

Benzimidazole-Branched Isomeric Dyes: Effect of Molecular Constitution on Photophysical, Electrochemical and Photovoltaic Properties

Govardhana Babu Bodedla,[†] K. R. Justin Thomas,^{*,†} Miao-Syuan Fan,[‡] Kuo-Chuan Ho.[‡]

[†] Organic Materials Chemistry, Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee – 247 667, India. E-mail: krjt8fcy@iitr.ac.in

[‡] Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

Supplementary Information

Figure S1.	Absorption spectra of 7b recorded in different solvents.	S2
Figure S2.	Absorption spectra of 7c recorded in different solvents.	S3
Figure S3.	Absorption spectra of 7b recorded in THF before and after addition of TFA or TEA.	S3
Figure S4.	Absorption spectra of 7c recorded in THF before and after addition of TFA or TEA.	S4
Figure S5.	Absorption spectra of the intermediates 4 , 6 and 12 recorded in THF.	S4
Figure S6.	Absorption spectra of the intermediates 5 , 11 and 13 recorded in THF.	S5
Figure S7.	Emission spectra of the intermediates 4 , 6 and 12 recorded in THF.	S5
Figure S8.	Emission spectra of the intermediates 5 , 11 and 13 recorded in THF.	S6
Figure S9.	¹ H NMR spectra of 2 recorded in DMSO- <i>d</i> ₆ .	S7
Figure S10.	¹³ C NMR spectra of 2 recorded in DMSO- <i>d</i> ₆ .	S8
Figure S11.	¹ H NMR spectra of 3 recorded in CDCl ₃ .	S9
Figure S12.	¹³ C NMR spectra of 3 recorded in DMSO- <i>d</i> ₆ .	S10
Figure S13.	¹ H NMR spectra of 4 recorded in CDCl ₃ .	S11
Figure S14.	¹³ C NMR spectra of 4 recorded in CDCl ₃ .	S12
Figure S15.	¹ H NMR spectra of 5 recorded in CDCl ₃ .	S13
Figure S16.	¹³ C NMR spectra of 5 recorded in CDCl ₃ .	S14
Figure S17.	¹ H NMR spectra of 6 recorded in DMSO- <i>d</i> ₆ .	S15
Figure S18.	¹³ C NMR spectra of 6 recorded in CDCl ₃ .	S16
Figure S19.	¹ H NMR spectra of 8 recorded in DMSO- <i>d</i> ₆ .	S17
Figure S20.	¹³ C NMR spectra of 8 recorded in DMSO- <i>d</i> ₆ .	S18
Figure S21.	¹ H NMR spectra of 9 recorded in CDCl ₃ .	S19
Figure S22.	¹³ C NMR spectra of 9 recorded in CDCl ₃ .	S20
Figure S23.	¹ H NMR spectra of 10 recorded in CDCl ₃ .	S21
Figure S24.	¹³ C NMR spectra of 10 recorded in CDCl ₃ .	S22
Figure S25.	¹ H NMR spectra of 11 recorded in CDCl ₃ .	S23

Figure S26.	^{13}C NMR spectra of 11 recorded in CDCl_3	S24
Figure S27.	^1H NMR spectra of 12 recorded in $\text{DMSO-}d_6$.	S25
Figure S28.	^{13}C NMR spectra of 12 recorded in $\text{DMSO-}d_6$.	S26
Figure S29.	^1H NMR spectra of 13 recorded in CDCl_3 .	S27
Figure S30.	^{13}C NMR spectra of 13 recorded in CDCl_3 .	S28
Figure S31.	^1H NMR spectra of 7a recorded in $\text{DMSO-}d_6$.	S29
Figure S32.	^{13}C NMR spectra of 7a recorded in $\text{DMSO-}d_6$.	S30
Figure S33.	^1H NMR spectra of 7b recorded in $\text{DMSO-}d_6$.	S31
Figure S34.	^{13}C NMR spectra of 7b recorded in $\text{DMSO-}d_6$.	S32
Figure S35.	^1H NMR spectra of 7c recorded in $\text{DMSO-}d_6$.	S33
Figure S36.	^{13}C NMR spectra of 7c recorded in $\text{DMSO-}d_6$.	S34
	Computational and structure determination details	S35
Table S1	Crystal data and structure refinement for 6 .	S36
Figure S37.	Molecular structure of 6 (40% thermal ellipsoids).	S37
Figure S38.	Emission spectra of the dyes recorded in (a) THF and (b) toluene.	S38
Figure S39	Calculated interplanar angles between various aromatic segments in the dyes.	S38
Table S2.	Cartesian coordinates for the optimized structure of 7a	S39-S41
Table S3.	Cartesian coordinates for the optimized structure of 7b	S43-S44
Table S4.	Cartesian coordinates for the optimized structure of 7c	S44-S47
Figure 40.	Correlation between Stokes shift and ET(30) parameter for dye 7b .	S48

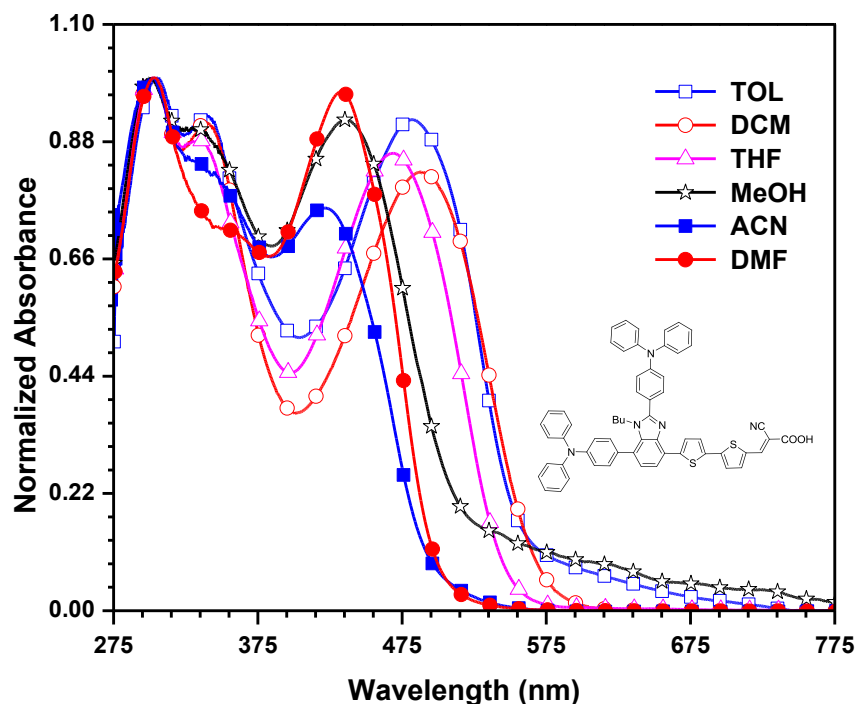


Figure S1. Absorption spectra of **7b** recorded in different solvents.

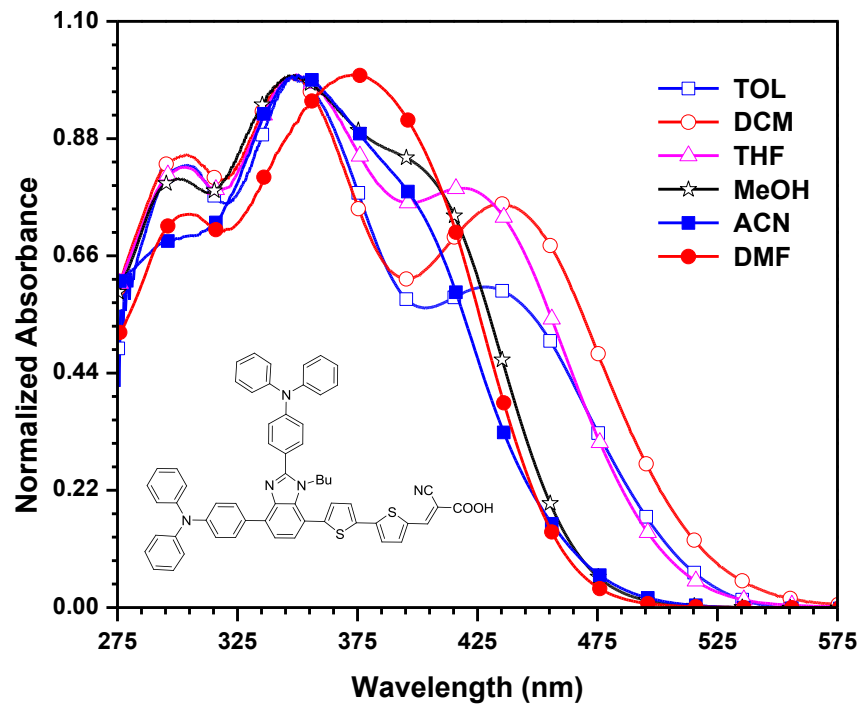


Figure S2. Absorption spectra of **7c** recorded in different solvents.

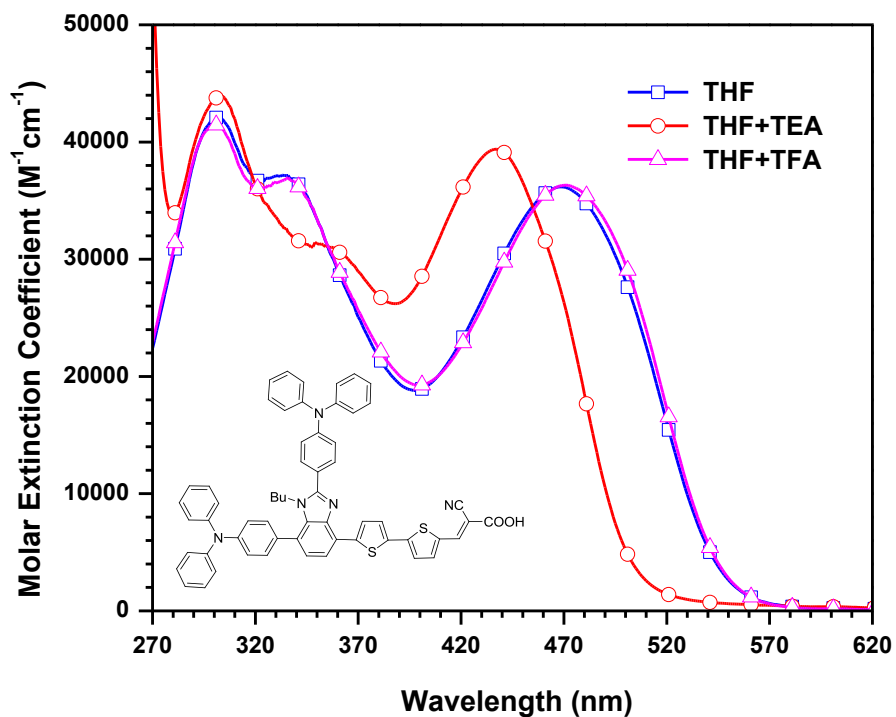


Figure S3. Absorption spectra of **7b** recorded in THF before and after addition of TFA or TEA.

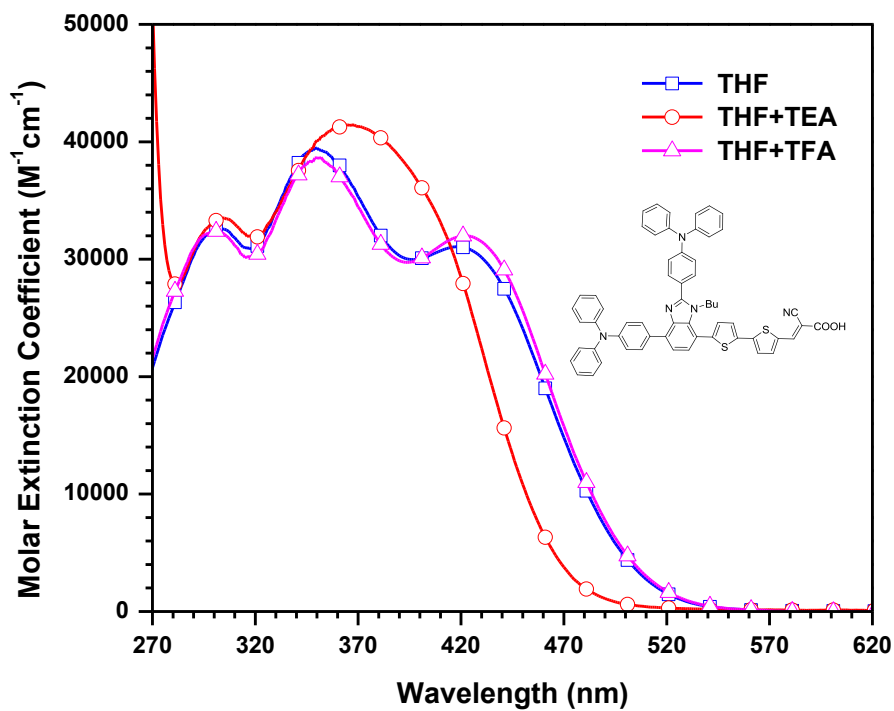


Figure S4. Absorption spectra of **7c** recorded in THF before and after addition of TFA or TEA.

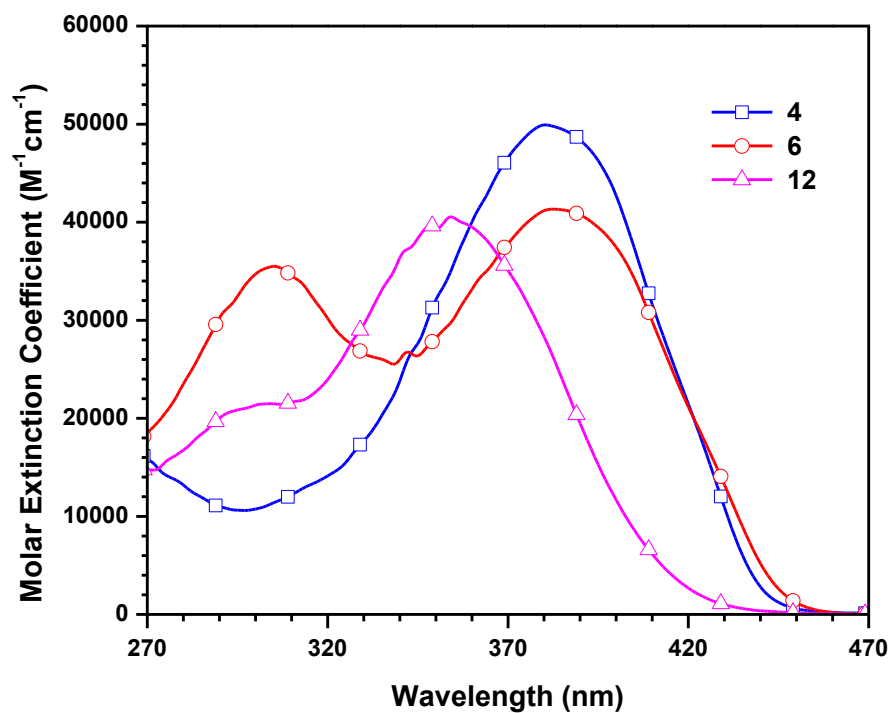


Figure S5. Absorption spectra of the intermediates **4**, **6** and **12** recorded in THF.

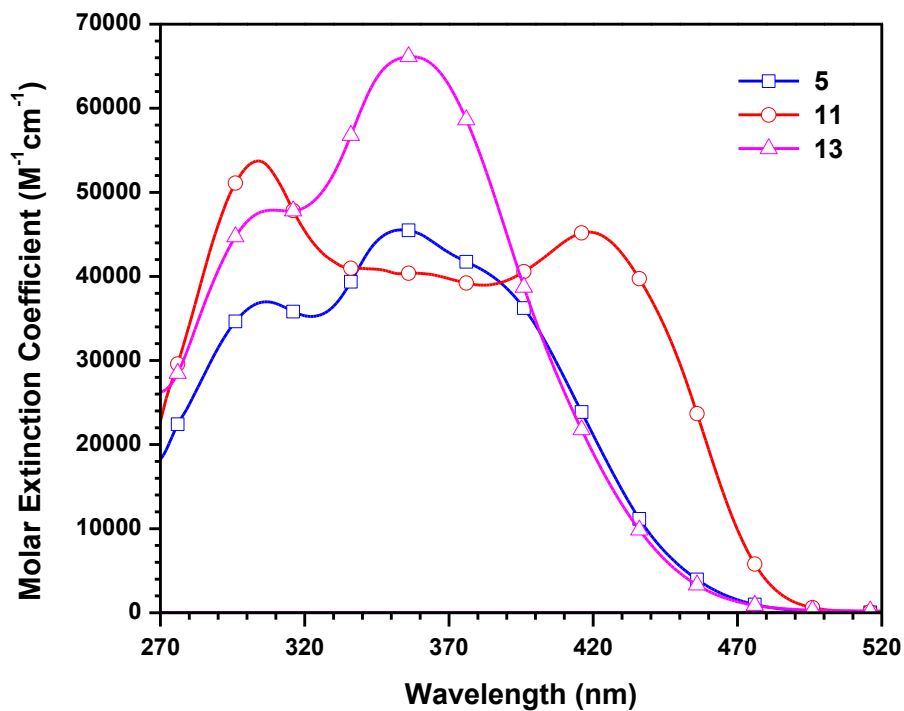


Figure S6. Absorption spectra of the intermediates **5**, **11** and **13** recorded in THF.

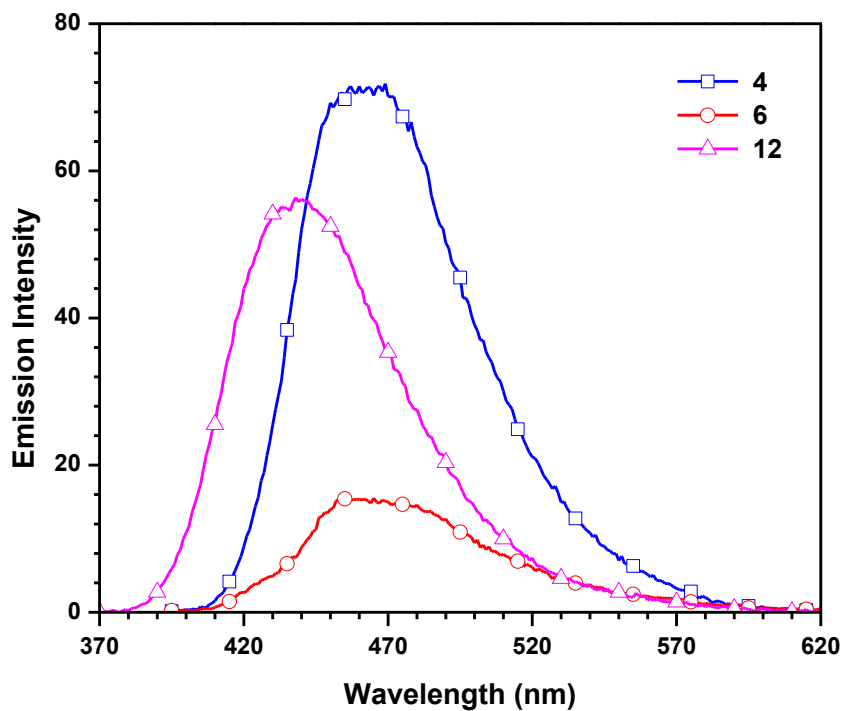


Figure S7. Emission spectra of the intermediates **4**, **6** and **12** recorded in THF.

