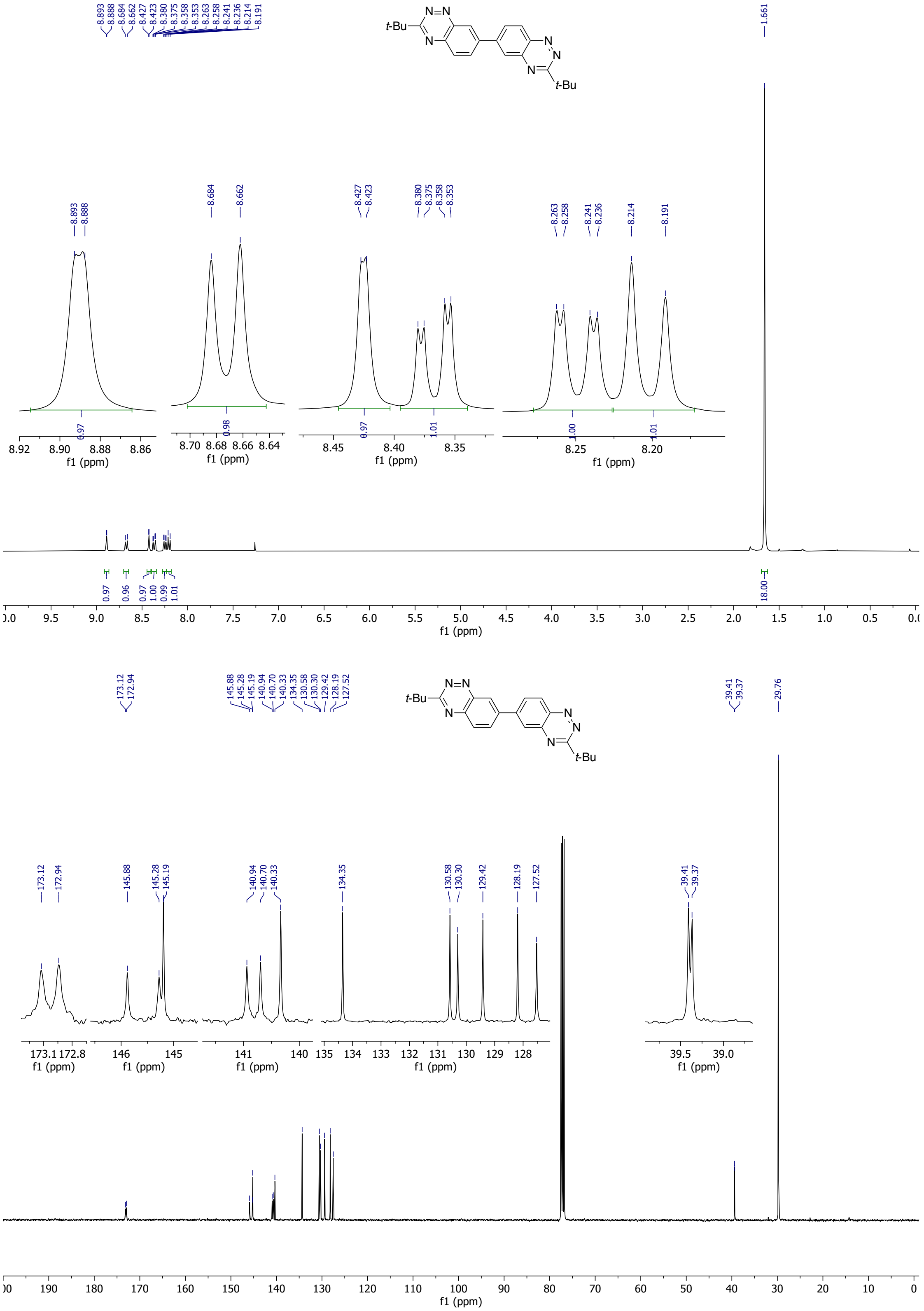


Figure S2. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3[6,7]** ($CDCl_3$).

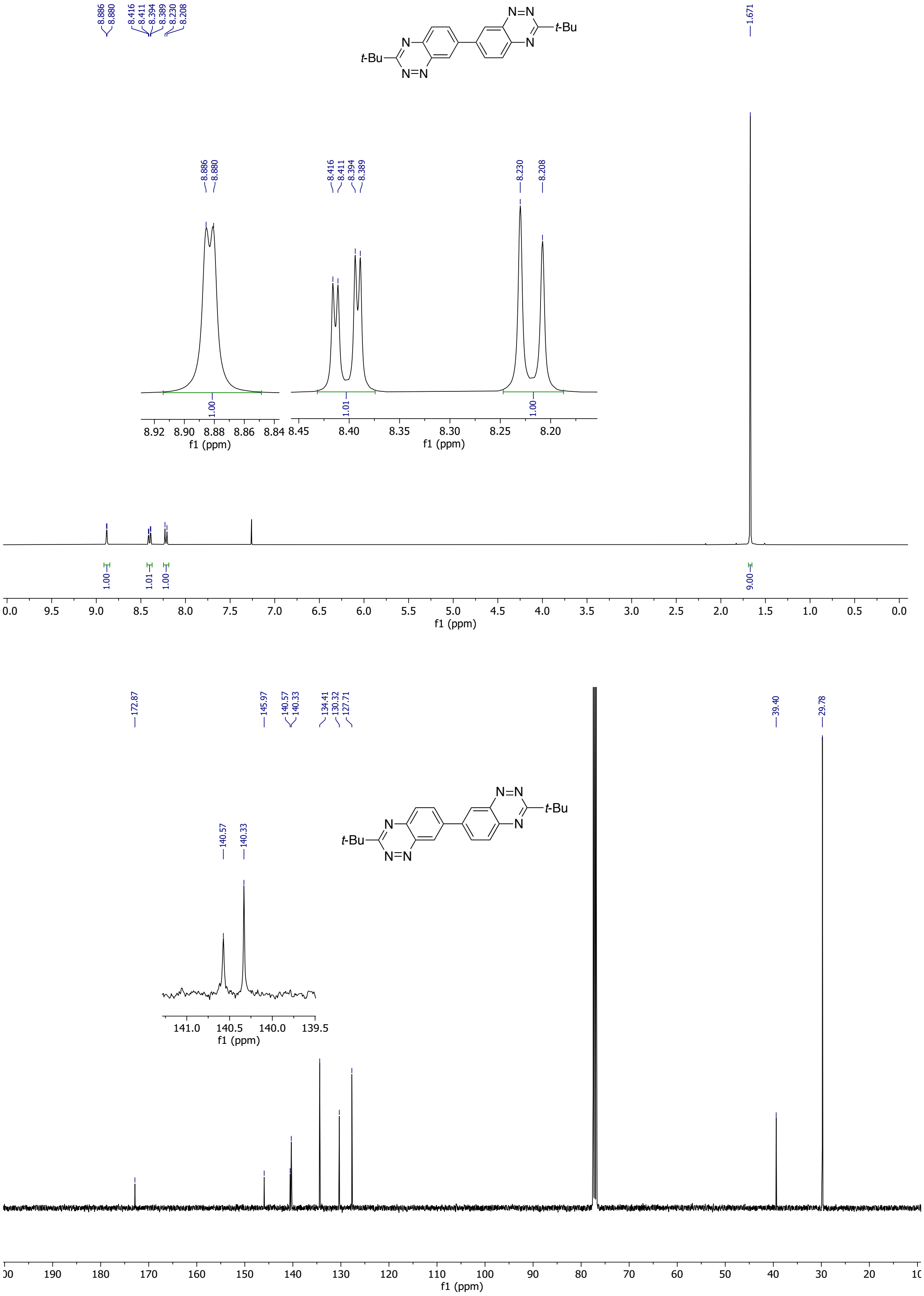
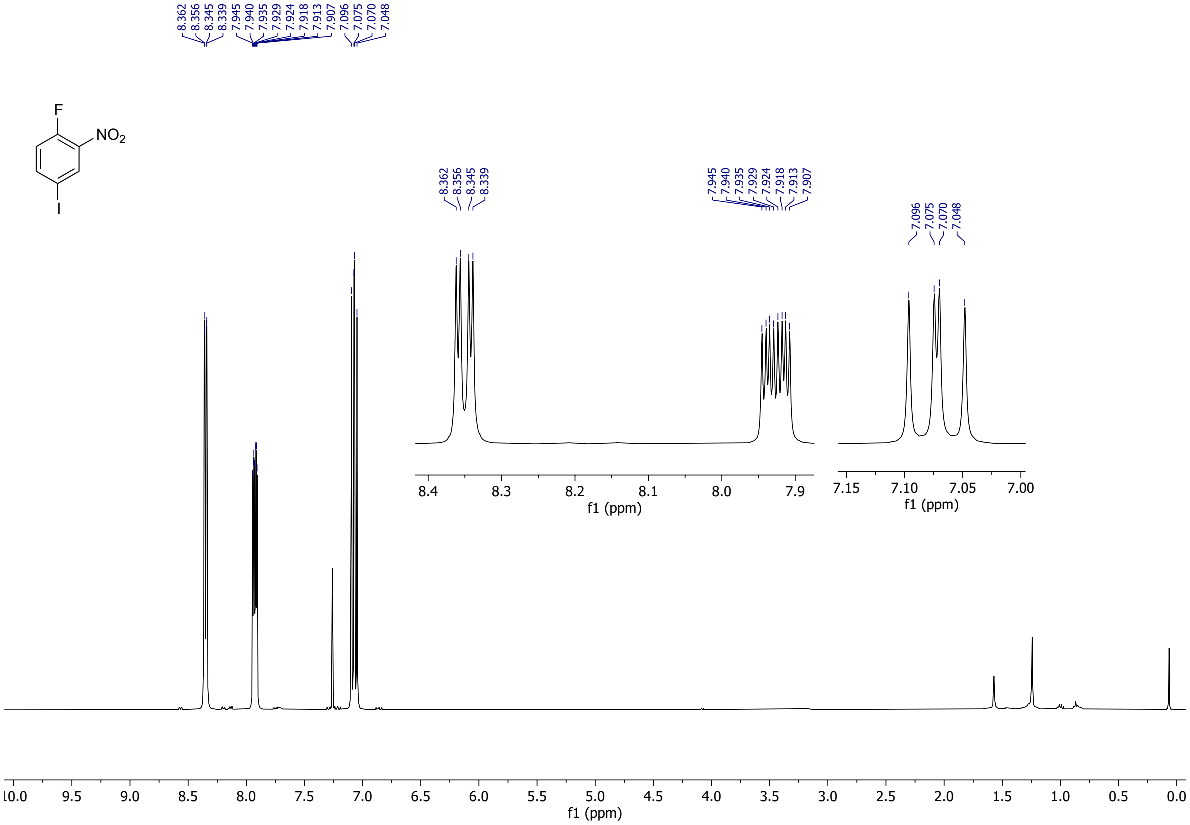
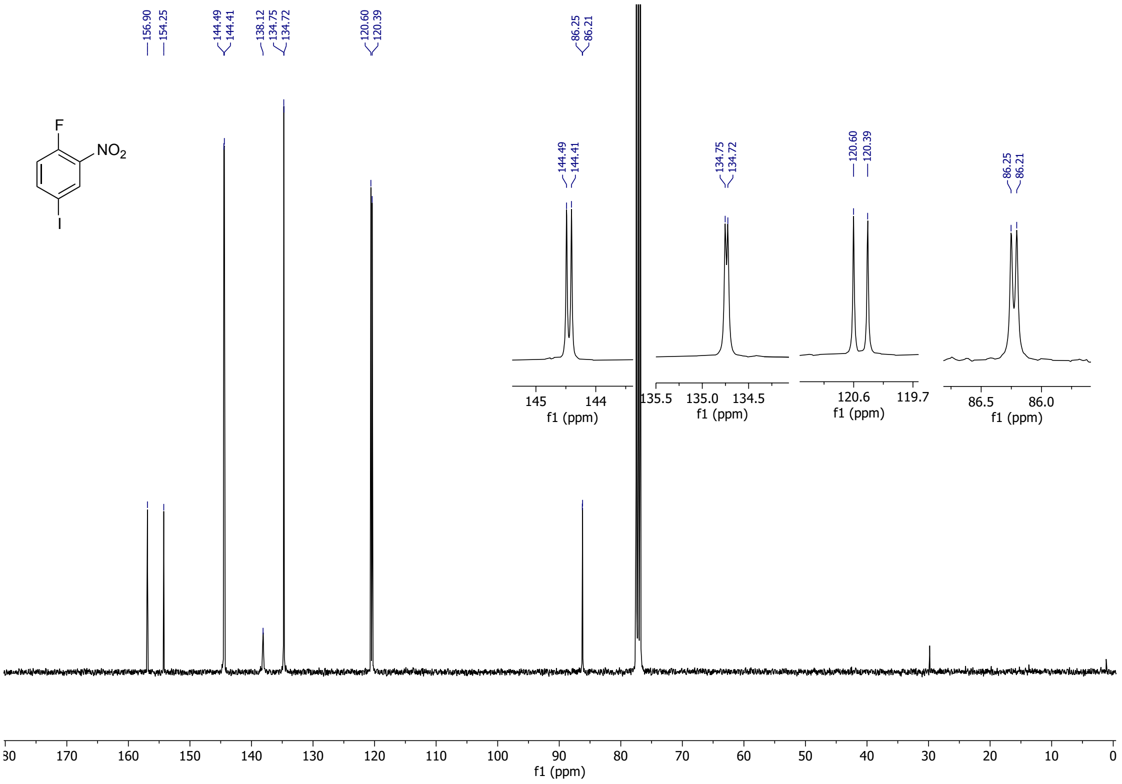


Figure S3. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3[7,7]** (CDCl$_3$).


8.362
8.356
8.345
8.339
7.945
7.940
7.935
7.929
7.924
7.918
7.913
7.907
7.096
7.075
7.070
7.048
F
NO2
I
f1 (ppm)
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
8.4 8.3 8.2 8.1 8.0 7.9
7.15 7.10 7.05 7.00


156.90
154.25
144.49
144.41
138.12
134.75
134.72
120.60
120.39
86.25
86.21
F
NO2
I
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
145 144
135.5 135.0 134.5
120.6 119.7
86.5 86.0

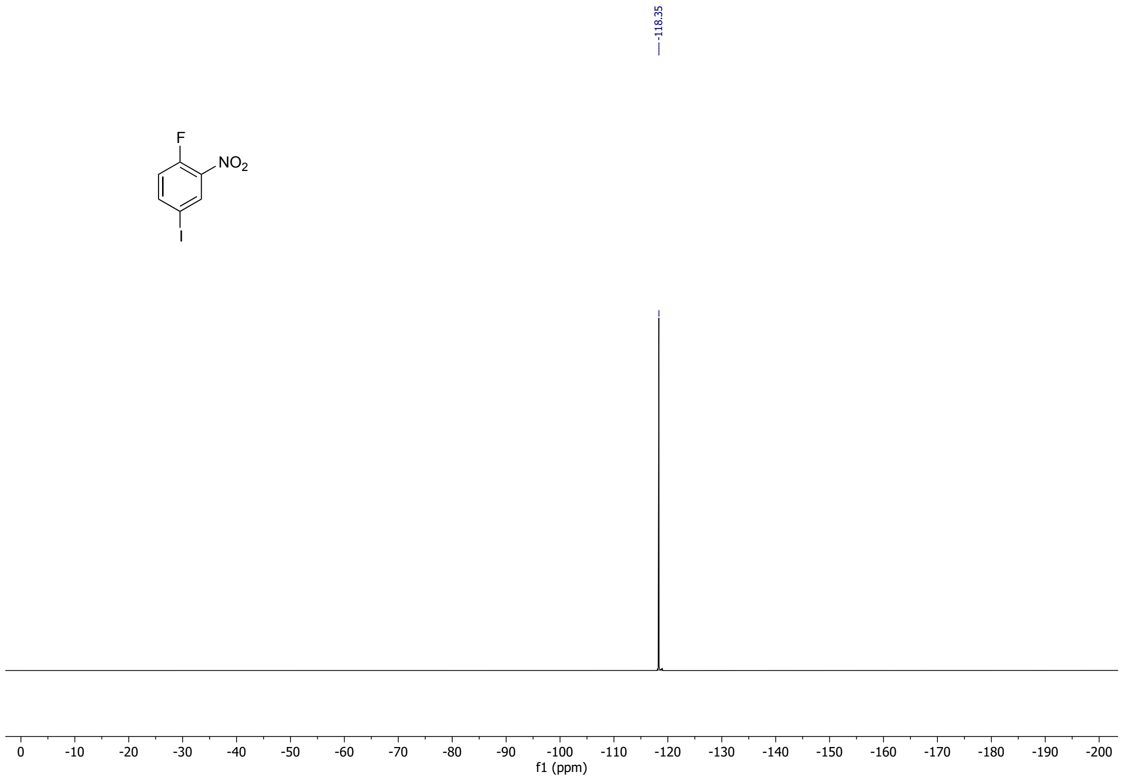
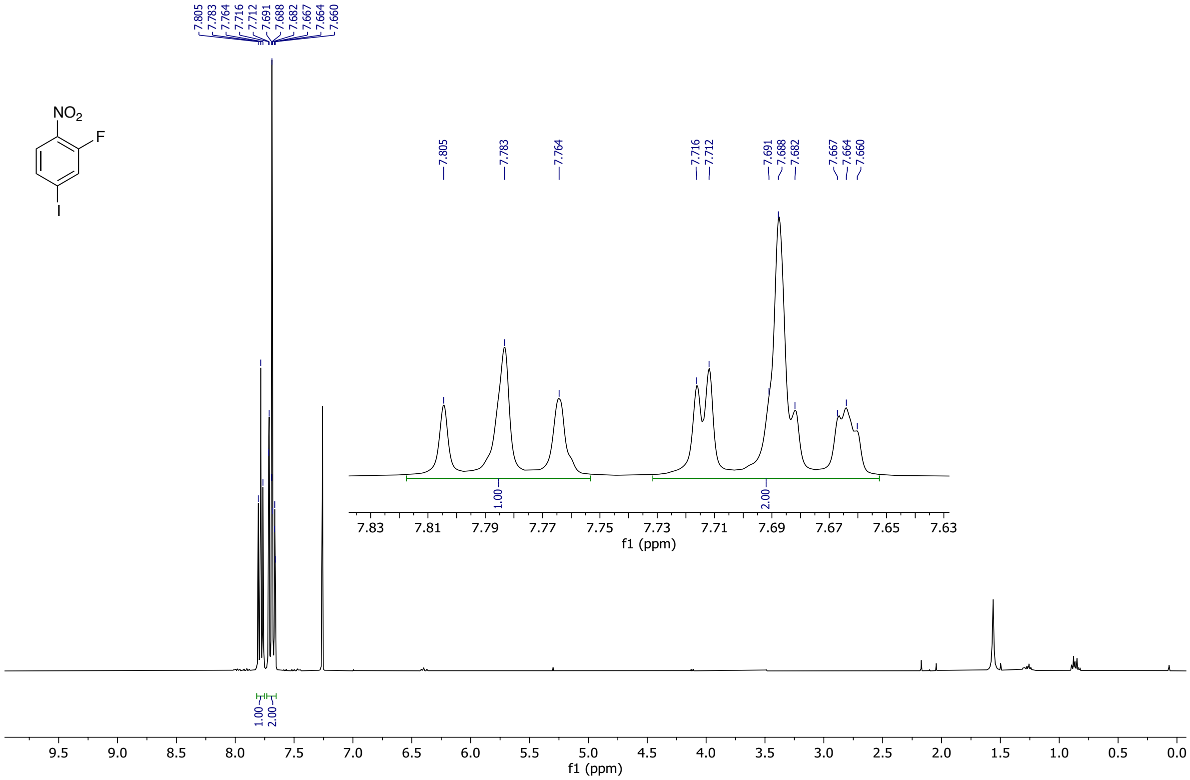


Figure S4. ^1H NMR (400 MHz), $^{13}C\{^1H\}$ NMR (100 MHz) and ^{19}F NMR (377 MHz) spectra of **4a** ($CDCl_3$).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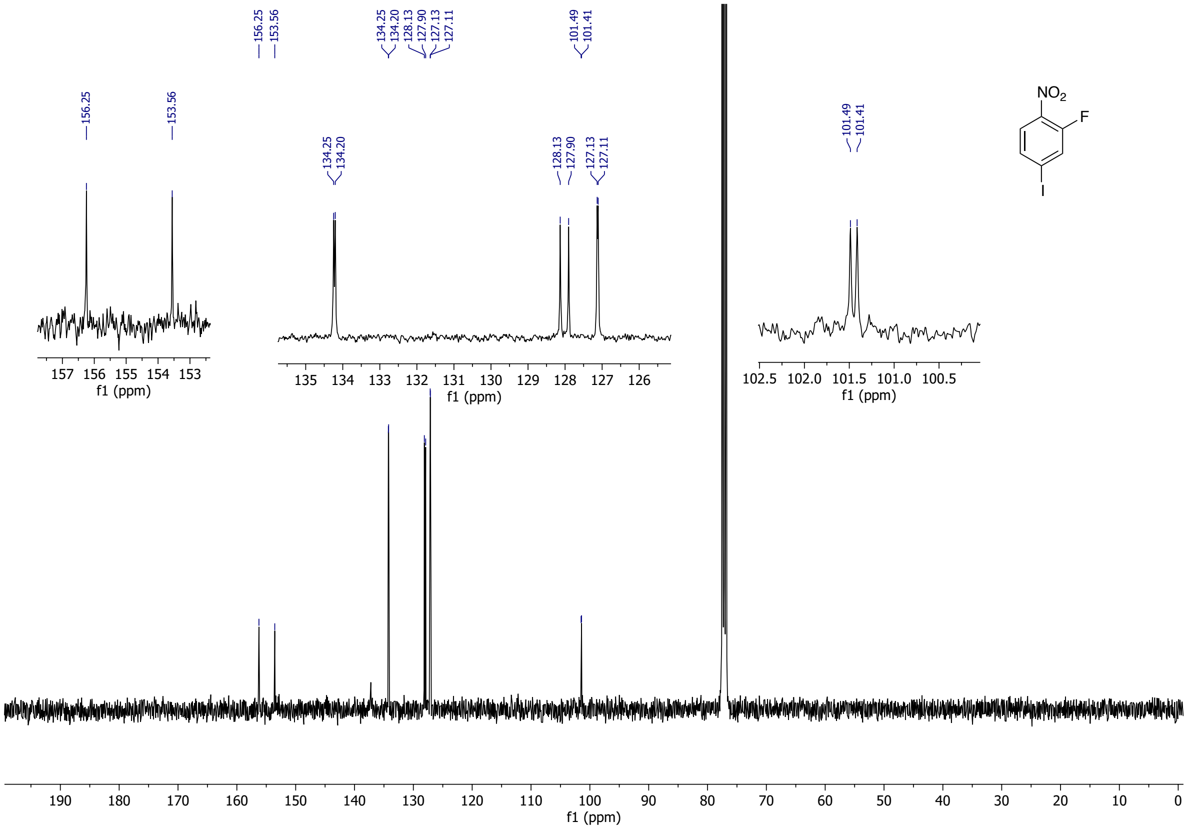
7.764
7.716
7.712
7.691
7.688
7.682
7.667
7.664
7.660
NO2
F
I
1.00
2.00
7.83 7.81 7.79 7.77 7.75 7.73 7.71 7.69 7.67 7.65 7.63
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


156.25
153.56
134.25
134.20
128.13
127.90
127.13
127.11
101.49
101.41
NO2
F
I
157 156 155 154 153
f1 (ppm)
135 134 133 132 131 130 129 128 127 126
f1 (ppm)
102.5 102.0 101.5 101.0 100.5
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

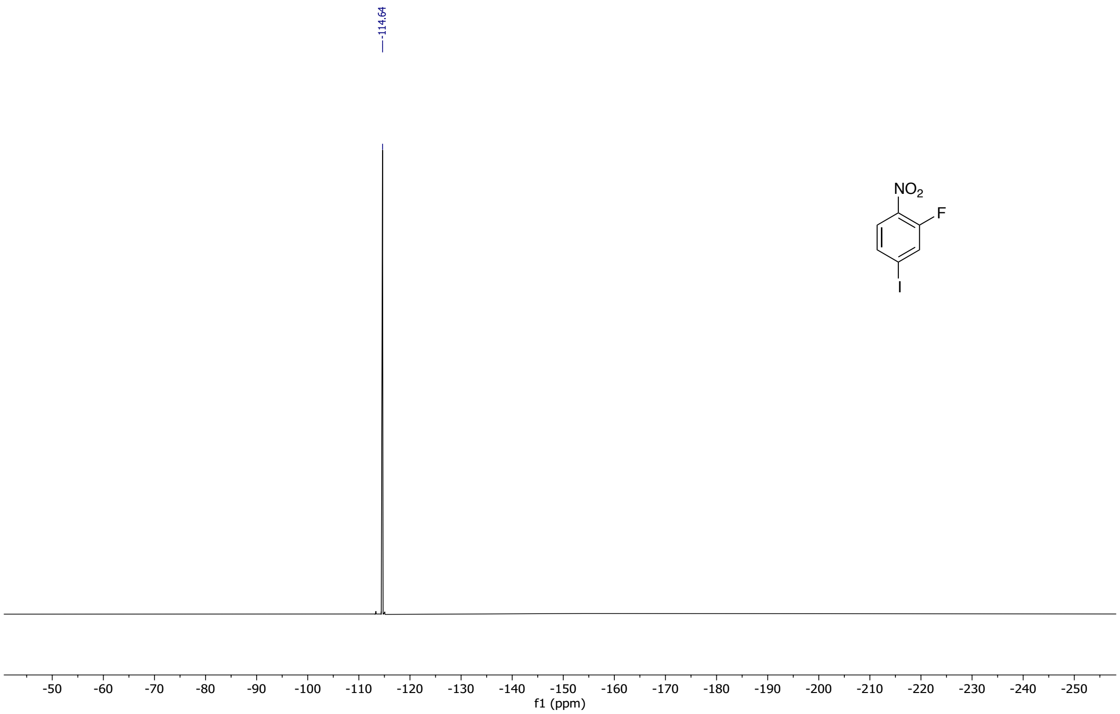
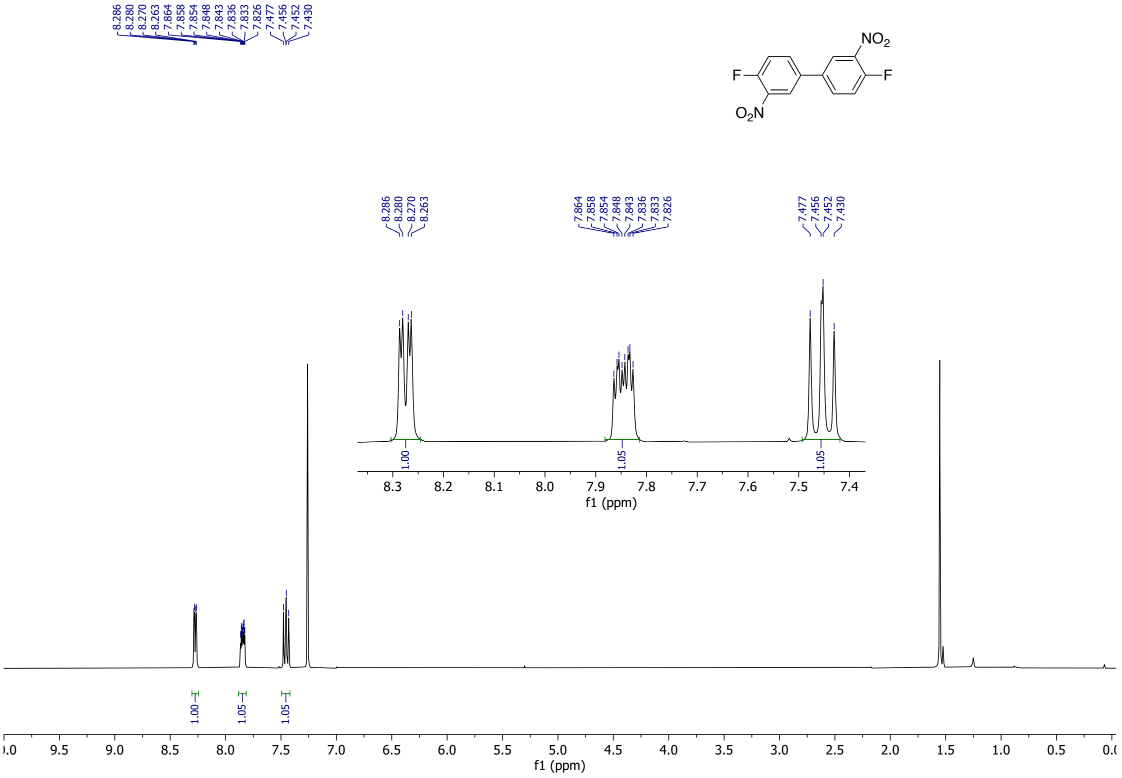


