Electronic Supplementary Information For:

Programmed twisting of phenylene-ethynylene linkages from aromatic stacking interactions in conjugated materials

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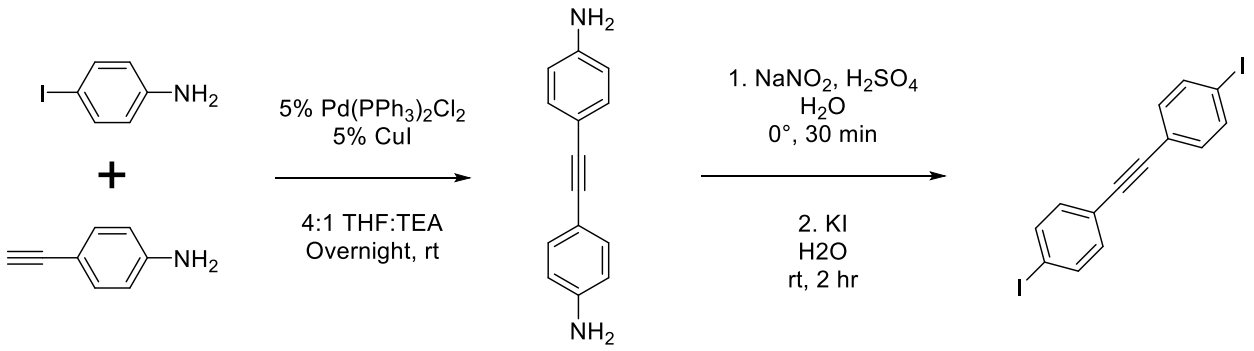
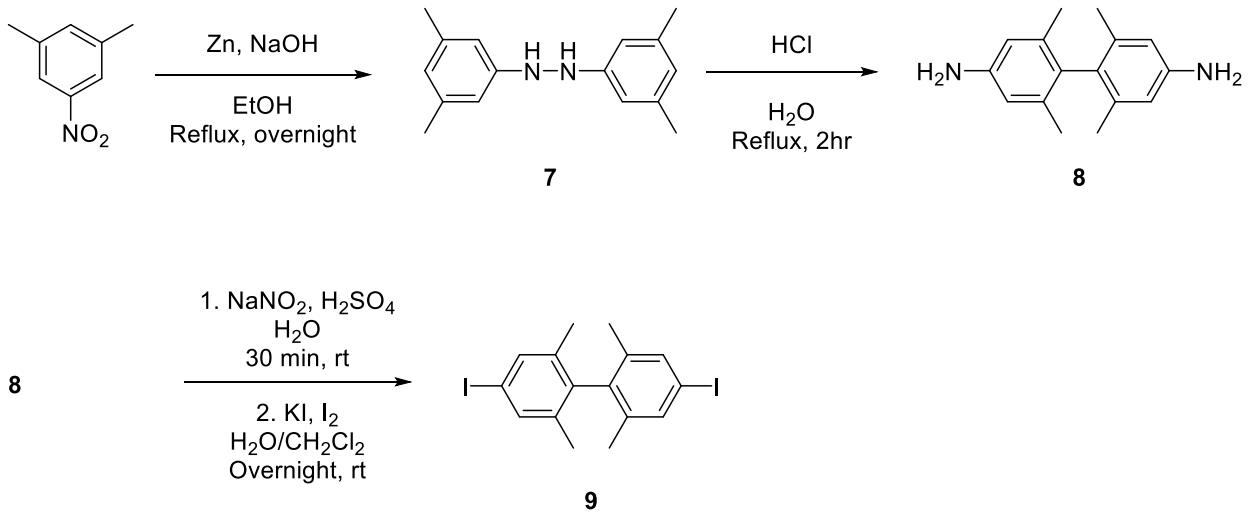