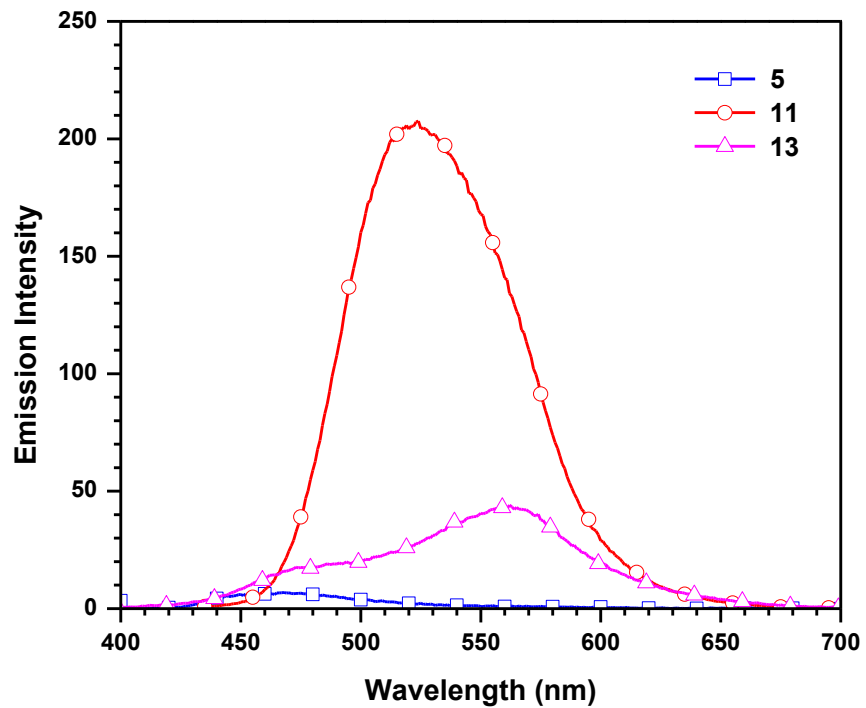
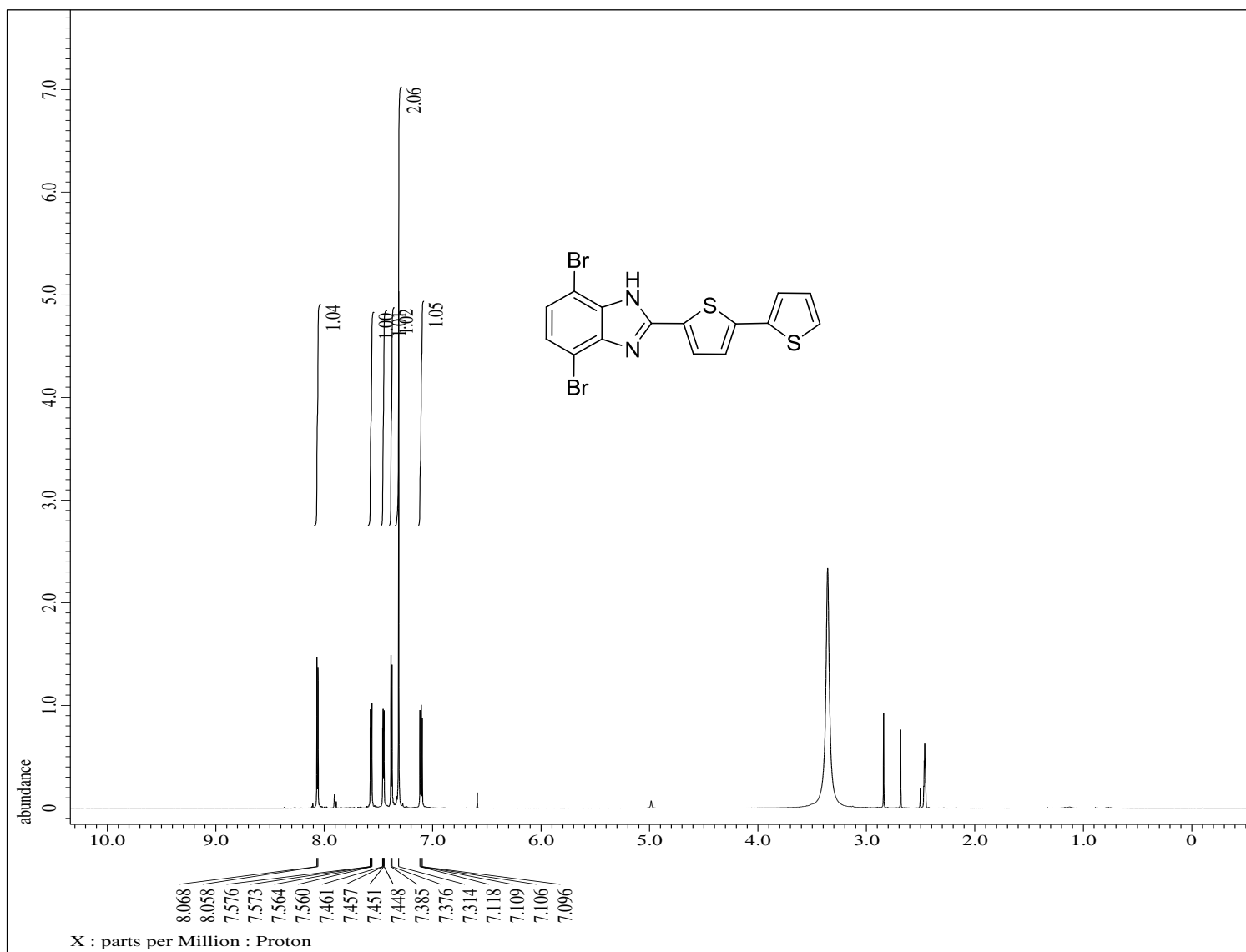


Figure S8. Emission spectra of the intermediates **5**, **11** and **13** recorded in THF.



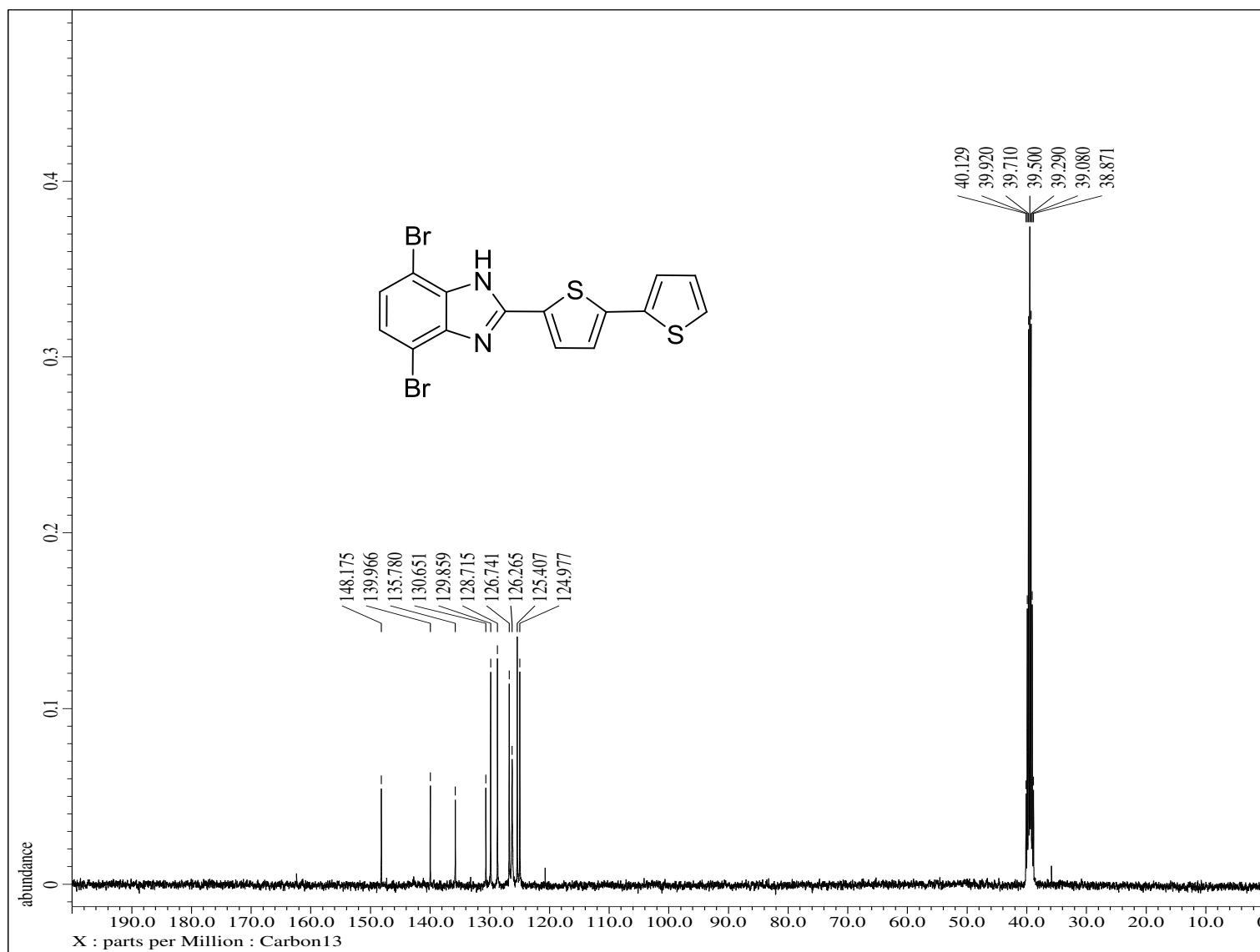


Figure S10. ^{13}C NMR spectra of **2** recorded in $\text{DMSO-}d_6$.

GB-1-151

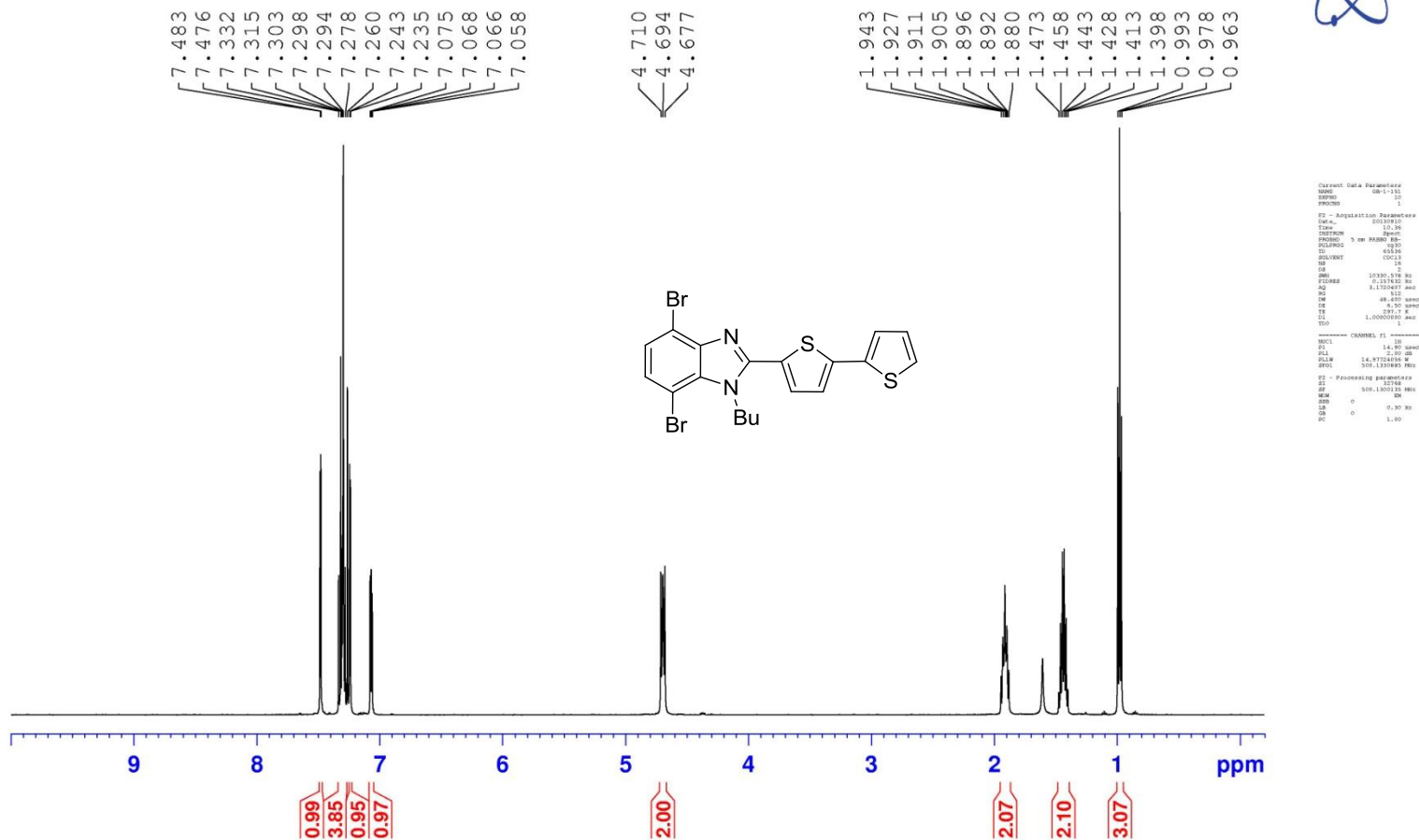


Figure S11. ¹H NMR spectra of 3 recorded in CDCl₃.

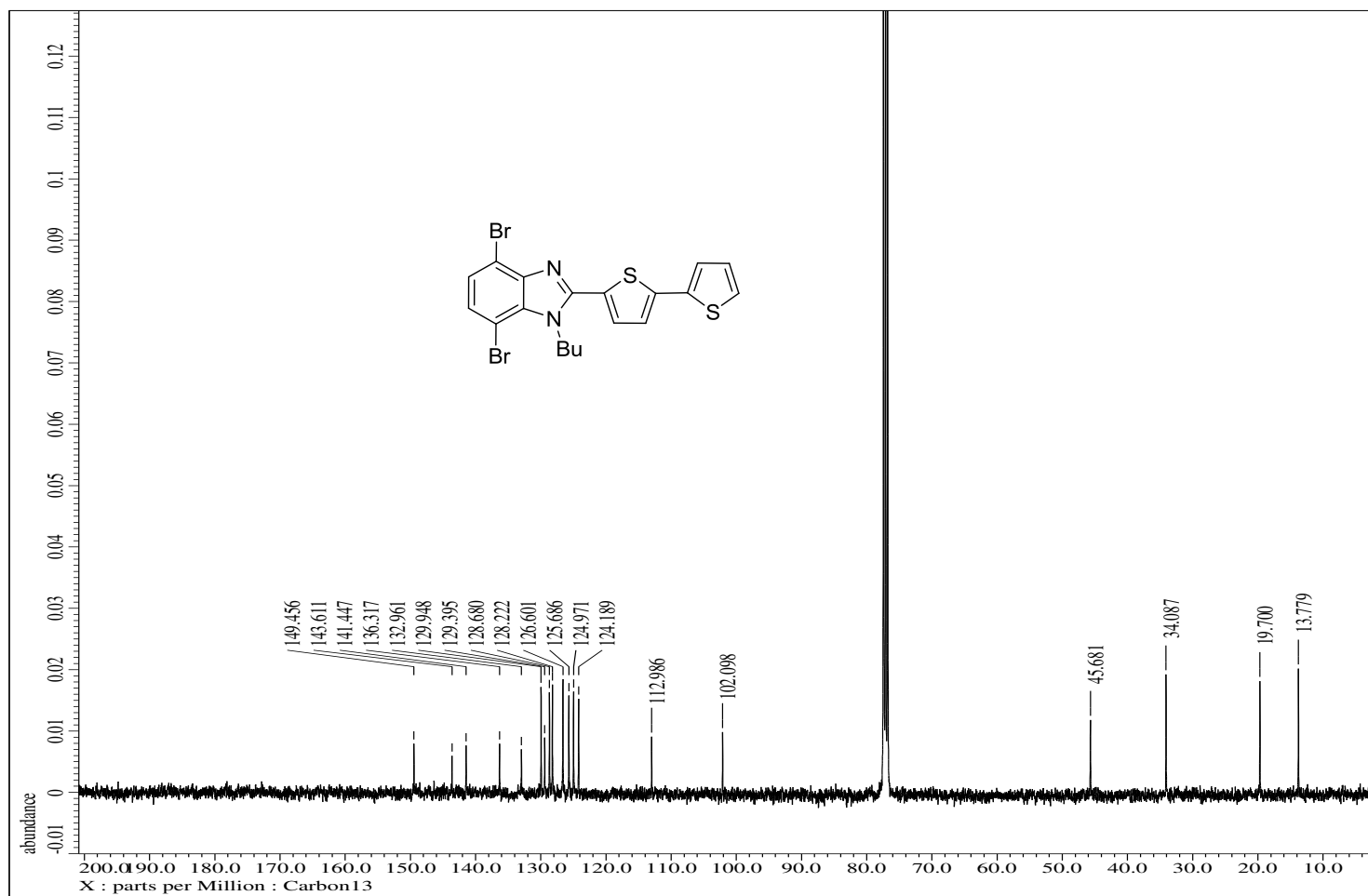


Figure S12. ^{13}C NMR spectra of **3** recorded in CDCl_3 .

GB-1-152

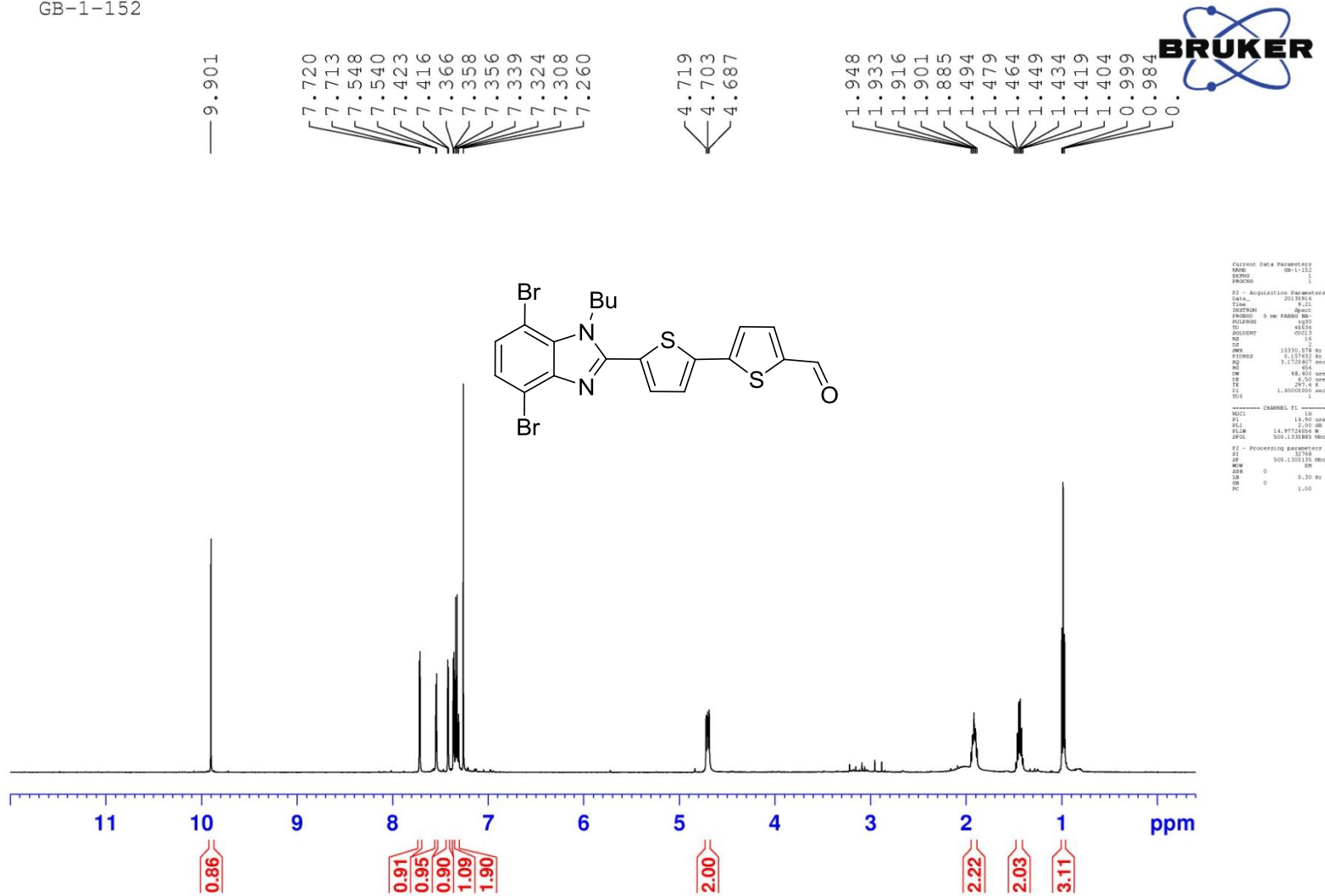
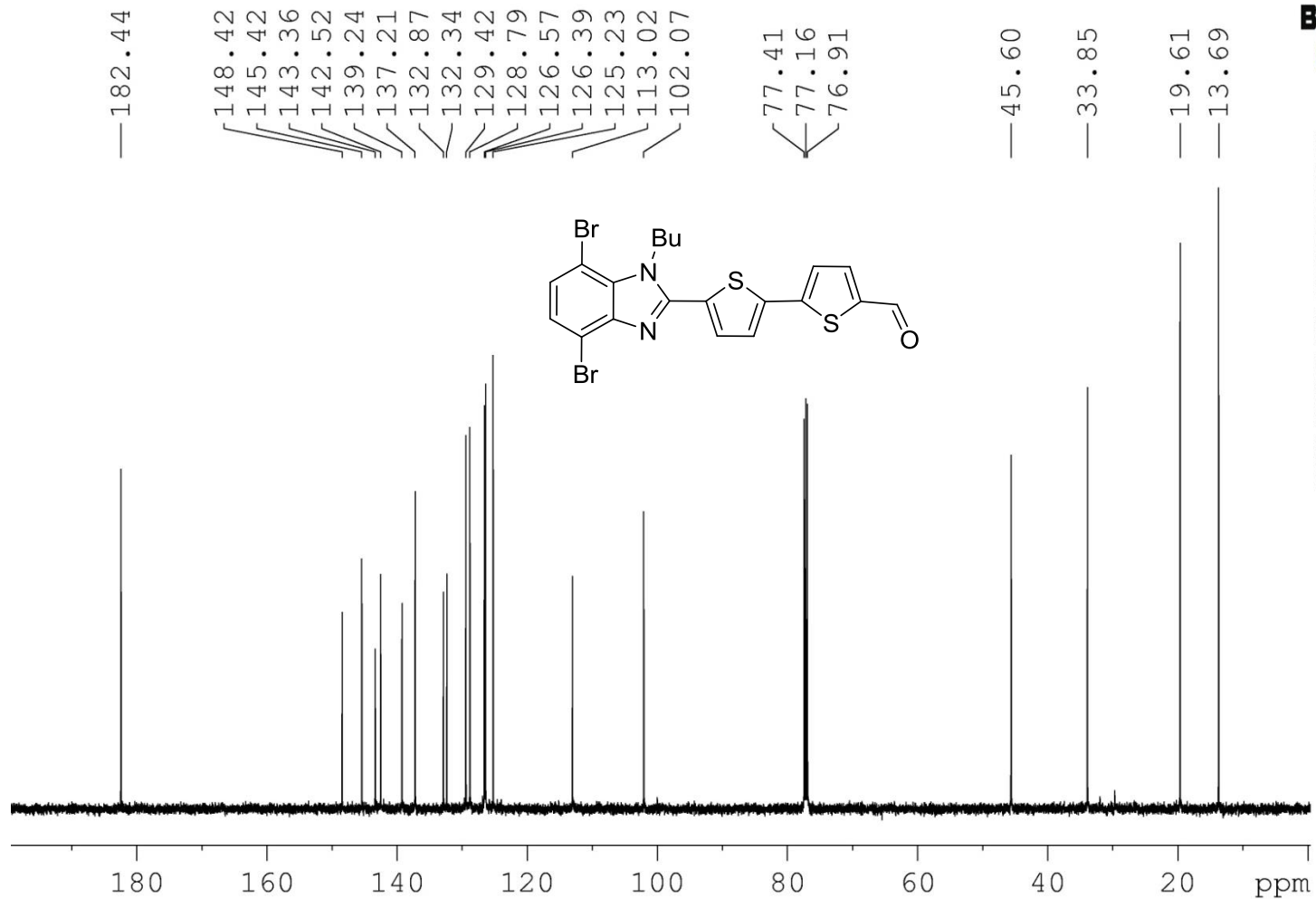