Figure S5. ^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (100 MHz) and ^{19}F NMR (377 MHz) spectra of **4b** (CDCl$_3$).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8.263
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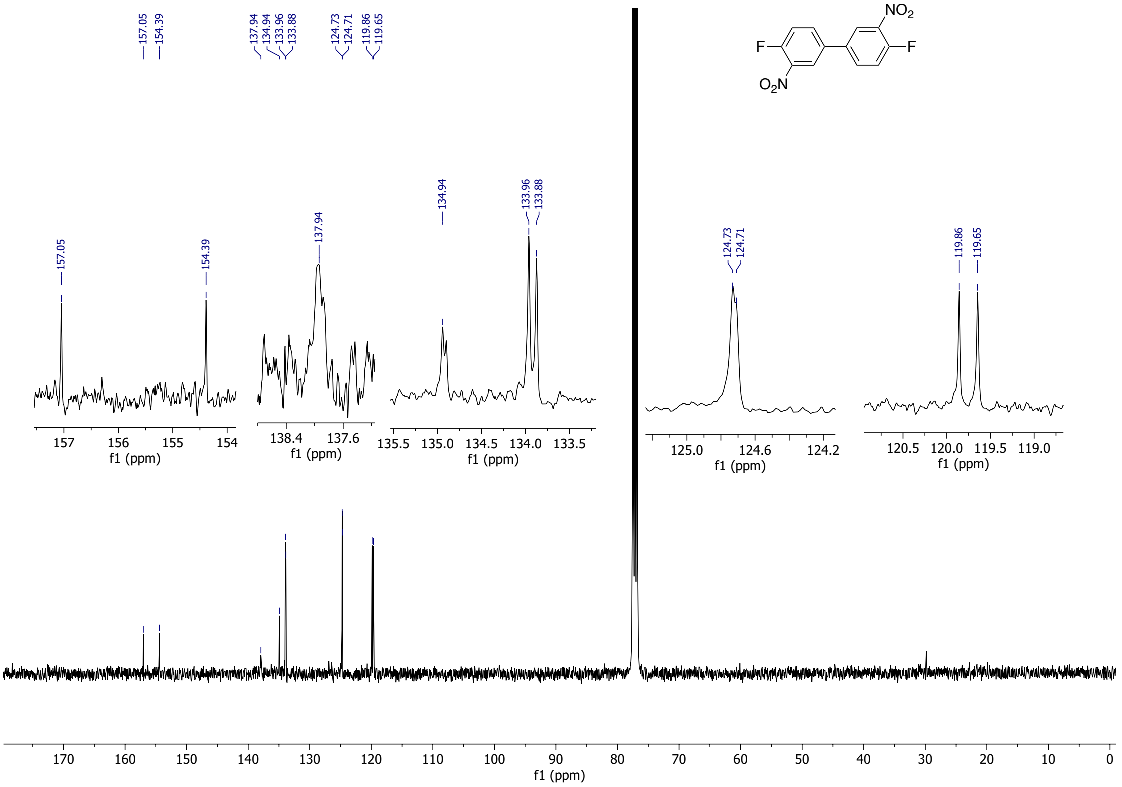
7.858
7.854
7.848
7.843
7.836
7.833
7.826
7.477
7.456
7.452
7.430
NO2
F
F
O2N
1.00
1.05
1.05
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


157.05
154.39
137.94
134.94
133.96
133.88
124.73
124.71
119.86
119.65
NO2
F
F
O2N
157 156 155 154
f1 (ppm)
138.4 137.6
f1 (ppm)
135.5 135.0 134.5 134.0 133.5
f1 (ppm)
125.0 124.6 124.2
f1 (ppm)
120.5 120.0 119.5 119.0
f1 (ppm)
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f1 (ppm)

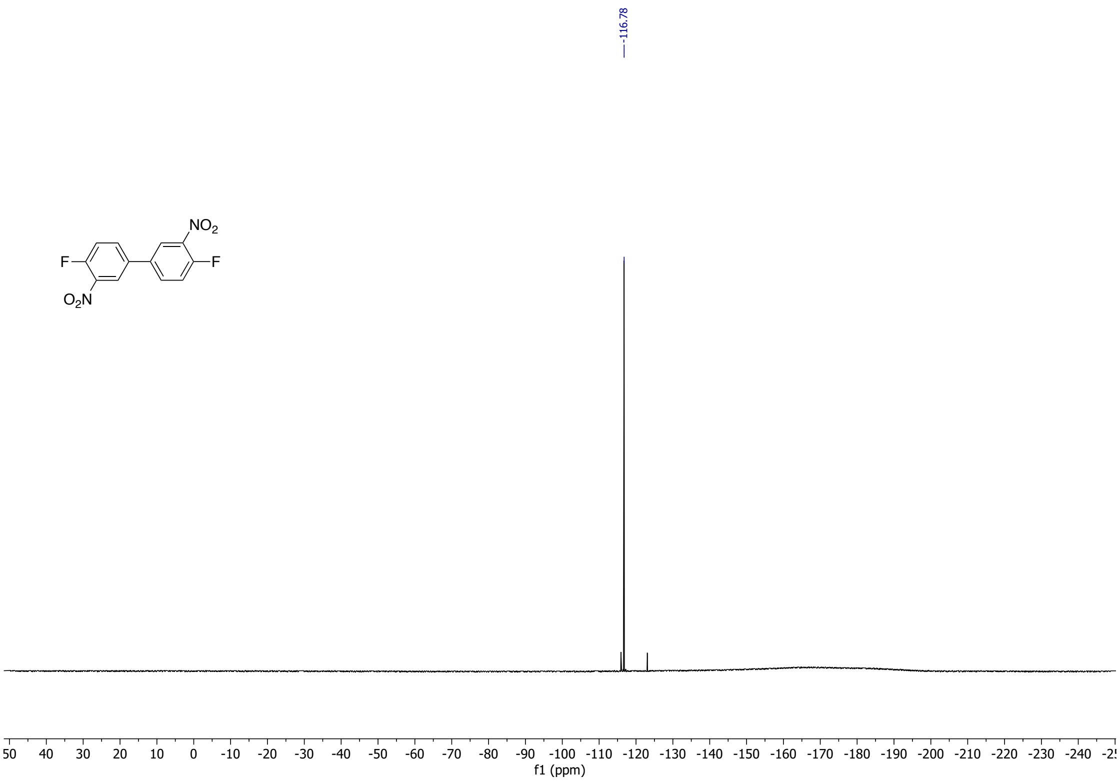
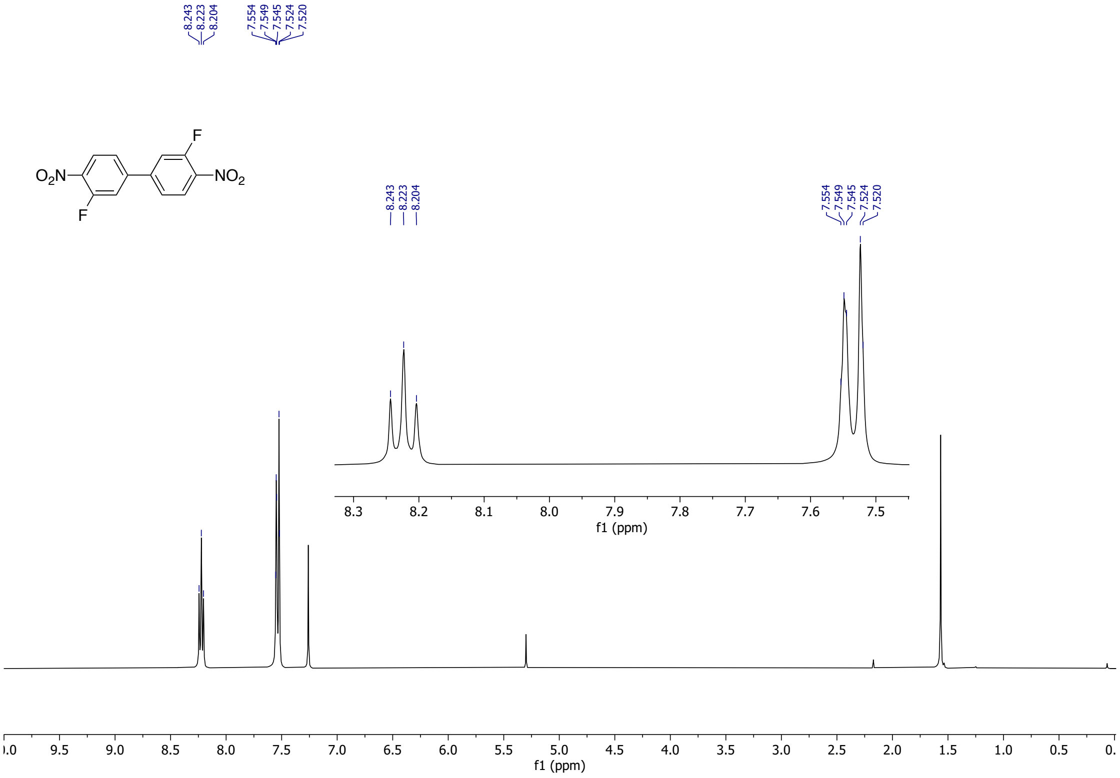


Figure S6. ^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (100 MHz) and ^{19}F (377 MHz) spectra of **5[6,6]** ($CDCl_3$).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8.223
8.204
7.554
7.549
7.545
7.524
7.520
F
O_2N
NO_2
F
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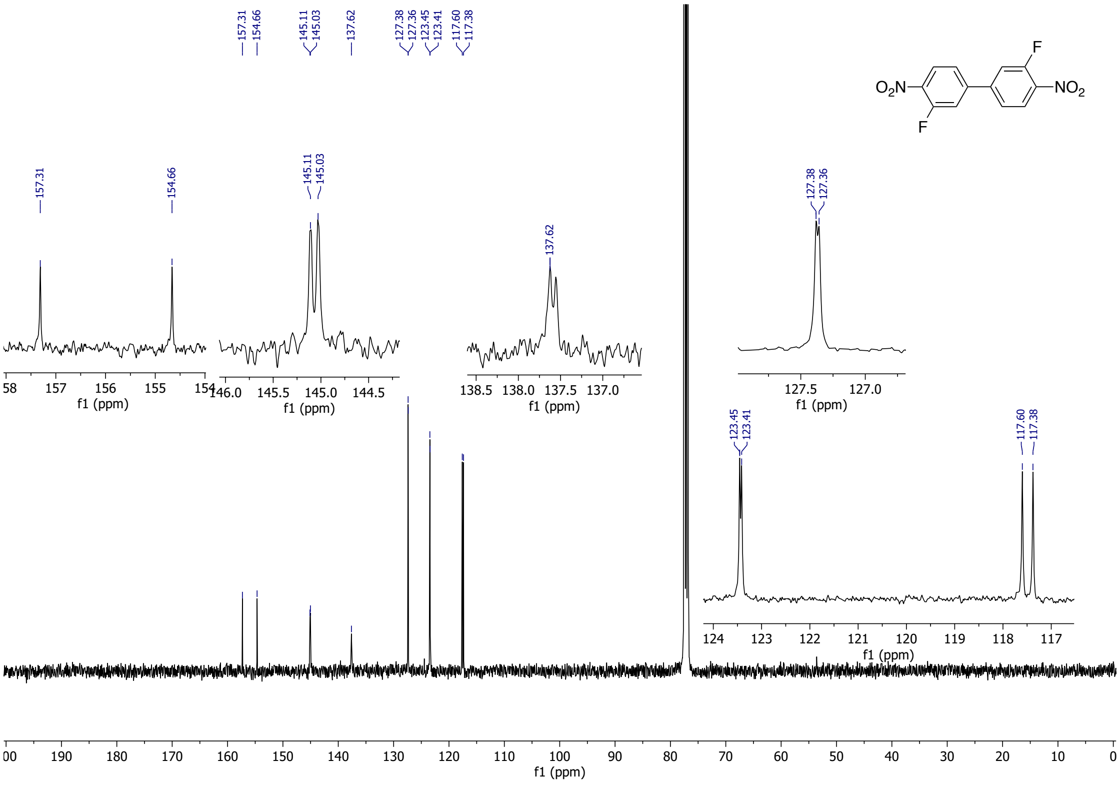
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


157.31
154.66
145.11
145.03
137.62
127.38
127.36
123.45
123.41
117.60
117.38
F
O_2N
NO_2
F
158 157 156 155 154
f1 (ppm)
146.0 145.5 145.0 144.5
f1 (ppm)
138.5 138.0 137.5 137.0
f1 (ppm)
127.5 127.0
f1 (ppm)
124 123 122 121 120 119 118 117
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

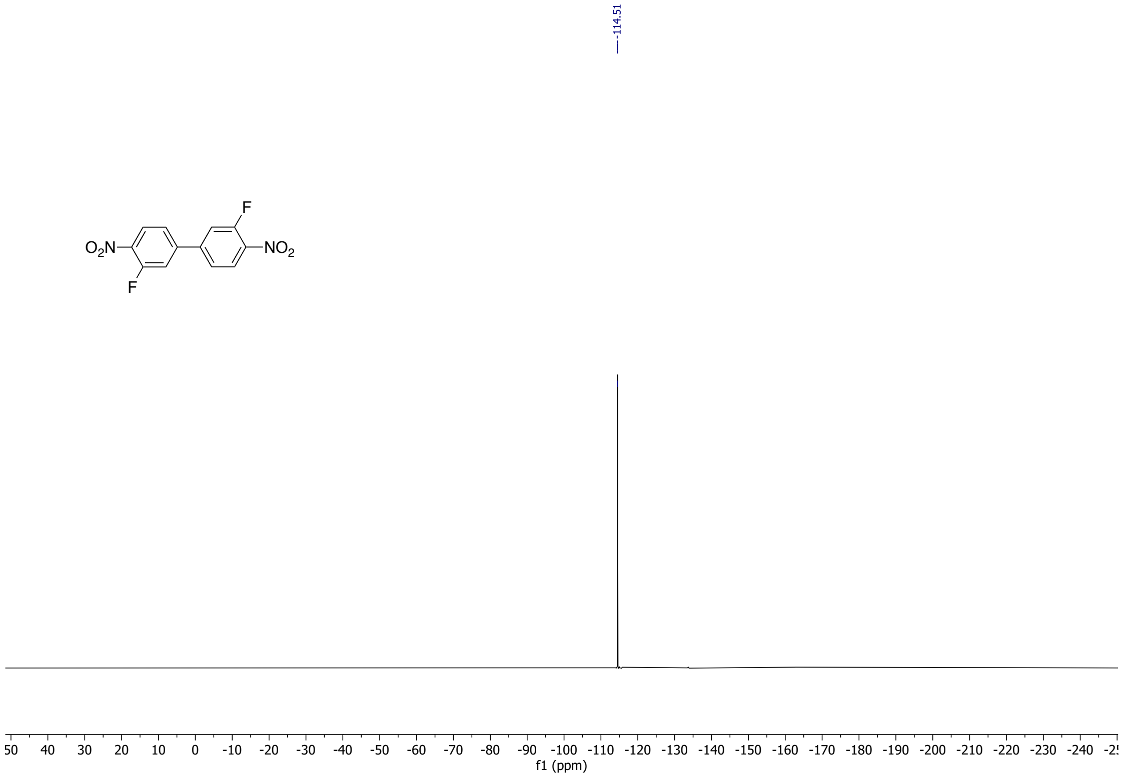


Figure S7. ^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (100 MHz) and ^{19}F NMR (377 MHz) spectra of **5[7,7]** (CDCl$_3$).

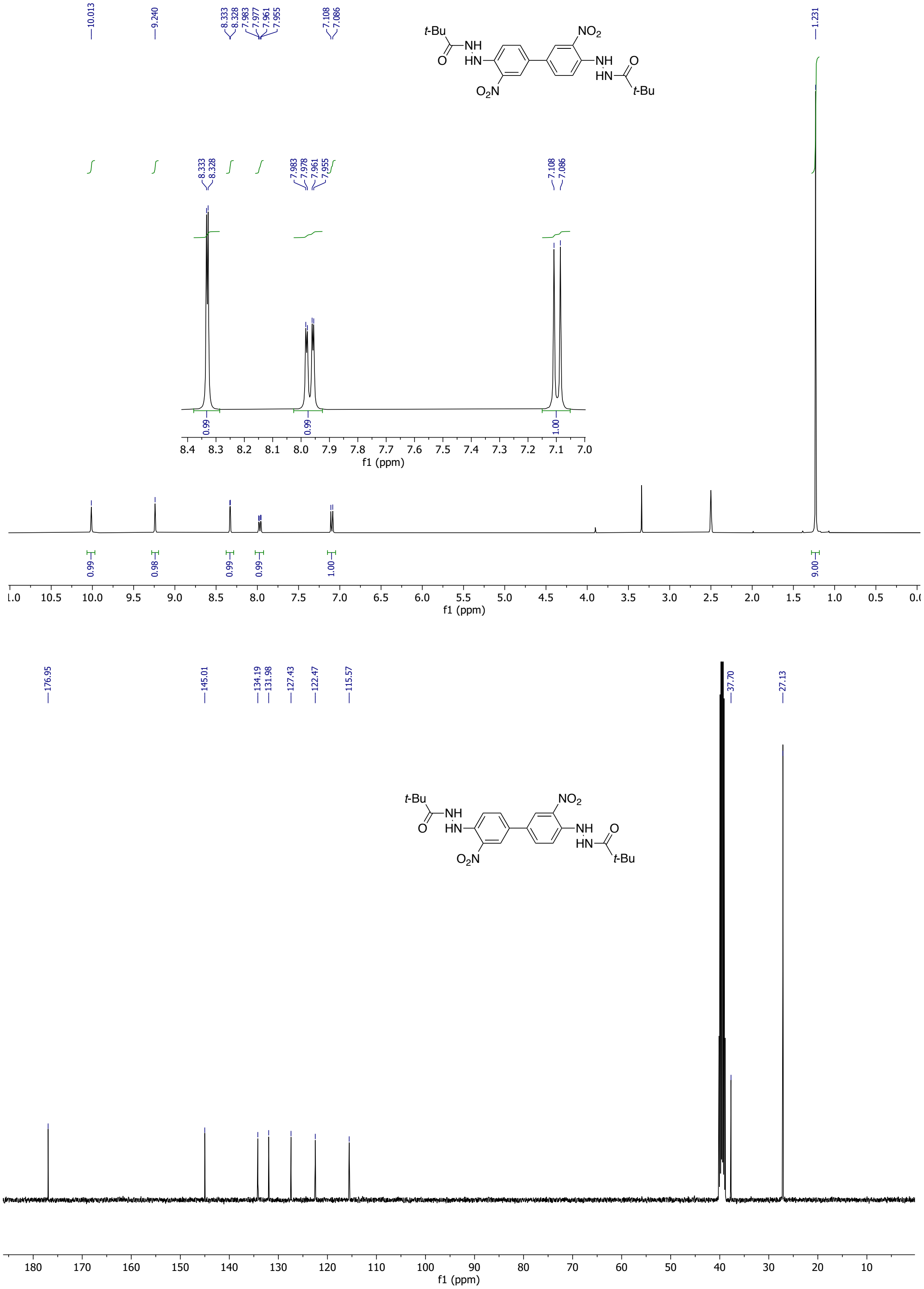


Figure S8. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **6[6,6]** (DMSO-d_6).

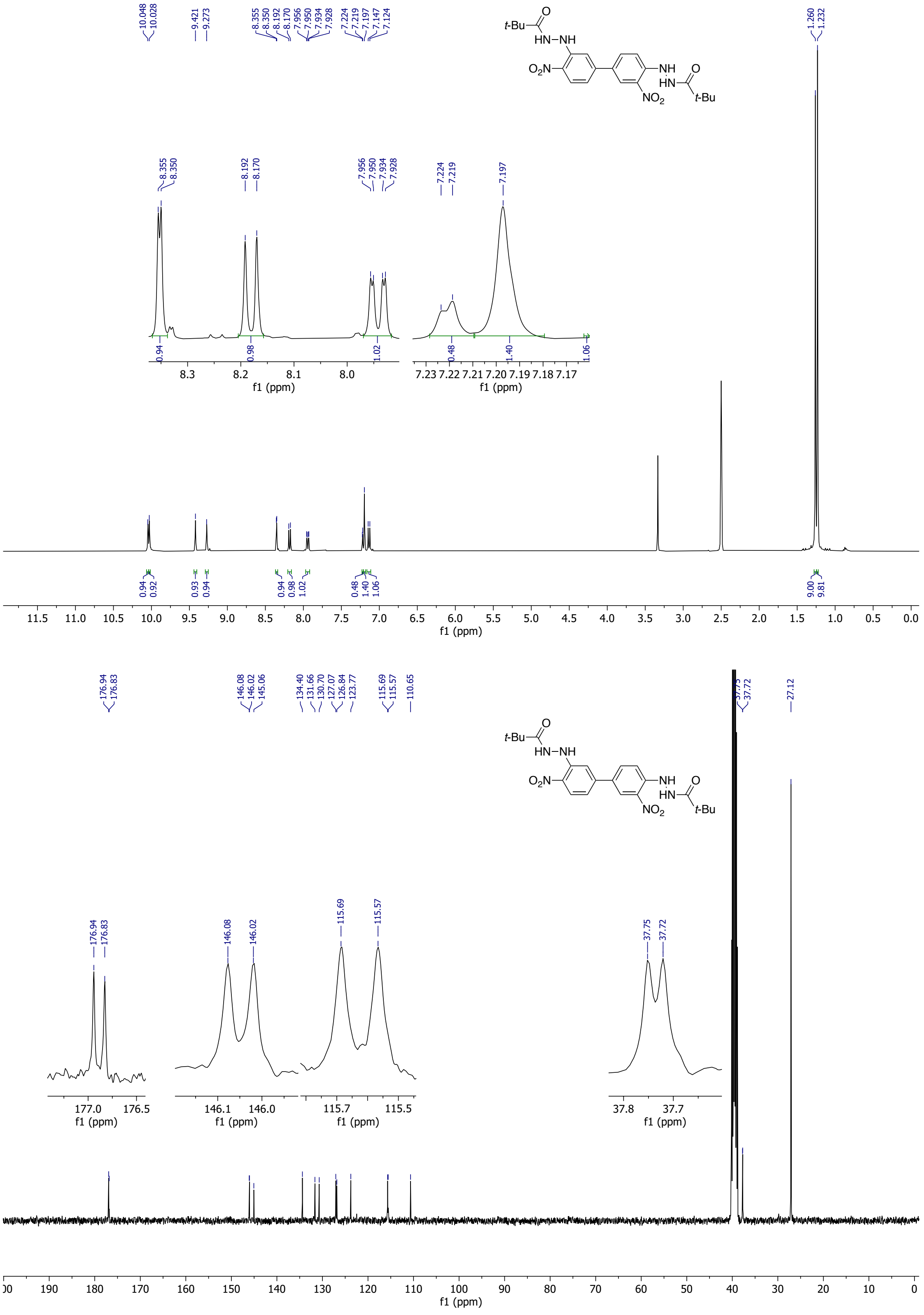


Figure S9. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **6[6,7]** (DMSO-d_6).

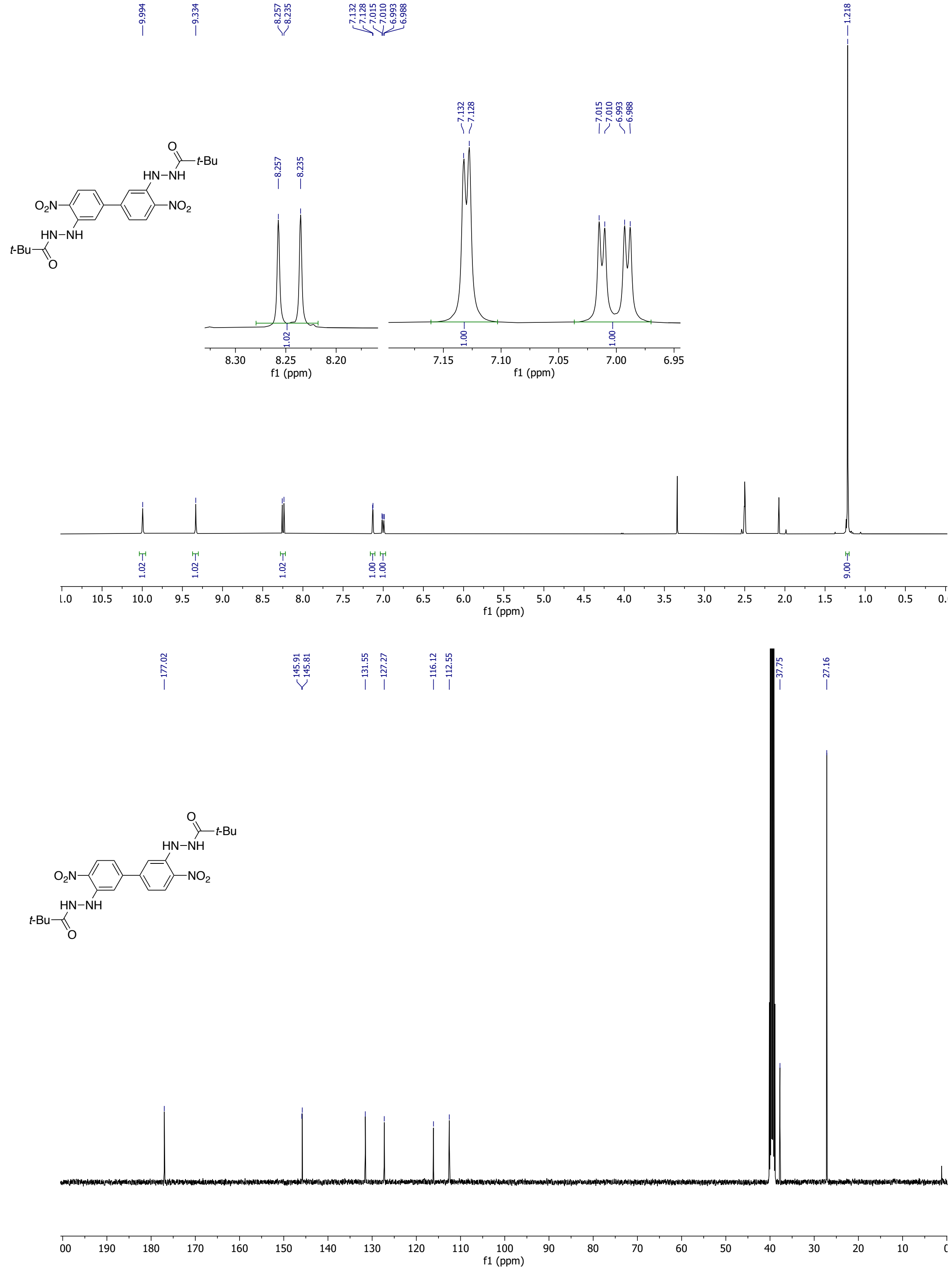
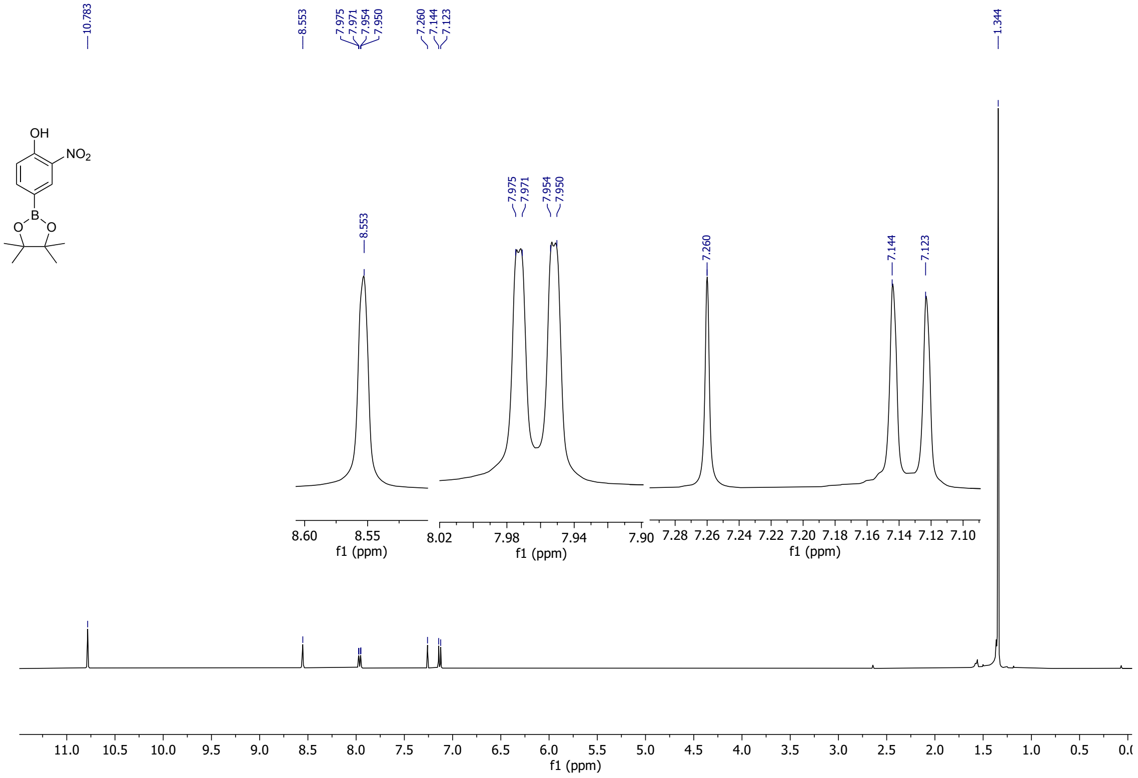