Scheme **S1:** Synthesis of *4,4'-Diiodotolane* **(6)**, the dihalide intermediate for **4-PE-F5** and **4-PE-H5**



5 **6**

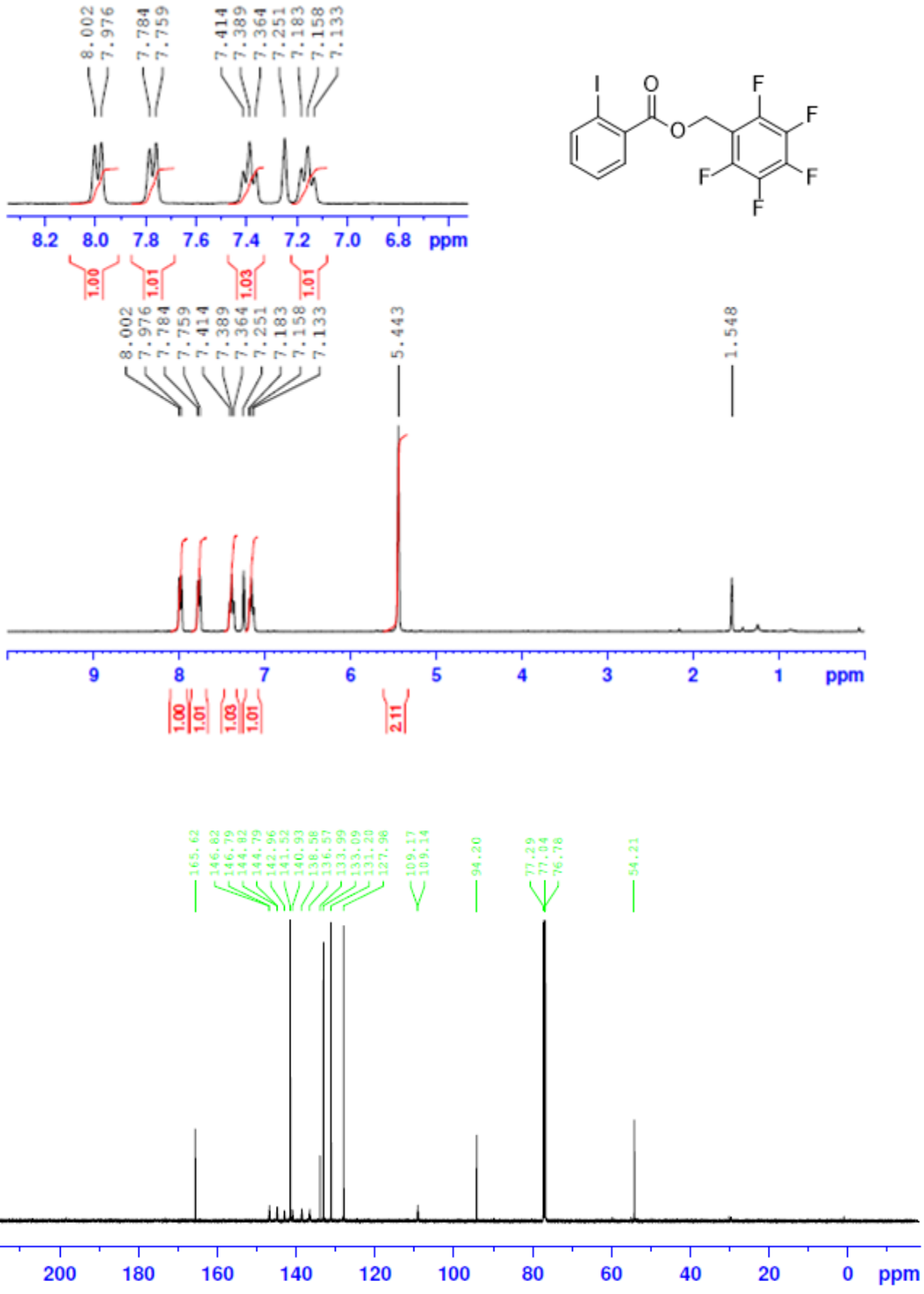
Scheme **S2**: Synthesis of *4,4'-diiodo-2,2',6,6'-tetramethylbiphenyl* (**9**), the dihalide intermediate for **4-TMBP-F5**.