Figure S13. ¹H NMR spectra of **4** recorded in CDCl₃.

GB-1-152 C13



```
Current Data Parameters
NAME: GB-1-152 C13
EXPNO: 13
PROCNO: 1

F2 - Acquisition Parameters
Date_: 20120905
Time: 12.57
INSTRUM: spect
PROBHD: 5 mm PABBO QNP
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 250
DS: 4
SWH: 30030.024 Kz
FIDRES: 0.43612 Kz
AQ: 1.091210 sec
RG: 3840
DQ: 16.650 usec
DE: 16.00 usec
TE: 300.2 K
D1: 2.0000000 sec
d11: 0.0300000 sec
TSD: 0

===== CHANNEL f1 =====
NUC1: 13C
P1: 8.80 usec
PL1: 1.00 dB
PC1M: 64.4667971 M
SFO1: 125.7697643 MHz

===== CHANNEL f2 =====
CPDPRG2: waltz16
NUC2: 1H
PCPD2: 80.00 usec
PL12: 19.00 dB
PL13: 16.60 dB
PL14: 25.00 dB
PL1M: 14.9724084 M
PL1M2: 0.3182408 M
PL1M3: 0.23737324 M
SFO2: 500.1320000 MHz

F2 - Processing parameters
SI: 32768
SF: 125.7677890 MHz
WDW: EM
SSB: 0
LB: 1.00 Kz
GB: 0
PC: 1.40
```

Figure S14. ^{13}C NMR spectra of **4** recorded in CDCl_3 .

GB-1-170

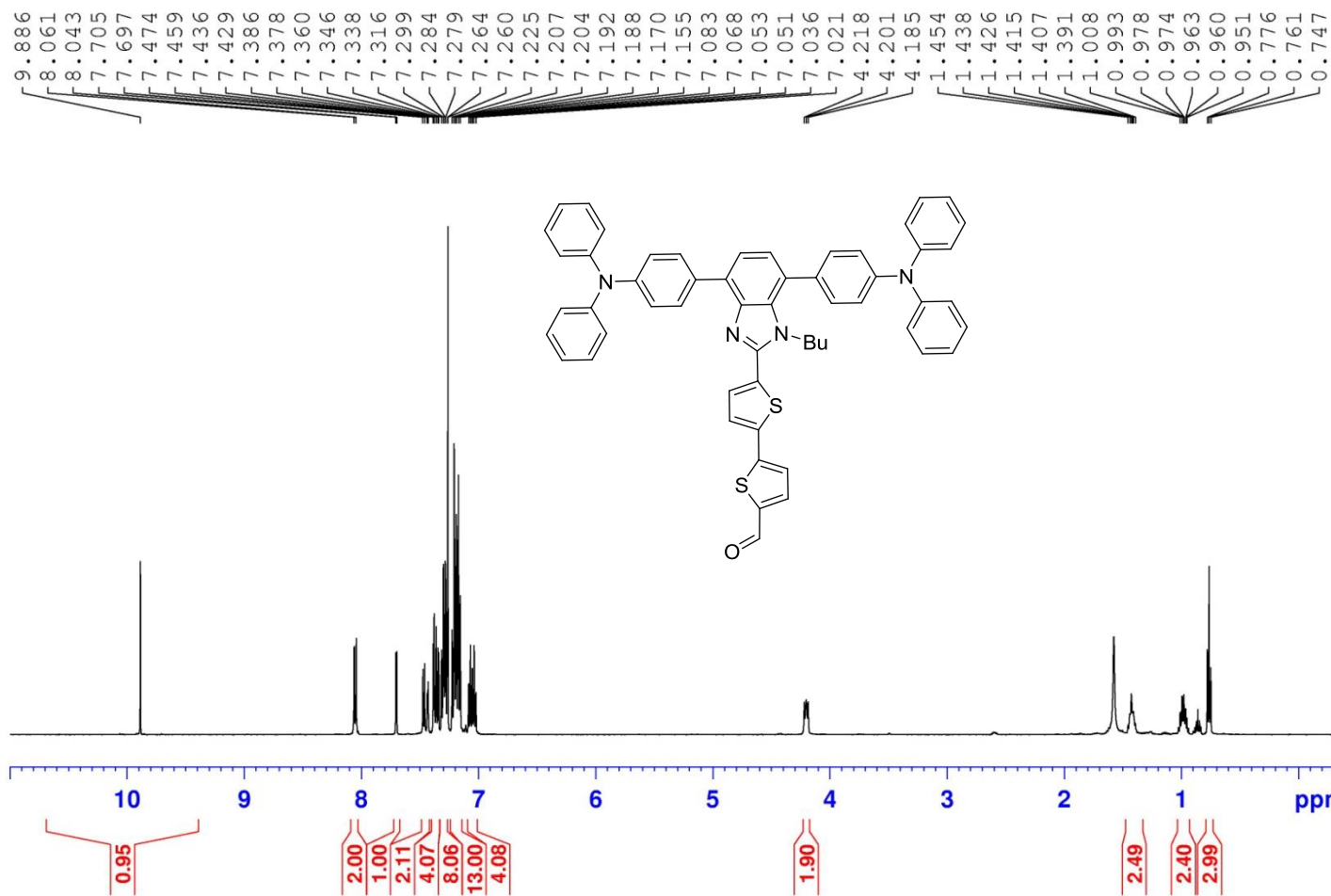


Figure S15. ¹H NMR spectra of **5** recorded in CDCl₃.

GB-1-169-2 C13

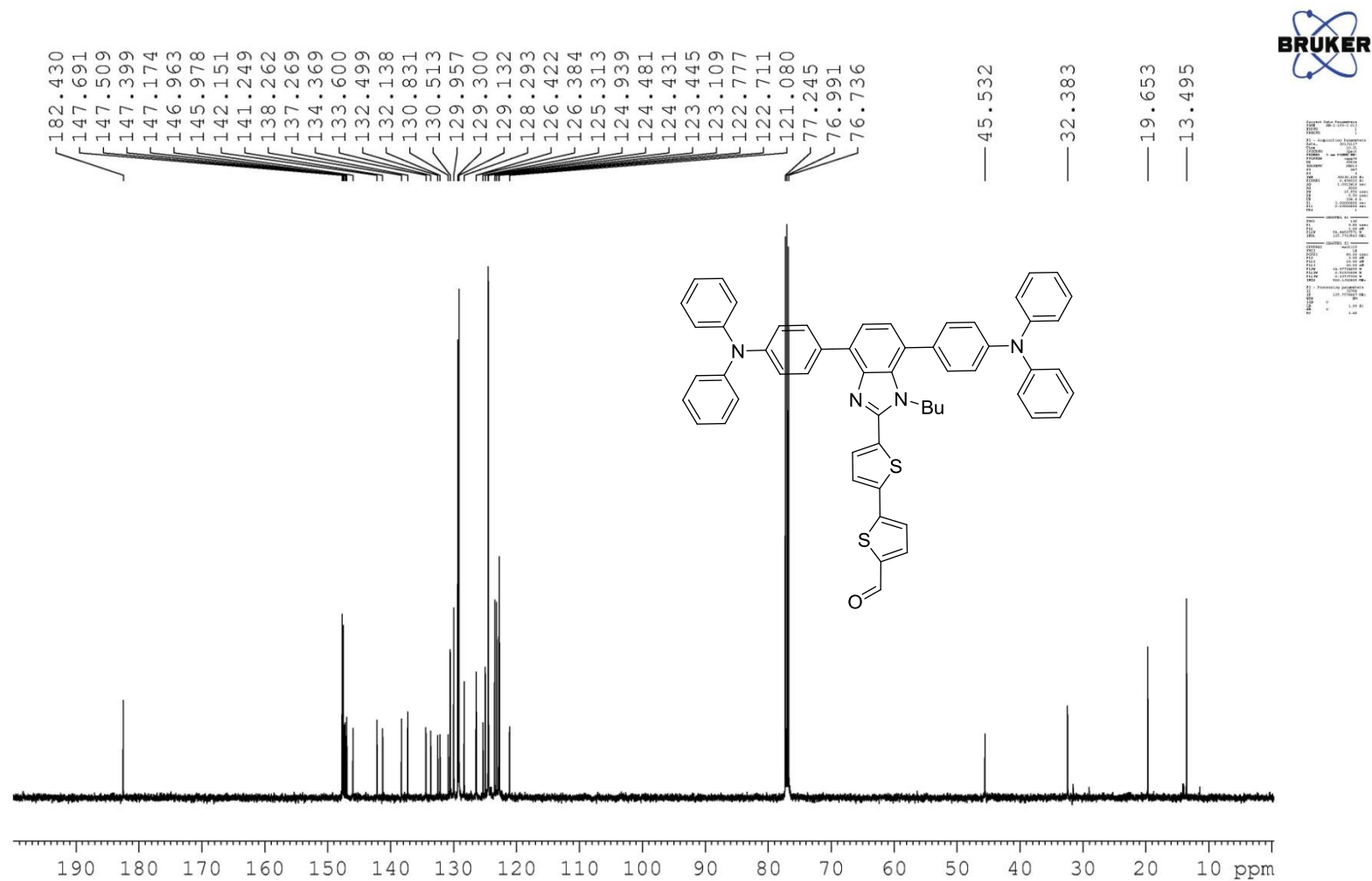
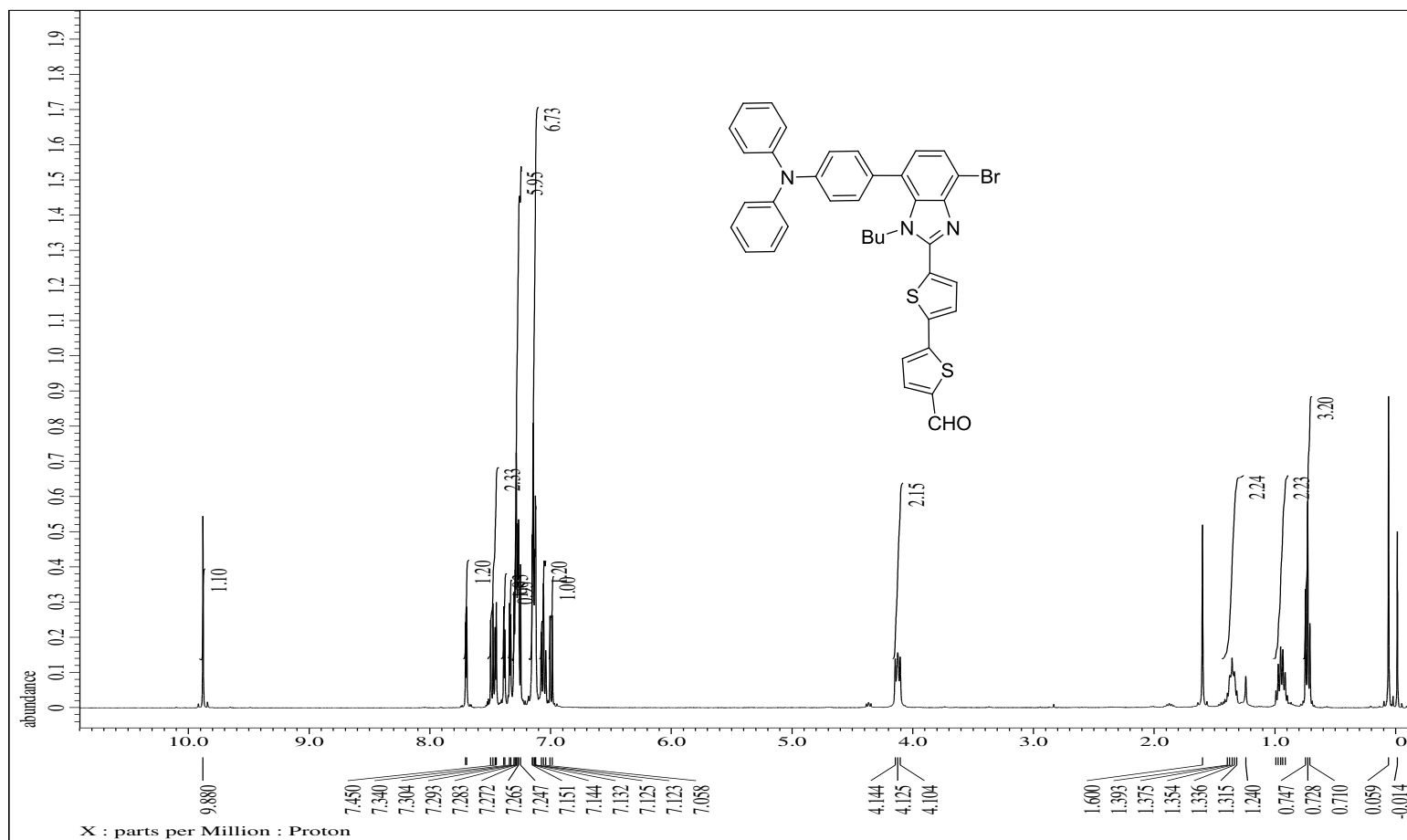


Figure S16. ¹³C NMR spectra of **5** recorded in CDCl₃.



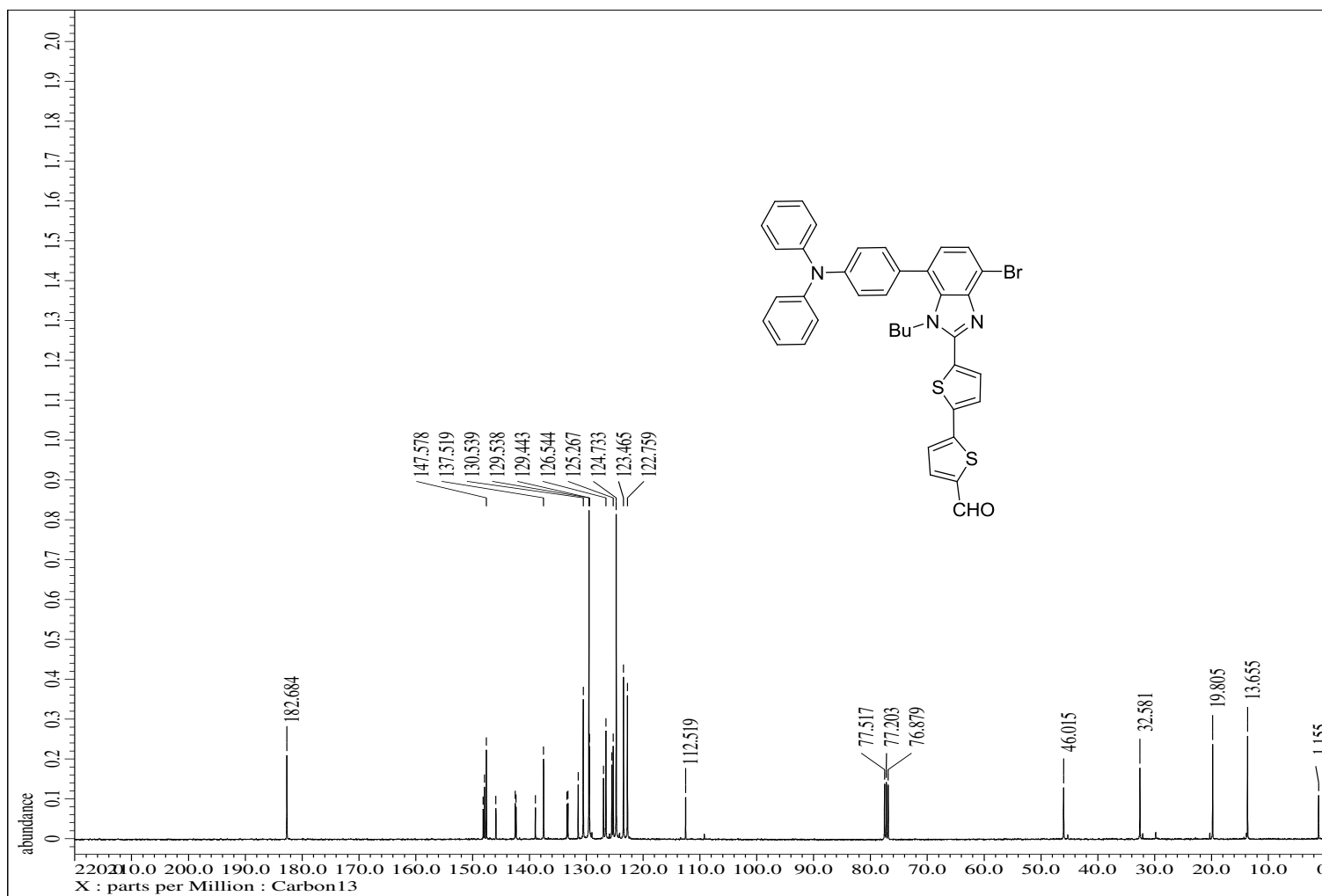


Figure S18. ^{13}C NMR spectra of **6** recorded in CDCl_3 .