Figure S10. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **6[7,7]** (DMSO-d_6).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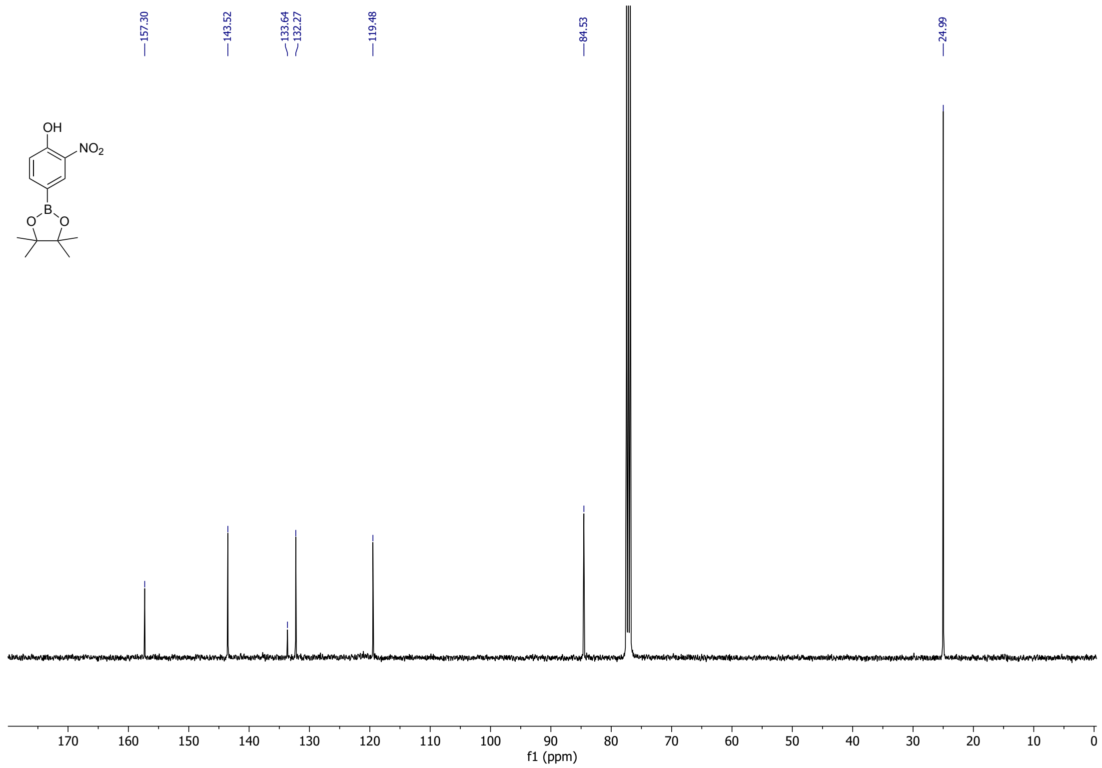
7.971
7.954
7.950
7.260
7.144
7.123
1.344
OH
NO2
B
O
O
8.60
8.55
f1 (ppm)
8.02
7.98
7.94
7.90
f1 (ppm)
7.28
7.26
7.24
7.22
7.20
7.18
7.16
7.14
7.12
7.10
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


157.30
143.52
133.64
132.27
119.48
84.53
24.99
OH
NO2
B
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

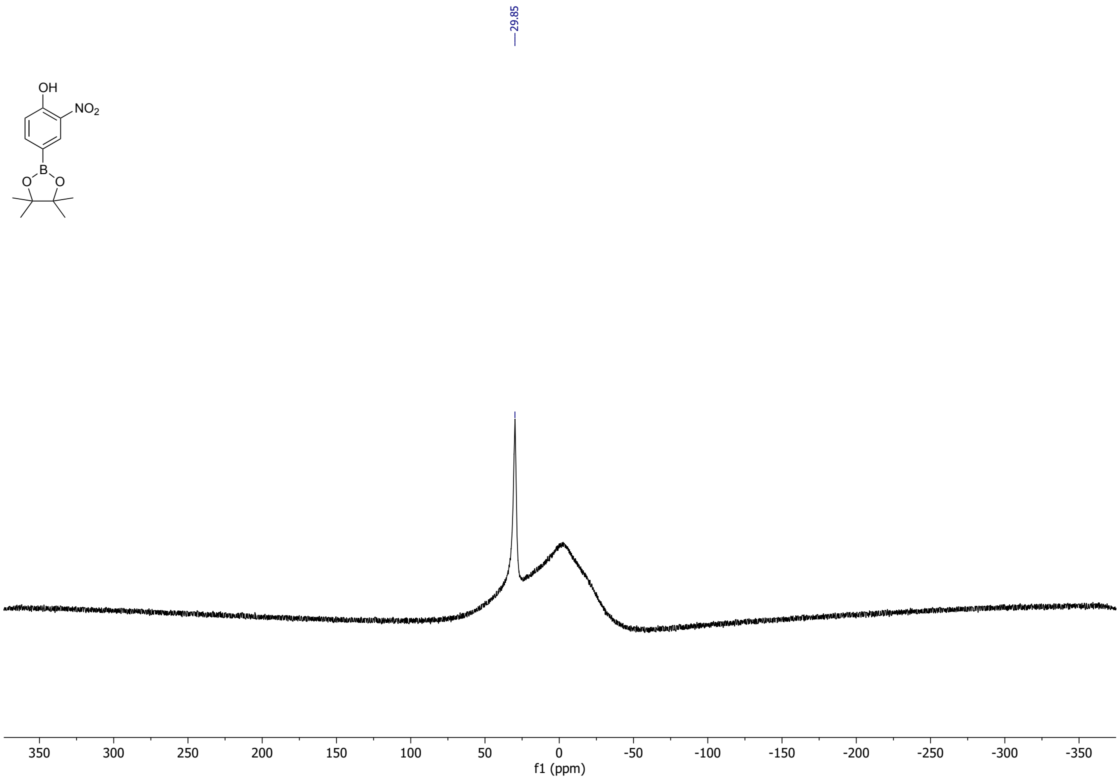


Figure S11. ^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (100 MHz) and ^{11}B{^{1}H} NMR (128 MHz) spectra of **7** ($CDCl_3$).

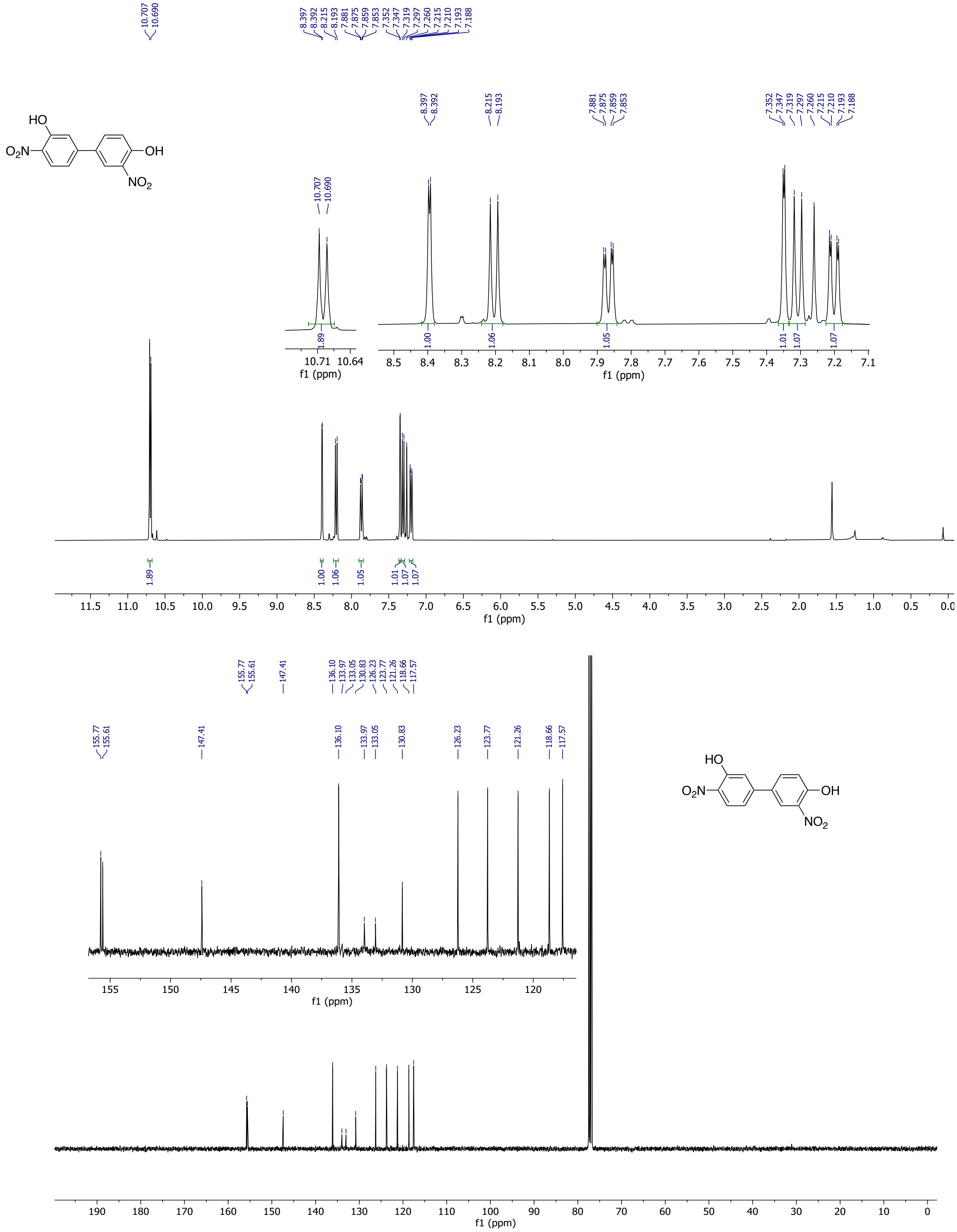
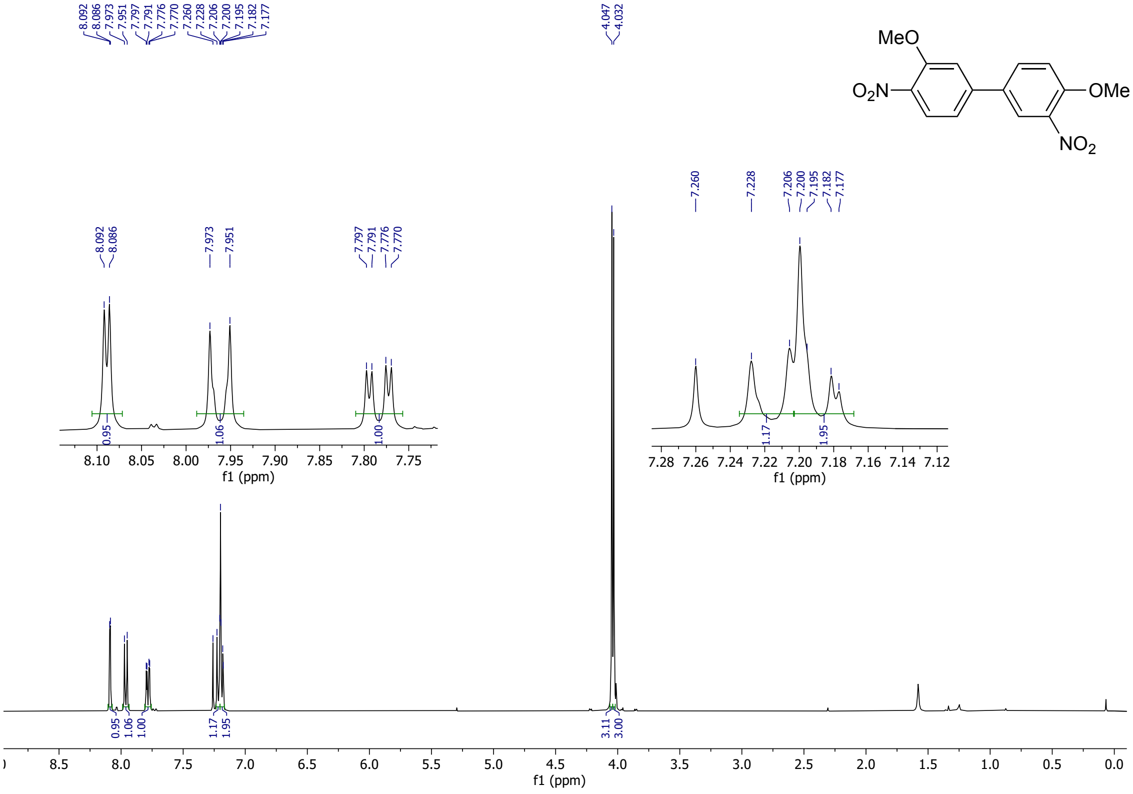
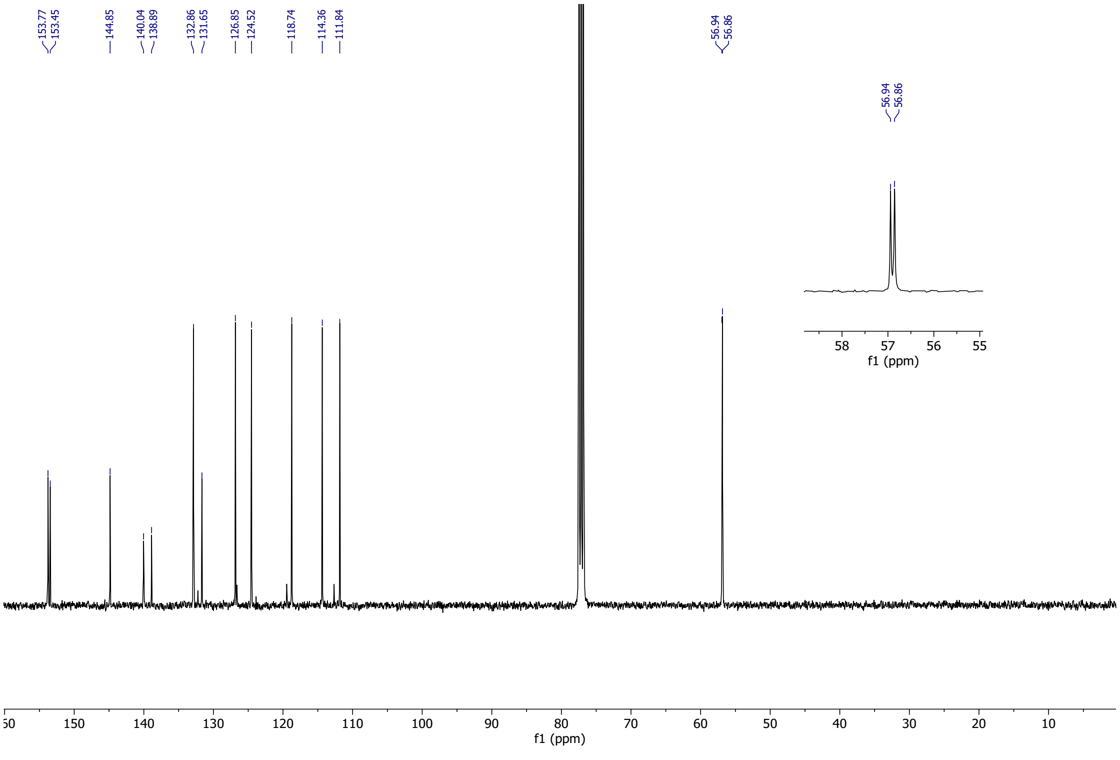


Figure S12. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **9[6,7]** (CDCl$_3$).

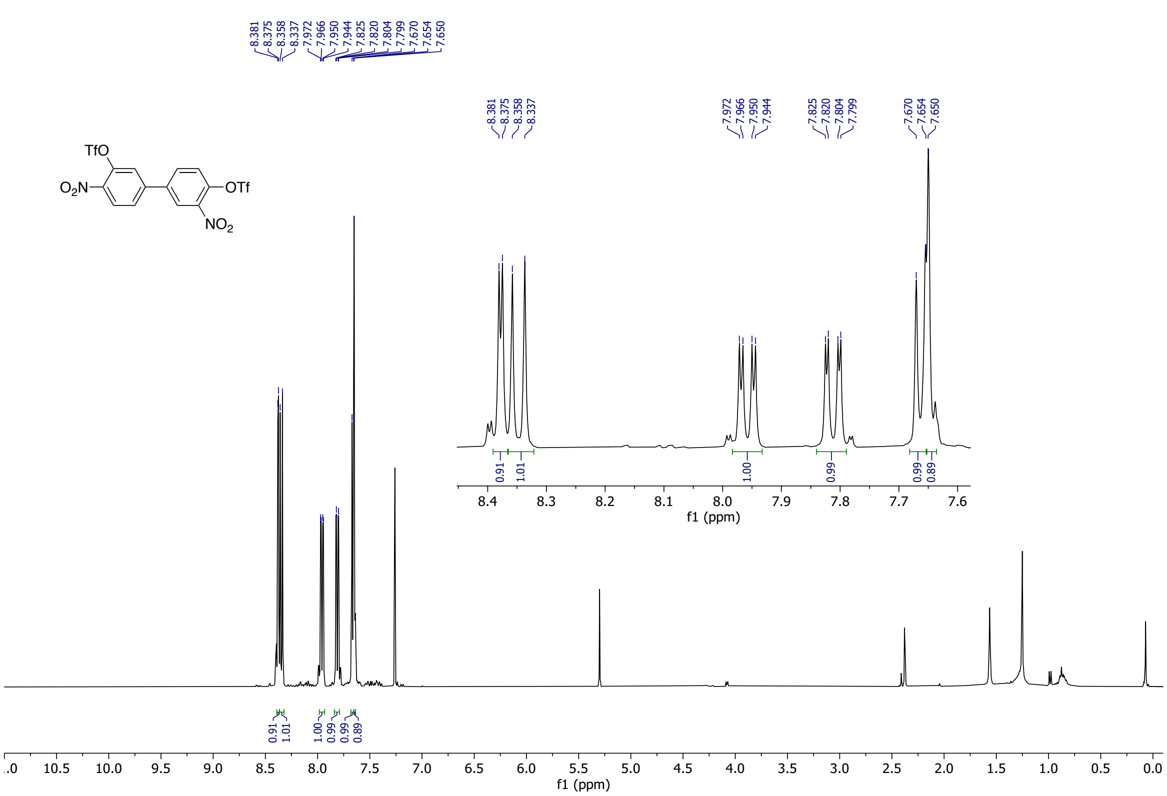


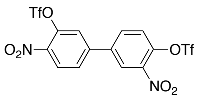
8.092
8.086
7.973
7.951
7.797
7.791
7.776
7.770
7.260
7.228
7.206
7.200
7.195
7.182
7.177
4.047
4.032
MeO
O_2N
OMe
NO_2
0.95
1.06
1.00
1.17
1.95
3.11
3.00
f1 (ppm)

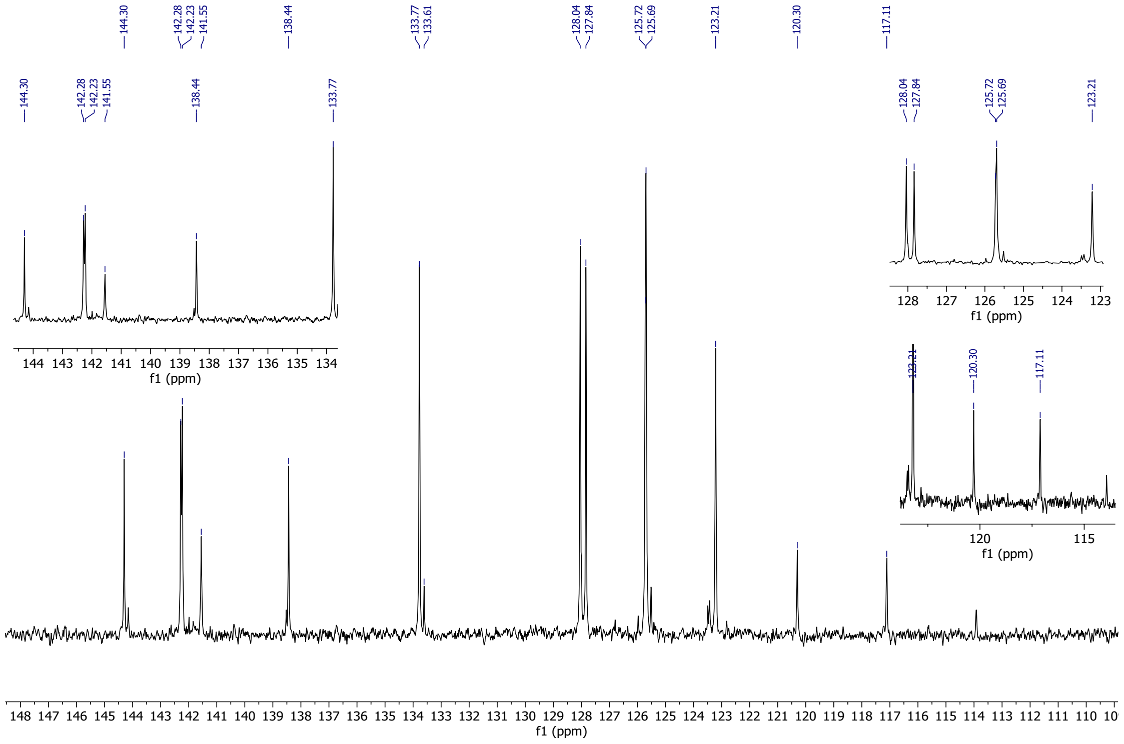


153.77
153.45
144.85
140.04
138.89
132.86
131.65
126.85
124.52
118.74
114.36
111.84
56.94
56.86
f1 (ppm)

Figure S13. ^{1}H NMR (400 MHz) and $^{13}C\{^1H\}$ NMR (100 MHz) spectra of **12[6,7]** ($CDCl_3$).






144.30
142.28
142.23
141.55
138.44
133.77
133.61
128.04
127.84
125.72
125.69
123.21
120.30
117.11
144 143 142 141 140 139 138 137 136 135 134
f1 (ppm)
128 127 126 125 124 123
f1 (ppm)
120 115
f1 (ppm)
148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112 111 110 10
f1 (ppm)

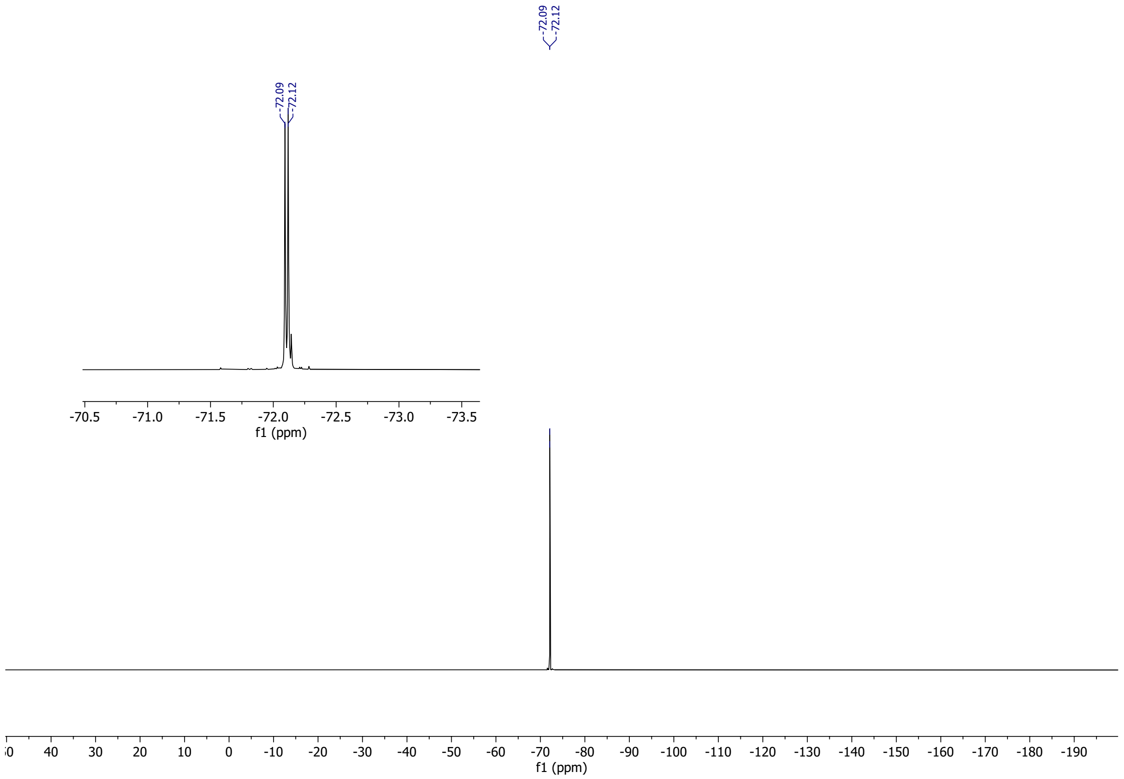
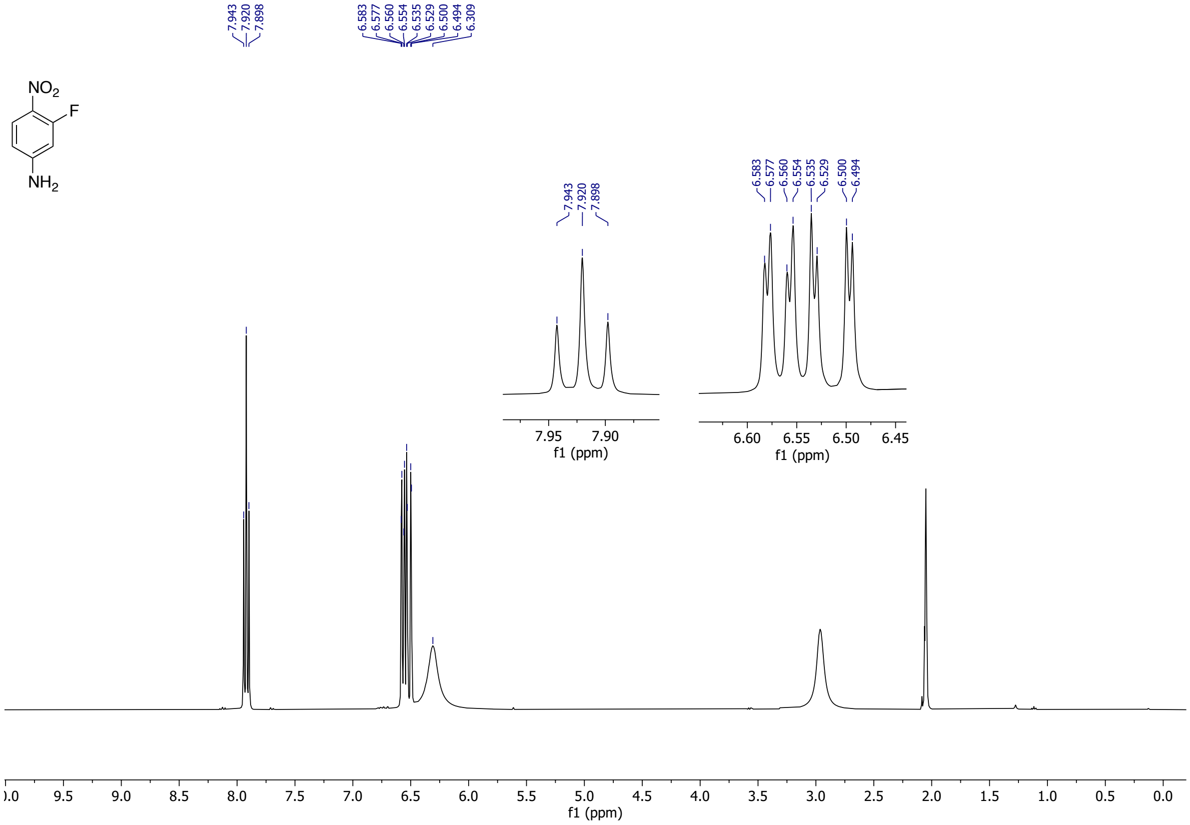
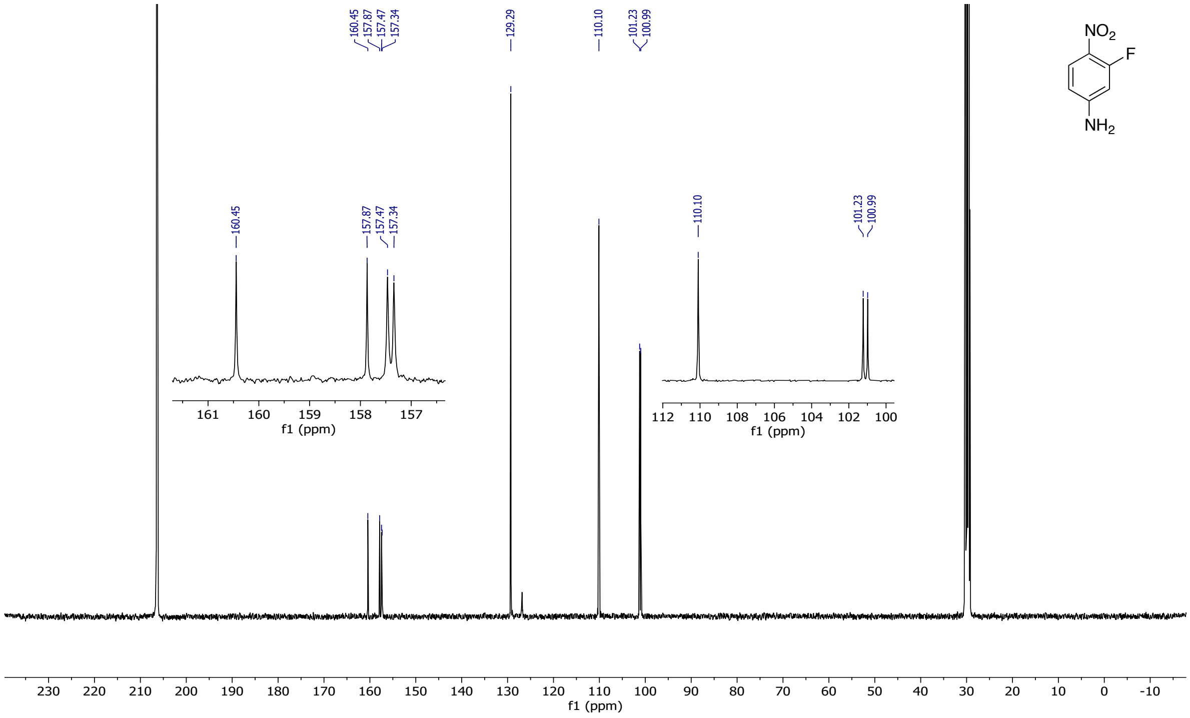

-72.09
-72.12
-70.5 -71.0 -71.5 -72.0 -72.5 -73.0 -73.5
f1 (ppm)
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

Figure S14. ^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (100 MHz) and ^{19}F NMR (377 MHz) spectra of **13[6,7]** ($CDCl_3$).