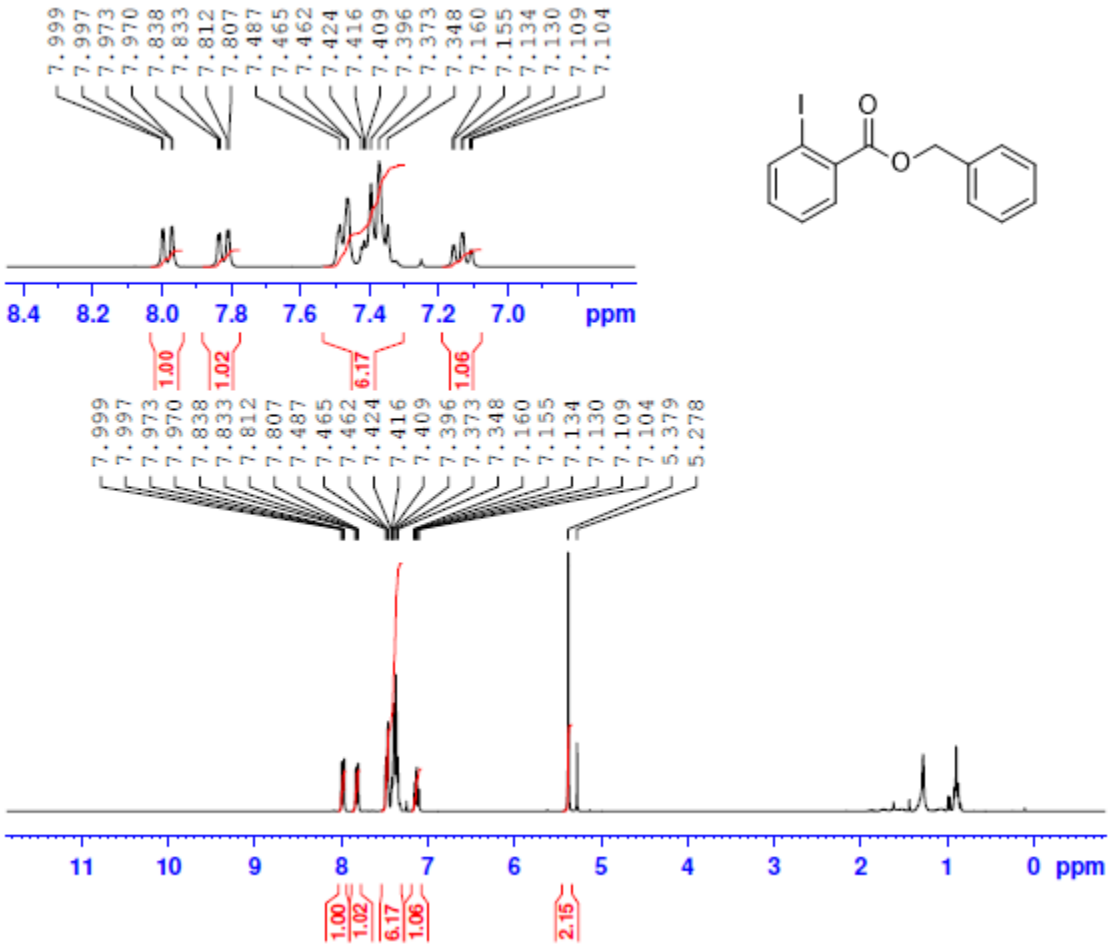
7 **8**

9

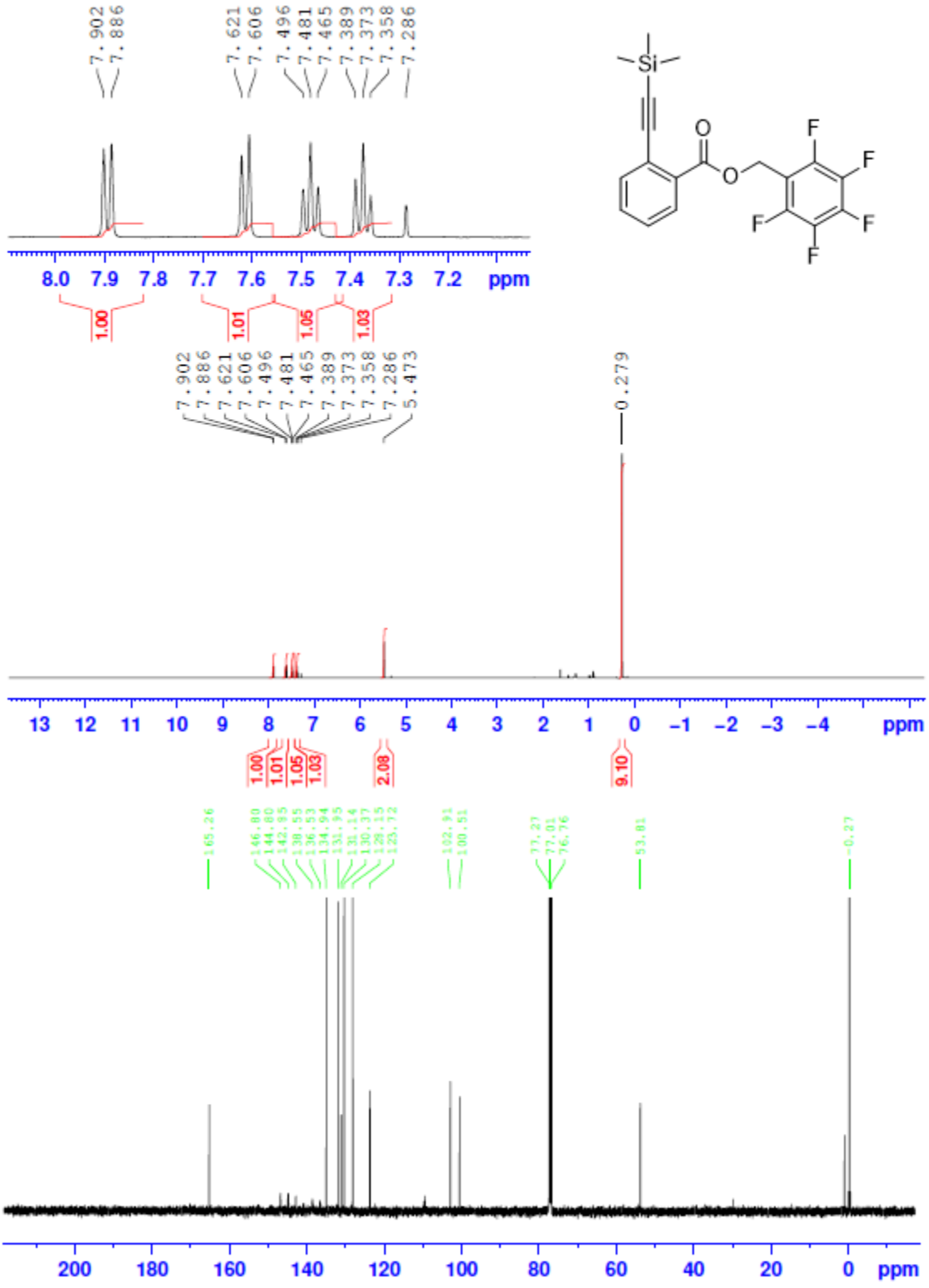