GB-1-13E

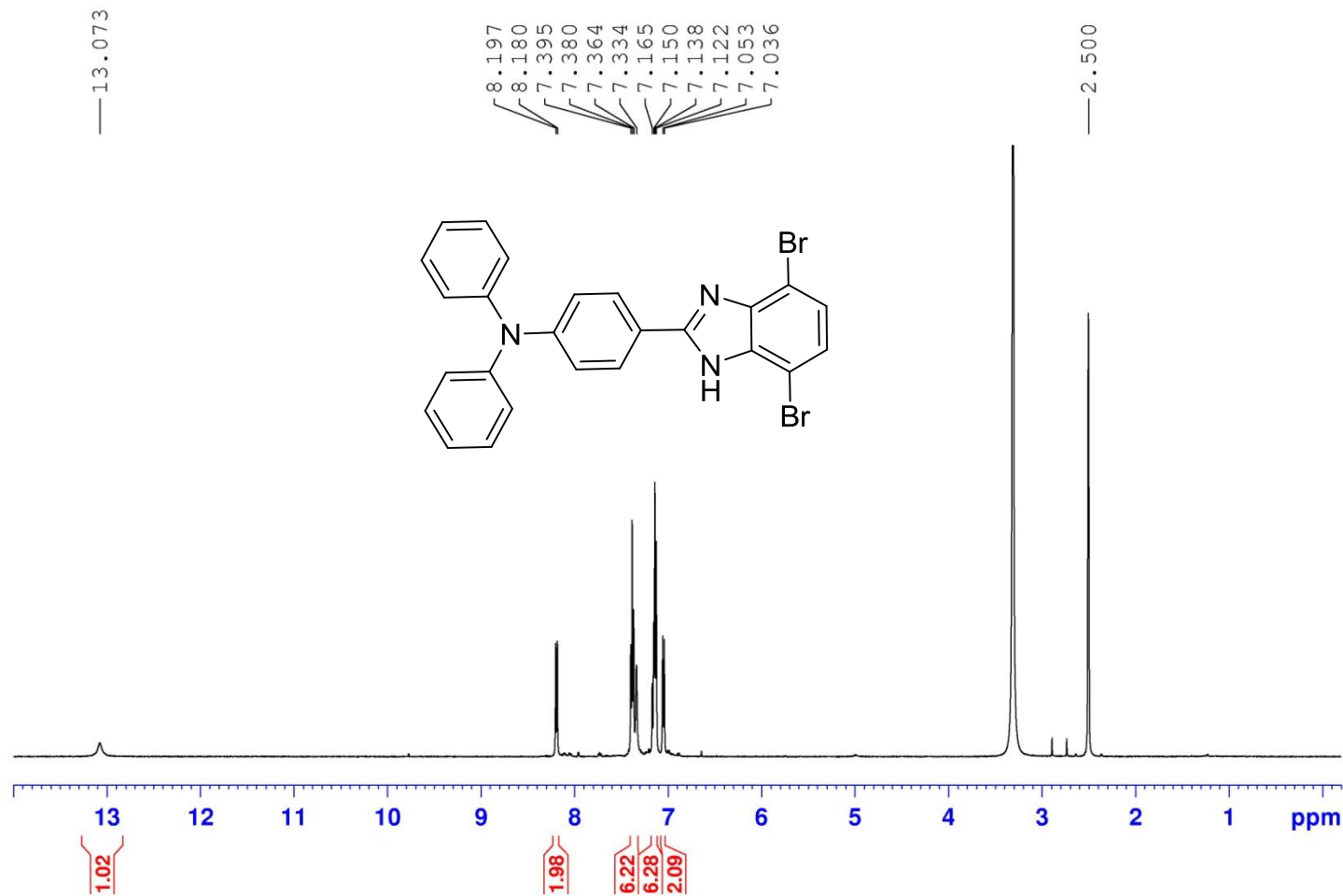


Figure S19. ¹H NMR spectra of **8** recorded in DMSO-*d*₆.

GB-1-135-2 C13

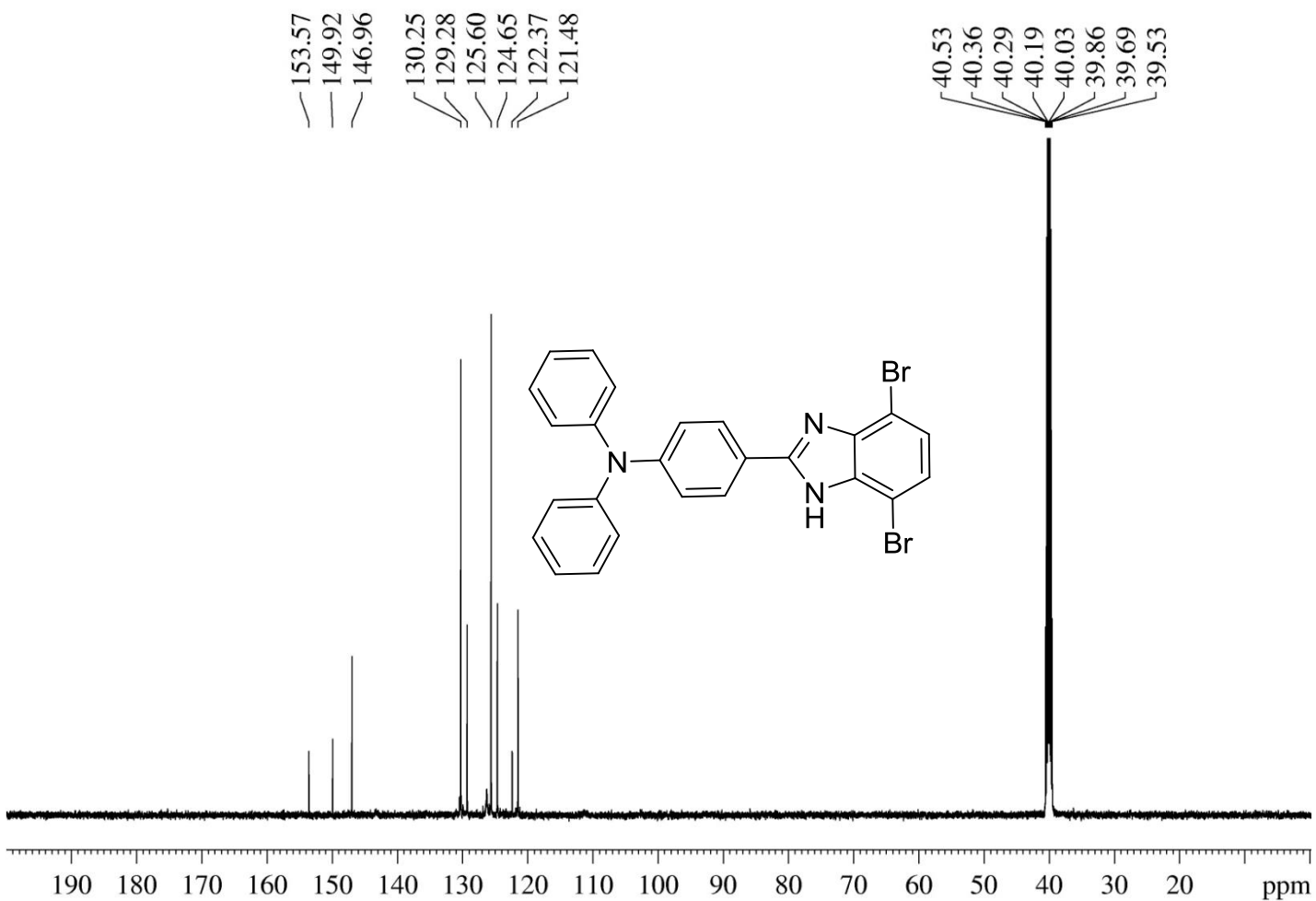


Figure S20. ^{13}C NMR spectra of **8** recorded in $\text{DMSO-}d_6$.

GB-1-136-

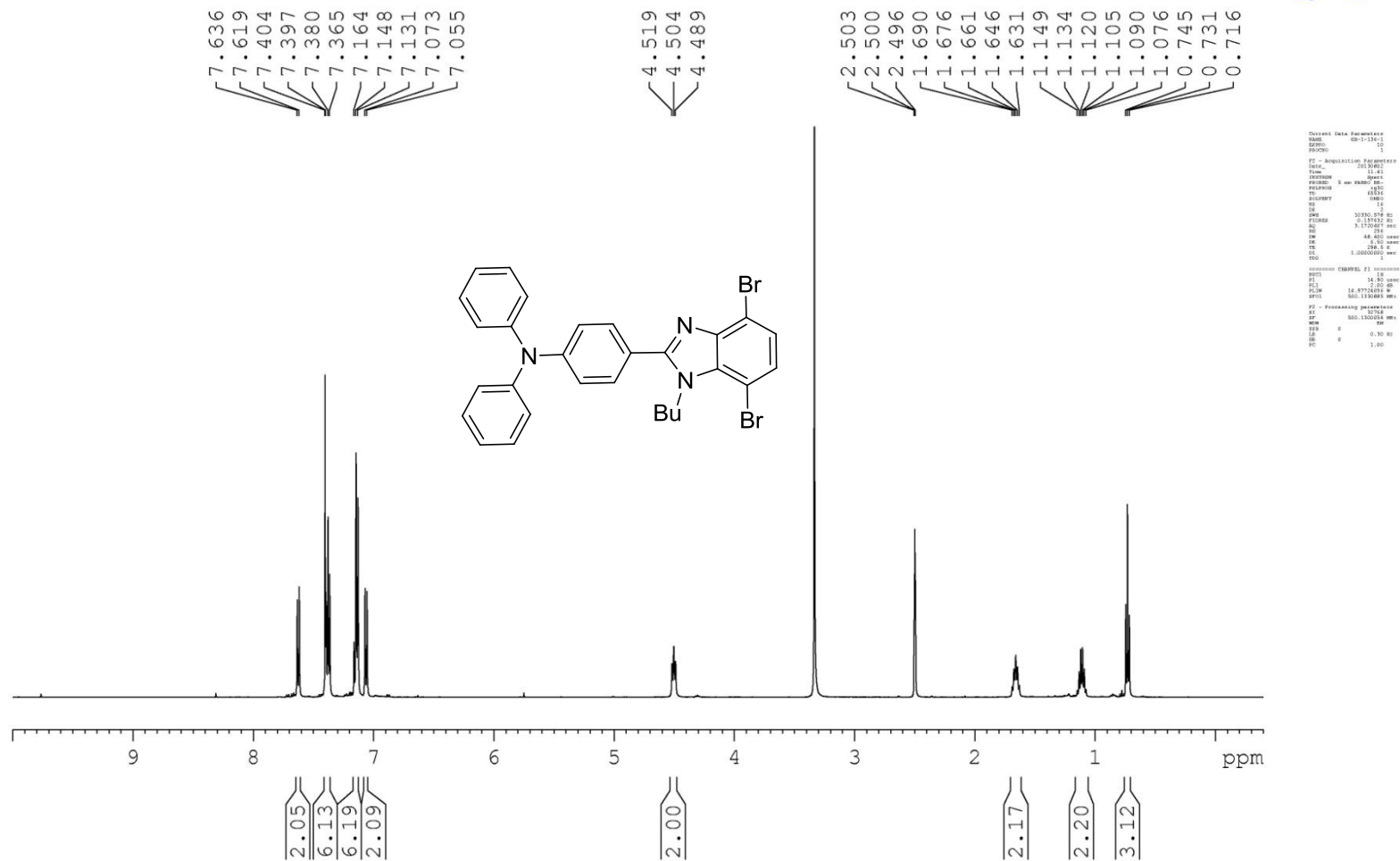
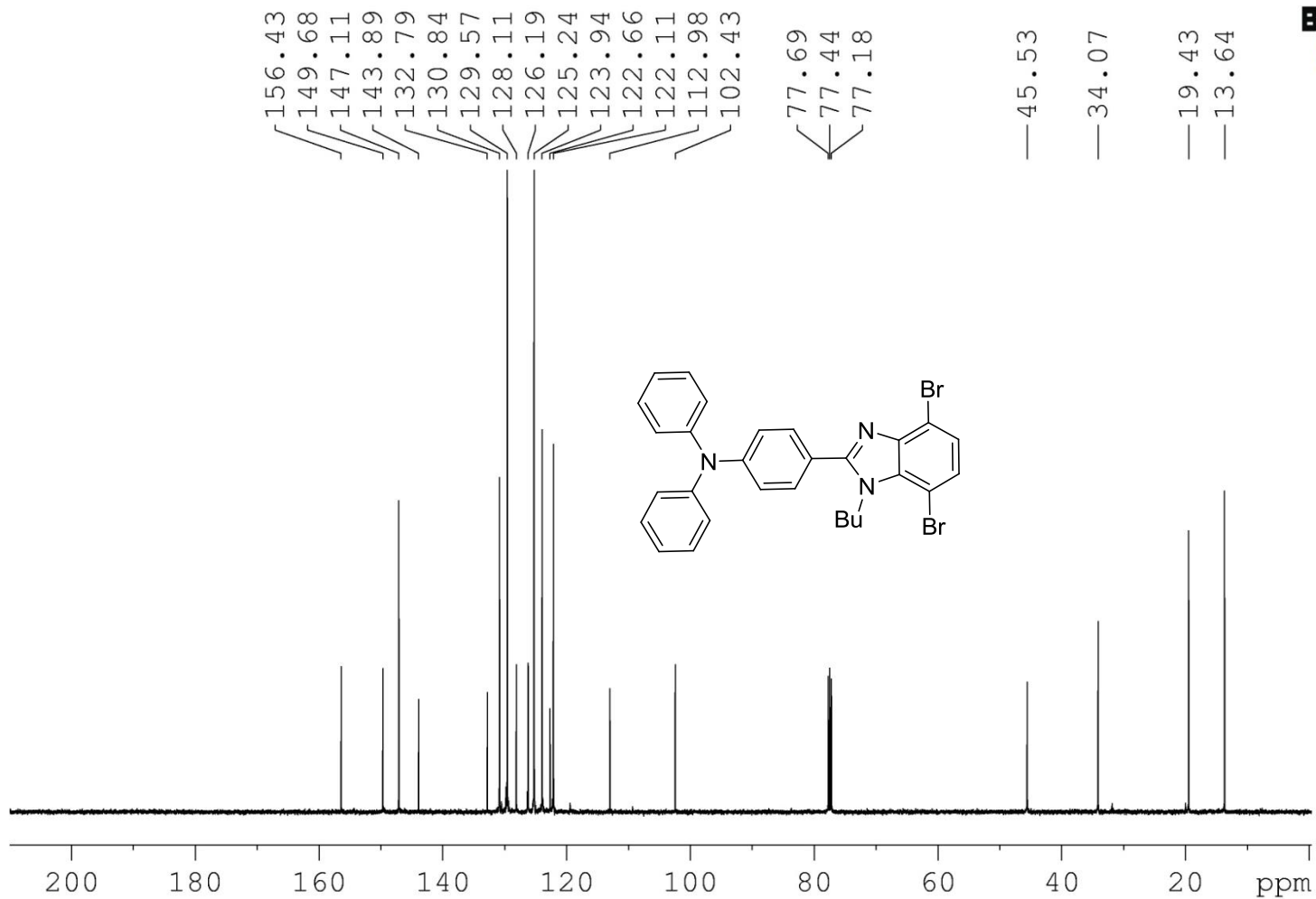


Figure S21. ¹H NMR spectra of **9** recorded in DMSO-*d*₆.

GB-1-136 C13



```
Current Data Parameters
NAME      GB-1-136 C13
EXPNO    13
PROCNO   13

F2 - Acquisition Parameters
Date_    20120902
Time     12.48
INSTRUM  spect
PROBHD   5 mm QNP5B
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        122
DS        4
SWH       30030.029 KHz
FIDRES   0.446112 KHz
AQ        1.191516 sec
RG         3200
AQ        16.480 usec
DE         6.40 usec
TE        300.2 K
D1         2.0000000 sec
d11        0.0200000 sec
TD0        1

===== CHANNEL f1 =====
NUC1      13C
P1         8.80 usec
PL1       1.00 dB
PL12      64.46697913 W
SFO1      125.7693643 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     80.00 usec
PL2       19.00 dB
PL12      16.40 dB
PL13      25.00 dB
PL14      14.9724084 W
PL15      0.18291408 W
PL16      0.23737324 W
SFO2      500.1320000 MHz

F2 - Processing parameters
SI         32768
SF        125.767890 MHz
WDW        EM
SSB         0
LB         1.00 KHz
GB         0
PC         1.40
```

Figure S22. ¹³C NMR spectra of **9** recorded in CDCl₃.

GB-1-175

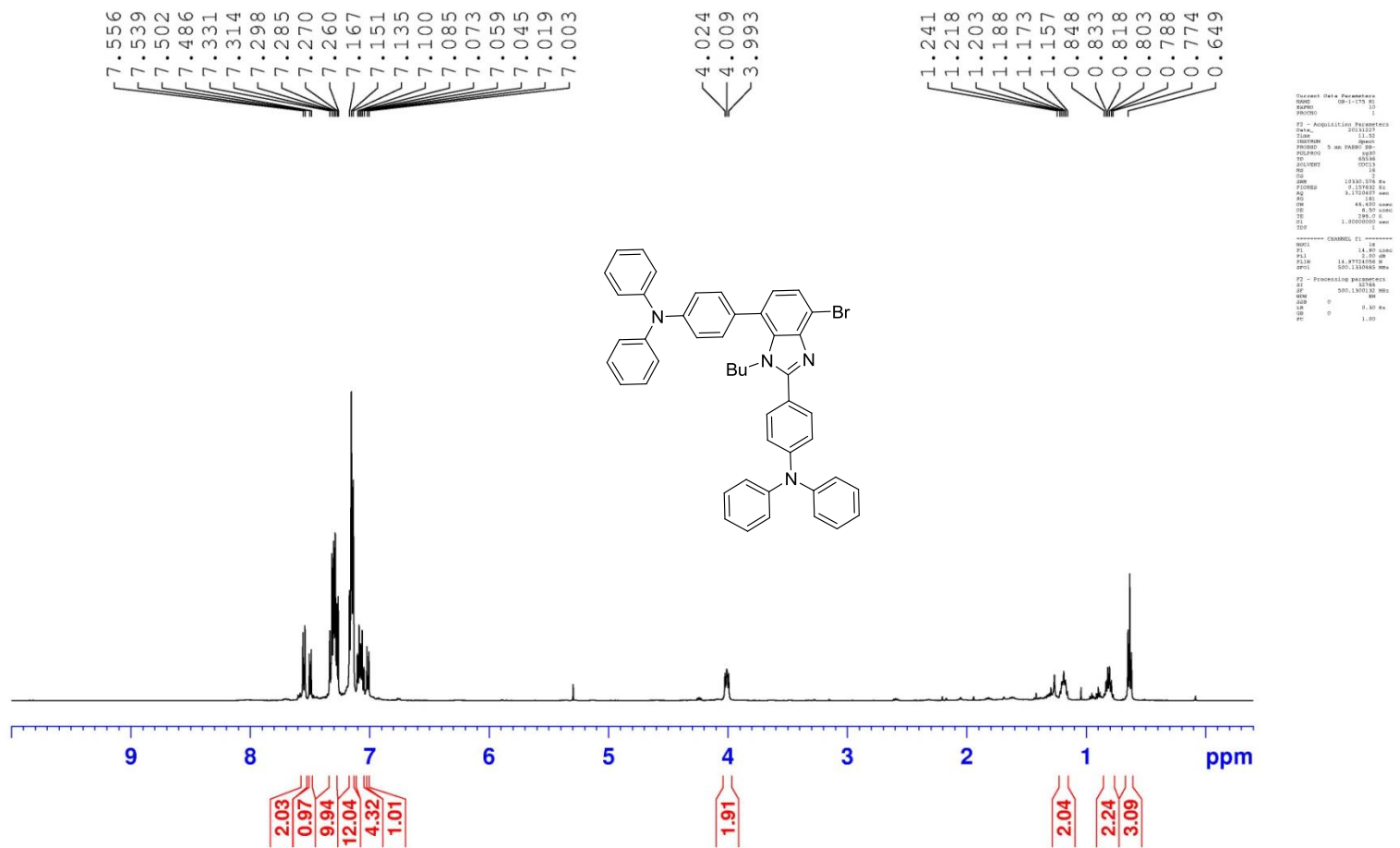


Figure S23. ^1H NMR spectra of **10** recorded in CDCl_3 .