7.943
7.920
7.898
6.583
6.577
6.560
6.554
6.535
6.529
6.500
6.494
6.309
NO2
F
NH2
7.95
7.90
f1 (ppm)
6.60
6.55
6.50
6.45
f1 (ppm)
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
f1 (ppm)


160.45
157.87
157.47
157.34
129.29
110.10
101.23
100.99
NO2
F
NH2
161
160
159
158
157
f1 (ppm)
112
110
108
106
104
102
100
f1 (ppm)
230
220
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)

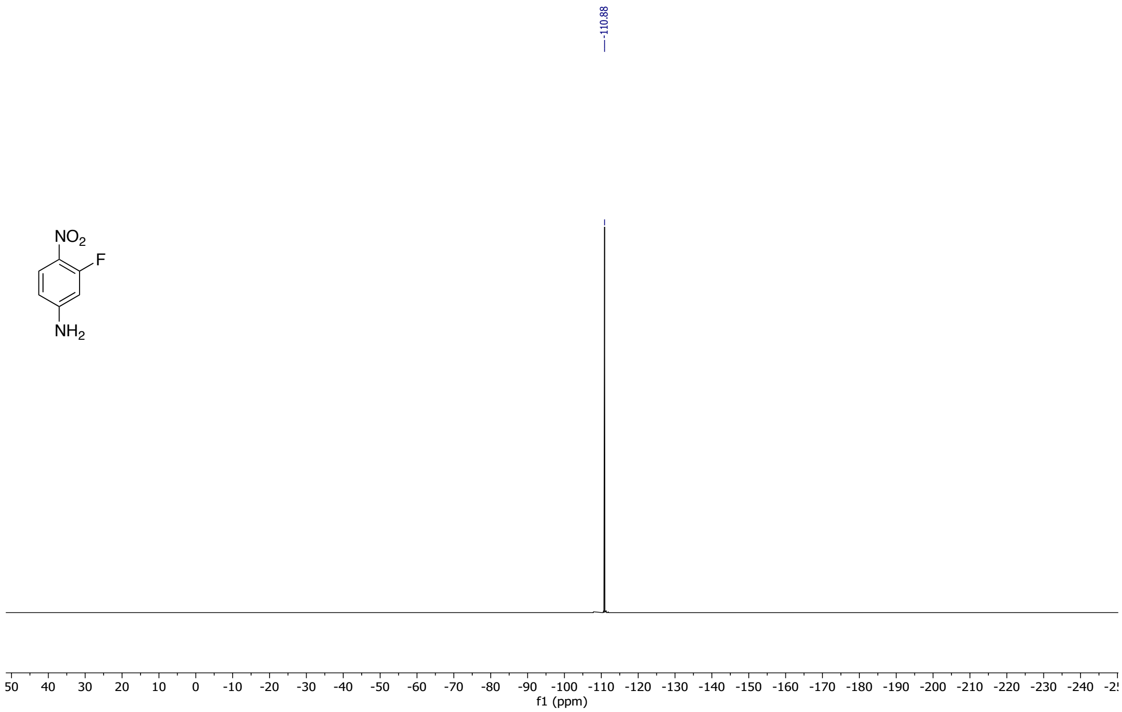


Figure S15. ^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (100 MHz) and ^{19}F NMR (377 MHz) spectra of **14** (acetone-*d*$_6$).

3. IR spectra

FT-IR spectra were recorded in KBr pellets and results are shown in Figures S16–S18.

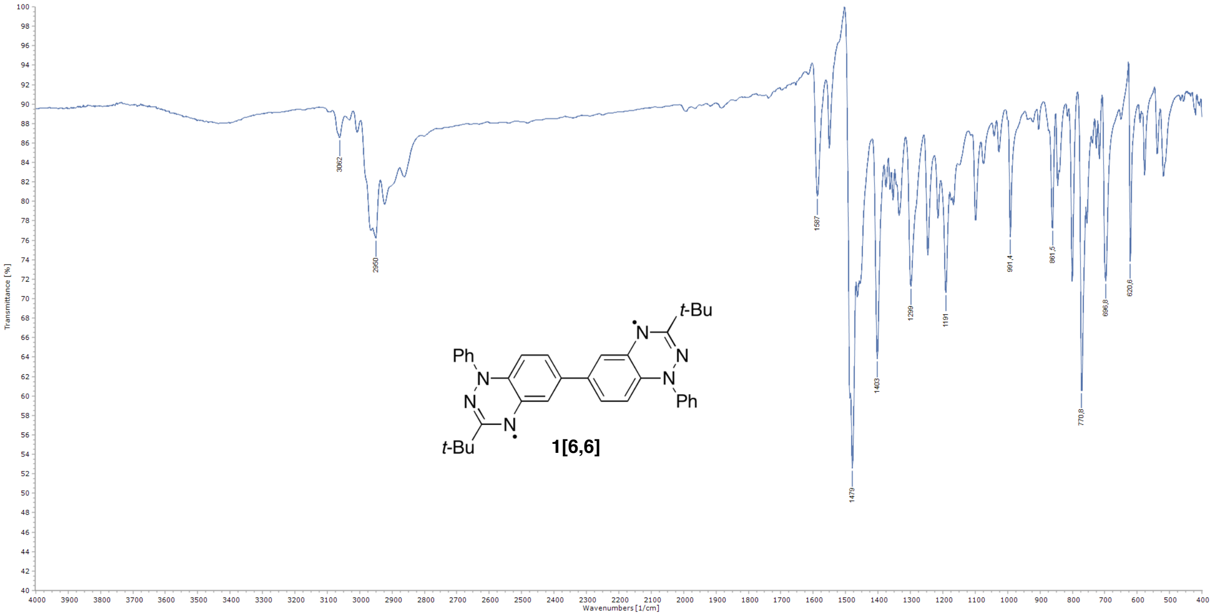


Figure S16. IR spectrum for diradical **1[6,6]** recorded in KBr.

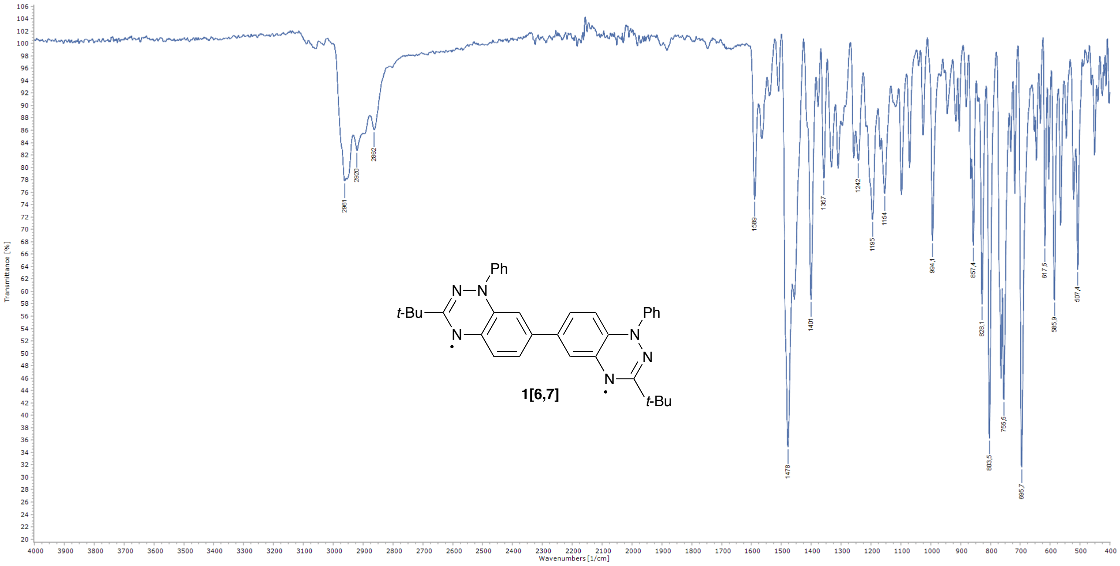


Figure S17. IR spectrum for diradical **1[6,7]** recorded in KBr.

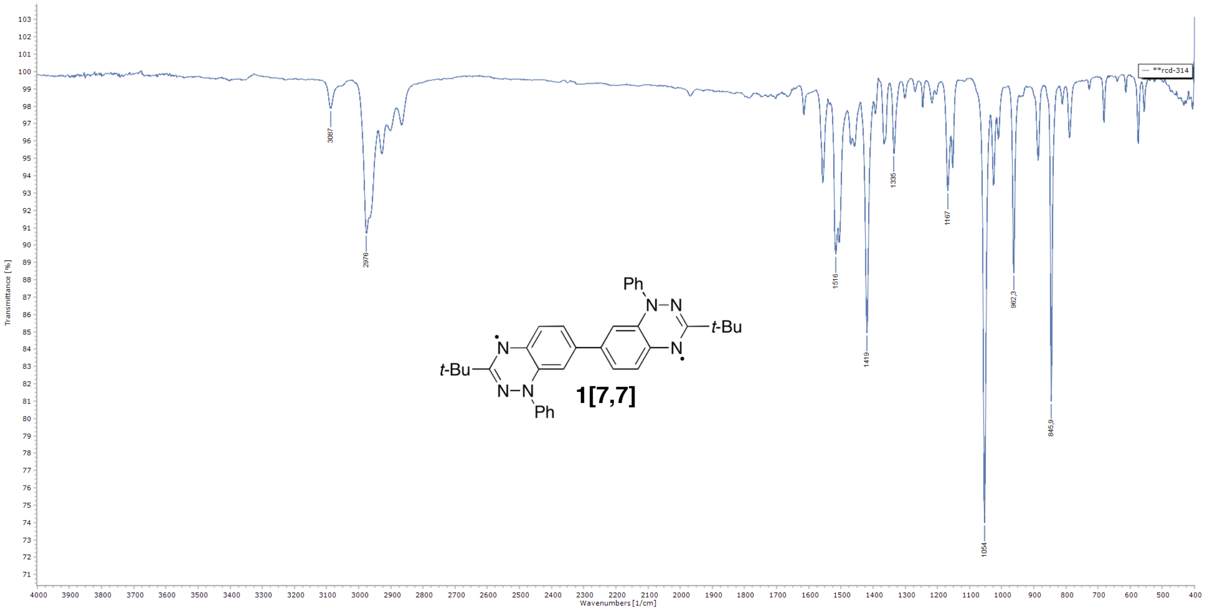


Figure S18. IR spectrum for diradical **1[7,7]** recorded in KBr.

4. XRD data collection and refinement

Data Collection

Crystals of diradicals **1[6,6], 1[6,7]** and **1[7,7]** were grown by liquid-liquid diffusion method using CH_2Cl_2/hexane solvent system.

Single-crystal X-ray diffraction measurements for **1[6,6], 1[6,7]** and **1[7,7]** were performed with XtaLAB Synergy, Pilatus 300 K diffractometer. All measurements were conducted at 100.0(1) K using Cu$K\alpha$ radiation (λ = 1.54184 Å). The data were integrated using CrysAlisPro program. Intensities for absorption were corrected using SCALE3 ABSPACK scaling algorithm implemented in CrysALisPro program.[12]

Structure solution and refinement

All structures were solved with the ShelXT structure solution program[13] using Intrinsic Phasing and refined by the full-matrix least-squares minimization on F^2 with the ShelXL refinement package.[14] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated geometrically and refined isotropically using the riding model.

The crystal data and structure refinement descriptors are presented in Table S1, while molecular structures are shown in Figures S19–S21.

Table S1. Crystal data and refinement details for diradicals **1[m,n]**.

Compound CCDC	**1[6,6]** 2250028	**1[6,7]** 2255380	**1[7,7]** 2250029
Empirical formula	$C_{34}H_{34}N_6$	$C_{34}H_{34}N_6$	$C_{34}H_{34}N_6$
Formula weight	526.28	526.28	526.28
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$I2$/a	$P2_1/c$
a/Å	9.1253(10)	30.2422(10)	31.6231(5)
b/Å	11.2591(2)	10.3658(3)	8.2908(10)
c/Å	13.6478(2)	39.1965(13)	21.4175(4)
α/°	90	90	90
β/°	90.020(1)	114.998(4)	96.233(2)
γ/°	90	90	90
Volume/Å^3	1402.21(4)	11136.4(7)	5582.1(2)
Z	2	16	8
Goodness-of-fit	1.037	1.061	1.057
Final R indexes [I>=2δ (I)]	R_1 = 0.0340 wR_2 =0.0854	R_1 = 0.0657 wR_2 =0.1456	R_1 = 0.0461 wR_2 =0.1250
Final R indexes [all data]	R_1 = 0.0362 wR_2 =0.0869	R_1 = 0.1043 wR_2 =0.1647	R_1 = 0.0585 wR_2 =0.1334

Selected geometrical parameters of **1[6,6]**, **1[7,7]** and **1[6,7]** are listed in Tables S2–S4. For comparison purposes Table S4 contains literature data for diradical **L.**[15]

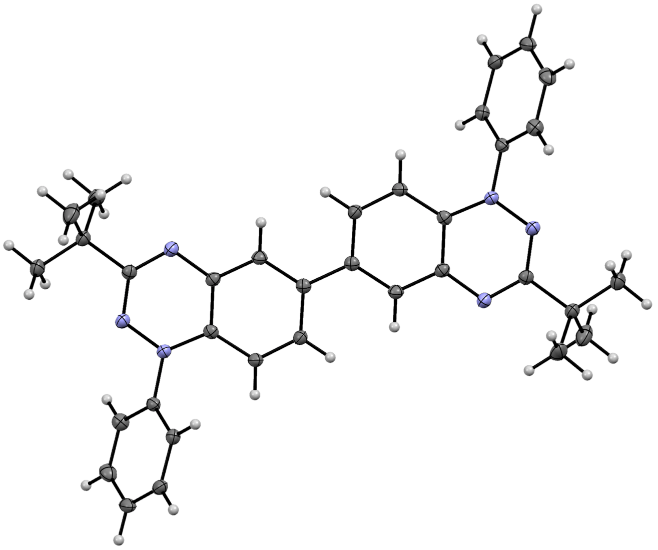


Figure S19. Atomic displacement ellipsoid diagram for diradical **1[6,6]**. Ellipsoids are drawn at 50% probability level.

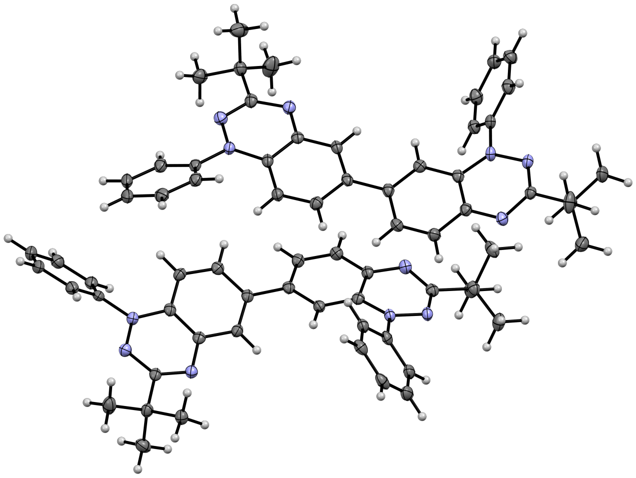


Figure S20. Atomic displacement ellipsoid diagram for two unique molecules of diradical **1[6,7]**. Ellipsoids are drawn at 50% probability level.

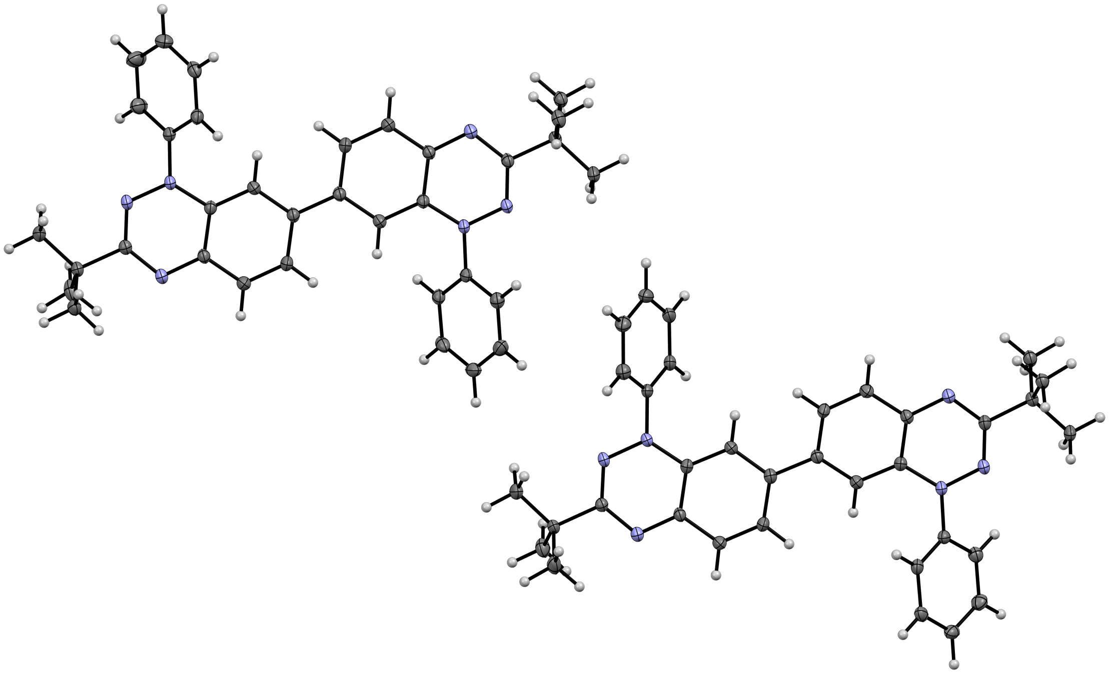
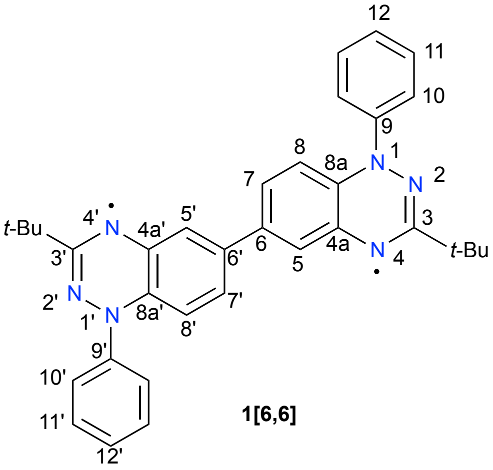


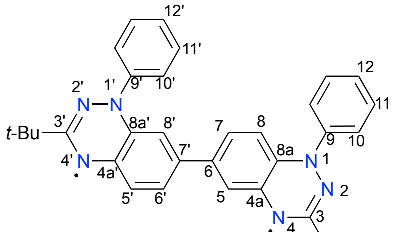
Figure S21. Atomic displacement ellipsoid diagram for two unique molecules of diradical **1[7,7]**. Ellipsoids are drawn at 50% probability level.

Table S2. Selected interatomic distances and angles for diradical **1[6,6]**.

	1[6,6]
N(1)-C(9)	1.431(1)
N(1)-N(2)	1.377(1)
N(2)-C(3)	1.332(1)
C(3)-N(4)	1.337(1)
C(3)-*t*Bu	1.528(1)
N(4)-C(4a)	1.372(1)
C(4a)-C(5)	1.400(1)
C(5)-C(6)	1.392(1)
C(6)-C(7)	1.412(1)
C(7)-C(8)	1.378(1)
C(8)-C(8a)	1.403(1)
C(8a)-N(1)	1.381(1)
C(8a)-C(4a)	1.417(1)
C(6)-C(6’)	1.481(1)
C(9)-C(10)	1.391(1)
C(10)-C(11)	1.390(2)
C(11)-C(12)	1.388(2)
N(1)-N(2)-C(3)	115.60(8)
N(2)-C(3)-N(4)	127.97(9)
N(2)-N(1)-C(9)-C(10)	40.5(1)



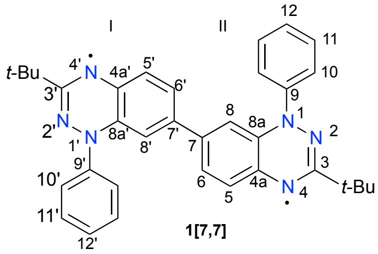
1[6,6]



1[6,7]

Table S3. Selected interatomic distances and angles for diradical **1[6,7]**.

	molecule 1	molecule 2		molecule 1	molecule 2
N(1)-C(9)	1.426(4)	1.439(4)	N(1’)-C(9’)	1.424(4)	1.429(4)
N(1)-N(2)	1.380(3)	1.381(4)	N(1’)-N(2’)	1.387(4)	1.388(4)
N(2)-C(3)	1.332(4)	1.333(4)	N(2’)-C(3’)	1.323(4)	1.310(4)
C(3)-N(4)	1.335(4)	1.340(4)	C(3’)-N(4’)	1.343(4)	1.350(4)
C(3)-*t*Bu	1.534(4)	1.522(4)	C(3’)-*t*Bu	1.526(4)	1.529(5)
N(4)-C(4a)	1.371(4)	1.367(4)	N(4’)-C(4a’)	1.366(4)	1.360(4)
C(4a)-C(5)	1.399(4)	1.405(5)	C(4a’)-C(5’)	1.409(5)	1.419(5)
C(5)-C(6)	1.393(4)	1.388(4)	C(5’)-C(6’)	1.373(5)	1.364(5)
C(6)-C(7)	1.406(4)	1.411(5)	C(6’)-C(7’)	1.407(4)	1.405(4)
C(7)-C(8)	1.374(4)	1.376(5)	C(7’)-C(8’)	1.399(4)	1.407(5)
C(8)-C(8a)	1.400(4)	1.394(4)	C(8’)-C(8a’)	1.392(5)	1.397(5)
C(8a)-N(1)	1.388(4)	1.387(4)	C(8a’)-N(1’)	1.389(4)	1.392(4)
C(8a)-C(4a)	1.406(4)	1.423(5)	C(8a’)-C(4a’)	1.417(4)	1.406(4)
C(6)-C(7’)	1.481(5)	1.475(5)	C(6)-C(7’)	1.481(2)	1.475(5)
C(9)-C(10)	1.376(4)	1.392(5)	C(9’)-C(10’)	1.388(4)	1.387(5)
C(10)-C(11)	1.385(4)	1.385(5)	C(10’)-C(11’)	1.378(4)	1.376(4)
C(11)-C(12)	1.390(5)	1.380(5)	C(11’)-C(12’)	1.395(4)	1.386(5)
N(1)-N(2)-C(3)	115.3(2)	116.5(3)	N(1’)-N(2’)-C(3’)	116.2(2)	116.0(2)
N(2)-C(3)-N(4)	128.2(3)	127.3(3)	N(2’)-C(3’)-N(4’)	127.4(3)	128.0(3)
N(2)-N(1)-C(9)-C(10)	41.2 (4)	30.0(4)	N(2’)-N(1’)-C(9’)-C(10’)	-37.0(4)	- 49.4(4)



1[7,7]

Table S4. Selected interatomic distances and angles for diradical **1[7,7]** and **L**.