^{1}H and ^{13}C NMR spectra for **Compound 1**



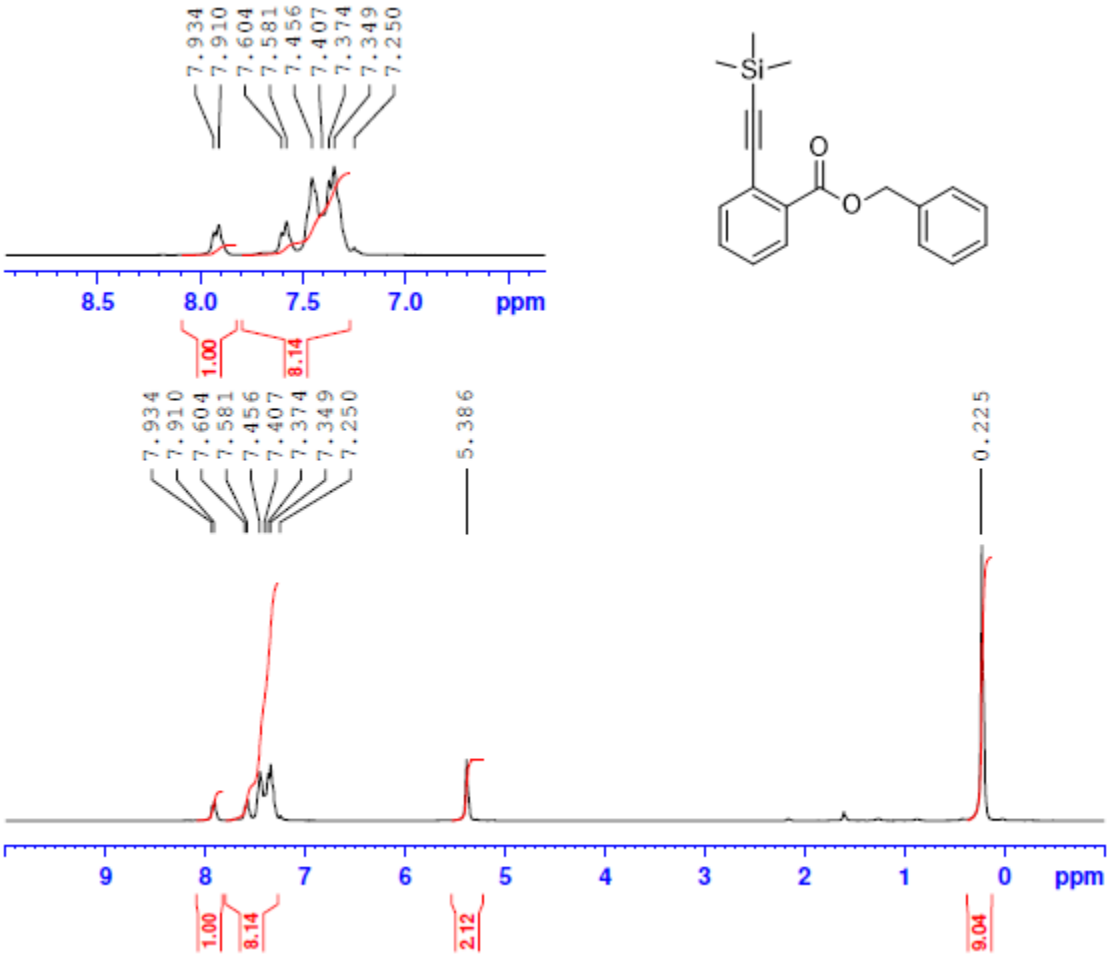
^{1}H NMR spectrum for **Compound 3**