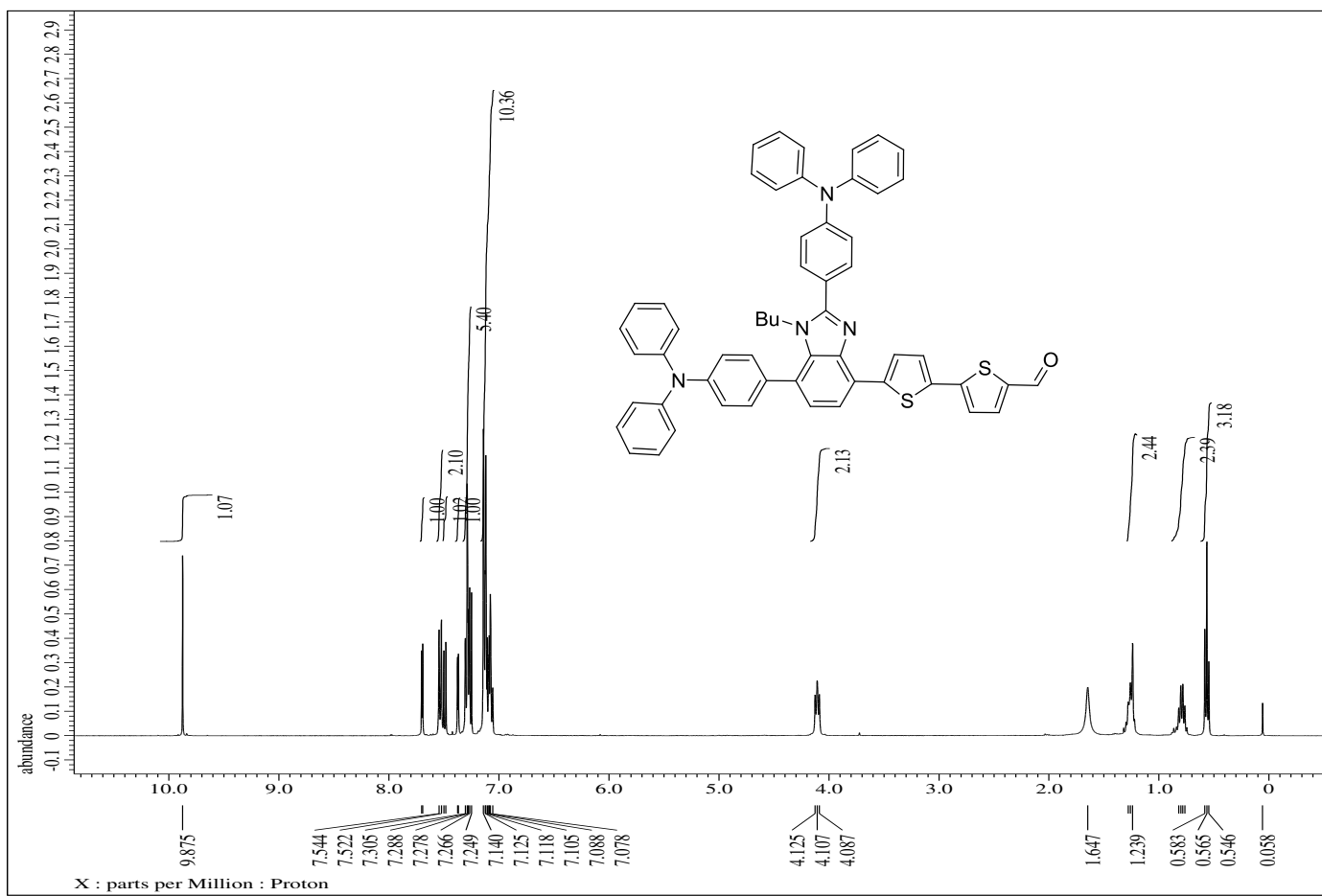


Figure S25. ¹H NMR spectra of **11** recorded in CDCl₃.

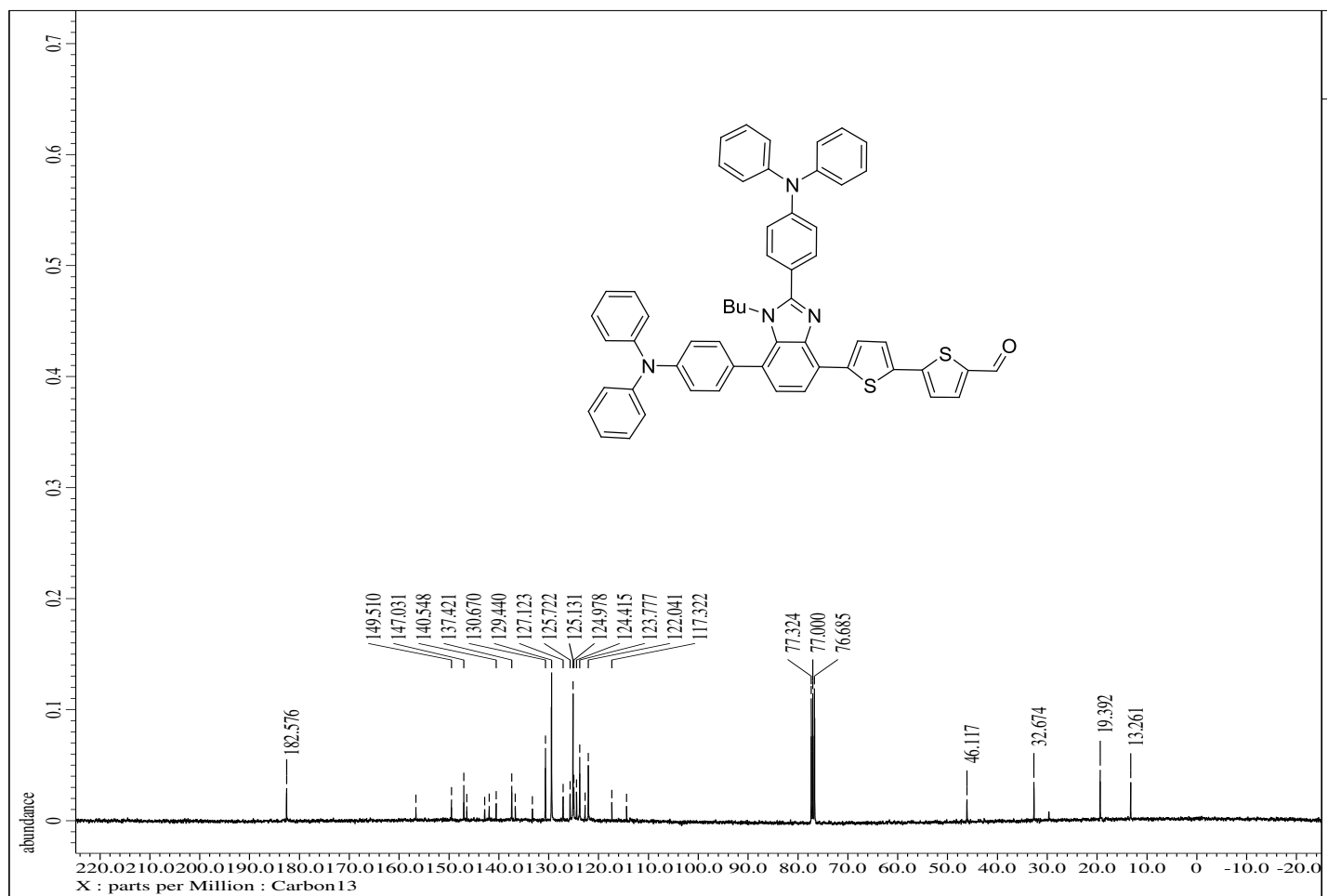


Figure S26. ^{13}C NMR spectra of **11** recorded in CDCl_3 .

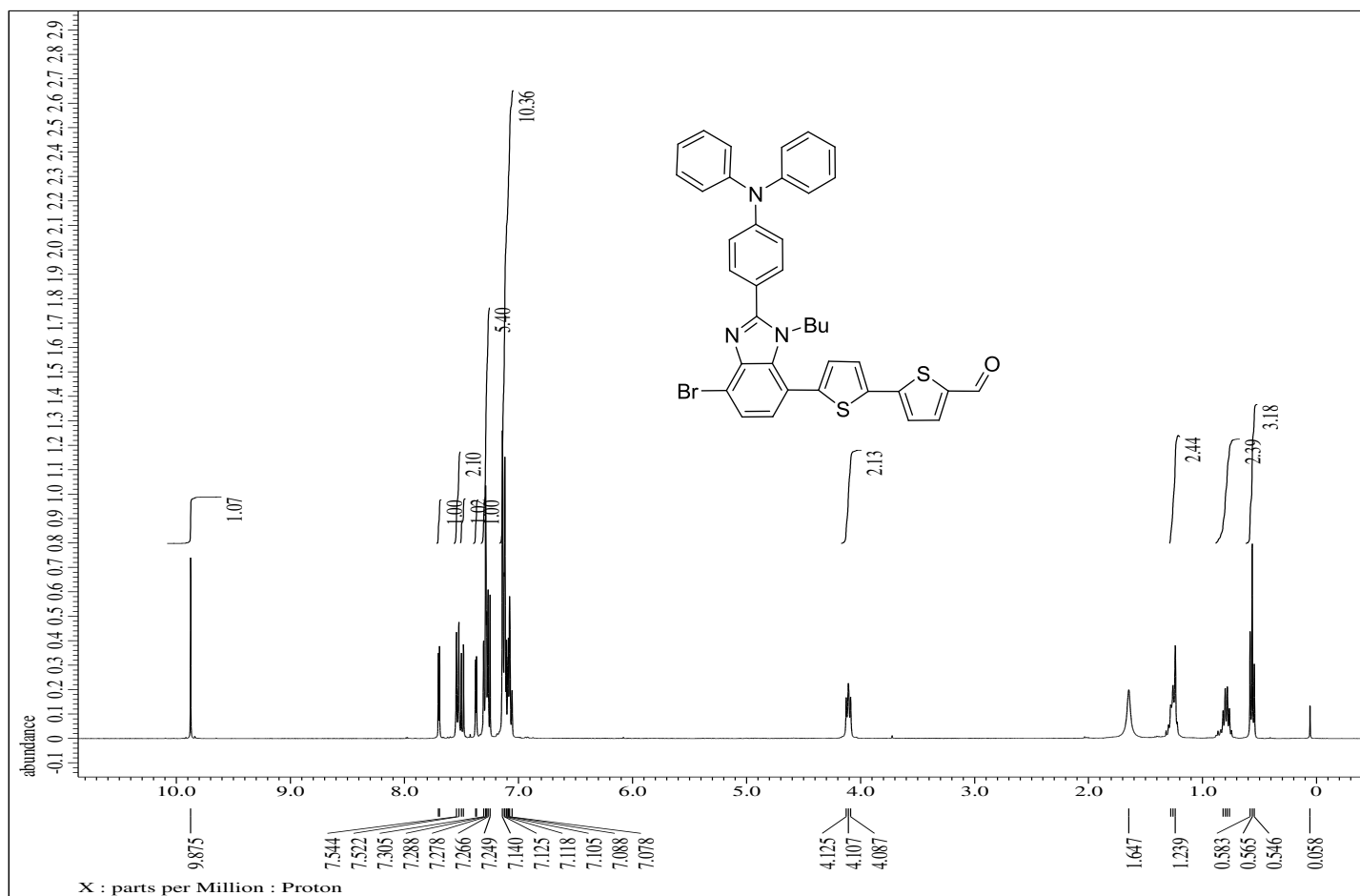


Figure S27. ¹H NMR spectra of **12** recorded in CDCl₃.

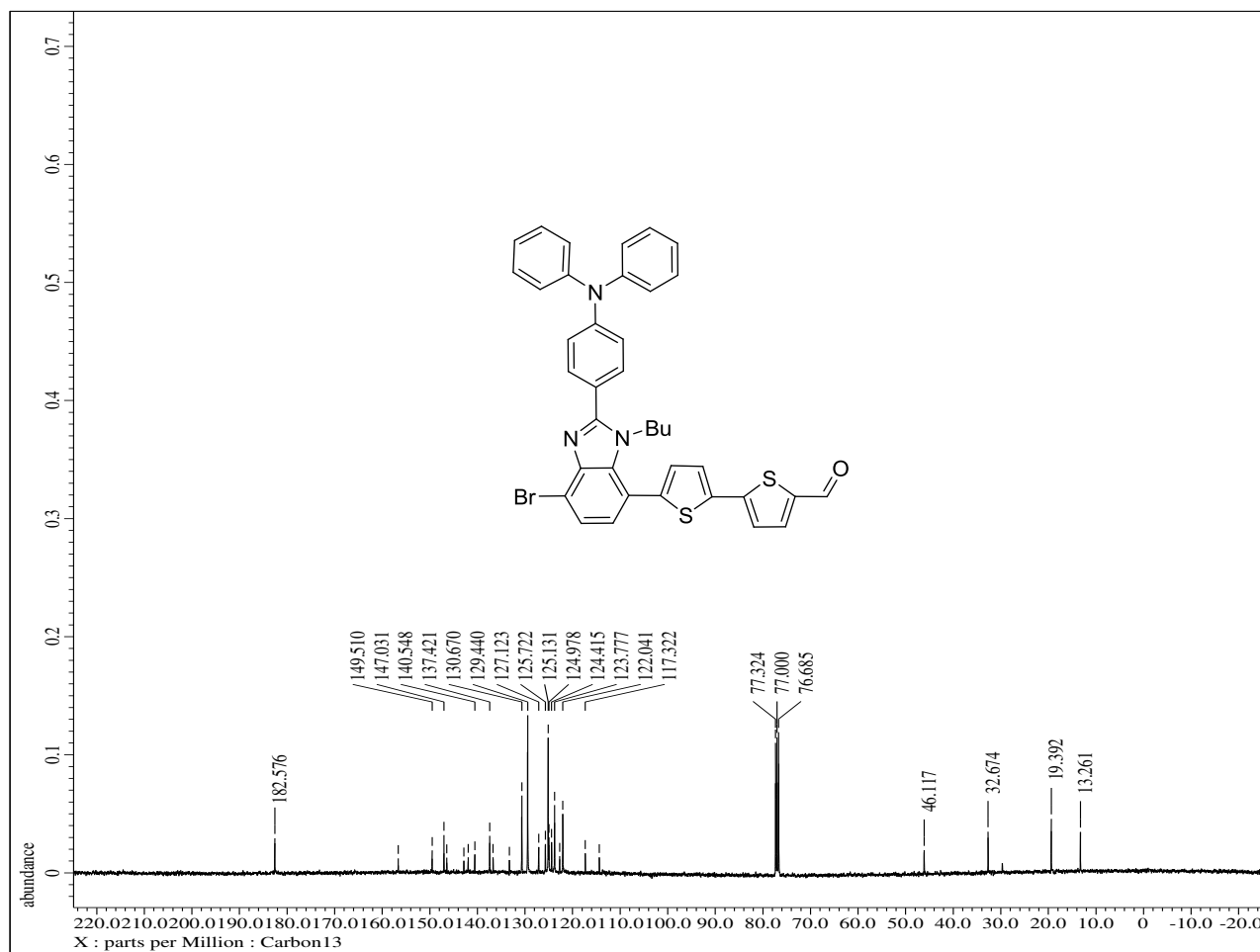


Figure S28. ^{13}C NMR spectra of **12** recorded in CDCl_3 .

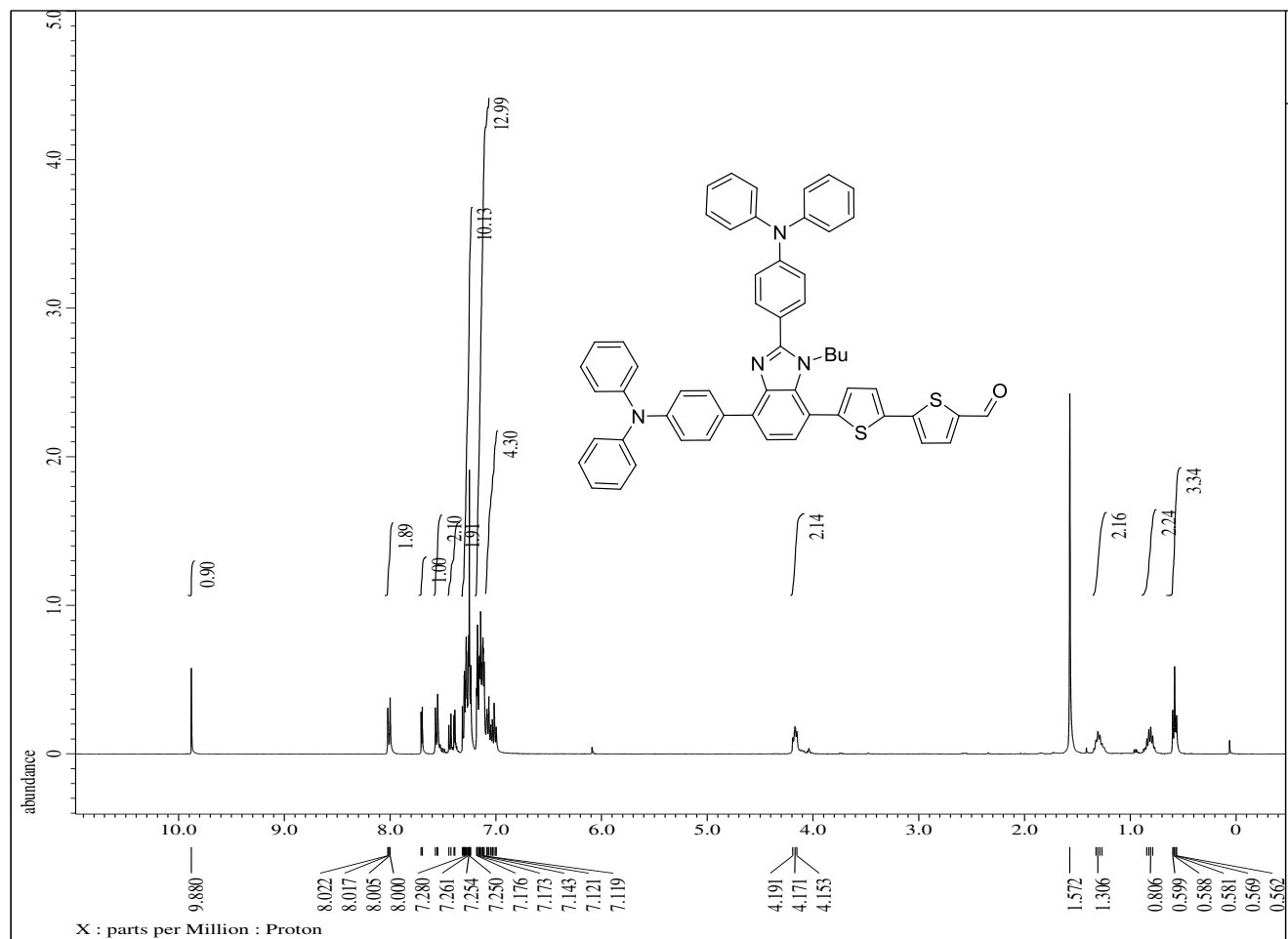


Figure S29. ¹H NMR spectra of **13** recorded in CDCl₃.