	1[7,7] (two molecules)					**L** ^{a}
	molecule 1	molecule 2		molecule 1	molecule 2	
N(1)-C(9)	1.427(2)	1.429(2)	N(1’)-C(9’)	1.427(2)	1.422(2)	1.431(3)
N(1)-N(2)	1.377(1)	1.375(2)	N(1’)-N(2’)	1.376(1)	1.375(1)	1.375(2)
N(2)-C(3)	1.313(2)	1.316(2)	N(2’)-C(3’)	1.317(2)	1.313(2)	1.317(3)
C(3)-N(4)	1.359(2)	1.354(2)	C(3’)-N(4’)	1.357(2)	1.360(2)	1.356(3)
C(3)-*t*Bu	1.525(2)	1.528(2)	C(3’)-*t*Bu	1.528(2)	1.525(2)	1.483(3)
N(4)-C(4a)	1.346(2)	1.353(2)	N(4’)-C(4a’)	1.354(2)	1.349(2)	1.353(3)
C(4a)-C(5)	1.420(2)	1.416(2)	C(4a’)-C(5’)	1.419(2)	1.419(2)	1.411(3)
C(5)-C(6)	1.367(2)	1.372(2)	C(5’)-C(6’)	1.370(2)	1.369(2)	1.366(3)
C(6)-C(7)	1.424(2)	1.421(2)	C(6’)-C(7’)	1.421(2)	1.421(2)	1.412(3)
C(7)-C(8)	1.404(2)	1.404(2)	C(7’)-C(8’)	1.403(2)	1.406(2)	1.406(3)
C(8)-C(8a)	1.389(2)	1.384(2)	C(8’)-C(8a’)	1.388(2)	1.388(2)	1.384(3)
C(8a)-N(1)	1.396(2)	1.399(2)	C(8a’)-N(1’)	1.394(2)	1.396(2)	1.392(3)
C(8a)-C(4a)	1.428(2)	1.426(2)	C(8a’)-C(4a’)	1.424(2)	1.424(2)	1.416(3)
C(6)-C(7’)	1.467(2)	1.468(2)	C(6)-C(7’)	1.467(2)	1.468(2)	1.463(4)
C(9)-C(10)	1.392(2)	1.389(2)	C(9’)-C(10’)	1.389(2)	1.390(2)	1.380(3)
C(10)-C(11)	1.387(2)	1.388(3)	C(10’)-C(11’)	1.392(2)	1.388(2)	1.390(3)
C(11)-C(12)	1.390(2)	1.380(2)	C(11’)-C(12’)	1.383(2)	1.383(2)	1.390(4)
N(1)-N(2)-C(3)	116.8(1)	116.5(1)	N(1’)-N(2’)-C(3’)	116.4(1)	116.9(1)	116.19 (19)
N(2)-C(3)-N(4)	127.1(1)	127.3(1)	N(2’)-C(3’)-N(4’)	127.4(1)	127.0(1)	127.30(19)
N(2)-N(1)-C(9)-C	-37.9 (2)	- 46.9(2)	N(2’)-N(1’)-C(9’)-C	46.0(2)	42.7(2)	55.6 (3)

[a] Ref [15]

5. Electronic absorption spectroscopy

Electronic absorption spectra of diradicals **1[m,n]** were recorded on a Jasco V770 spectrophotometer in spectroscopic grade CH_2Cl_2 at concentrations in a range of 1.9 to 10.0×10^{-5} mol·L^{-1} and the measurements were recorded immediately after. The measured UV-vis spectra were fitted to the Beer–Lambert law ($A = \varepsilon c l$), the molar absorption coefficient (ε) was derived from the linear plots. Results are shown in Figures S22–S24.

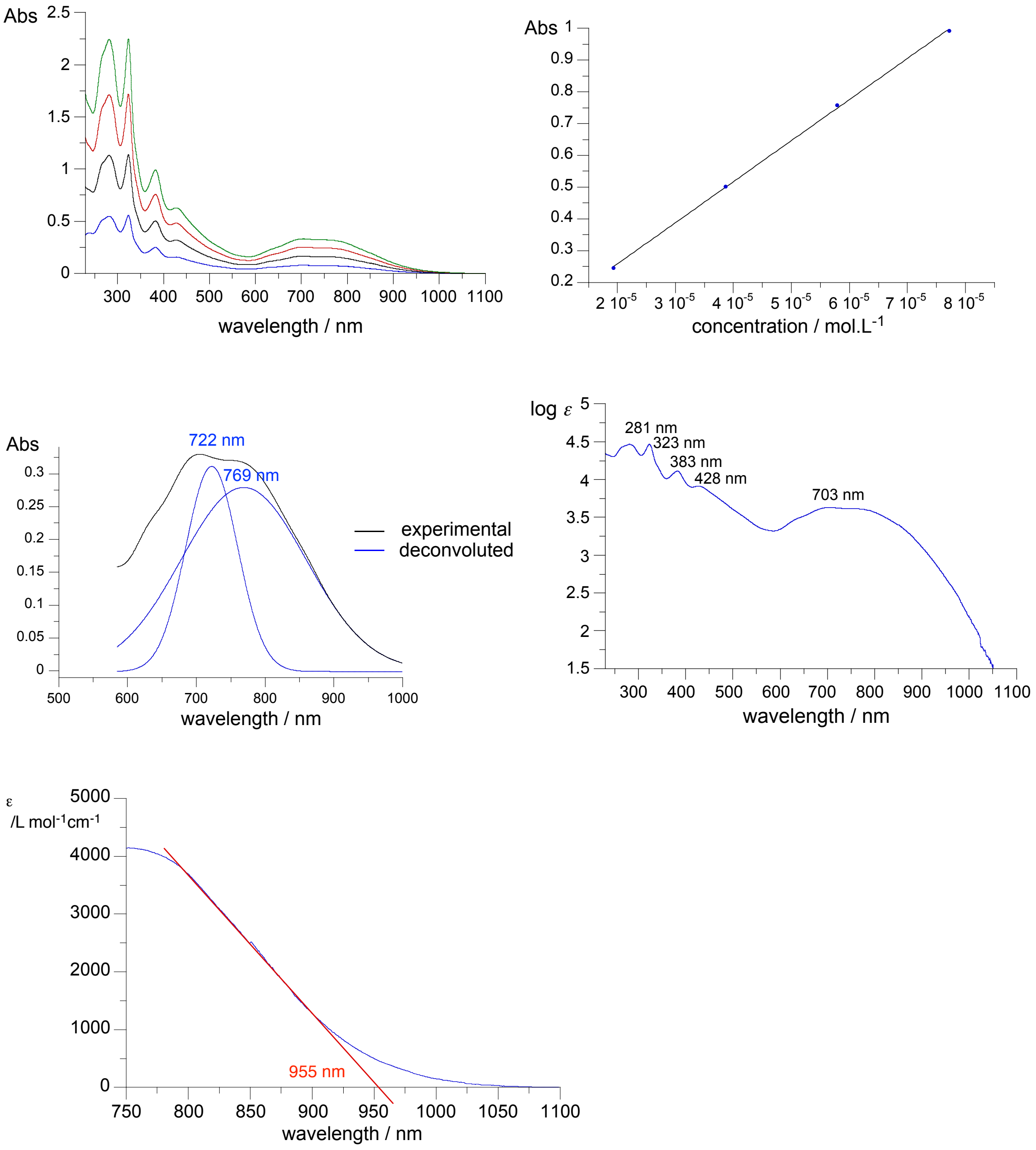


Figure S22. Clockwise: electronic absorption spectra of diradical **1[6,6]** in CH_2Cl_2 for four different concentrations, determination of molar extinction coefficient ε at λ = 382.6 nm (best fit function: ε = 12934(65)×conc, r^2 = 0.9996), molar extinction log (ε) plot, deconvolution of the lowest energy portion of the spectrum and the onset of absorption.

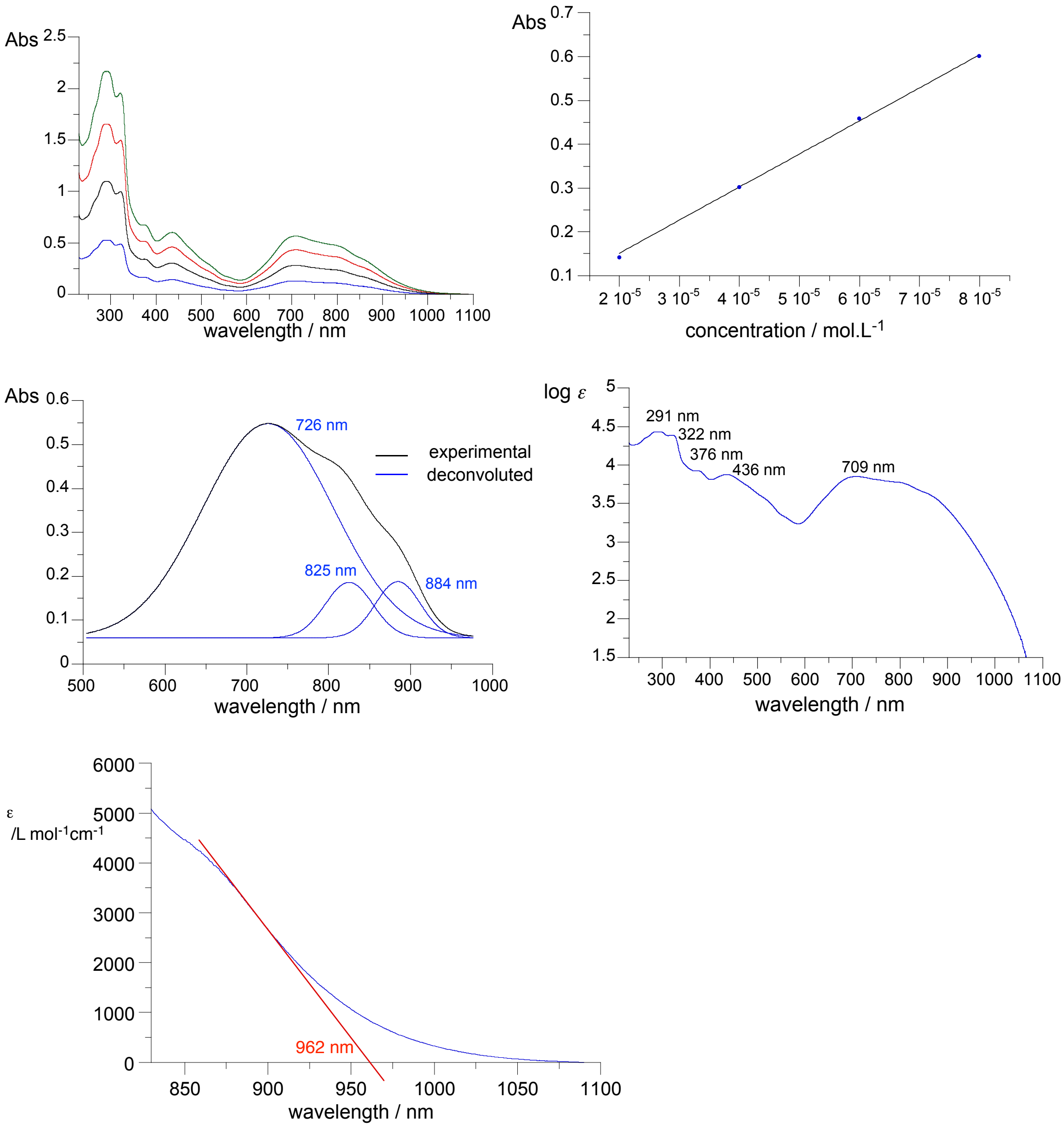


Figure S23. Clockwise: electronic absorption spectra of diradical **1[6,7]** in CH_2Cl_2 for four different concentrations, determination of molar extinction coefficient ε at λ = 435.6 nm (best fit function: ε = 7554.5(62)×conc, r^2 = 0.9988), molar extinction log (ε) plot, deconvolution of the lowest energy portion of the spectrum and the onset of absorption.

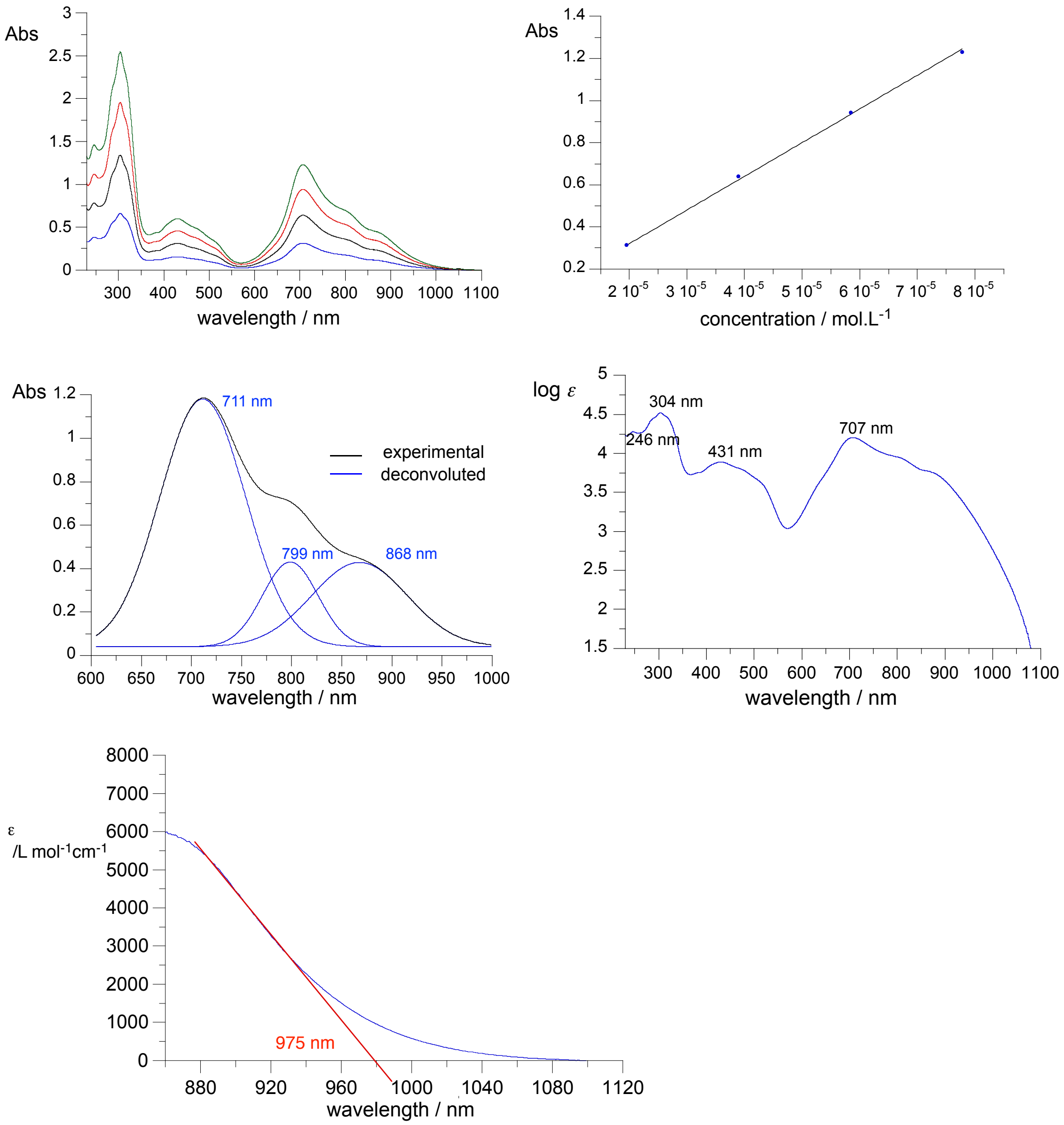


Figure S24. Clockwise: electronic absorption spectra of diradical **1[7,7]** in CH_2Cl_2 for four different concentrations, determination of molar extinction coefficient ε at λ = 706.2 nm (best fit function: ε = 16000(129)×conc, r^2 = 0.9988), molar extinction log (ε) plot, deconvolution of the lowest energy portion of the spectrum and the onset of absorption.

6. Electrochemical results

Electrochemical characterization of diradicals **1[m,n]** was conducted using a Metrohm Autolab PGSTAT 128N potentiostat/galvanostat instrument. Diradical **1[m,n]** was dissolved in dry, spectroscopic grade CH_2Cl_2 (concentration 1.5 mM) in the presence of $[n\text{-}Bu_4N]^+[PF_6]^-$ as an electrolyte (concentration 100 mM) and the resulting solution was degassed by purging with Ar gas for 20 minutes. A three-electrode electrochemical cell was used with glassy carbon disk as the working electrode (ϕ 2 mm, alumina polished), Pt wire as the counter electrode and Ag/AgCl wire as the pseudoreference electrode. All samples were measured without internal reference once and afterwards with $FcMe_{10}$ as the internal reference couple with a scan rate of 50 mV s^{-1} (CV) or 5 mV s^{-1} (DPV) at *ca.* 20 °C. The oxidation potential for the $FcMe_{10}/FcMe_{10}^{+}$couple was established at -0.556 V in CH_2Cl_2 *vs* Fc/Fc^{+}, by comparison with the oxidation potential for the Fc/Fc^{+} couple (0.0 V).

Cyclic voltammetry (CV) measurements were started from 0.0 V in the oxidative direction, while differential pulse voltammetry (DPV) measurements were conducted starting from -1.6 V in the oxidative direction (black line) and starting from 0.9 V in the reductive direction (red line). Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) plots are shown in Figures S25–S27 and numerical results are shown in Table S5.

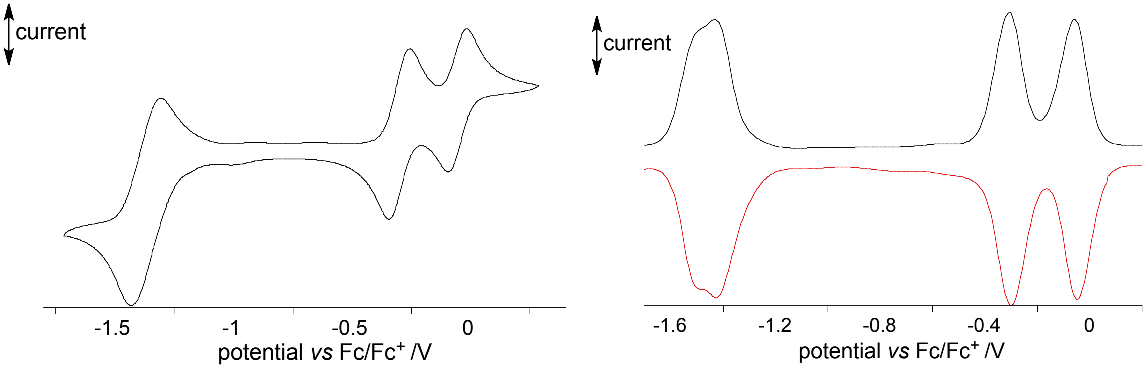


Figure S25. Cyclic voltammogram (CV, left) and differential pulse voltammogram (DPV, right) for **1[6,6]** in CH_2Cl_2 referenced to the Fc/Fc^{+} couple.

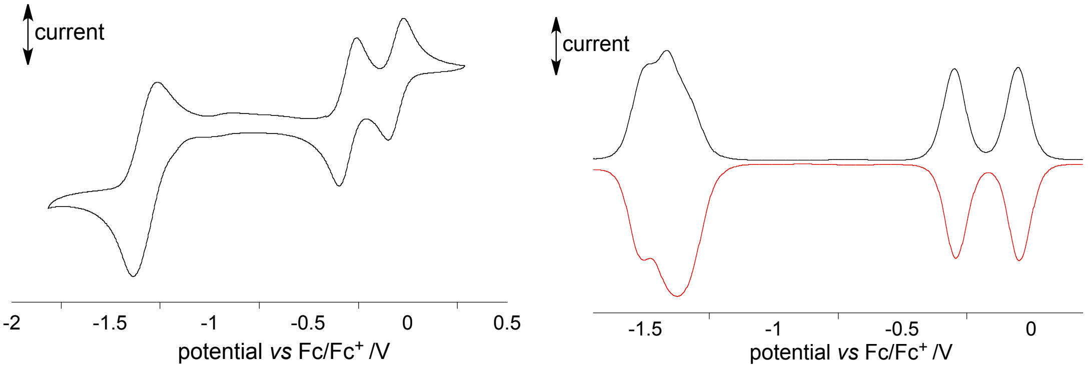


Figure S26. Cyclic voltammogram (CV, left) and differential pulse voltammogram (DPV, right) for **1[6,7]** in CH_2Cl_2 referenced to the Fc/Fc$^+$ couple.

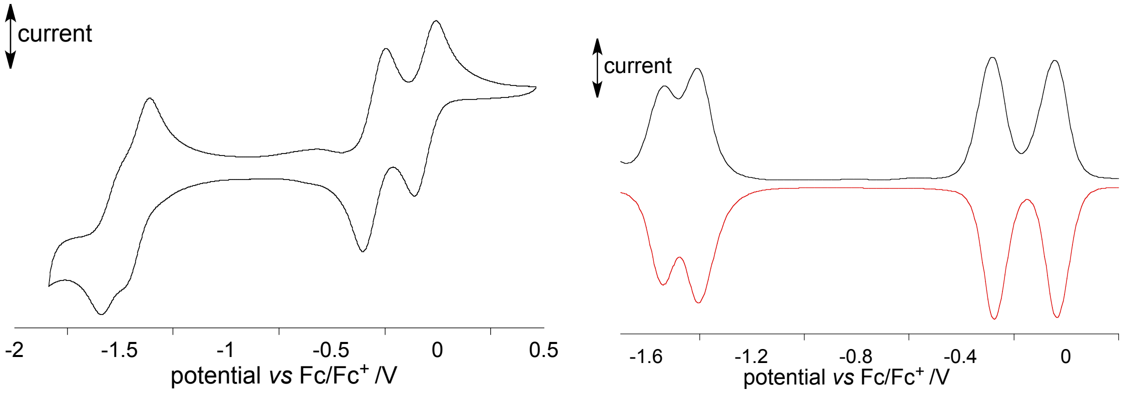


Figure S27. Cyclic voltammogram (CV, left) and differential pulse voltammogram (DPV, right) for **1[7,7]** in CH_2Cl_2 referenced to the Fc/Fc$^+$ couple.

Table S5. Electrochemical properties of diradicals **1[m,n]**.[a]

diradical	$E_{1/2}^{2-/-}$ (V)	$E_{1/2}^{-/0}$ (V)	$E_{1/2}^{0/+}$ (V)	$E_{1/2}^{+/2+}$ (V)	ΔE_{cell} (1)[b] (V)	ΔE_{cell} (2)[b] (V)
1[6,6] [c]	-1.49	-1.43	-0.30	-0.06	1.13	1.43
1[6,7] [c]	-1.52	-1.37	-0.30	-0.05	1.07	1.47
1[7,7] [c]	-1.53	-1.40	-0.28	-0.04	1.12	1.49

[a]Measured in CH_2Cl_2 $[n\text{-}Bu_4N]^+[PF_6]^-$ (100 mM), *ca.* 20 °C, 50 mVs^{-1} (CV); 5 mVs^{-1} (DPV), glassy carbon electrode. Potentials referenced to Fc/Fc$^+$). [b]$\Delta E_{\text{cell}}(1) = E_{1/2}^{+/0} - E_{1/2}^{-/0}$; $\Delta E_{\text{cell}}(2) = E_{1/2}^{+/2+} - E_{1/2}^{2-/-}$. [c] Data from DPV measurements.

7. VT EPR spectroscopy

a) sample preparation

A solution of polystyrene (500.2 mg, d = 1.04 g cm^{-3}) in dry and distilled CH_2Cl_2 (4 mL) was degassed in vacuum and diradical **1[m,n]** (1.317 mg, 2.5×10^{-3} mmol) was added and mixed till a homogenous mixture was formed. The resulting mixture was degassed in vacuum till complete evaporation of the solvent and formation of a fragile polystyrene film. The film was then dried for 1 h, divided into smaller pieces, placed in EPR tube and tightly packed using a glass rod. The EPR tube containing the sample was blown with argon gas, tightly closed, and variable temperature measurement was performed.

b) measurement

Variable temperature EPR spectra for diradicals **1[m,n]** were recorded on an X-band EMX-Nano EPR spectrometer equipped with a frequency counter and nitrogen flow temperature control (120 K to 340 K) in degassed solid polystyrene solutions (5.2 mM) at 120 K exhibit patterns with randomly oriented triplets contaminated with signal from the doublet impurity (the middle singlet). No half-field transition $|\Delta m_s| = 2$ was observed in either of the diradicals. Variable-temperature EPR spectra for diradicals **1[m,n]** are shown in the Figures S28–S30.

c) spectra analysis and simulation

EPR spectra were double integrated and the resulting DI intensities were normalized for the intensity at the lowest temperature. The resulting DI_{rel} values are shown in Tables S6–S8.

Table S6. Double integral and normalized data for **1[6,6]**.

Temp /K	DI	DI/DI$_{130}$	DI$_{rel}$•T	Temp /K	DI	DI/DI$_{130}$	DI$_{rel}$•T
130	9040	1	130	234	9930	1.0985	257.04
136	9400	1.0398	141.42	239	9890	1.094	261.47
140	9460	1.0465	146.5	244	9870	1.0918	266.4
144	9680	1.0708	154.19	249	9740	1.0774	268.28
150	9820	1.0863	162.94	254	9860	1.0907	277.04
154	9780	1.0819	166.61	259	9680	1.0708	277.34
159	9910	1.0962	174.3	264	9590	1.0608	280.06
164	9990	1.1051	181.23	269	9610	1.0631	285.96
169	9970	1.1029	186.39	274	9570	1.0586	290.06
174	10100	1.1173	194.4	279	9470	1.0476	292.27
179	10100	1.1173	199.99	284	9360	1.0354	294.05
184	10000	1.1062	203.54	289	9250	1.0232	295.71
189	10100	1.1173	211.16	294	9260	1.0243	301.15
194	10100	1.1173	216.75	299	9220	1.0199	304.95
199	10000	1.1062	220.13	304	9150	1.0122	307.7
204	10100	1.1173	227.92	309	9110	1.0077	311.39
209	10000	1.1062	231.19	314	8970	0.99226	311.57
214	10000	1.1062	236.73	319	8970	0.99226	316.53
219	10100	1.1173	244.68	324	9090	1.0055	325.79
224	9990	1.1051	247.54	329	8910	0.98562	324.27
229	9980	1.104	252.81	334	8860	0.98009	327.35

Table S7. Double integral and normalized data for **1[6,7]**.

Temp /K	DI	DI/DI_{120}	DI_{rel}•T	Temp /K	DI	DI/DI_{120}	DI_{rel}•T
120	2670	1	120	228	5060	1.8951	432.09
123	2850	1.0674	131.29	234	5070	1.8989	444.34
129	3040	1.1386	146.88	239	5030	1.8839	450.25
134	3310	1.2397	166.12	244	5130	1.9213	468.81
138	3330	1.2472	172.11	248	5210	1.9513	483.93
144	3460	1.2959	186.61	253	5320	1.9925	504.1
149	3530	1.3221	196.99	258	5340	2	516
154	3650	1.367	210.52	263	5580	2.0899	549.64
159	3950	1.4794	235.22	269	5280	1.9775	531.96
163	4170	1.5618	254.57	273	5370	2.0112	549.07
169	3980	1.4906	251.92	279	5540	2.0749	578.9
174	4370	1.6367	284.79	284	5430	2.0337	577.57
178	4330	1.6217	288.67	288	5440	2.0375	586.79
183	4350	1.6292	298.15	294	5440	2.0375	599.01
188	4430	1.6592	311.93	298	5640	2.1124	629.48
193	4620	1.7303	333.96	304	5720	2.1423	651.27
199	4630	1.7341	345.08	308	5580	2.0899	643.69
204	4640	1.7378	354.52	313	5560	2.0824	651.79
208	4840	1.8127	377.05	318	5650	2.1161	672.92
213	4870	1.824	388.51	323	5690	2.1311	688.34
219	4980	1.8652	408.47	328	5700	2.1348	700.22
224	5020	1.8801	421.15	333	5620	2.1049	700.92

Table S8. Double integral and normalized data for **1[7,7]**.

Temp /K	DI	$\mathrm{DI/DI_{149}}$	$\mathrm{DI_{rel}}$•T	Temp /K	DI	$\mathrm{DI/DI_{149}}$	$\mathrm{DI_{rel}}$•T
149	82	1	149	244	1300	15.854	3868.3
154	257	3.1341	482.66	248	1300	15.854	3931.7
159	491	5.9878	952.06	254	1380	16.829	4274.6
163	523	6.378	1039.6	258	1340	16.341	4216.1
169	641	7.8171	1321.1	263	1420	17.317	4554.4
173	701	8.5488	1478.9	269	1560	19.024	5117.6
179	741	9.0366	1617.5	274	1520	18.537	5079
184	721	8.7927	1617.9	279	1790	21.829	6090.4
188	826	10.073	1893.8	283	1490	18.171	5142.3
193	842	10.268	1981.8	288	1620	19.756	5689.8
198	879	10.72	2122.5	293	1800	21.951	6431.7
203	945	11.524	2339.5	299	1770	21.585	6454
208	892	10.878	2262.6	304	1880	22.927	6969.8
213	1040	12.683	2701.5	309	1660	20.244	6255.4
219	1120	13.659	2991.2	314	1670	20.366	6394.9
223	1180	14.39	3209	319	1780	21.707	6924.6
228	1200	14.634	3336.6	324	1640	20	6480
234	1170	14.268	3338.8	328	1720	20.976	6880
239	1350	16.463	3934.8	333	1890	23.049	7675.2

The singlet-triplet energy gap $\Delta E_{S\text{-}T}$ $(2J)$ was estimated by fitting $\mathrm{DI_{rel}}$•T to a modified Bleaney-Bowers equation[16] (eq S1).

$$\chi \bullet T = \frac{Ng^2\mu_B^2}{k}\left(\frac{2}{3+e^{-\frac{2J}{kT}}}\right)(1-\rho)+\frac{Ng^2\mu_B^2}{2k}\,\rho \qquad \text{eq S1}$$

For numeral fitting to the eq S1, a three-parameter equation S2 was used.

$$DI_{rel}\times T = m1\left(\frac{2}{3+e^{-\frac{m2}{m0}}}\right)(1-m3)+0.5\times m1\times m3 \qquad \text{eq S2}$$

Results are shown in Figures S27–S29 and in Table S9.