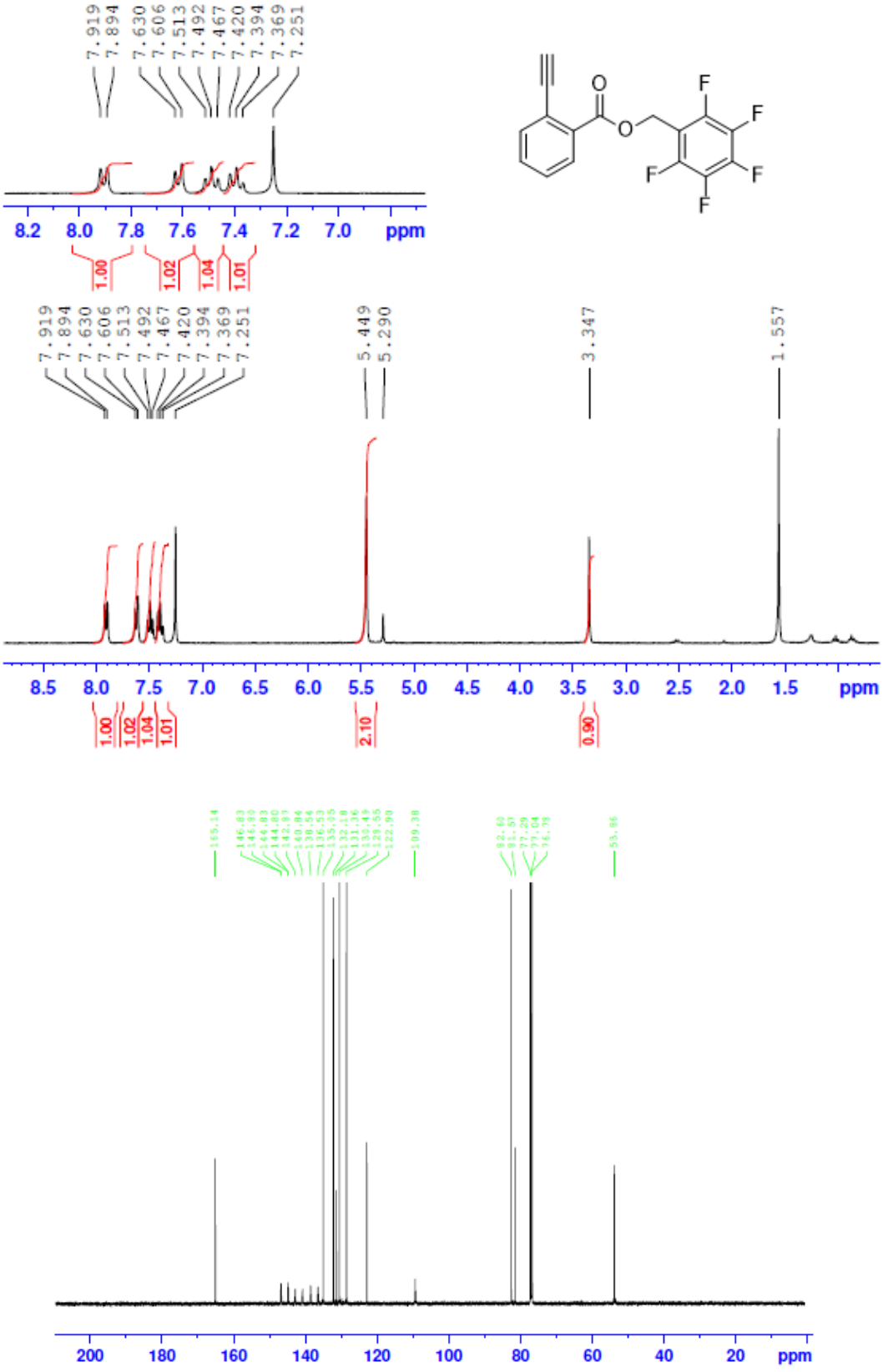
^{1}H and ^{13}C NMR spectra for **TMS-alkyne derived from 1**