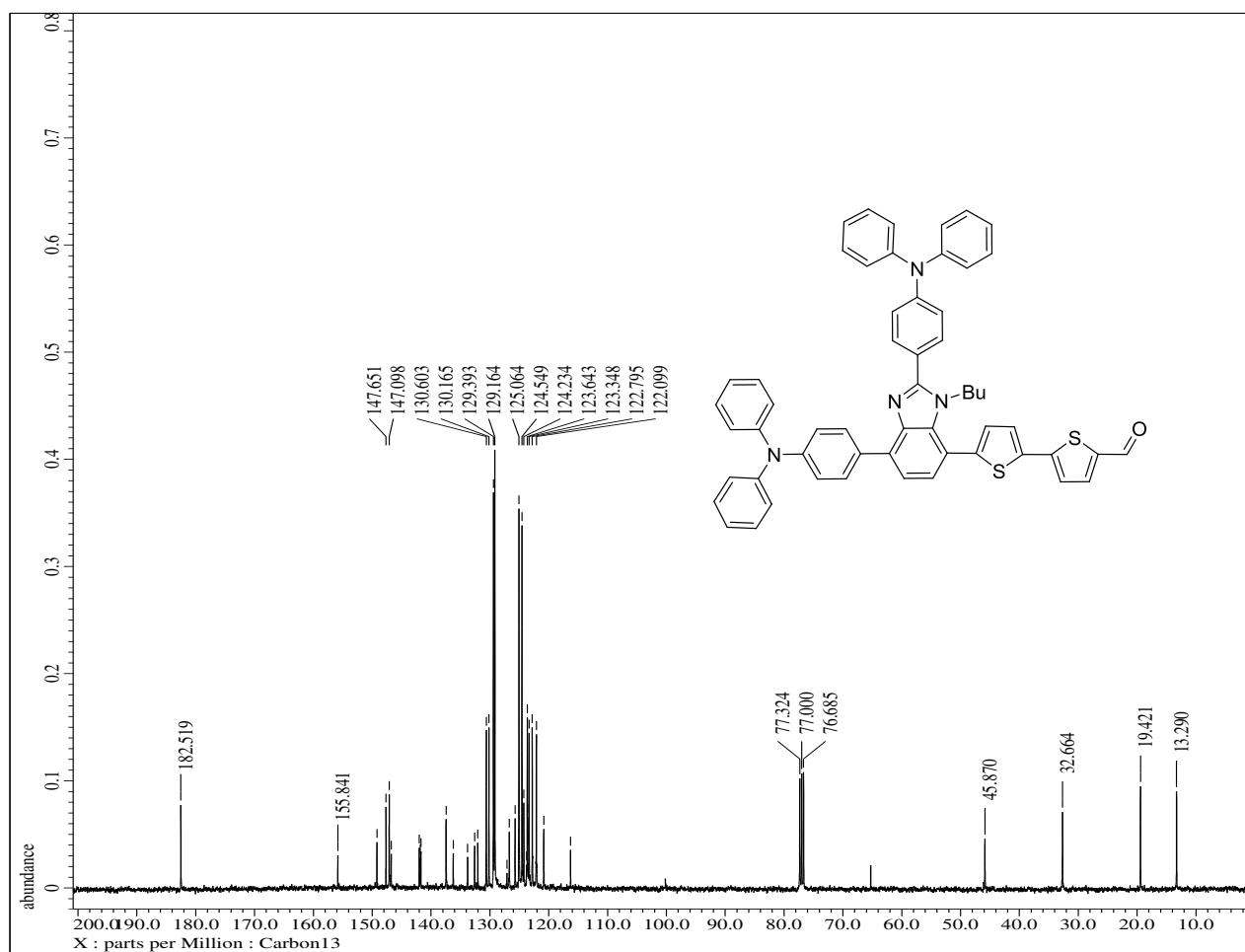


Figure S30. ^{13}C NMR spectra of **13** recorded in CDCl_3 .

GB-1-173-2

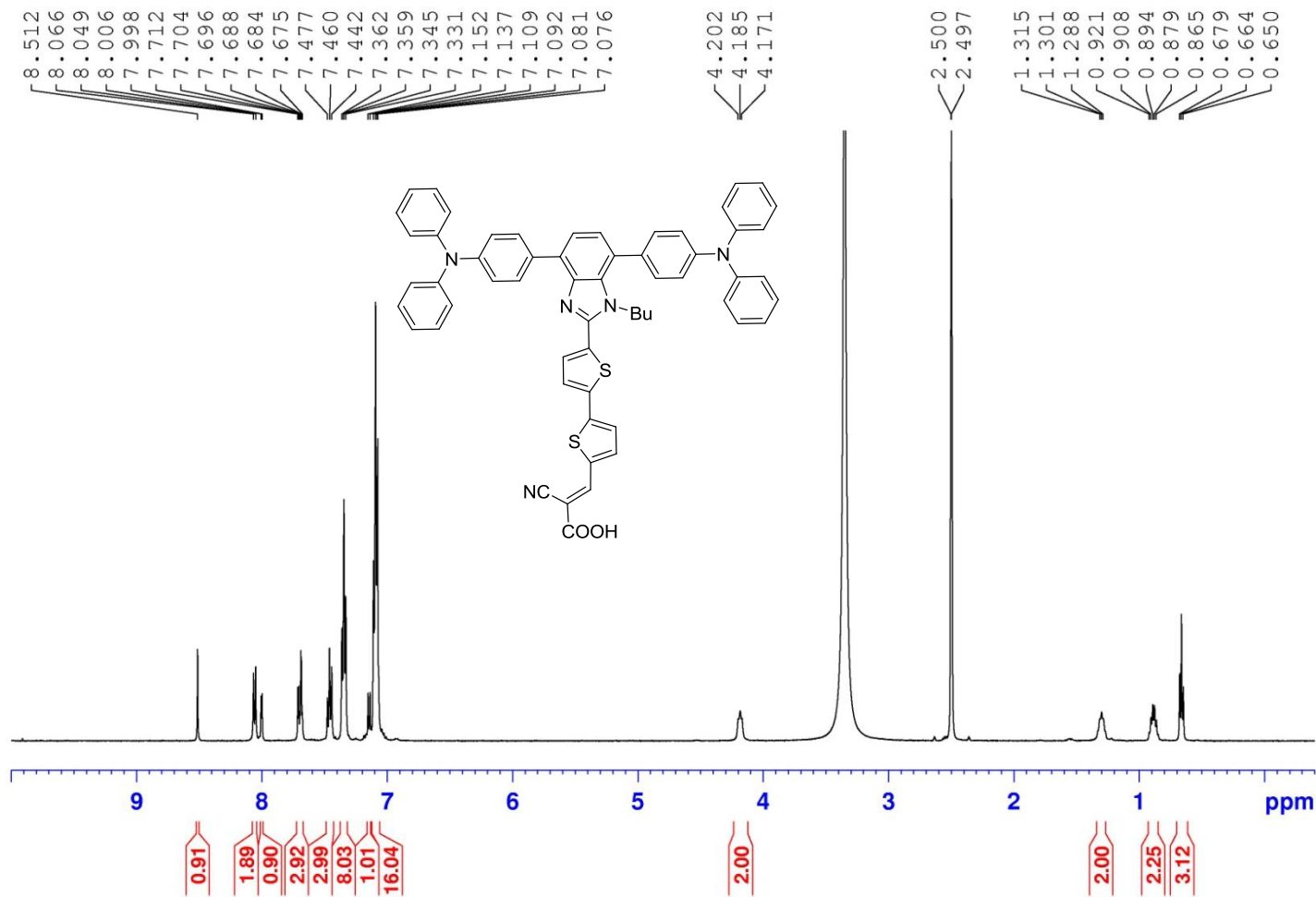


Figure S31. ^1H NMR spectra of **7a** recorded in $\text{DMSO-}d_6$.

GB-1-173C13

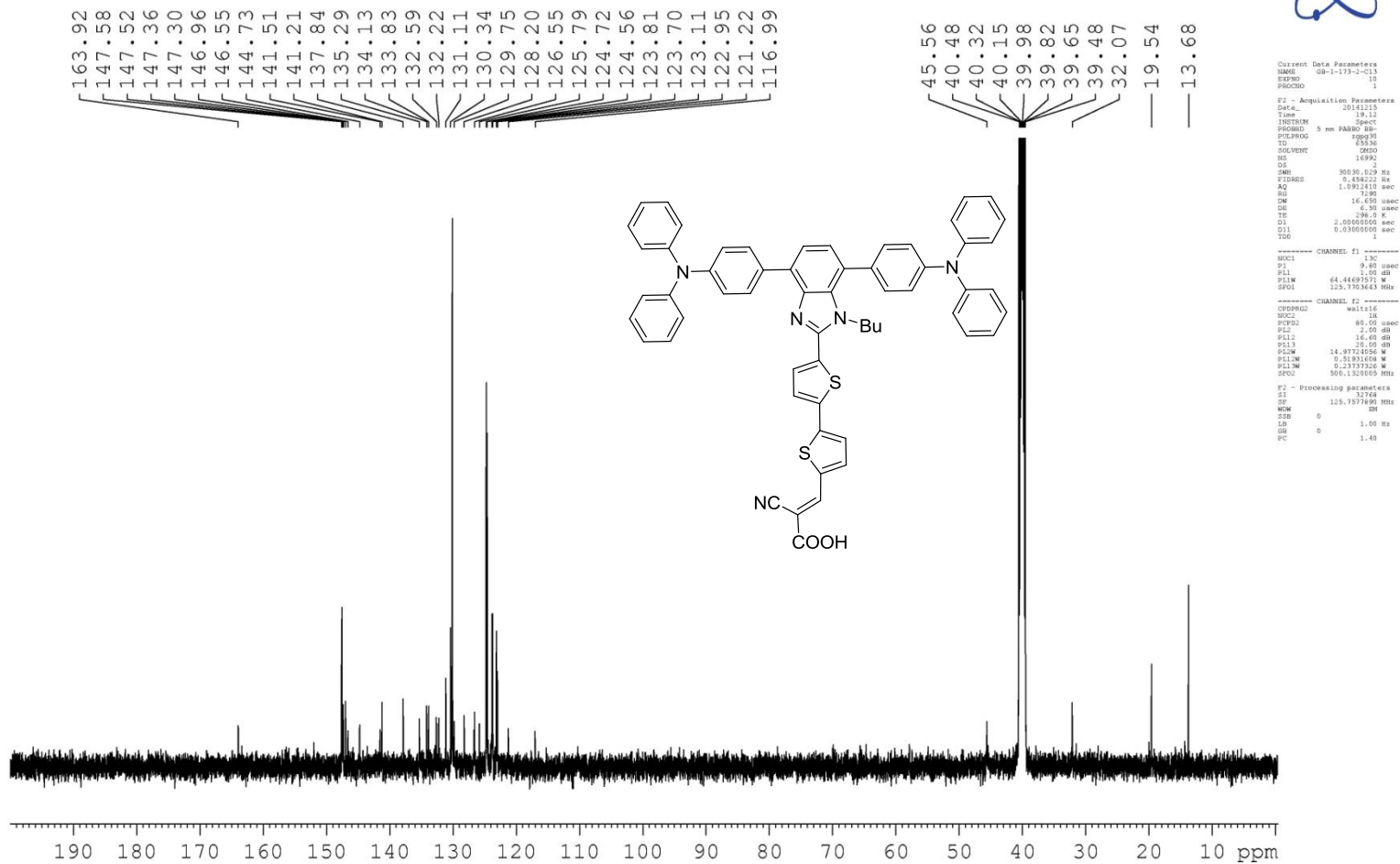
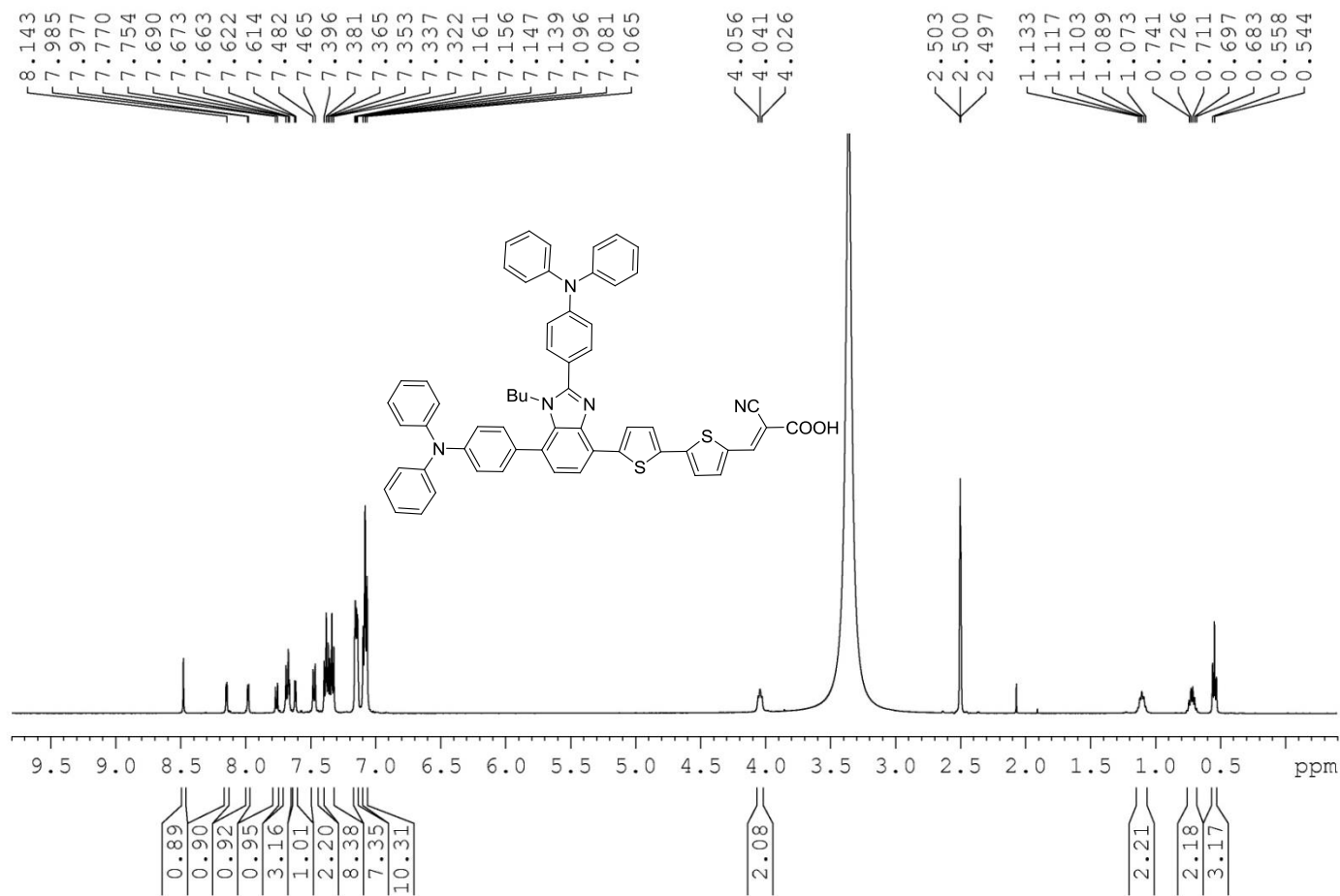


Figure S32. ^{13}C NMR spectra of **7a** recorded in $\text{DMSO-}d_6$.

GB-1-219 R



```
===== CHANNEL f1 =====
NUC1  13
P1  1.00000000
PC1  2.00 dB
PC2  14.97144000
SFO1  500.1320880 MHz
F2 - Processing parameters
SF  500.1320880 MHz
AQ  0.37500000
RG  64
SI  0
LS  0
GB  0
PC  1.00
```

Figure S33. ¹H NMR spectra of **7b** recorded in DMSO-d₆.

GB-1-219 C13

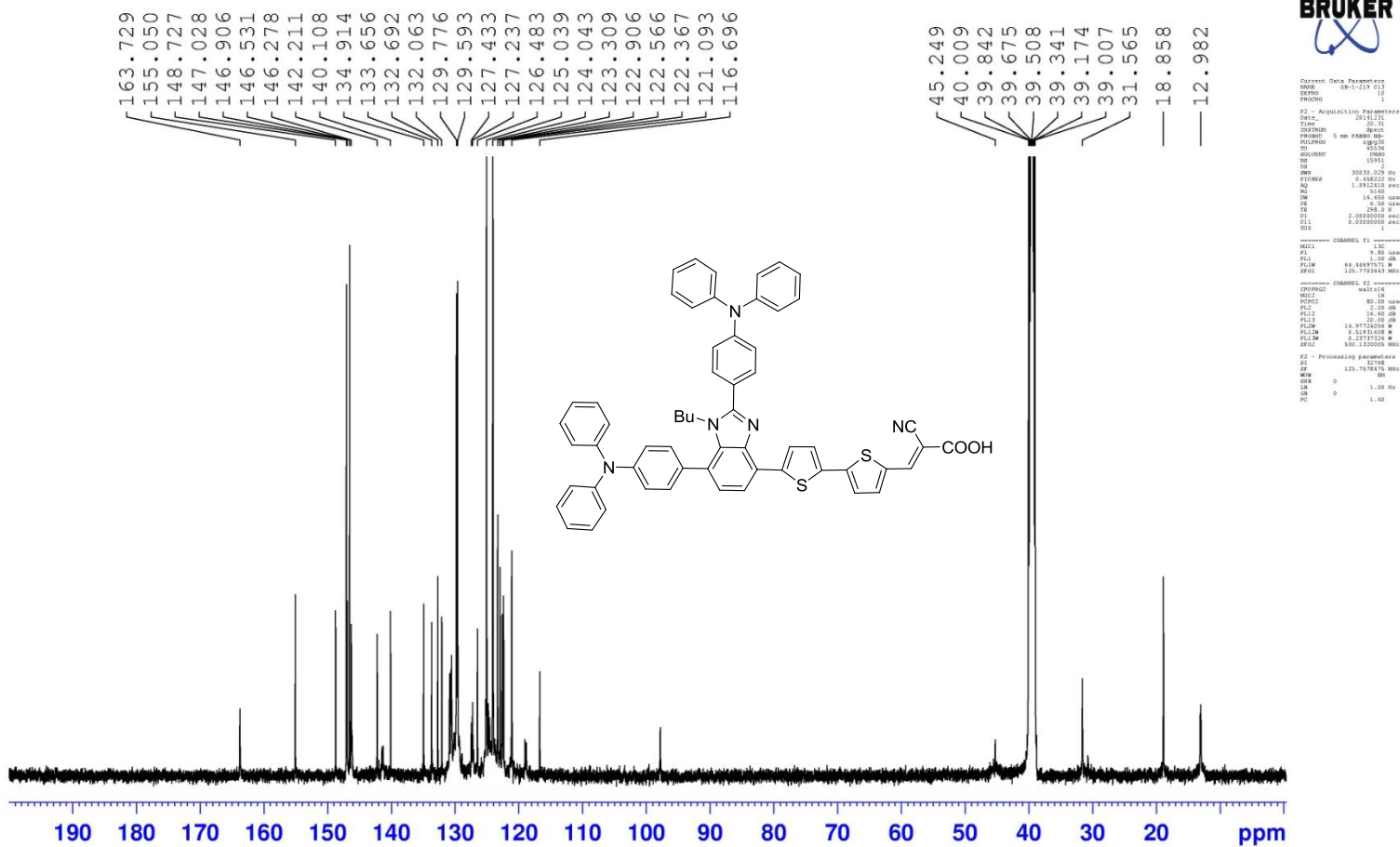


Figure S34. ^{13}C NMR spectra of **7b** recorded in $\text{DMSO-}d_6$.