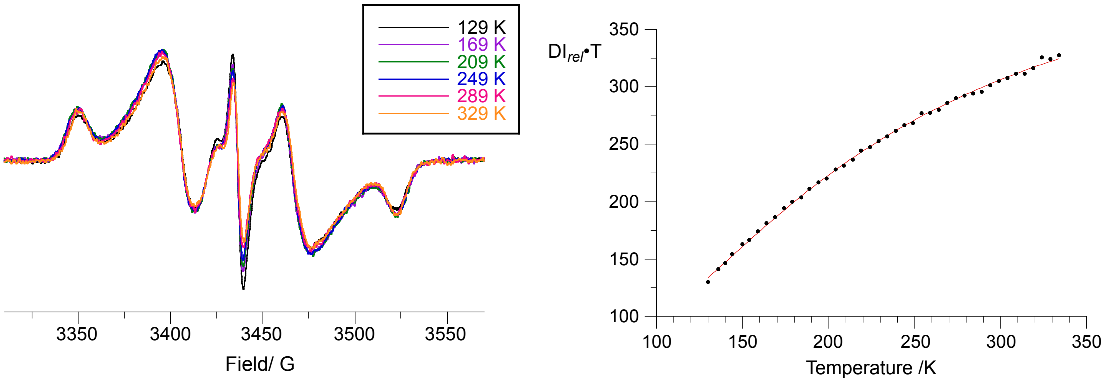


Figure S28. Determination of ΔE_{ST} for 5.2 mM diradical **1[6,6]** in polystyrene. Left: variable temperature spectra in the temperature range 129–329 K. Right: plot of DI$_{rel}$•T *vs* *T*, in the temperature range 130–334 K. Red line represents the best fitting function (eq. S2) with the following parameters: $m1$ = 950(6), $m2$ = $2J/k$ = -406(7) K, $m3$ = 0.150, r^2 = 0.999.

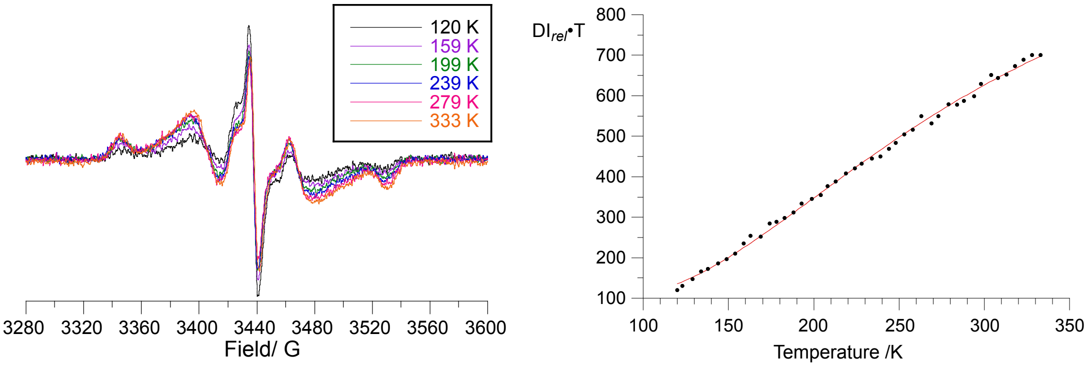


Figure S29. Determination of ΔE_{ST} for 5.2 mM diradical **1[6,7]** in polystyrene. Left: variable temperature spectra in the temperature range 120–333 K. Right: a plot of DI$_{rel}$•T *vs* *T* in the temperature range 120–333 K. The red line represents the best fitting function (eq. S2) with the following parameters: $m1$ = 2764(50), $m2$ = $2J/k$ = -569(10) K, $m3$ = 0.066, r^2 = 0.997.

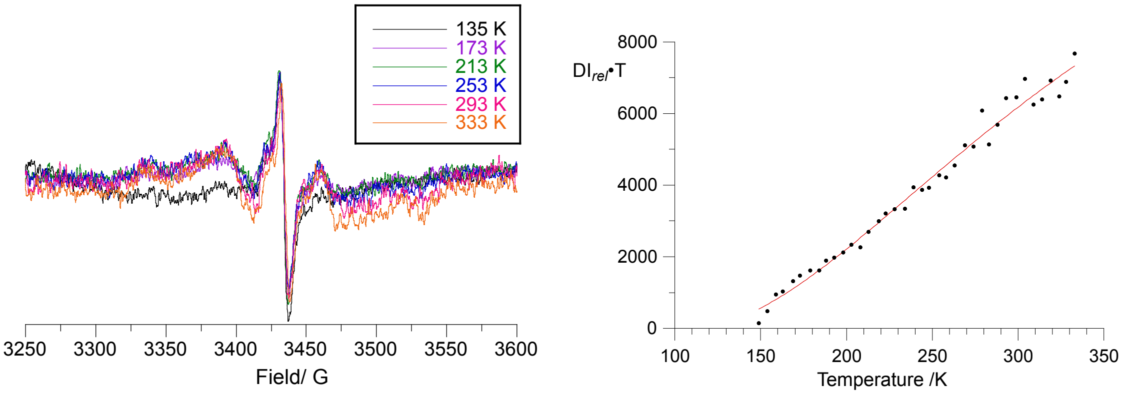


Figure S30. Determination of ΔE_{ST} for 5.2 mM diradical **1[7,7]** in polystyrene. Left: variable temperature spectra in the temperature range 135–333 K. Right: a plot of DI_{rel}•T *vs* T in the temperature range 149–333 K. The red line represents the best fitting function (eq. S2) with the following parameters: $m1$ = 39640(2965), $m2 = 2J/k$ = -673(38) K, $m3$ = -0.016(15), r^2 = 0.983.

Table S9. The singlet-triplet energy gap $\Delta E_{S\text{-}T}$ $(2J)$ for diradicals **1[m,n]** determined by fitting to the Bleaney-Bowers equation eq S1.

	Matrix	$\Delta E_{S\text{-}T}$ /kcal/mol
1[6,6]	PS	-0.81(1)
1[6,7]	PS	-1.13(2)
1[7,7]	PS	-1.33(8)

Simulation of triplet EPR spectra for diradicals **1[m,n]** was conducted using the *pepper* module in *EasySpin* (Matlab),[17] and results are shown in Figures S31–S33. Assuming an isotropic *g* value, the resulting absolute values of zero field splitting parameters (*zfp*), $|D/hc|$ and $|E/hc|$, are shown in Table S10. Assuming a point dipole approximation, the mean distance between the spin centers was estimated using equation S3.

$$r = ((D/2\mathrm{g})\times 7.19\times 10^{-5})^{-1/3} \qquad \text{eq S3}$$

where D (in gauss) is the fitting parameter in the simulated EPR spectrum.

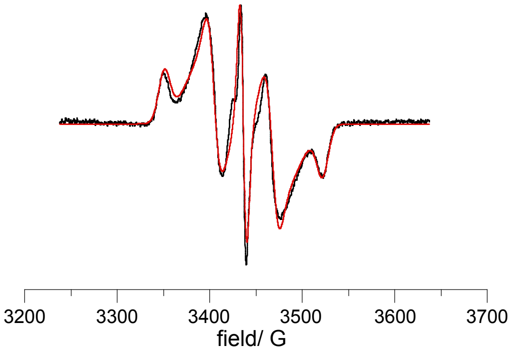


Figure S31. A complete set of fitting parameters for EPR spectrum of 5.2 mM diradical **1[6,6]** in polystyrene (119 K, ν = 9.644 GHz). Simulation $|\Delta m_S|$ = 1 region (*pepper*, *EasySpin*, rmsd = 0.0821065): Component A, weight = 1.0000, S = 1, D = 238.77 MHz, E = 16.63 MHz, g_{iso} = 2.00492; H-strain (MHz): H_x = 37.0232, H_y = 120.226, H_z = 40.7546; D-strain (MHz): D = 80.00, E = 30.00; component B, S =1/2, weight = 0.146923, g_{iso}= 2.00497, H-strain (MHz): H_x = 50.00, H_y = 50.00, H_z = 87.00.

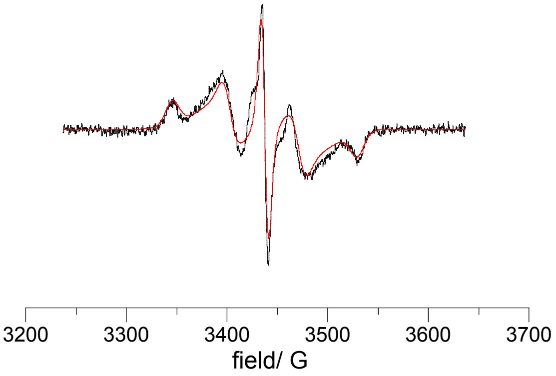


Figure S32. A complete set of fitting parameters for EPR spectrum of 5.2 mM diradical **1[6,7]** in polystyrene (253 K, ν = 9.644 GHz). Simulation $|\Delta m_S|$ = 1 region (*pepper*, *EasySpin*, rmsd = 0.0464004): Component A, weight = 1.0000, S = 1, D = 255.30 MHz, E = 16.72 MHz, g_{iso} = 2.00455, H-strain (MHz): H_x = 38.376, H_y = 169.137, H_z = 43.438; D-strain (MHz): D = 80.00, E = 30.00; component B, S =1/2, weight = 0.2324777, g_{iso} = 2.00443; H-strain (MHz): H_x = 50.00, H_y = 50.00, H_z = 87.00.

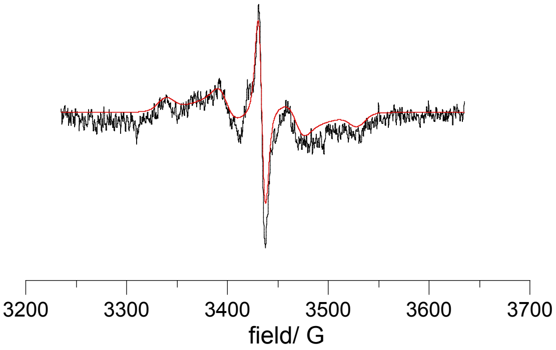


Figure S33. A complete set of fitting parameters for the EPR spectrum of 5.2 mM diradical **1[7,7]** in polystyrene (253 K, ν = 9.644 GHz). Simulation $|\Delta m_S| = 1$ region (pepper, EasySpin, rmsd = 0.0443615): Component A, weight = 1.0000, $S = 1$, $D = 263.629$ MHz, $E = 17.876$ MHz, $g_{\text{iso}} = 2.00666$; H-strain (MHz): $H_x = 42.446$, $H_y = 191.877$, $H_z = 50.029$; D-strain (MHz): $D = 80.00$, $E = 30.00$; component B, $S = 1/2$, weight = 0.294611, $g_{\text{iso}} = 2.0065$; H-strain (MHz): $H_x = 50.00$, $H_y = 50.00$, $H_z = 87.00$.

Table S10. Zero field splitting parameters simulated for di-Blatter diradicals **1[m,n]**.

compound	Matrix, temp/ K	$\|D/hc\|$ /cm^{-1}	$\|E/hc\|$ /cm^{-1}	g	r /Å ^{a}
1[6,6]	PS, 119	7.96×10^{-3}	5.54×10^{-4}	2.00492	8.68
1[6,7]	PS, 253	8.51×10^{-3}	5.57×10^{-4}	2.00455	8.49
1[7,7]	PS, 253	8.79×10^{-3}	5.96×10^{-4}	2.00666	8.40

^{a} Calculated using equation S3.

8. Stability testing

a) thermal stability

Thermal stability of diradicals **1[m,n]** was investigated with a thermogravimetric method (TGA) using a TA Instruments TGA 5500 at a heating rate of 10 K min^{-1} under nitrogen atmosphere. Results are shown in Figures S34–S36.

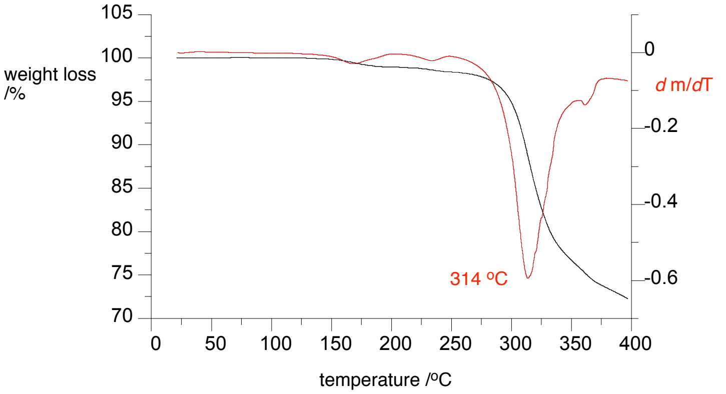


Figure S34. Termogravimetric analysis of diradical **1[6,6]**. Heating rate of 10 K min^{-1}.

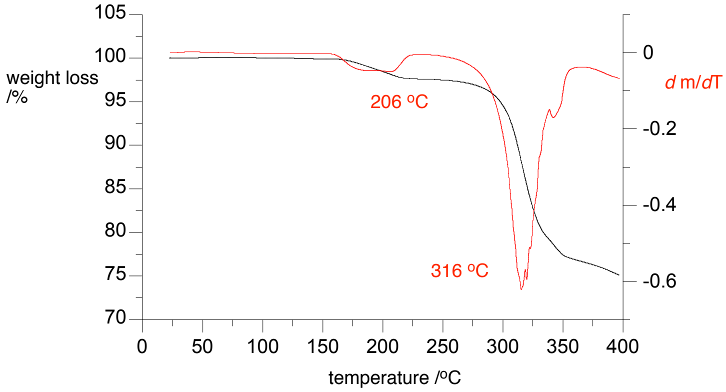


Figure S35. Termogravimetric analysis of diradical **1[6,7]**. Heating rate of 10 K min^{-1}.

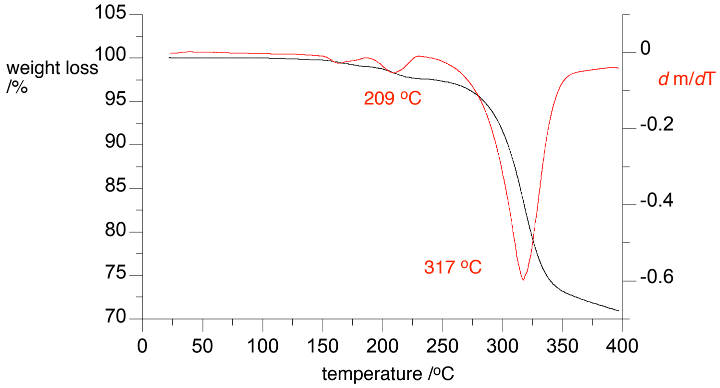


Figure S36. Termogravimetric analysis of diradical **1[7,7]**. Heating rate of 10 K min^{-1}.

b) photostability

Photostability of diradicals **1[m,n]** was investigated in CH_2Cl_2 solutions in a quartz cuvette and the absorbance at 705 nm was measured periodically. If needed, fresh solvent was added to maintain the original volume of the solution before each measurement.

Solutions of diradicals **1[m,n]** in spectroscopic grade CH_2Cl_2 and concentration of 1.0×10^{-4} mol·L^{-1} in a quartz cuvette with the optical path of 1.0 cm were irradiated with unfiltered light produced by a 400 W halogen lamp placed in a distance of 30 cm. Cuvettes were cooled during irradiation with a fan. Electronic absorption spectra of diradicals were recorded on a Jasco V770 spectrophotometer. Results are shown in Figure S37.

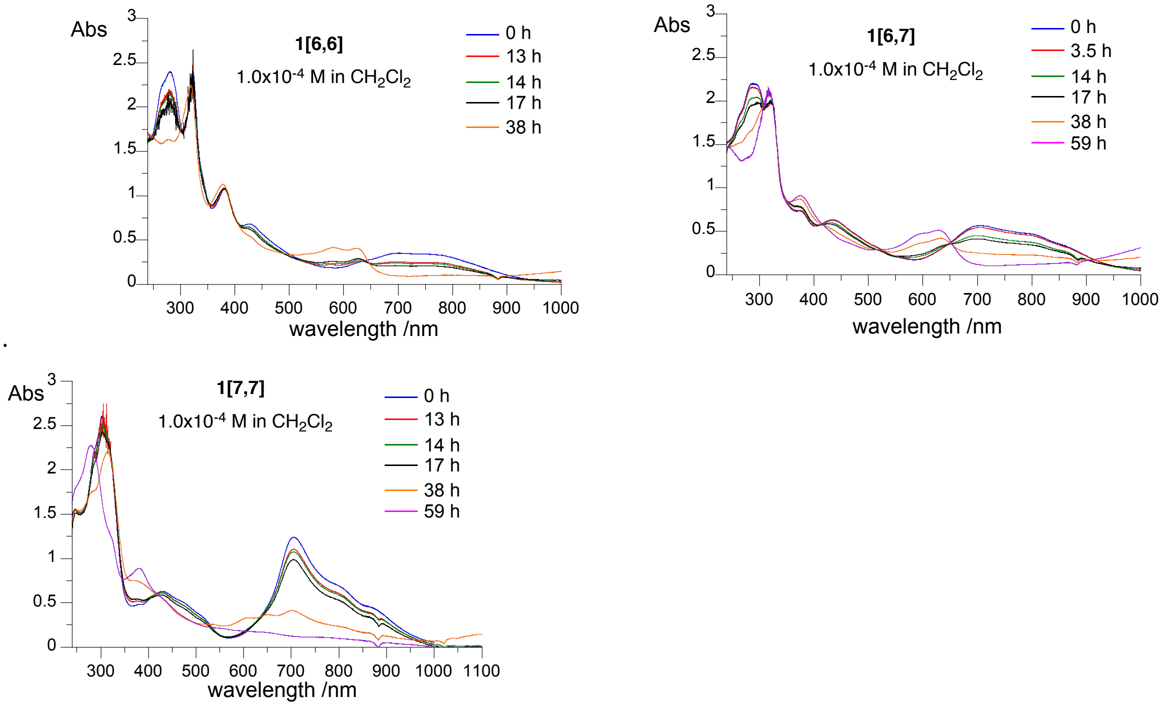
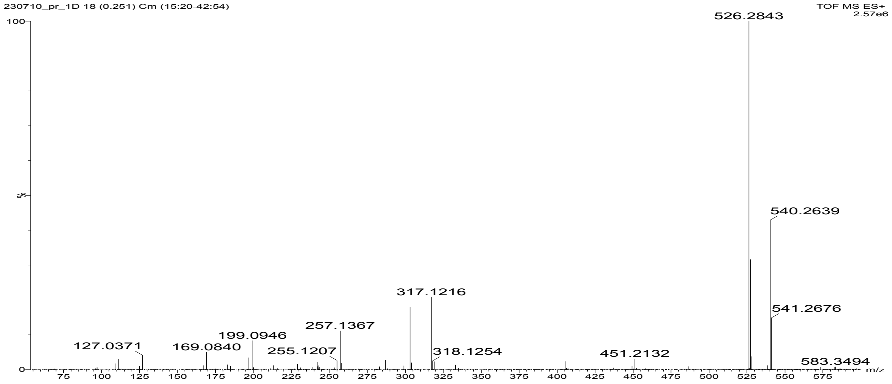


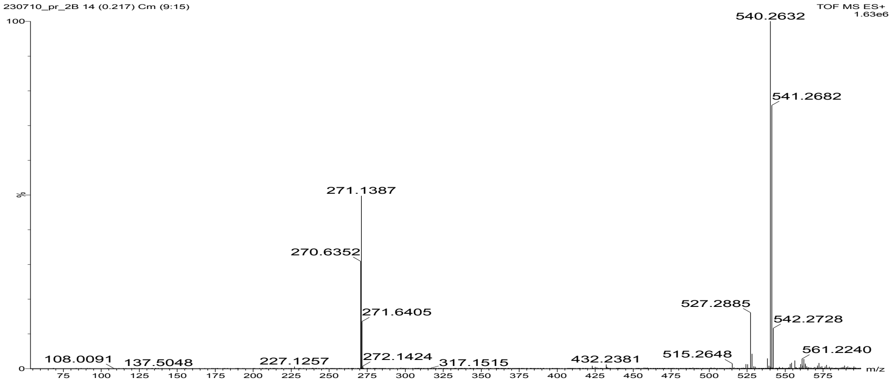
Figure S37. Electronic absorption spectra of 1.0x10-4 M solution of diradicals **1[m,n]** in CH_2Cl_2 irradiated with unfiltered white light (400 W halogen lamp)

Photodecomposition products of **1[7,7]** diradical were separated using semipreparative TLC and hexane / ethyl acetate / methanol (6:6:1) as the eluent. The resulting 6 fractions and the baseline material were analyzed by TOF MS ES(+) analysis and results are shown in Figure S38.

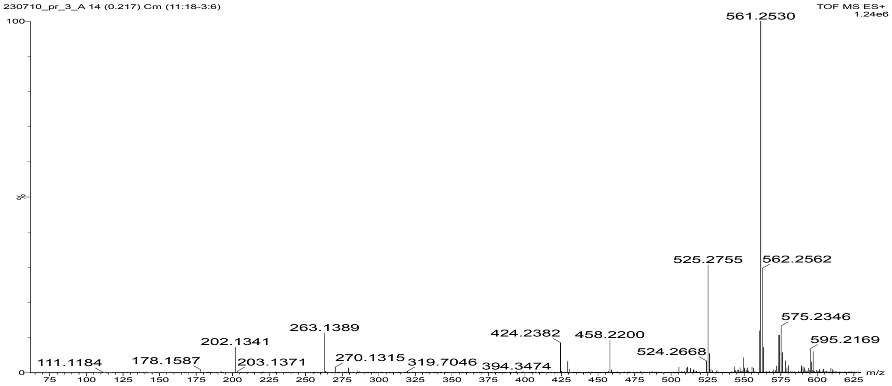
fraction 1



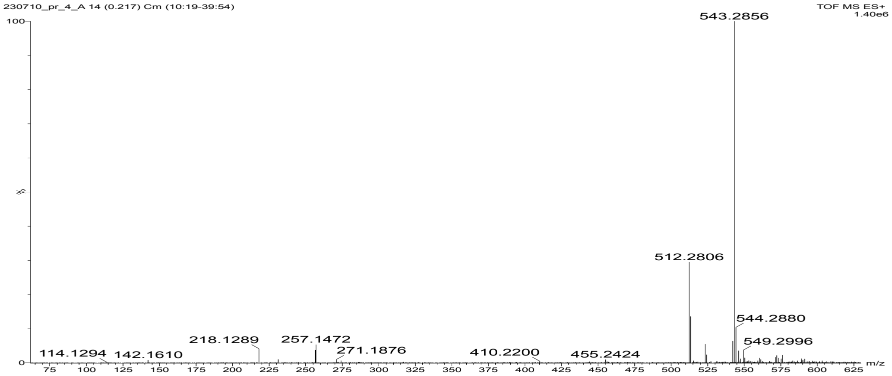
fraction 2



fraction 3



fraction 4



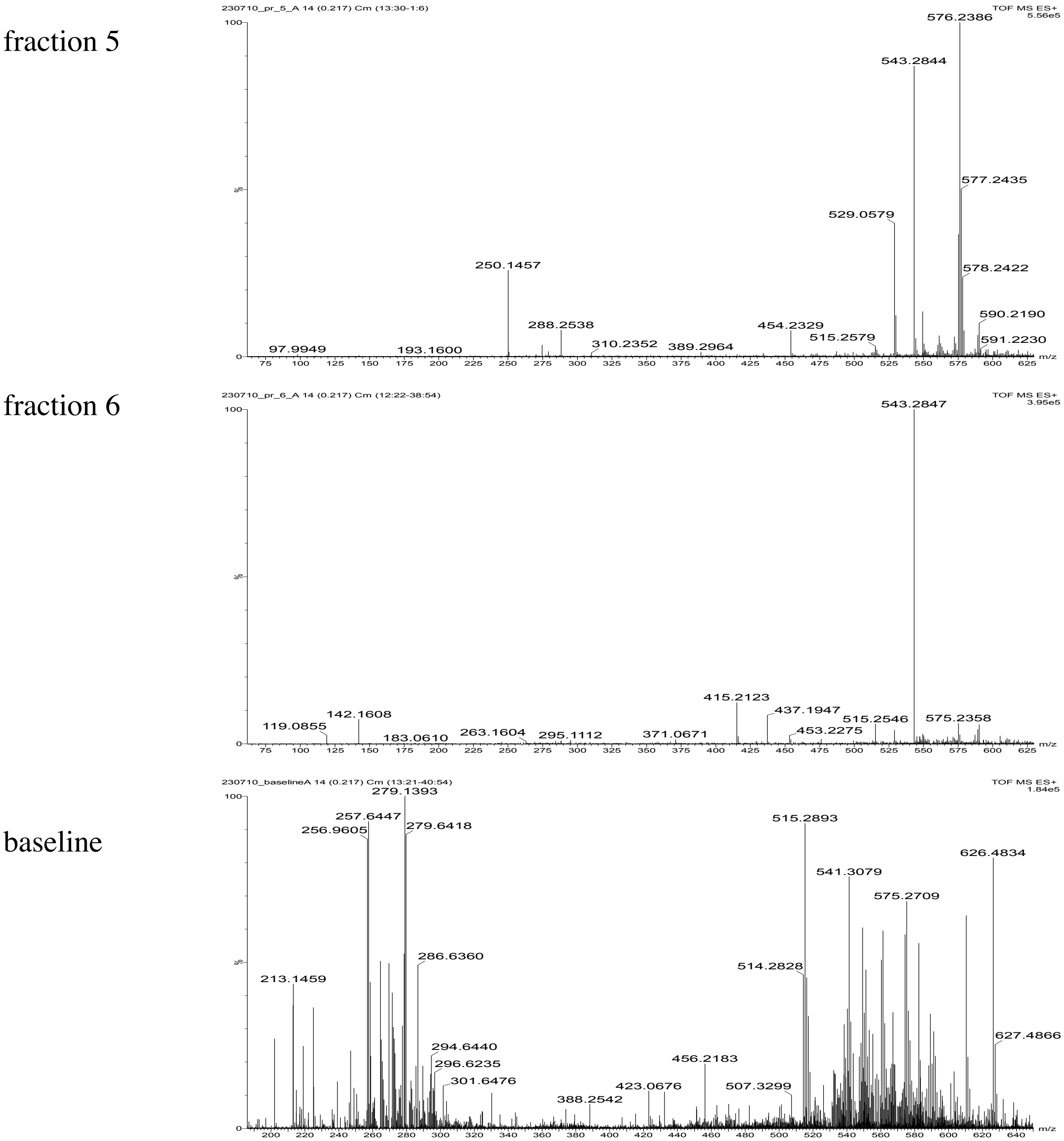


Figure S38. Mass spectra of six fractions in the order of increasing polarity from the top and the baseline material (bottom).

High-resolution mass spectrometry (HRMS) analysis was conducted for selected *m/z* peaks and results are listed in Table S11.

Table S11. High-resolution mass spectra (HRMS) results for selected *m/z* signals in the photodegradation products of diradical **1[7,7]**.[a]

Measured mass	Calculated mass	Error /mDa	/ppm	Conf /%	formula
577.2477	577.2483	-0.6	-1.0	100	$C_{34}H_{34}N_6ClO$
576.2386	576.2404	-1.8	-3.1	n/a	$C_{34}H_{33}N_6ClO$
561.2530	561.2533	-0.3	-0.5		$C_{34}H_{34}N_6Cl$
543.2857	543.2872	-1.5	-2.8	94	$C_{34}H_{34}N_9O$
540.2639	540.2638	1.5	32.8	51	$C_{34}H_{32}N_9O$
527.2923[b]	527.2901				$C_{34}H_{35}N_6$ $[M+H]^+$

[a] Obtained using the TOF MS ES(+) method. [b] HRMS for diradical **1[7,7]**.

9. Computational details

a) geometry optimization and relative energies

Quantum-mechanical calculations were carried out using Gaussian 09 suite of programs.[18] Geometry optimizations for open-shell singlet (using the broken symmetry approach **1[m,n]-OSS**), triplet (**1[m,n]-T**) and the closed-shell analoge (**1[m,n]-CS**) were undertaken at the (U)B3LYP/6-311G(d,p) level of theory in the gas phase. Vibrational frequency calculations were used to characterize the nature of the stationary points and to obtain thermodynamic parameters. The resulting energies and spin expectation values before spin annihilation are listed in Table S12.

The effective spin-spin exchange interaction J_{DFT} for each diradical was determined using the Yamaguchi procedure[19-21] (eq S3):

$$\Delta E_{S-T} = 2J = 2\frac{E_{BS}-E_T}{\langle S^2\rangle_T-\langle S^2\rangle_{BS}} \qquad \text{eq. S3}$$

where the SCF energies of the triplet (E_T) and broken symmetry singlet (E_{BS}) corrected for ZPE and total spin angular momenta $\langle S^2\rangle$ before spin annihilation. The results are shown in Table S12.

Table S12. DFT results for diradicals **1[m,n]**.[a]

Diradical	E_{SCF} /Ha	$\langle S^2 \rangle$	ZPE	ΔE_{ST} [b] /kcal mol^{-1}	ΔE_{rel} [c] /kcal mol^{-1}
1[6,6]					
OSS [d]	-1644.9505675	1.010001	0.606762		0
T	-1644.9503396	2.028708	0.606774	-0.30	0.15
CS	-1644.9304335	–	0.607068		6.02
1[6,7]					
OSS [d]	-1644.9513165	0.979631	0.606814		0
T	-1644.9503693	2.029147	0.606859	-1.19	0.62
CS	-1644.9380562	–	0.607316		8.64
1[7,7]					
OSS [d]	-1644.9517064	0.966223	0.606767		0
T	-1644.9501868	2.027059	0.606844	-1.89	1.00
CS	-1644.9412747	–	0.607415		6.95

[a] Obtained with the (U)B3LYP/6-311G(d,p) method in vacuum. [b] Calculated with the Yamaguchi protocol, ref. [19-21] using SCF energies with ZPE correction. [c] Calculates as difference of SCF energies with ZPE correction. [d] Calculated as the broken symmetry singlet[22] using the "guess(mix, always)" keyword.

b) population analysis

Bond order and electron occupancy of the bond connecting the two benzo[*e*][1,2,4]triazinyl units was obtained by NBO analysis of the UB3LYP/6-31G(2d,p) wavefunction for **1[m,n]-OSS** using keywords "Pop=NBORead" and "$nbo bndidx $end". Results are shown in Table S13.

Table S13. Results of NBO analysis of the bonding between the benzo[*e*][1,2,4]triazinyl units in **1[m,n]-OSS**.[a]

Diradical	bond	WBI	e pop BD	e pop BD*
1[6,6]	C(6)–C(6’)	1.0503	0.98302	0.0161
1[6,7]	C(6)–C(7’)	1.0640	0.98313	0.01574
1[7,7]	C(7)–C(7’)	1.0764	0.98323	0.01527

[a] Obtained from the analysis of the UB3LYP/6-311G(d,p) wavefunction.

c) diradicaloid character y_0 and alternative calculations of the S–T energy gap

Diradical character index *y* was calculated using the occupancy *n* of the lowest unoccupied natural orbital (LUNO) using the Yamaguchi equation:[19]

$$y = 1 - \frac{2T}{1+T^2} \qquad \text{eq S4}$$

where *T* is calculated using the occupation number *n* of natural orbitals derived with the UHF method

$$T = \frac{n_{HONO} - n_{LUNO}}{2} \qquad \text{eq S5}$$

y = 0 for the closed-shell and *y* = 1 for the pure singlet diradical. The occupancy numbers n_{HOMO} and n_{LUMO} were obtained from natural orbital population analysis (pop=no) using the broken symmetry UHF/6-311G(d,p) // UB3LYP/6-311G(d,p) method in gas phase.

Adiabatic singlet-triplet energy gaps, ΔE_{ST}, were obtained from the spin-flip non-collinear time-dependent DFT calculations (SF-NC-TDDFT)[23-26] at the PBE5050/6-311G(d) // UB3LYP/6-311G(d,p) level of theory using the Q-Chem 5.4 computational package.

d) electronic excitation data

Electronic excitation energies in CH_2Cl_2 dielectric medium were obtained for diradicals **1[m,n]** at the UB3LYP/6-311++G(d,p) // UB3LYP/6-311G(d,p) level of theory using time-dependent DFT method supplied in the Gaussian 09 package. Solvation models in calculations were implemented by PCM model using the SCRF(solvent=CH2CL2) keyword. Other keywords: “guess=mix SCF=xqc nosymm”. Energies of FMOs involved in the low energy transitions are listed in Table S14.

Table S14. Calculated energies for selected MOs.[a]

Radical	α-HOMO-1 /eV	α-HOMO /eV	α-LUMO /eV	α-LUMO+1 /eV	β-HOMO-1 /eV	β-HOMO /eV	β-LUMO /eV	β-LUMO+1 /eV
1[6,6]	-6.584	-4.865	-2.932	-1.530	-6.586	-4.866	-2.927	-1.531
1[6,7]	-6.508	-4.878	-2.949	-1.530	-6.533	-4.852	-2.947	-1.551
1[7,7]	-6.502	-4.863	-2.957	-1.511	-6.496	-4.861	-2.965	-1.511
2	-6.9215	-4.869	-1.122	-0.992	-6.607	–	-2.871	-1.033

[a] Obtained with the TD UB3LYP/6-311++G(d,p) // UB3LYP/6-311G(d,p) method in CH_2Cl_2 dielectric medium.

e) partial output from TD-DFT calculations

```
Open-shell singlet at
UB3LYP/6-311++G(d,p)// UB3LYP/6-311G(d,p) in CH2Cl2
```

1[6,6]-OSS

```
Excited state symmetry could not be determined.
 Excited State   1:  1.257-?Sym    1.4929 eV  830.50 nm  f=0.0065  <S**2>=0.145
    140A -> 141A       0.84574
    140B -> 141B      -0.52015
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -1644.92229668
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited state symmetry could not be determined.
 Excited State   2:  1.238-?Sym    1.5048 eV  823.91 nm  f=0.0957  <S**2>=0.133
    140A -> 141A       0.51496
    140B -> 141B       0.84249

 Excited state symmetry could not be determined.
 Excited State   3:  2.249-?Sym    2.3782 eV  521.35 nm  f=0.0006  <S**2>=1.014
    140A -> 142A       0.60622
    140A -> 143A       0.14979
    140A -> 145A      -0.11631
    140A -> 146A      -0.16815
    140B -> 142B       0.65019
    140B -> 143B      -0.16257
    140B -> 145B       0.12294
```

```
   140B -> 146B       0.16258

Excited state symmetry could not be determined.
Excited State   4:  2.340-?Sym    2.4331 eV  509.57 nm  f=0.0509  <S**2>=1.119
   140A -> 142A       0.65402
   140A -> 143A       0.12567
   140A -> 145A      -0.13760
   140A -> 146A      -0.17734
   140B -> 142B      -0.61301
   140B -> 143B       0.11728
   140B -> 145B      -0.12976
   140B -> 146B      -0.15058

Excited state symmetry could not be determined.
Excited State   5:  2.350-?Sym    2.6123 eV  474.62 nm  f=0.0053  <S**2>=1.131
   137A -> 141A       0.10471
   138A -> 141A       0.16145
   139A -> 141A       0.66108
   137B -> 141B      -0.11308
   138B -> 141B       0.14131
   139B -> 141B      -0.61688
   140B -> 143B      -0.10909

Excited state symmetry could not be determined.
Excited State   6:  2.355-?Sym    2.6582 eV  466.43 nm  f=0.0603  <S**2>=1.136
   137A -> 141A       0.17196
   138A -> 141A       0.18130
   139A -> 141A       0.58703
   140A -> 143A      -0.12800
   137B -> 141B       0.21418
   138B -> 141B      -0.18099
   139B -> 141B       0.62584
   140B -> 143B      -0.12643

Excited state symmetry could not be determined.
Excited State   7:  2.288-?Sym    2.8187 eV  439.86 nm  f=0.0014  <S**2>=1.059
   134A -> 141A       0.19440
   136A -> 141A      -0.42474
   137A -> 141A       0.69453
   138A -> 141A       0.14395
   139A -> 141A      -0.17674
   136B -> 141B      -0.20757
   137B -> 141B      -0.34722
   140B -> 143B       0.11723

Excited state symmetry could not be determined.
Excited State   8:  2.298-?Sym    2.8270 eV  438.56 nm  f=0.0171  <S**2>=1.071
   136A -> 141A      -0.21279
   137A -> 141A       0.30012
   140A -> 143A       0.28370
   134B -> 141B       0.17665
   135B -> 141B      -0.10743
   136B -> 141B       0.43131
   137B -> 141B       0.63713
   139B -> 141B      -0.17781
   140B -> 143B       0.18051

Excited state symmetry could not be determined.
```

```
 Excited State   9:  2.320-?Sym    2.8674 eV  432.40 nm  f=0.1470  <S**2>=1.095
    137A -> 141A      -0.17551
    138A -> 141A      -0.13494
    139A -> 141A       0.26804
    140A -> 143A       0.37253
    140A -> 144A      -0.10447
    137B -> 141B      -0.20396
    139B -> 141B       0.20481
    140B -> 142B       0.21007
    140B -> 143B       0.69442
    140B -> 144B      -0.17701
    140B -> 146B      -0.11354

 Excited state symmetry could not be determined.
 Excited State  10:  2.333-?Sym    2.8726 eV  431.61 nm  f=0.0120  <S**2>=1.111
    140A -> 142A      -0.23276
    140A -> 143A       0.70370
    140A -> 144A      -0.15398
    140A -> 146A      -0.14809
    137B -> 141B      -0.18809
    138B -> 141B       0.13161
    139B -> 141B       0.22182
    140B -> 142B      -0.15424
    140B -> 143B      -0.42925
```

1[6,7]-OSS

```
Excited State   1:  1.307-?Sym    1.4204 eV  872.90 nm  f=0.0030  <S**2>=0.177
    140A -> 141A      -0.64685
    140B -> 141B       0.75210
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -1644.92558327
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited state symmetry could not be determined.
 Excited State   2:  1.194-?Sym    1.5134 eV  819.22 nm  f=0.1862  <S**2>=0.106
    140A -> 141A       0.74707
    140B -> 141B       0.64628

 Excited state symmetry could not be determined.
 Excited State   3:  2.257-?Sym    2.3658 eV  524.08 nm  f=0.0106  <S**2>=1.024
    140A -> 142A      -0.24128
    140B -> 142B       0.86050
    140B -> 143B      -0.23482
    140B -> 147B       0.25417

 Excited state symmetry could not be determined.
 Excited State   4:  2.327-?Sym    2.4213 eV  512.05 nm  f=0.0139  <S**2>=1.103
    140A -> 141A       0.10924
    140A -> 142A       0.87335
    140A -> 143A      -0.10605
    140A -> 144A       0.15907
    140A -> 146A      -0.14587
    140A -> 147A       0.20748
    140B -> 142B       0.25475

 Excited state symmetry could not be determined.
```

```
Excited State   5:  2.311-?Sym    2.5782 eV  480.89 nm  f=0.0476  <S**2>=1.086
   137A -> 141A      -0.13449
   138A -> 141A       0.15088
   139A -> 141A       0.86805
   138B -> 141B       0.13903
   139B -> 141B       0.28035
   140B -> 143B      -0.18252

Excited state symmetry could not be determined.
Excited State   6:  2.375-?Sym    2.6345 eV  470.63 nm  f=0.0229  <S**2>=1.160
   139A -> 141A      -0.30596
   137B -> 141B       0.18142
   138B -> 141B       0.33937
   139B -> 141B       0.81054

Excited state symmetry could not be determined.
Excited State   7:  2.308-?Sym    2.8233 eV  439.14 nm  f=0.0194  <S**2>=1.081
   135A -> 141A      -0.13823
   137A -> 141A      -0.52001
   140A -> 143A       0.18068
   135B -> 141B      -0.15959
   137B -> 141B       0.60770
   139B -> 141B      -0.11218
   140B -> 143B       0.40679

Excited state symmetry could not be determined.
Excited State   8:  2.313-?Sym    2.8268 eV  438.61 nm  f=0.0226  <S**2>=1.088
   135A -> 141A       0.10879
   137A -> 141A       0.43106
   140A -> 143A      -0.10245
   135B -> 141B      -0.17094
   137B -> 141B       0.66800
   138B -> 141B       0.12011
   139B -> 141B      -0.22712
   140B -> 142B      -0.10774
   140B -> 143B      -0.41002

Excited state symmetry could not be determined.
Excited State   9:  2.348-?Sym    2.8466 eV  435.55 nm  f=0.0812  <S**2>=1.129
   134A -> 141A       0.13518
   135A -> 141A       0.11763
   137A -> 141A       0.59182
   139A -> 141A       0.21099
   140A -> 143A       0.35844
   140A -> 144A      -0.19652
   140B -> 142B       0.15787
   140B -> 143B       0.51843
   140B -> 144B      -0.10976

Excited state symmetry could not be determined.
Excited State  10:  2.306-?Sym    2.8941 eV  428.40 nm  f=0.0165  <S**2>=1.079
   137A -> 141A      -0.12149
   140A -> 142A       0.21937
   140A -> 143A       0.60977
   140A -> 144A      -0.41113
   140A -> 147A      -0.10488
   138B -> 141B      -0.16352
   139B -> 141B       0.20415
```

```
    140B -> 142B      -0.15418
    140B -> 143B      -0.43800
    140B -> 144B       0.13111

 Excited state symmetry could not be determined.
 Excited State  11:  2.371-?Sym    3.2396 eV  382.72 nm  f=0.1455  <S**2>=1.156
    138A -> 141A       0.17348
    140A -> 143A       0.29821
    140A -> 144A      -0.16321
    140A -> 146A      -0.13248
    140A -> 147A       0.19207
    132B -> 141B       0.12724
    133B -> 141B      -0.11138
    134B -> 141B      -0.10382
    137B -> 141B      -0.15518
    138B -> 141B       0.75954
    139B -> 141B      -0.24751

 Excited state symmetry could not be determined.
 Excited State  12:  2.468-?Sym    3.2753 eV  378.55 nm  f=0.0157  <S**2>=1.272
    134A -> 141A      -0.13071
    136A -> 141A       0.17135
    138A -> 141A      -0.30145
    140A -> 142A      -0.13487
    140A -> 143A       0.23858
    140A -> 144A       0.25422
    140A -> 145A       0.57248
    140A -> 147A       0.32966
    140A -> 148A      -0.13903
    132B -> 141B       0.21743
    140B -> 144B      -0.12613
    140B -> 145B      -0.21535
    140B -> 146B      -0.10301
    140B -> 148B      -0.14293
```

1[7,7]-OSS

```
Excited state symmetry could not be determined.
 Excited State   1:  1.344-?Sym    1.3732 eV  902.87 nm  f=0.0005  <S**2>=0.202
    140A -> 141A      -0.67194
    140B -> 141B       0.72529
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -1644.92759468
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited state symmetry could not be determined.
 Excited State   2:  1.185-?Sym    1.4909 eV  831.61 nm  f=0.2018  <S**2>=0.101
    140A -> 141A       0.72500
    140B -> 141B       0.67172

 Excited state symmetry could not be determined.
 Excited State   3:  2.187-?Sym    2.4142 eV  513.56 nm  f=0.0004  <S**2>=0.946
    140A -> 142A      -0.53929
    140A -> 143A      -0.19749
    140A -> 147A      -0.14228
    140B -> 142B       0.68461
    140B -> 143B      -0.23805
    140B -> 147B      -0.17687
```

```
Excited state symmetry could not be determined.
Excited State   4:  2.396-?Sym    2.4267 eV  510.91 nm  f=0.0142  <S**2>=1.185
   140A -> 142A       0.70108
   140A -> 143A       0.17868
   140A -> 147A       0.18811
   139B -> 141B       0.11381
   140B -> 142B       0.56086
   140B -> 143B      -0.13412
   140B -> 147B      -0.14573

Excited state symmetry could not be determined.
Excited State   5:  2.288-?Sym    2.5902 eV  478.66 nm  f=0.0133  <S**2>=1.059
   138A -> 141A       0.13157
   139A -> 141A      -0.31219
   140A -> 143A      -0.19206
   137B -> 141B      -0.15395
   138B -> 141B       0.24789
   139B -> 141B       0.82653

Excited state symmetry could not be determined.
Excited State   6:  2.363-?Sym    2.6225 eV  472.77 nm  f=0.0439  <S**2>=1.146
   137A -> 141A       0.13409
   138A -> 141A      -0.25084
   139A -> 141A       0.82547
   139B -> 141B       0.32425
   140B -> 143B       0.19995

Excited state symmetry could not be determined.
Excited State   7:  2.304-?Sym    2.8158 eV  440.31 nm  f=0.1214  <S**2>=1.077
   135A -> 141A      -0.11558
   137A -> 141A      -0.37652
   138A -> 141A       0.12554
   140A -> 142A       0.13310
   140A -> 143A      -0.47657
   140A -> 144A       0.22466
   137B -> 141B       0.27104
   140B -> 142B       0.16332
   140B -> 143B       0.54177
   140B -> 144B      -0.25423

Excited state symmetry could not be determined.
Excited State   8:  2.342-?Sym    2.8239 eV  439.05 nm  f=0.0046  <S**2>=1.121
   135A -> 141A      -0.12602
   137A -> 141A      -0.41027
   140A -> 142A      -0.19730
   140A -> 143A       0.53611
   140A -> 144A      -0.17414
   135B -> 141B       0.13595
   137B -> 141B      -0.41861
   140B -> 142B       0.16230
   140B -> 143B       0.39758
   140B -> 144B      -0.11493

Excited state symmetry could not be determined.
Excited State   9:  2.330-?Sym    2.8462 eV  435.61 nm  f=0.0522  <S**2>=1.107
   135A -> 141A       0.20223
   137A -> 141A       0.71904
```

```
      139A -> 141A      -0.25152
      140B -> 142B       0.21534
      140B -> 143B       0.48380
      140B -> 144B      -0.17747

 Excited state symmetry could not be determined.
 Excited State  10:  2.326-?Sym    2.8559 eV  434.13 nm  f=0.0487  <S**2>=1.103
      140A -> 142A      -0.19101
      140A -> 143A       0.43061
      140A -> 144A      -0.14888
      135B -> 141B      -0.22337
      137B -> 141B       0.76144
      139B -> 141B       0.24864

 Excited state symmetry could not be determined.
 Excited State  11:  2.405-?Sym    3.2609 eV  380.22 nm  f=0.0004  <S**2>=1.197
      132A -> 141A       0.11000
      137A -> 141A       0.10657
      138A -> 141A       0.57370
      139A -> 141A       0.18343
      140A -> 144A      -0.12908
      140A -> 145A       0.10074
      140A -> 148A       0.10029
      132B -> 141B      -0.11881
      138B -> 141B       0.60982
      139B -> 141B      -0.18295
      140B -> 144B      -0.19624

 Excited state symmetry could not be determined.
 Excited State  12:  2.470-?Sym    3.2741 eV  378.69 nm  f=0.0357  <S**2>=1.275
      132A -> 141A      -0.11362
      138A -> 141A      -0.35592
      139A -> 141A      -0.11321
      140A -> 143A       0.13130
      140A -> 144A       0.44340
      140A -> 145A       0.21387
      140A -> 146A      -0.21093
      140A -> 147A       0.28988
      140A -> 148A       0.13931
      133B -> 141B      -0.13029
      138B -> 141B       0.27029
      140B -> 143B      -0.10391
      140B -> 144B      -0.29186
      140B -> 145B      -0.15281
      140B -> 146B       0.13669
      140B -> 147B      -0.19619
      140B -> 148B       0.10981
```

2

```
Excited State   1:  2.086-A      2.5329 eV  489.49 nm  f=0.0079  <S**2>=0.838
      71A -> 72A        0.85409
      71A -> 73A        0.43562
      71A -> 74A       -0.15575
      66B -> 71B        0.11413
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -822.995471851
 Copying the excited state density for this state as the 1-particle RhoCI
density.
```

```
 Excited State   2:  2.108-A      2.6522 eV  467.48 nm  f=0.0352  <S**2>=0.861
     71A -> 72A        -0.17265
     71A -> 73A         0.11542
     67B -> 71B        -0.10023
     69B -> 71B         0.26339
     70B -> 71B         0.90787

 Excited State   3:  2.053-A      2.8379 eV  436.88 nm  f=0.0037  <S**2>=0.804
     71A -> 72A         0.11567
     71A -> 73A        -0.17071
     68B -> 71B        -0.23193
     69B -> 71B         0.90088
     70B -> 71B        -0.23105

 Excited State   4:  2.105-A      2.9486 eV  420.48 nm  f=0.0831  <S**2>=0.858
     71A -> 72A        -0.41221
     71A -> 73A         0.81710
     71A -> 74A        -0.11739
     66B -> 71B         0.12709
     67B -> 71B         0.10870
     69B -> 71B         0.16135
     70B -> 71B        -0.22246

 Excited State   5:  2.123-A      3.2961 eV  376.15 nm  f=0.0057  <S**2>=0.877
     71A -> 73A         0.19244
     71A -> 74A         0.92796
     71A -> 75A         0.12781
     67B -> 71B        -0.11399
     68B -> 71B        -0.15296

 Excited State   6:  2.393-A      3.4684 eV  357.46 nm  f=0.0050  <S**2>=1.181
     68A -> 74A        -0.11483
     70A -> 72A        -0.12517
     70A -> 73A         0.13332
     71A -> 74A        -0.20673
     71A -> 75A         0.71946
     66B -> 71B         0.32512
     67B -> 71B        -0.34970
     67B -> 72B         0.13890
     67B -> 73B         0.11102
     68B -> 74B         0.11979
     70B -> 73B         0.14441

 Excited State   7:  2.236-A      3.6616 eV  338.61 nm  f=0.0987  <S**2>=1.000
     70A -> 72A         0.13370
     71A -> 72A         0.11027
     71A -> 73A        -0.14025
     71A -> 74A         0.15754
     71A -> 75A         0.31916
     66B -> 71B         0.40895
     67B -> 71B         0.59076
     68B -> 71B         0.40126
     69B -> 71B         0.14698
     70B -> 73B        -0.13351

 Excited State   8:  2.103-A      3.7790 eV  328.09 nm  f=0.0146  <S**2>=0.856
     65B -> 71B         0.10539
```

```
      66B -> 71B        -0.35818
      67B -> 71B        -0.33021
      68B -> 71B         0.80664
      69B -> 71B         0.17935

 Excited State   9:  2.127-A      3.8408 eV  322.81 nm  f=0.1085  <S**2>=0.881
      70A -> 73A         0.10041
      71A -> 72A        -0.12396
      71A -> 75A        -0.51293
      66B -> 71B         0.66096
      67B -> 71B        -0.29929
      68B -> 71B         0.22470
      70B -> 72B         0.21875
```

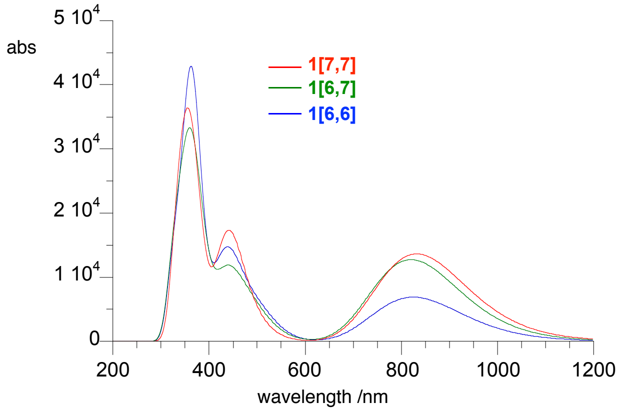


Figure S39. Results of UV-vis spectral simulation based on the TD UB3LYP/6-311++G(d,p) // UB3LYP/6-311G(d,p) results. The Half-Width (HWHH) in the Gaussian line-shape function is set at 0.2 eV.

f) MO energies obtained with UB3LYP/6-311++G(d,p) method

```
UB3LYP/6-311++G(d,p)// UB3LYP/6-311G(d,p) in CH2Cl2
Open-shell singlet (OSS)
```

1[6,6]-OSS

```
Alpha  occ. eigenvalues --   -0.28409  -0.27820  -0.27575  -0.27303  -0.27179
Alpha  occ. eigenvalues --   -0.26660  -0.26346  -0.25395  -0.24195  -0.17879
Alpha virt. eigenvalues --   -0.10776  -0.05622  -0.03819  -0.03394  -0.02971
Alpha virt. eigenvalues --   -0.02839  -0.02737  -0.01290  -0.01064  -0.00739

Beta  occ. eigenvalues --   -0.28499  -0.27784  -0.27570  -0.27311  -0.27113
Beta  occ. eigenvalues --   -0.26726  -0.26298  -0.25425  -0.24202  -0.17882
Beta virt. eigenvalues --   -0.10756  -0.05625  -0.03814  -0.03408  -0.02974
Beta virt. eigenvalues --   -0.02841  -0.02722  -0.01257  -0.01096  -0.00737
```

1[6,7]-OSS

```
Alpha  occ. eigenvalues --   -0.28510  -0.27686  -0.27602  -0.27255  -0.27229
Alpha  occ. eigenvalues --   -0.26844  -0.26436  -0.25678  -0.23918  -0.17927
Alpha virt. eigenvalues --   -0.10839  -0.05623  -0.03977  -0.03590  -0.02975
Alpha virt. eigenvalues --   -0.02836  -0.02441  -0.01281  -0.01145  -0.00657
```

```
Beta  occ. eigenvalues --   -0.27979  -0.27923  -0.27663  -0.27459  -0.27353
Beta  occ. eigenvalues --   -0.26958  -0.26443  -0.25327  -0.24009  -0.17830
Beta virt. eigenvalues --   -0.10831  -0.05699  -0.04090  -0.03455  -0.02925
Beta virt. eigenvalues --   -0.02815  -0.02304  -0.01456  -0.01140  -0.00674
```

1[7,7]-OSS

```
Alpha  occ. eigenvalues --   -0.28147  -0.27871  -0.27712  -0.27572  -0.27306
 Alpha  occ. eigenvalues --   -0.27027  -0.26489  -0.25642  -0.23896  -0.17870
 Alpha virt. eigenvalues --   -0.10868  -0.05553  -0.04248  -0.03693  -0.02985
 Alpha virt. eigenvalues --   -0.02863  -0.02064  -0.01288  -0.01106  -0.00700

Beta  occ. eigenvalues --   -0.28109  -0.27889  -0.27719  -0.27531  -0.27314
Beta  occ. eigenvalues --   -0.27013  -0.26512  -0.25664  -0.23874  -0.17865
Beta virt. eigenvalues --   -0.10897  -0.05552  -0.04234  -0.03696  -0.02991
Beta virt. eigenvalues --   -0.02847  -0.02076  -0.01251  -0.01108  -0.00738
```

2

```
Alpha  occ. eigenvalues --   -0.29713  -0.27884  -0.27506  -0.26923  -0.25436
Alpha  occ. eigenvalues --   -0.17894

Alpha virt. eigenvalues --  -0.04124  -0.03644 -0.02838 -0.01253 -0.00944

Beta occ. eigenvalues --  -0.35321  -0.34406  -0.33228 -0.32423  -0.31345
Beta occ. eigenvalues --  -0.27963  -0.27590  -0.27245 -0.26321  -0.24280
Beta virt. eigenvalues --  -0.10550  -0.03795  -0.03289 -0.02674 -0.00944
Beta virt. eigenvalues --  -0.00306  -0.00036   0.00210 0.01259   0.01695
```

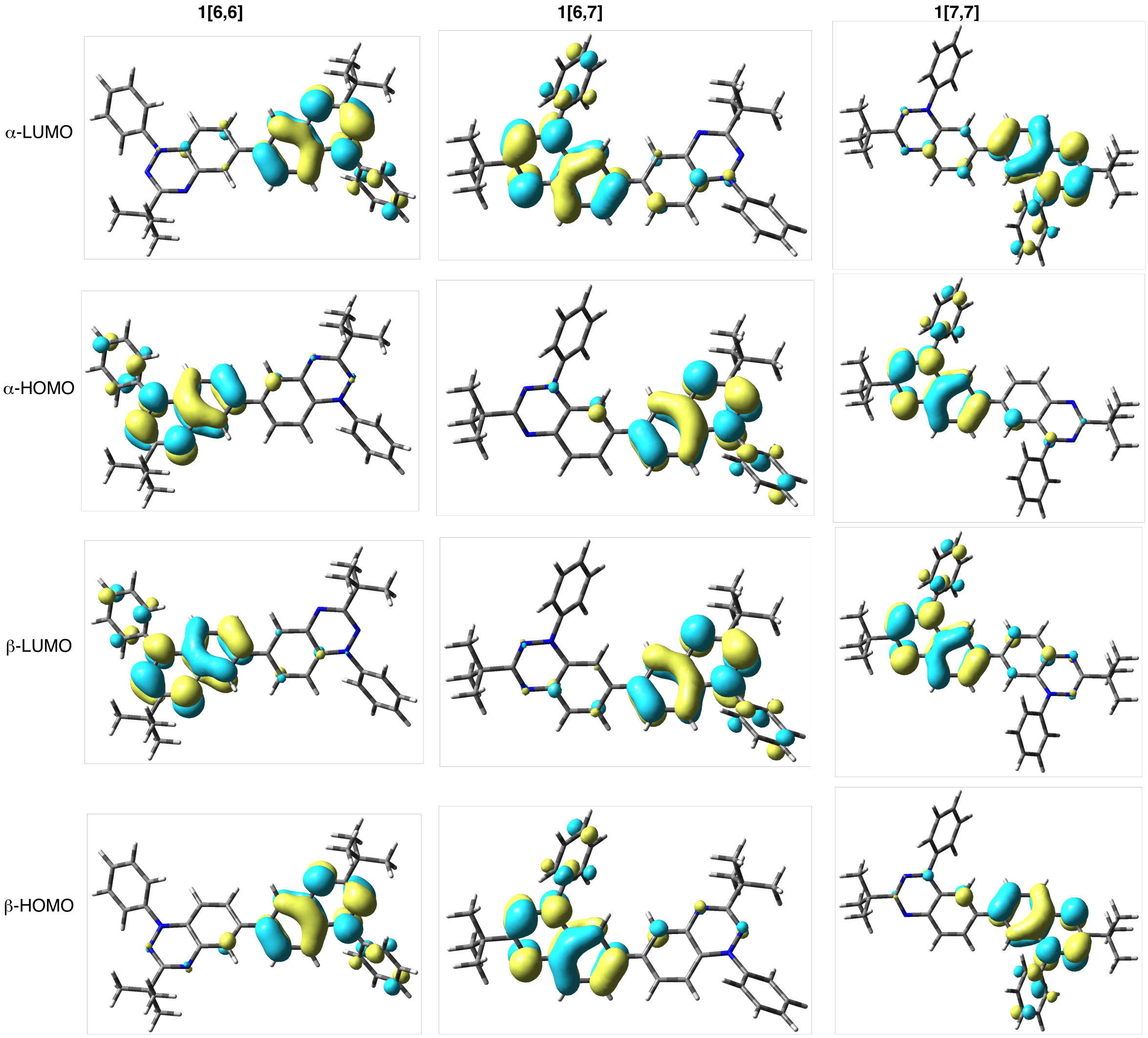


Figure S40. Contours of FMOs for OSS **1[m,n]** in CH_2Cl_2 dielectric medium. Level of theory: UB3LYP/6-311++G(d,p) // UB3LYP/6-311G(d,p), MO isovalue = 0.03, density = 0.0004.

g) details of the NEVPT2 calculations

First, the spin restricted MP2 calculation for a given geometry to obtain the MP2 unrelaxed natural orbitals was performed. The MP2 natural orbitals were used as the initial guess orbitals for the CASSCF calculations. In the state-averaged (SA***k***-)CASSCF(***m***,***n***), the numbers of active electrons (***m***), active orbitals (***n***) as well as the number of singlet states to be solved (***k***) should be specified. In the present case, we set ***k*** = 3 (i.e., S_0, S_1, and S_2 states) and compared the results of *m* (= *n*) = 2, 4, 6 and 8 (i.e., CASSCF(2,2), CASSCF(4,4), CASSCF(6,6), and CASSCF(8,8)). During the calculations, the def2-SVP basis set and the def2-SVP/C auxiliary basis set for the resolution-of-the-identity (RI) approximation were employed. Then, the quasi-degenerate second-order *n*-

electron valence state perturbation theory (QD-NEVPT2) calculation was performed based on the CASSCF wavefunctions to obtain the energies of the ground and excited states. Here, the strongly-contracted version of NEVPT2 (SC-NEVPT2) was employed. Electron configurations of each state were analyzed based on the CASSCF wavefunction. No solvent effect was assumed. All these calculations were performed using ORCA 4.2 program package.