GB-1-220 OLD

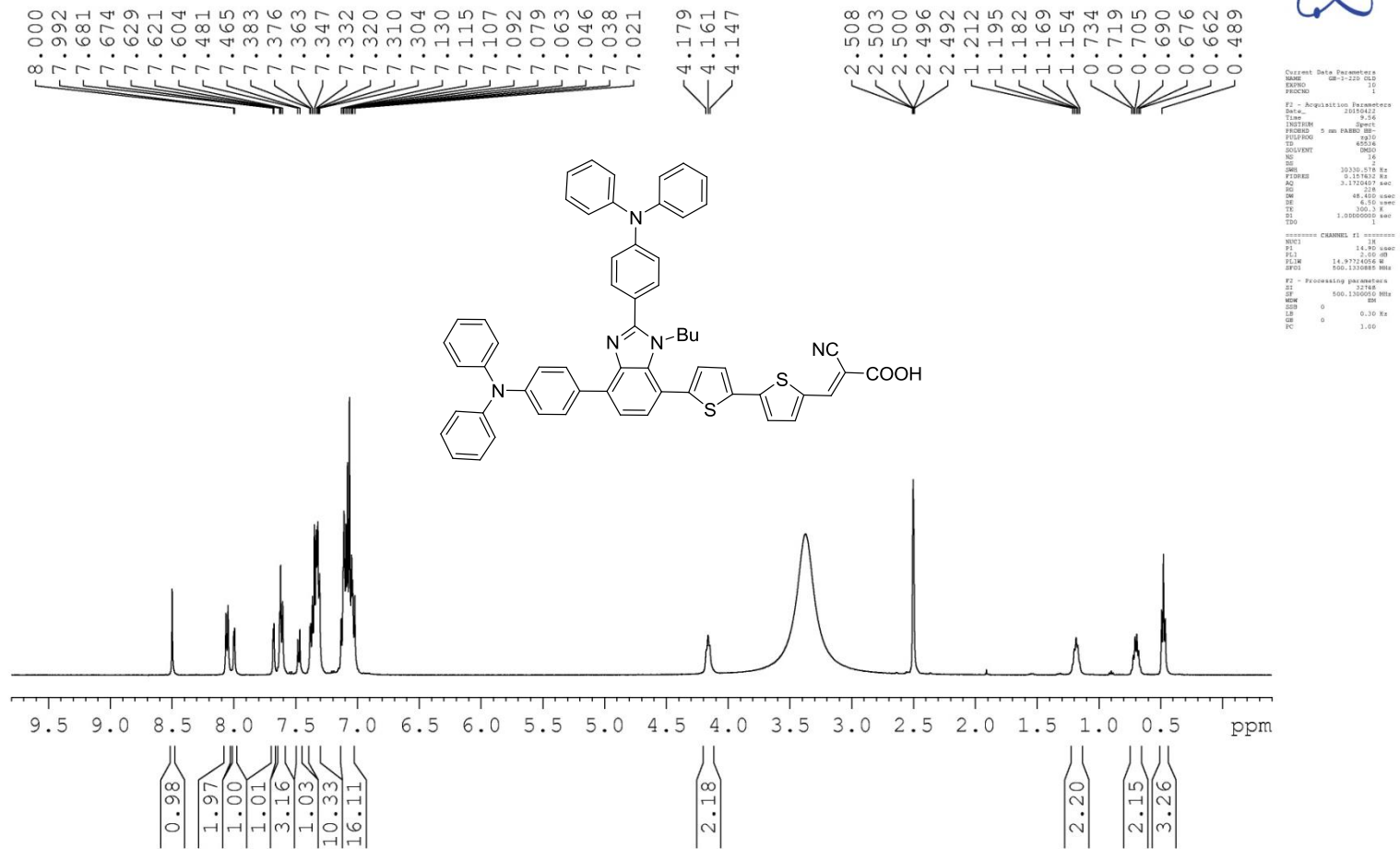
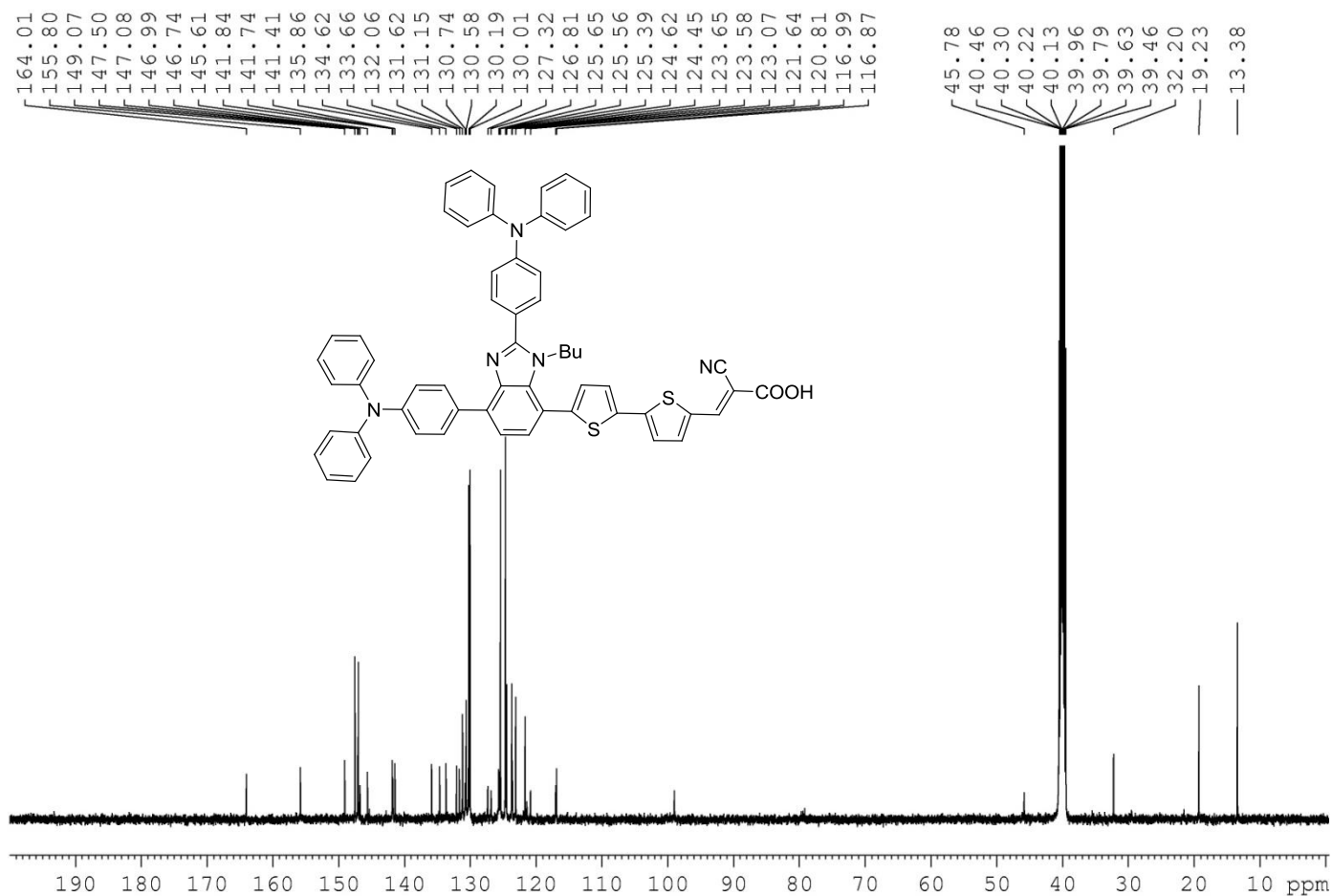


Figure S35. ¹H NMR spectra of 7c recorded in DMSO-d₆.

GB-1-220



===== CHANNEL F1 =====
NUC1 13
P1 1.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F2 =====
NUC2 13
P2 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F3 =====
NUC3 13
P3 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F4 =====
NUC4 13
P4 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F5 =====
NUC5 13
P5 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F6 =====
NUC6 13
P6 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F7 =====
NUC7 13
P7 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F8 =====
NUC8 13
P8 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F9 =====
NUC9 13
P9 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F10 =====
NUC10 13
P10 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F11 =====
NUC11 13
P11 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F12 =====
NUC12 13
P12 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F13 =====
NUC13 13
P13 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F14 =====
NUC14 13
P14 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F15 =====
NUC15 13
P15 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F16 =====
NUC16 13
P16 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F17 =====
NUC17 13
P17 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F18 =====
NUC18 13
P18 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F19 =====
NUC19 13
P19 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F20 =====
NUC20 13
P20 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F21 =====
NUC21 13
P21 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F22 =====
NUC22 13
P22 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F23 =====
NUC23 13
P23 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F24 =====
NUC24 13
P24 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F25 =====
NUC25 13
P25 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F26 =====
NUC26 13
P26 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F27 =====
NUC27 13
P27 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F28 =====
NUC28 13
P28 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F29 =====
NUC29 13
P29 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F30 =====
NUC30 13
P30 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F31 =====
NUC31 13
P31 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F32 =====
NUC32 13
P32 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F33 =====
NUC33 13
P33 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F34 =====
NUC34 13
P34 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F35 =====
NUC35 13
P35 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F36 =====
NUC36 13
P36 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F37 =====
NUC37 13
P37 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F38 =====
NUC38 13
P38 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F39 =====
NUC39 13
P39 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F40 =====
NUC40 13
P40 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F41 =====
NUC41 13
P41 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F42 =====
NUC42 13
P42 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F43 =====
NUC43 13
P43 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F44 =====
NUC44 13
P44 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F45 =====
NUC45 13
P45 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F46 =====
NUC46 13
P46 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F47 =====
NUC47 13
P47 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F48 =====
NUC48 13
P48 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F49 =====
NUC49 13
P49 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F50 =====
NUC50 13
P50 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F51 =====
NUC51 13
P51 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F52 =====
NUC52 13
P52 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F53 =====
NUC53 13
P53 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F54 =====
NUC54 13
P54 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F55 =====
NUC55 13
P55 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F56 =====
NUC56 13
P56 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F57 =====
NUC57 13
P57 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F58 =====
NUC58 13
P58 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F59 =====
NUC59 13
P59 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F60 =====
NUC60 13
P60 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F61 =====
NUC61 13
P61 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F62 =====
NUC62 13
P62 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F63 =====
NUC63 13
P63 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F64 =====
NUC64 13
P64 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F65 =====
NUC65 13
P65 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F66 =====
NUC66 13
P66 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F67 =====
NUC67 13
P67 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F68 =====
NUC68 13
P68 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F69 =====
NUC69 13
P69 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F70 =====
NUC70 13
P70 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F71 =====
NUC71 13
P71 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F72 =====
NUC72 13
P72 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F73 =====
NUC73 13
P73 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F74 =====
NUC74 13
P74 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F75 =====
NUC75 13
P75 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F76 =====
NUC76 13
P76 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F77 =====
NUC77 13
P77 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F78 =====
NUC78 13
P78 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F79 =====
NUC79 13
P79 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F80 =====
NUC80 13
P80 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F81 =====
NUC81 13
P81 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F82 =====
NUC82 13
P82 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F83 =====
NUC83 13
P83 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F84 =====
NUC84 13
P84 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F85 =====
NUC85 13
P85 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F86 =====
NUC86 13
P86 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F87 =====
NUC87 13
P87 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F88 =====
NUC88 13
P88 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F89 =====
NUC89 13
P89 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F90 =====
NUC90 13
P90 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F91 =====
NUC91 13
P91 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F92 =====
NUC92 13
P92 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F93 =====
NUC93 13
P93 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F94 =====
NUC94 13
P94 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F95 =====
NUC95 13
P95 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F96 =====
NUC96 13
P96 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F97 =====
NUC97 13
P97 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F98 =====
NUC98 13
P98 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F99 =====
NUC99 13
P99 0.00
PL 0.00
SFO 125.760348 MHz
===== CHANNEL F100 =====
NUC100 13
P100 0.00
PL 0.00
SFO 125.760348 MHz

Figure S36. ^{13}C NMR spectra of 7c recorded in $\text{DMSO-}d_6$.

Computational Methods. All the computations were performed with the Gaussian 09 program package. The ground-state geometries were fully optimized without any symmetry constraints at the DFT level with Becke's three parameters hybrid functional and Lee, Yang and Parr's correlational functional (B3LYP) using 6-31G(D, P) basis set on all atoms. The default parameters for the convergence criteria were used. Vibrational analyses on the optimized structures were performed to confirm the structure. No negative frequency vibrations were observed for the optimized geometries. The excitation energies and oscillator strengths for the lowest 10 singlet transitions for the optimized geometry in the ground state were obtained by TD-DFT calculations using the same basis set.

X-ray Crystal Structure Determination. Crystals of the compounds **6** suitable for X-ray data collection were grown from dichloromethane/hexane mixture. X-ray data of **6** was collected on a CCD diffractometer using Mo K α ($\lambda=0.71073$). The data were corrected for Lorentz and polarization effects. A total of 29055 reflections were measured out of which 8174 were independent and 2383 were observed [$I>2\sigma(I)$] for maximum theta 28.341° at room temperature. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares refinement methods based on F^2 , using SHELXL-2014/7. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with their U_{iso} values 1.2 times of the phenylene and methylene carbons and 1.5 times of the methyl carbons. All calculations were performed using Bruker SHELXTL package. A final refinement of 410 parameters gave $R_1 = 0.0534$, $wR_2 = 0.1326$ for the observed data and $R_1 = 0.2493$, $wR_2 = 0.2249$ for all data.

Table S1. Crystal data and structure refinement for **6**.

Empirical formula	C ₃₈ H ₃₀ Br N ₃ O S ₂	
Formula weight	688.68	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.0416(5) Å	a = 99.687(3)°.
	b = 12.3341(6) Å	b = 97.512(3)°.
	c = 14.3639(7) Å	g = 104.946(3)°.
Volume	1665.77(14) Å ³	
Z	2	
Density (calculated)	1.373 Mg/m ³	
Absorption coefficient	1.394 mm ⁻¹	
F(000)	708	
Crystal size	0.12 x 0.09 x 0.07 mm ³	
Theta range for data collection	1.463 to 28.341°.	
Index ranges	-13<=h<=13, -16<=k<=12, -19<=l<=19	
Reflections collected	29055	
Independent reflections	8174 [R(int) = 0.1032]	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8174 / 0 / 410	
Goodness-of-fit on F ²	0.877	
Final R indices [I>2sigma(I)]	R1 = 0.0534, wR2 = 0.1326	
R indices (all data)	R1 = 0.2493, wR2 = 0.2249	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.324 and -0.330 e.Å ⁻³	

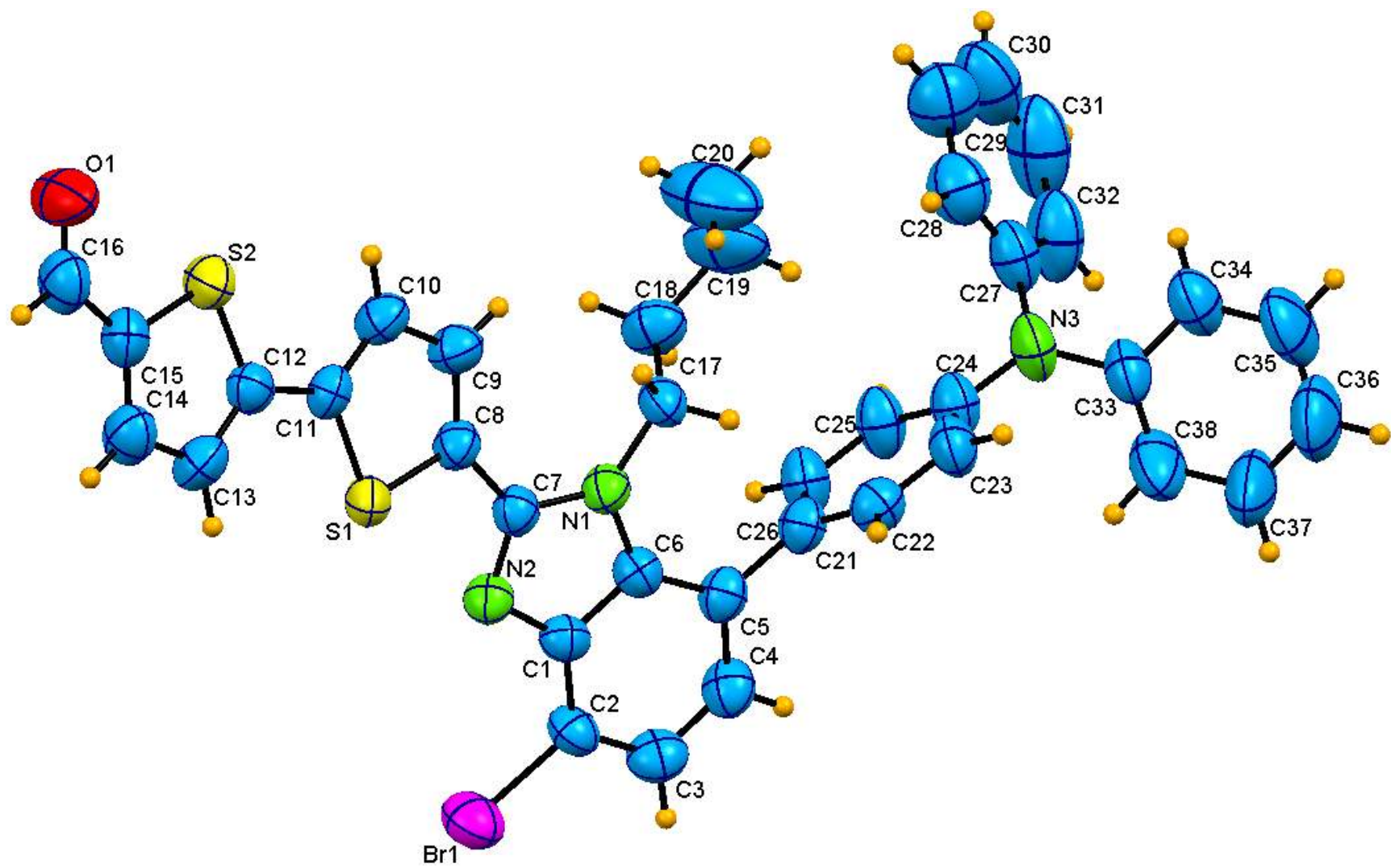


Figure S37. Molecular structure of **6** (40% thermal ellipsoids).

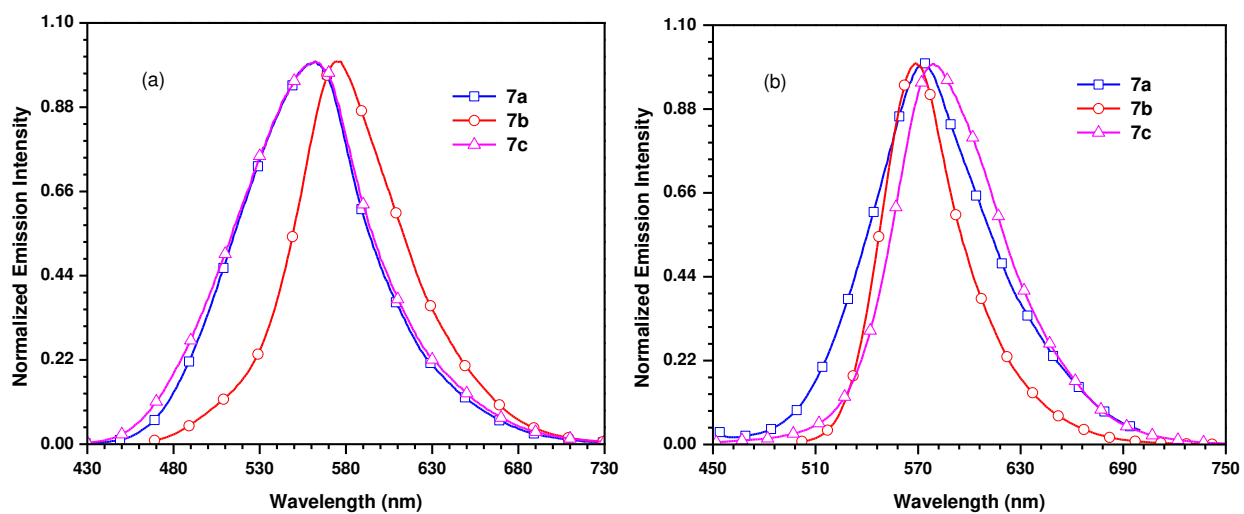


Figure S38. Emission spectra of the dyes recorded in (a) THF and (b) toluene.

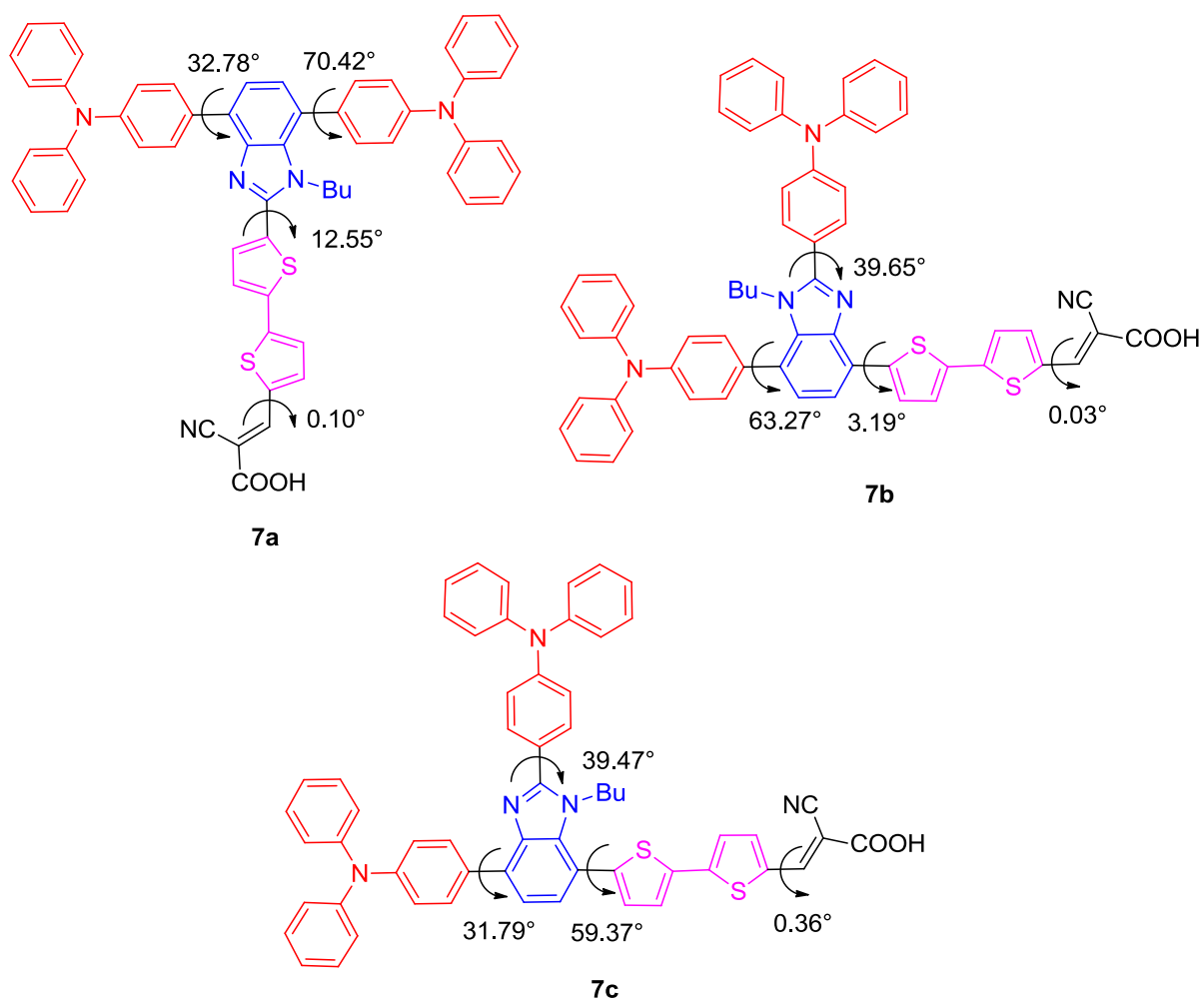


Figure S39. Calculated interplanar angles between various aromatic segments in the dyes.

Table S1. Cartesian coordinates for the optimized structure of **7a**.

Total Energy: -3495.97535867 hartrees

At. No.	X	Y	Z
6	0.334352	0.298817	-0.0765742
7	1.102609	-0.777009	-0.096339
7	-1.020005	-0.012184	-0.067714
6	0.250673	-1.851807	-0.079954
6	-1.100368	-1.405536	-0.072385
6	0.582845	-3.230604	-0.063396
6	-2.188191	-2.305266	-0.066237
6	-0.505009	-4.106533	-0.018144
6	-1.833379	-3.657903	-0.021700
1	-0.321521	-5.174994	0.038060
1	-2.633931	-4.392329	-0.003970
6	-2.141171	0.916935	0.085991
6	-2.523984	1.168740	1.550744
1	-2.992850	0.504906	-0.455315
1	-1.878444	1.850925	-0.417611
6	-3.715099	2.126135	1.680381
1	-2.769743	0.207601	2.019179
1	-1.659088	1.572865	2.093114
6	-4.111068	2.388467	3.136835
1	-3.474538	3.079337	1.188075
1	-4.573870	1.706693	1.137486
1	-4.963449	3.074022	3.199856
1	-4.393494	1.457619	3.642824
1	-3.281550	2.833646	3.699270
6	-3.636210	-1.947341	-0.124377
6	-4.479532	-2.178554	0.973289
6	-4.223565	-1.453149	-1.301346
6	-5.843692	-1.903477	0.913267
1	-4.054798	-2.565908	1.895713
6	-5.588409	-1.191608	-1.378563
1	-3.603987	-1.300176	-2.181647
6	-6.422223	-1.408220	-0.267452
1	-6.468517	-2.075366	1.783618
1	-6.018339	-0.829814	-2.306827
7	-7.811758	-1.142535	-0.339483
6	-8.740098	-2.001304	0.316302
6	-8.294253	-0.028161	-1.081969
6	-9.811325	-1.461631	1.045183
6	-8.601534	-3.396062	0.238519

6	-9.414995	-0.162281	-1.916812
6	-7.663873	1.222647	-0.985431
6	-10.726384	-2.302987	1.675443
1	-9.920795	-0.383758	1.111601
6	-9.510865	-4.229324	0.887603
1	-7.780396	-3.819851	-0.331035
6	-9.894716	0.933933	-2.631261
1	-9.904926	-1.127242	-1.999587
6	-8.139575	2.308774	-1.717660
1	-6.803435	1.337264	-0.333291
6	-10.580224	-3.690013	1.605826
1	-11.550556	-1.869117	2.235571
1	-9.389233	-5.307063	0.817561
6	-9.259050	2.174065	-2.541475
1	-10.763560	0.811853	-3.272667
1	-7.639584	3.269947	-1.630408
1	-11.291217	-4.342555	2.104380
1	-9.631646	3.024462	-3.105217
6	1.973993	-3.732722	-0.090310
6	2.279547	-4.953675	-0.720359
6	3.035260	-3.042772	0.524811
6	3.571037	-5.465914	-0.735493
1	1.498023	-5.495140	-1.245893
6	4.326686	-3.557231	0.529640
1	2.838991	-2.097586	1.015871
6	4.618543	-4.777523	-0.101608
1	3.777606	-6.398947	-1.249898
1	5.120682	-3.013654	1.031825
7	5.937837	-5.298842	-0.105968
6	6.153006	-6.693788	0.064979
6	7.048707	-4.428717	-0.286834
6	7.102278	-7.370947	-0.717747
6	5.420652	-7.416527	1.021017
6	8.207922	-4.583026	0.490340
6	7.003670	-3.404303	-1.246157
6	7.316304	-8.736361	-0.539091
1	7.668111	-6.821161	-1.463133
6	5.629037	-8.785183	1.179582
1	4.690860	-6.899105	1.635640
6	9.298386	-3.735968	0.301948
1	8.246537	-5.368300	1.238615
6	8.092384	-2.550834	-1.414553
1	6.113169	-3.283153	-1.854665
6	6.579714	-9.454143	0.405638
1	8.055140	-9.243451	-1.154325
1	5.053125	-9.327666	1.924981

6	9.247792	-2.712595	-0.646922
1	10.187524	-3.869627	0.912724
1	8.040221	-1.763154	-2.161728
1	6.744633	-10.519748	0.537201
1	10.096861	-2.049439	-0.785679
6	0.950663	1.618573	-0.102399
6	2.299226	1.808753	-0.353181
16	0.180631	3.156907	0.231899
6	2.707766	3.154628	-0.290663
1	2.951759	0.973839	-0.573815
6	1.684557	4.035705	0.014773
1	3.728280	3.476251	-0.470459
6	1.729764	5.468173	0.150220
6	0.685861	6.342685	0.434767
16	3.237148	6.334777	-0.044669
6	1.090509	7.683356	0.493671
1	-0.335642	6.014481	0.592061
6	2.449157	7.879953	0.257852
1	0.418565	8.509568	0.702497
6	3.075910	9.159156	0.266900
6	4.381182	9.519620	0.054994
1	2.395036	9.979495	0.477890
6	5.410148	8.574684	-0.235385
6	4.819396	10.933950	0.112564
7	6.228850	7.780617	-0.471108
8	5.958122	11.311396	-0.066197
8	3.800796	11.792944	0.391400
1	4.206666	12.678986	0.402701

Table S2. Cartesian coordinates for the optimized structure of **7b**.

Total Energy: -3495.98141070 hartrees

At. No.	X	Y	Z
6	-0.116307	0.553529	0.080237
7	0.785825	-0.408937	0.019363
7	-1.415587	0.059590	0.095439
6	0.083670	-1.585948	0.011476
6	-1.312828	-1.333085	0.040713
6	0.615660	-2.895592	0.010449
6	-2.255864	-2.382906	0.029811
6	-0.331370	-3.930015	0.050071
6	-1.704375	-3.674246	0.055827
1	-0.002994	-4.963687	0.065124
1	-2.390407	-4.516400	0.049355
6	-2.644042	0.854753	0.148342
6	-3.303709	0.885772	1.533353
1	-3.346961	0.452377	-0.583696
1	-2.384967	1.864973	-0.176267
6	-4.541079	1.792148	1.556522
1	-3.587203	-0.133890	1.818719
1	-2.575579	1.226652	2.281818
6	-5.245116	1.802887	2.917234
1	-4.249959	2.816968	1.284599
1	-5.245348	1.459196	0.781199
1	-6.119890	2.462668	2.908314
1	-5.586370	0.797856	3.192264
1	-4.571915	2.152956	3.709144
6	0.268566	1.974767	0.077142
6	-0.338300	2.966249	0.866468
6	1.362863	2.356387	-0.721131
6	0.111605	4.281826	0.845751
1	-1.139438	2.708275	1.550695
6	1.808000	3.669767	-0.758686
1	1.852313	1.601746	-1.327701
6	1.186597	4.661801	0.023580
1	-0.361038	5.020747	1.483909
1	2.638862	3.938138	-1.402425
7	1.635116	5.999999	-0.009754
6	0.710863	7.075693	0.129499
6	3.020128	6.294028	-0.176645
6	1.004810	8.156591	0.974657
6	-0.497094	7.075735	-0.585409
6	3.426689	7.294592	-1.072283

6	3.991703	5.597760	0.558735
6	0.107408	9.216129	1.096666
1	1.937287	8.160104	1.530243
6	-1.396469	8.130924	-0.443426
1	-0.722783	6.248111	-1.250613
6	4.779536	7.594257	-1.222388
1	2.678187	7.832644	-1.645430
6	5.343504	5.891977	0.388791
1	3.681871	4.829195	1.260028
6	-1.099420	9.208250	0.394219
1	0.349505	10.045997	1.755312
1	-2.327210	8.116997	-1.004521
6	5.745764	6.893108	-0.497919
1	5.078731	8.371979	-1.920036
1	6.084172	5.344403	0.965622
1	-1.799151	10.032754	0.496580
1	6.799701	7.124797	-0.622067
6	-3.738232	-2.254572	-0.039875
6	-4.549332	-2.779025	0.980416
6	-4.383727	-1.712663	-1.164299
6	-5.938374	-2.739447	0.899791
1	-4.080107	-3.207674	1.862047
6	-5.771783	-1.683772	-1.263572
1	-3.787566	-1.351186	-1.998500
6	-6.574442	-2.194004	-0.228507
1	-6.538499	-3.135217	1.712648
1	-6.241242	-1.281768	-2.155462
7	-7.986734	-2.170282	-0.325615
6	-8.758757	-3.264535	0.159608
6	-8.646022	-1.067553	-0.938804
6	-9.931222	-3.031825	0.895337
6	-8.365219	-4.587308	-0.097228
6	-9.686780	-1.281665	-1.855902
6	-8.270883	0.249294	-0.629069
6	-10.694988	-4.102645	1.356161
1	-10.238001	-2.010913	1.100026
6	-9.125669	-5.651867	0.383381
1	-7.464815	-4.773658	-0.674070
6	-10.338721	-0.199182	-2.443884
1	-9.978958	-2.297615	-2.101952
6	-8.916197	1.325416	-1.235451
1	-7.477587	0.420868	0.092060
6	-10.296007	-5.417783	1.108430
1	-11.600421	-3.905446	1.924078
1	-8.807399	-6.670055	0.175493
6	-9.955650	1.109540	-2.142837

1	-11.142549	-0.382715	-3.151943
1	-8.613953	2.338711	-0.983849
1	-10.890004	-6.249903	1.475304
1	-10.461761	1.950551	-2.608019
6	2.048549	-3.168981	-0.020812
6	2.660436	-4.412991	-0.083973
16	3.265217	-1.903897	0.027244
6	4.066445	-4.365374	-0.090058
1	2.106229	-5.342838	-0.130114
6	4.571151	-3.076688	-0.032813
1	4.692905	-5.250298	-0.137208
6	5.946211	-2.655959	-0.023364
6	6.450709	-1.358595	0.033342
16	7.245928	-3.827558	-0.086541
6	7.849806	-1.309688	0.025861
1	5.815306	-0.481266	0.079031
6	8.467115	-2.558529	-0.036164
1	8.423295	-0.388925	0.064524
6	9.876663	-2.741196	-0.054233
6	10.637034	-3.882825	-0.112704
1	10.438803	-1.811882	-0.014500
6	10.071111	-5.191106	-0.170240
6	12.115406	-3.833782	-0.119926
7	9.584135	-6.248262	-0.216410
8	12.841670	-4.805071	-0.169818
8	12.606298	-2.563428	-0.063812
1	13.575432	-2.664794	-0.074717

Table S3. Cartesian coordinates for the optimized structure of **7c**.

Total Energy: -3495.97736545 hartrees

At. No.	X	Y	Z
6	0.690349	0.810167	-0.117194
7	1.540734	-0.194897	-0.143868
7	-0.635406	0.390223	-0.195827
6	0.777995	-1.337836	-0.222123
6	-0.603466	-1.001425	-0.277246
6	1.226176	-2.680327	-0.232943
6	-1.602554	-1.997962	-0.385846
6	0.219583	-3.652664	-0.288233
6	-1.135352	-3.322438	-0.363075
1	0.493680	-4.702430	-0.259452
1	-1.866272	-4.122533	-0.435023
6	-1.815295	1.256762	-0.205158
6	-2.573027	1.289687	1.128598
1	-2.484710	0.921833	-0.999127
1	-1.474226	2.258231	-0.476006
6	-3.792157	2.219748	1.073335
1	-2.895287	0.274087	1.386876
1	-1.892935	1.609212	1.929943
6	-4.567158	2.264016	2.394096
1	-3.466914	3.235143	0.804798
1	-4.461798	1.888854	0.267728
1	-5.432711	2.931747	2.323461
1	-4.934741	1.268417	2.669379
1	-3.934038	2.623081	3.214641
6	1.149799	2.209216	-0.066313
6	0.554002	3.217781	0.709332
6	2.307373	2.543687	-0.793008
6	1.075123	4.506884	0.741568
1	-0.298440	2.992225	1.341330
6	2.824123	3.831151	-0.778579
1	2.790244	1.772291	-1.383555
6	2.213395	4.841696	-0.012045
1	0.607346	5.259445	1.367322
1	3.703973	4.064527	-1.368545
7	2.732787	6.155132	0.005981
6	1.856859	7.274732	0.106238
6	4.137919	6.378430	-0.078382
6	2.154650	8.331053	0.980703
6	0.692731	7.342106	-0.675103
6	4.645142	7.382822	-0.916959

6	5.030940	5.606776	0.681363
6	1.305003	9.432756	1.065376
1	3.052913	8.282516	1.588138
6	-0.160278	8.439322	-0.570617
1	0.463697	6.532969	-1.361496
6	6.018106	7.612185	-0.986281
1	3.958840	7.979147	-1.509844
6	6.403646	5.830529	0.590827
1	4.644168	4.834191	1.338391
6	0.141289	9.492281	0.295860
1	1.549716	10.242767	1.747402
1	-1.057503	8.476931	-1.182858
6	6.905726	6.835883	-0.238336
1	6.394970	8.394125	-1.640286
1	7.081997	5.223524	1.184540
1	-0.521827	10.349480	0.369193
1	7.975730	7.012415	-0.300352
6	2.654932	-3.060562	-0.187126
6	3.102485	-4.234225	-0.822635
6	3.614204	-2.296481	0.504097
6	4.432736	-4.632269	-0.771286
1	2.404089	-4.827778	-1.405590
6	4.942643	-2.698608	0.576507
1	3.308336	-1.380978	0.994805
6	5.376588	-3.872698	-0.060537
1	4.750309	-5.529852	-1.292203
1	5.655689	-2.100261	1.134678
7	6.735249	-4.276345	0.003837
6	7.064653	-5.650845	0.157589
6	7.771522	-3.306726	-0.093260
6	8.120336	-6.218239	-0.574576
6	6.340838	-6.462324	1.046612
6	8.895626	-3.377811	0.745439
6	7.687303	-2.264836	-1.030973
6	8.445484	-7.563549	-0.412140
1	8.681027	-5.599250	-1.267667
6	6.661939	-7.810852	1.188363
1	5.529331	-6.028921	1.622412
6	9.913752	-2.432271	0.638202
1	8.964449	-4.176523	1.477120
6	8.701935	-1.313700	-1.118183
1	6.824192	-2.206233	-1.686251
6	7.717565	-8.370252	0.465118
1	9.265404	-7.985526	-0.987628
1	6.090835	-8.423373	1.881332
6	9.823336	-1.392434	-0.289567

1	10.776516	-2.503069	1.295594
1	8.619546	-0.514162	-1.849903
1	7.969669	-9.420201	0.583769
1	10.615852	-0.653346	-0.365454
6	-3.050134	-1.773231	-0.546836
6	-3.741422	-1.140537	-1.558783
16	-4.175792	-2.473321	0.601221
6	-5.150202	-1.203688	-1.421678
1	-3.243870	-0.686864	-2.408943
6	-5.567331	-1.899568	-0.302604
1	-5.840527	-0.778396	-2.142998
6	-6.912066	-2.165938	0.145846
6	-7.331548	-3.047170	1.135429
16	-8.271390	-1.325890	-0.564439
6	-8.723095	-3.054968	1.311811
1	-6.647623	-3.673448	1.697433
6	-9.409543	-2.184365	0.469130
1	-9.237935	-3.683129	2.031644
6	-10.826187	-2.032557	0.473614
6	-11.645126	-1.233071	-0.280185
1	-11.331814	-2.660512	1.202390
6	-11.153972	-0.344007	-1.282510
6	-13.116365	-1.235809	-0.103405
7	-10.724054	0.372969	-2.093372
8	-13.889006	-0.551039	-0.740066
8	-13.531795	-2.098985	0.863630
1	-14.502365	-2.012922	0.886616

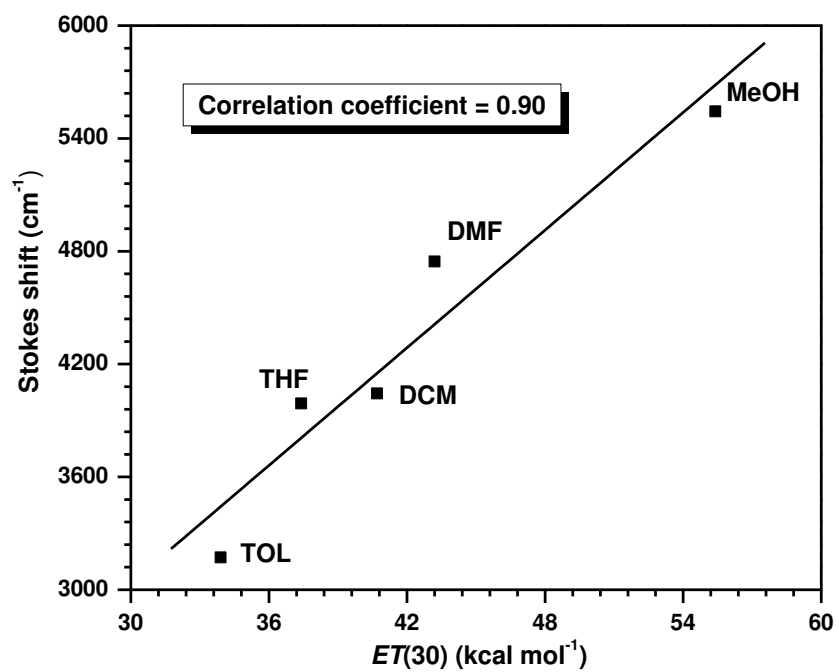


Figure S40. Correlation between Stokes shift and ET(30) parameter for dye **7b**.