Figure S41 shows the QD-NEVPT2 excitation energies for the excited states that are characterized by single excitation (Single) and double excitation (Double), respectively, as a function of *m* (= *n*). As increasing *m* (*n*), in principle, the degree of freedom of the wavefunction increases, thus an improved description of excited states is expected. However, the convergence of QD-NEVPT2 excitation energies was not smooth, and with the increase of *m* (= *n*), the excitation energies tend to be overestimated. Excitation energy for the single excitation state at the QD-NEVPT2 with SA3-CASSCF(2,2) appears to be close to the experimental result. However, it is difficult to evaluate the effect of this approximation on the energy of the double excitation state, because optical transition to this state (very weak or forbidden) is difficult to be assigned from experiment.

These calculations are consistent with the results of TD-DFT calculations. All three methods correctly predict the position of the main low energy absorption band, however the position of the double excitation band cannot be verified experimentally without additional more advanced experiments.

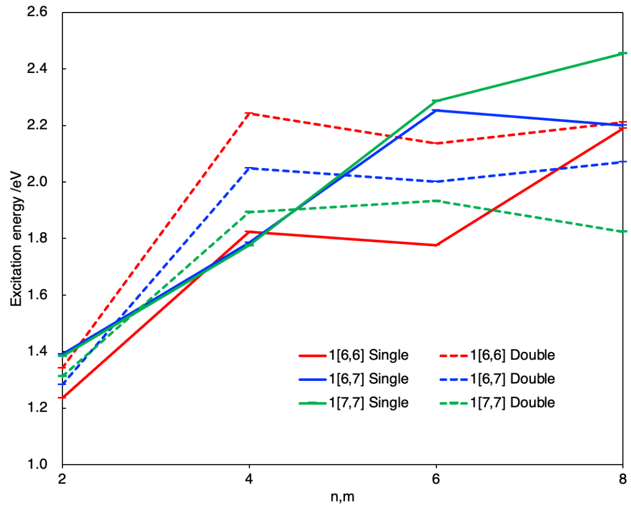


Figure S41. Dependence of QD-NEVPT2 excitation energies for the single and double excitation states on the numbers of active electrons (*m*) and orbitals (*n*) in the SA3-CASSCF(*m*,*n*) wavefunction.

10. Archive for DFT calculations at the UB3LYP/6-311G(d,p) level of theory

1[6,6]-OSS

```
1\1\GINC-LOCALHOST\FOpt\UB3LYP\6-311G(d,p)\C34H34N6\PIOTR\10-Apr-2023\
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  2nd orient\\0,1\N,4.9239689651,-0.4569551959,-0.1068003493\N,5.702416
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 ,-1.5402685014,-1.2994672465\C,5.3438602715,-2.8606640138,0.1621956492
 \C,7.4997871037,-2.6751269663,-1.5947740719\C,6.0960161963,-3.99125168
 32,-0.1438881529\C,7.1720891388,-3.9043892196,-1.0245395363\C,-0.74240
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 8501\C,-1.3451910119,1.3577363651,-0.3459950452\C,-2.9732502917,-0.865
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 4\H,-5.9938481485,3.8266044202,-3.0760892527\H,-7.834116012,4.6373412
 614,-1.6207049237\C,5.9423380094,2.9142372201,1.0088105507\C,-5.915638
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 20797796,-3.3782148417,2.4076201994\H,-5.960746313,-4.2580380128,2.739
 9994995\H,-4.342250536,-3.6318271505,2.3617074407\H,-5.5341920479,-2.5
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 drupole=3.2312454,3.4229427,-6.6541881,-21.7457874,-4.600813,-2.521235
 3\PG=C01 [X(C34H34N6)]\\
```

1[6,6]-T

```
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```

```
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 fcheck\\6,6-bis(benzo[e][1,2,4]triazinyl) tBu triplet 2nd oriet\\0,3\N
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 224854923\C,-1.5744991308,-0.987450323,0.1178598122\C,-1.3448812059,1.
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 N,-5.7027102644,-0.6039402833,0.2867957364\C,-5.0594946076,-1.73397175
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 )]\\
```

1[6,6]-CS

```
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 5371368\N,3.7771752355,1.9447124311,0.67566032\C,5.0902792281,1.763594
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```
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69794\C,5.3525262182,-2.8220576614,0.3456361784\C,7.3911298466,-2.7449
73186,-1.5549443453\C,6.0926306813,-3.9677548622,0.0675172625\C,7.1089
337022,-3.9349448687,-0.8848939663\C,-0.7332273089,0.0864780114,0.0663
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,7.6844366622,-4.8284786153,-1.0966437138\H,-1.1850393423,-2.001061114
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379904,0.4977448764\C,-5.6568699381,1.6043440401,-0.4455409577\C,-6.71
91128299,2.0111548317,0.3638576483\C,-5.3604412709,2.2964411777,-1.621
6658501\C,-7.4641386978,3.1293714421,0.0070805381\H,-6.9515123386,1.44
09149218,1.2529283204\C,-6.1129401108,3.4145556805,-1.9689073023\H,-4.
5639923861,1.9498012399,-2.2680469484\C,-7.1619973825,3.8376034559,-1.
1553532756\H,-8.2842472632,3.4480284222,0.6400483632\H,-5.8859949234,3
.9458721591,-2.8859344928\H,-7.7468685259,4.7074372745,-1.4305555403\C
,5.9846344193,2.9734829978,0.8385338207\C,-5.9629728031,-2.9834528888,
0.8451943103\C,7.4732148876,2.6615782473,0.6198911388\H,7.8097435157,1
.8429946244,1.2583745371\H,7.6749506866,2.3764871644,-0.4147949328\H,8
.0681046578,3.5497433383,0.8526358346\C,5.5574801683,4.132842114,-0.08
76060509\H,5.723461921,3.8761819984,-1.1383309945\H,4.4998248422,4.363
1030691,0.0453785371\H,6.1448882303,5.027941042,0.1375450234\C,5.75318
77538,3.3823394779,2.3101548726\H,6.3386436582,4.275787041,2.546783148
\H,4.6986769383,3.5953612947,2.4902861204\H,6.064007556,2.5844948809,2
.9911530461\C,-5.7244877576,-4.0695040415,-0.2272154306\H,-6.042319755
8,-3.7199789838,-1.2140512018\H,-4.6674418315,-4.3332097273,-0.2805782
895\H,-6.3003099485,-4.9677093134,0.014945254\C,-5.5247633094,-3.52117
46622,2.2246785953\H,-6.1001180985,-4.416618516,2.4780246368\H,-4.4638
367222,-3.7739424818,2.2214424902\H,-5.6972823213,-2.77711956,3.008282
779\C,-7.4553239083,-2.6199374778,0.8846451741\H,-7.6626728613,-1.8608
403098,1.6418254858\H,-7.7990349377,-2.2306338332,-0.0751704749\H,-8.0
400159075,-3.5125000721,1.1262115652\\Version=ES64L-G09RevD.01\State=1
-A\HF=-1644.9304335\RMSD=9.385e-09\RMSF=1.147e-05\Dipole=0.0145657,0.0
1181,-0.7539998\Quadrupole=3.21894,3.5952282,-6.8141683,-26.3672506,-4
.8668405,-2.7107893\PG=C01 [X(C34H34N6)]\\
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1[6,7]-OSS

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1\1\GINC-LOCALHOST\FOpt\UB3LYP\6-311G(d,p)\C34H34N6\PIOTR\10-Apr-2023\
 0\\#P UB3LYP/6-311G(d,p) FOpt SCF=Direct Geom=(NoDistance,NoAngle) #P
 guess=(mix, always)\\6,7-bis(3-tBu-benzo[e][1,2,4]triazinyl) OS single
 t 2nd orient\\0,1\N,4.6605763058,-0.542381679,0.0499523818\N,5.2033589
 729,0.6784699883,-0.2492495327\N,3.0184158364,1.5618479319,-0.59428257
 64\C,4.3502976131,1.6501968667,-0.5533753245\C,2.484225478,0.317765166
 5,-0.4039809218\C,1.100772055,0.1237516487,-0.5361602951\C,0.515006604
 3,-1.1371531021,-0.4228361261\C,1.3666443806,-2.2386888038,-0.1857378\
 C,2.7334673044,-2.0843213778,-0.0326613543\C,3.3072292769,-0.806247588
```

```
6,-0.1093513556\C,5.6158974142,-1.5137145334,0.4843862256\C,5.38370641
 54,-2.2712904132,1.6347524503\C,6.8102726838,-1.6591154251,-0.22413420
 84\C,6.3389756317,-3.1910737609,2.0576295214\C,7.759428124,-2.57804295
 71,0.2096698165\C,7.5263839785,-3.3507014362,1.3464746611\C,-0.9455316
 399,-1.3236679611,-0.5458883536\C,-1.4854773797,-2.5133152087,-1.08340
 27508\C,-1.828089778,-0.3166962687,-0.1377213119\C,-2.8481901852,-2.69
 66137593,-1.1847723124\C,-3.2095556601,-0.4783722548,-0.2680944929\C,-
 3.7517793864,-1.6996224935,-0.7637726738\C,4.9571003328,3.0225735662,-
 0.8713589252\H,0.5116749841,1.0010780981,-0.7705848848\H,0.9448016323,
 -3.2316353418,-0.0915588007\H,3.3543241525,-2.9505109347,0.1475819613\
 H,4.4741872067,-2.1260125717,2.2038192837\H,6.9829181477,-1.0429548176
 ,-1.0960499437\H,6.1585212086,-3.7726390203,2.9543103027\H,8.684127291
 3,-2.6914233766,-0.3443544099\H,8.2690610459,-4.0655645024,1.680905124
 3\H,-0.8192115898,-3.2885027577,-1.4416761641\H,-1.4366352627,0.583799
 3275,0.3127197892\H,-3.2698196541,-3.6104421597,-1.5848213415\C,-5.875
 8261181,-0.9702492749,-0.292532249\C,-3.8036483005,1.8132099111,0.5061
 670192\C,-4.3554225825,2.3332044538,1.6786850148\C,-2.9652971234,2.601
 8060723,-0.2856147462\C,-4.0498951702,3.6336318963,2.0651719457\H,-5.0
 231092264,1.7165454932,2.2650979743\C,-2.6622319793,3.9004018584,0.112
 9739348\H,-2.5697117288,2.2076850227,-1.2132605145\C,-3.1990888595,4.4
 194123486,1.2894032415\H,-4.4767076226,4.0327666609,2.9781367267\H,-2.
 01409104,4.5100251724,-0.5058654805\H,-2.961793437,5.431548408,1.59547
 48913\C,-7.3786767575,-1.2682984162,-0.2469248823\N,-5.0910967484,-1.9
 271398137,-0.8093662111\N,-4.1461737263,0.485599785,0.1018075305\N,-5.
 4847753046,0.2088172288,0.1658108959\C,-8.1775688414,-0.111119618,0.37
 18942779\H,-7.8714345854,0.0815239859,1.4022892106\H,-8.0433726339,0.8
 14787635,-0.1900824538\H,-9.2417264149,-0.3646078944,0.372808102\C,-7.
 5935830544,-2.5504054326,0.5870494289\H,-8.6545010642,-2.8172411843,0.
 5959221756\H,-7.0265345839,-3.3832870061,0.1691113448\H,-7.2739812223,
 -2.4029039244,1.6231051962\C,-7.861243185,-1.5138970884,-1.6938970916\
 H,-7.2948566684,-2.3219191446,-2.1588133354\H,-8.9215605131,-1.7830878
 058,-1.6930432421\H,-7.7412018999,-0.6138636219,-2.304025121\C,4.39519
 45192,4.0414345317,0.1445476369\H,4.7651494156,5.0442810499,-0.0883547
 994\H,3.3048859358,4.0540634571,0.1158399512\H,4.7097034855,3.79292853
 19,1.1624612663\C,4.5175668443,3.4259766979,-2.2960370101\H,4.91242906
 18,2.7283135788,-3.0407480306\H,3.4298396236,3.4338069483,-2.377518145
 8\H,4.8959002533,4.4241341071,-2.5350162779\C,6.4913686719,3.009408170
 4,-0.7911432528\H,6.8390243786,2.7242605066,0.2033569489\H,6.924539977
 8,2.3067246074,-1.5059765256\H,6.8744831236,4.0085154873,-1.0187782017
 \\Version=ES64L-G09RevD.01\State=1-A\HF=-1644.9513165\S2=0.979631\S2-1
 =0.\S2A=0.199119\RMSD=4.951e-09\RMSF=1.924e-06\Dipole=1.076197,-0.3845
 395,0.543905\Quadrupole=-3.0632431,5.9928597,-2.9296165,-15.1731281,-2
 .8279455,-1.061315\PG=C01 [X(C34H34N6)]\\
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1[6,7]-T

```
1\1\GINC-LOCALHOST\FOpt\UB3LYP\6-311G(d,p)\C34H34N6(3)\PIOTR\11-Apr-20
 23\0\\#P UB3LYP/6-311G(d,p) FOpt SCF=Direct Geom=(NoDistance,NoAngle)\
 \6,7-bis(3-tBu-benzo[e][1,2,4]triazinyl) triplet 2nd orient\\0,3\N,4.6
 615238057,-0.5329869478,0.0585691833\N,5.2078708846,0.6745200537,-0.28
 08759913\N,3.0293729187,1.5548862888,-0.6701385363\C,4.3631277659,1.63
 91675,-0.6230833704\C,2.4912277348,0.3204831188,-0.4416124966\C,1.1054
 964615,0.1296353363,-0.579173779\C,0.5146015903,-1.1225822283,-0.42844
 35834\C,1.3547321637,-2.2205659302,-0.1448358022\C,2.7229702191,-2.067
 5523983,0.0116176134\C,3.3036780781,-0.7973763306,-0.1036185975\C,5.60
 91455598,-1.4903957996,0.5349794969\C,5.3594739887,-2.2164378911,1.702
 3156673\C,6.8148926297,-1.6559075138,-0.1502106958\C,6.3078001963,-3.1
 240160447,2.165146304\C,7.7569729691,-2.5620779181,0.3237582052\C,7.50
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 62450789,-3.3033007479,1.4776180002\C,-0.9485777072,-1.3027449187,-0.5
 71644987\C,-1.4828104693,-2.4678562574,-1.1620089838\C,-1.8298435707,-
 0.3149578586,-0.1224092927\C,-2.8466470249,-2.6487491386,-1.2711090727
 \C,-3.2124795374,-0.4731261055,-0.2626581579\C,-3.750302025,-1.6721679
 517,-0.8092889476\C,4.9773144188,2.9983257902,-0.9802752167\H,0.521586
 5346,1.0005123275,-0.8488529208\H,0.923448048,-3.2063993912,-0.0212045
 999\H,3.3375975666,-2.9304536133,0.2260331516\H,4.4416705091,-2.055976
 1017,2.2536701048\H,7.001424957,-1.0647294775,-1.0364508686\H,6.112980
 1041,-3.6805580076,3.074646593\H,8.6900901005,-2.6904768361,-0.2126431
 894\H,8.2433141366,-4.0086560984,1.8431767784\H,-0.8120661772,-3.22493
 96486,-1.5500143199\H,-1.438101643,0.5654280716,0.3666619323\H,-3.2669
 456438,-3.5453141285,-1.7098355428\C,-5.8769388875,-0.9673041976,-0.31
 11829815\C,-3.8092053005,1.7876082609,0.596515262\C,-4.3652452342,2.26
 72119369,1.78420216\C,-2.9695683321,2.603336243,-0.1658920404\C,-4.062
 1424107,3.5541006668,2.215231125\H,-5.0343397866,1.6304423659,2.346990
 3057\C,-2.6689878654,3.8879954415,0.2772556162\H,-2.5717428851,2.24164
 15106,-1.1056554509\C,-3.209806056,4.3664261837,1.4689208243\H,-4.4922
 206788,3.9218651667,3.1397522261\H,-2.0199194007,4.5189322627,-0.31882
 77747\H,-2.9746776716,5.3679672828,1.8095542499\C,-7.3805789018,-1.265
 235352,-0.281168628\N,-5.0932043,-1.8987019988,-0.86725202\N,-4.149715
 9561,0.4744603349,0.1461005407\N,-5.4877696044,0.1942675181,0.19771582
 08\C,-8.1781492937,-0.1430147664,0.4007800508\H,-7.873583502,-0.009968
 6152,1.4410950791\H,-8.0411844136,0.8130249314,-0.107350051\H,-9.24277
 04172,-0.3941239689,0.3856257088\C,-7.598062305,-2.5909752718,0.480531
 8258\H,-8.6593400585,-2.8562026545,0.4740810297\H,-7.0315228838,-3.400
 3302042,0.0182831009\H,-7.2791972283,-2.500805813,1.5233667148\C,-7.86
 24821688,-1.428643051,-1.7400331644\H,-7.2974083264,-2.2108253483,-2.2
 487696621\H,-8.923471401,-1.6947391152,-1.7556055967\H,-7.7397524947,-
 0.4963803433,-2.2992188985\C,4.420582581,4.0479613455,0.0069945635\H,4
 .7962218546,5.0420339008,-0.2527136848\H,3.3303408046,4.0662709961,-0.
 0228816697\H,4.7331342757,3.8254898059,1.0315105295\C,4.5407029754,3.3
 644721747,-2.4158328964\H,4.932490833,2.6445623822,-3.1407344176\H,3.4
 531088391,3.3756748647,-2.4986990841\H,4.9242753375,4.3536989178,-2.68
 19725579\C,6.5113538284,2.9786993587,-0.8985950172\H,6.8568018232,2.71
 91271686,0.1036112411\H,6.9408306858,2.2540462366,-1.593514719\H,6.900
 4177445,3.9688517093,-1.1535289382\\Version=ES64L-G09RevD.01\State=3-A
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 =4.413e-06\Dipole=1.0481147,-0.3153004,0.6029795\Quadrupole=-3.371551,
 5.7098656,-2.3383145,-14.5904182,-2.7435472,-0.991422\PG=C01 [X(C34H34
 N6)]\\
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1[6,7]-CS

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 0\\#P B3LYP/6-311G(d,p) FOpt SCF=Direct Geom=(NoDistance,NoAngle)\\6,7
 -bis(3-tBu-benzo[e][1,2,4]triazinyl) zwitterion 2nd orient\\0,1\N,4.65
 8873386,-0.5759745097,0.0110656538\N,5.203897007,0.6836225646,-0.08040
 34338\N,3.0017578476,1.5787081674,-0.2381870863\C,4.3297938289,1.67697
 71377,-0.2038005937\C,2.4680520906,0.3224736843,-0.2193058316\C,1.0937
 6552,0.1240095419,-0.3139838038\C,0.5099874604,-1.1597157284,-0.349899
 5975\C,1.4015520659,-2.2666135028,-0.3055850955\C,2.7648431421,-2.1201
 183236,-0.1940439994\C,3.3293617955,-0.8270220099,-0.1199883316\C,5.64
 10618055,-1.6027626242,0.2145661854\C,5.5166050416,-2.4973928849,1.277
 8537407\C,6.7476860455,-1.6574865319,-0.6327180362\C,6.4939144905,-3.4
 693701821,1.4735043855\C,7.7177212407,-2.6327479166,-0.4287971678\C,7.
 592287609,-3.5433442804,0.6196390444\C,-0.9225555078,-1.365879715,-0.4
 09391089\C,-1.4816771284,-2.6402683764,-0.715034247\C,-1.8263503209,-0
 .2996477841,-0.1882124775\C,-2.8339956245,-2.8474677186,-0.7668850989\
 C,-3.19727396,-0.4819134444,-0.269872162\C,-3.7525569093,-1.7919803416
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,-0.5145498984\C,4.9150676658,3.0921484557,-0.2906210536\H,0.494875280
6,1.0205916131,-0.3909220823\H,1.0117243885,-3.2748022571,-0.336407902
6\H,3.4004657038,-2.9934469554,-0.1676427533\H,4.6745018508,-2.4201599
988,1.9542534927\H,6.8381960402,-0.9320884464,-1.4300610308\H,6.401110
6058,-4.1600616589,2.3035280599\H,8.5749089043,-2.6800048115,-1.090336
5035\H,8.3521886113,-4.2999527113,0.7764272218\H,-0.8307550976,-3.4760
631491,-0.9341201977\H,-1.444250025,0.675717115,0.0680956249\H,-3.2525
200244,-3.8214796751,-0.9868110671\C,-5.8656359853,-0.9821024455,-0.15
40241881\C,-3.8188169594,1.9103179793,0.0050440968\C,-4.4087022138,2.6
727028395,1.0162715875\C,-2.9630946833,2.5161509618,-0.9197970113\C,-4
.1260015141,4.0311251343,1.1095149633\H,-5.0891052197,2.1938407917,1.7
071127489\C,-2.6850730287,3.8751796649,-0.8149476691\H,-2.5340737299,1
.9319013071,-1.7237525767\C,-3.2603595262,4.6369922397,0.2005685168\H,
-4.582718428,4.6173243053,1.898724635\H,-2.024917938,4.3403806747,-1.5
378283842\H,-3.0405311206,5.6952747679,0.2785241674\C,-7.3572425346,-1
.2938110323,-0.0187031876\N,-5.0616459037,-2.0294036825,-0.484083997\N
,-4.1431397202,0.5239868743,-0.1054000206\N,-5.4805537662,0.2527956862
,0.0376952329\C,-8.1684699973,-0.0500277952,0.3735127953\H,-7.8490084,
0.347790823,1.3391346548\H,-8.0608125696,0.7475786179,-0.3637421736\H,
-9.2273824696,-0.3147097502,0.4455380575\C,-7.5293811344,-2.3867107249
,1.0594293918\H,-8.5841107618,-2.6637061211,1.1454363397\H,-6.95360277
54,-3.2775559272,0.8047115886\H,-7.193714969,-2.0284896102,2.037259995
3\C,-7.8579331755,-1.8326853664,-1.3774940375\H,-7.2790741982,-2.70471
12506,-1.6851667392\H,-8.9106794149,-2.1200989927,-1.3009045042\H,-7.7
716811678,-1.0691353939,-2.1561454774\C,4.3878797579,3.8997987042,0.91
60344741\H,4.7441672725,4.9327406108,0.859004588\H,3.297233613,3.90415
43225,0.9304324115\H,4.7427659416,3.4717162681,1.858257028\C,4.4168904
937,3.743427027,-1.5989938828\H,4.7834665299,3.1968580861,-2.473248430
4\H,3.3269711947,3.7541482877,-1.6345787385\H,4.7827244809,4.772224890
8,-1.6671127979\C,6.4517806883,3.0864431494,-0.2723873475\H,6.84097905
42,2.6265770909,0.6375220371\H,6.8607115174,2.534717506,-1.121461339\H
,6.8176863706,4.1160882094,-0.3248168756\\Version=ES64L-G09RevD.01\Sta
te=1-A\HF=-1644.9380562\RMSD=5.477e-09\RMSF=8.410e-06\Dipole=1.1869519
,-0.7644832,0.1727608\Quadrupole=-1.0405868,6.840036,-5.7994492,-18.19
06411,-3.6047801,-1.4463125\PG=C01 [X(C34H34N6)]\\
```

1[7,7]-OSS

```
1\1\GINC-LOCALHOST\FOpt\UB3LYP\6-311G(d,p)\C34H34N6\PIOTR\10-Apr-2023\
 0\\#P UB3LYP/6-311G(d,p) FOpt SCF=Direct Geom=(NoDistance,NoAngle) #P
 guess=(mix, always)\\7,7-bis(3-tBu-benzo[e][1,2,4]triazinyl) OS\\0,1\N
 ,4.6188232686,-0.6871478424,-0.7761155496\N,3.6826203542,-3.0791017223
 ,0.1934422244\C,2.7424442967,-2.1342813841,-0.2159403517\C,1.361581978
 7,-2.3028385821,-0.0982601394\C,0.4747051214,-1.3161557108,-0.55054362
 19\C,1.0156079663,-0.1405137353,-1.1217174844\C,2.376759545,0.05149174
 95,-1.2082701246\C,3.2831211397,-0.9238405201,-0.7407443293\C,-0.98355
 02081,-1.5012848096,-0.437809519\C,-1.5606309989,-2.7901543175,-0.5158
 462092\C,-1.8364724815,-0.4027827459,-0.2605670022\C,-2.9250687739,-2.
 968133954,-0.4538665611\C,-3.2178205724,-0.5753311451,-0.1620399114\C,
 -3.7984191635,-1.8713252601,-0.2943449755\H,0.9749585134,-3.1910033797
 ,0.3803732845\H,0.3478575325,0.6148889699,-1.5173587312\H,2.7968807749
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1[7,7]-T

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2

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