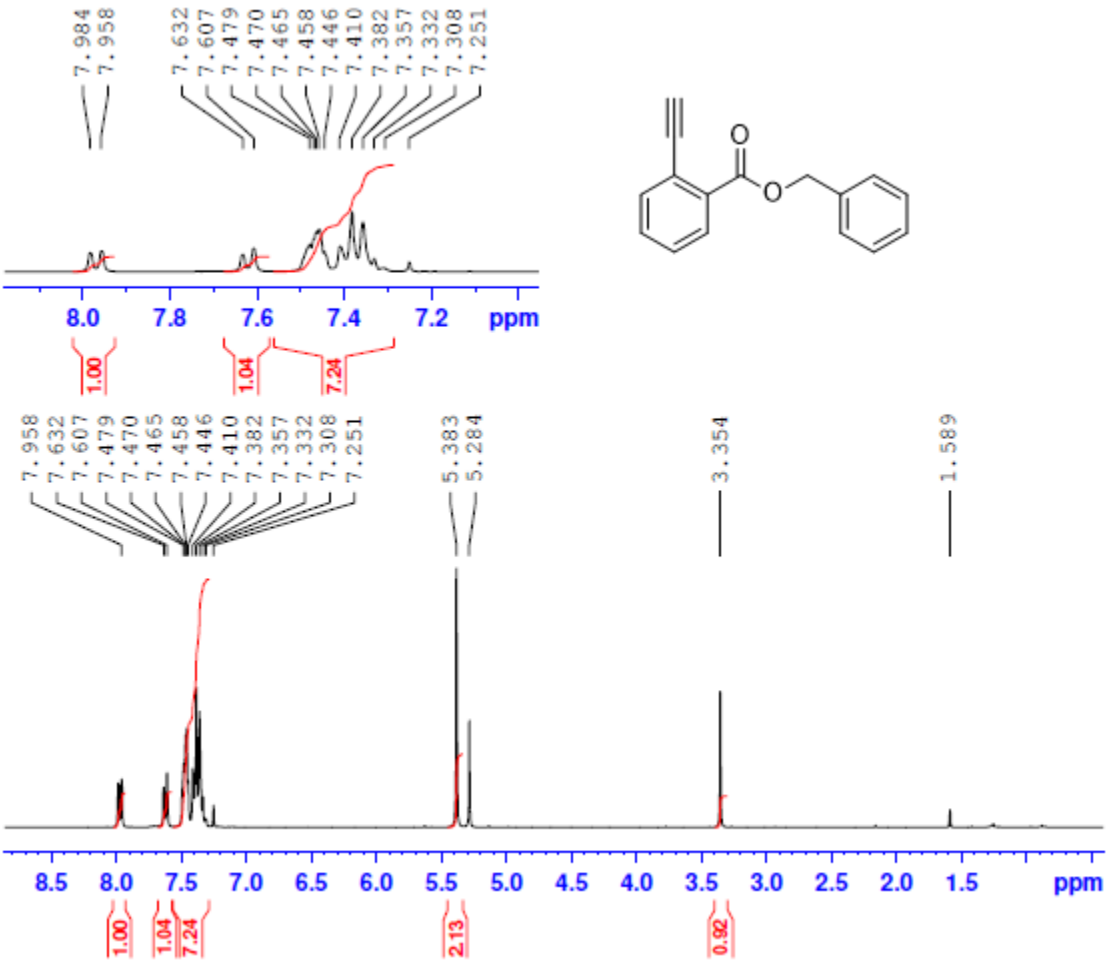
^{1}H NMR spectrum for **TMS-alkyne derived from 3**



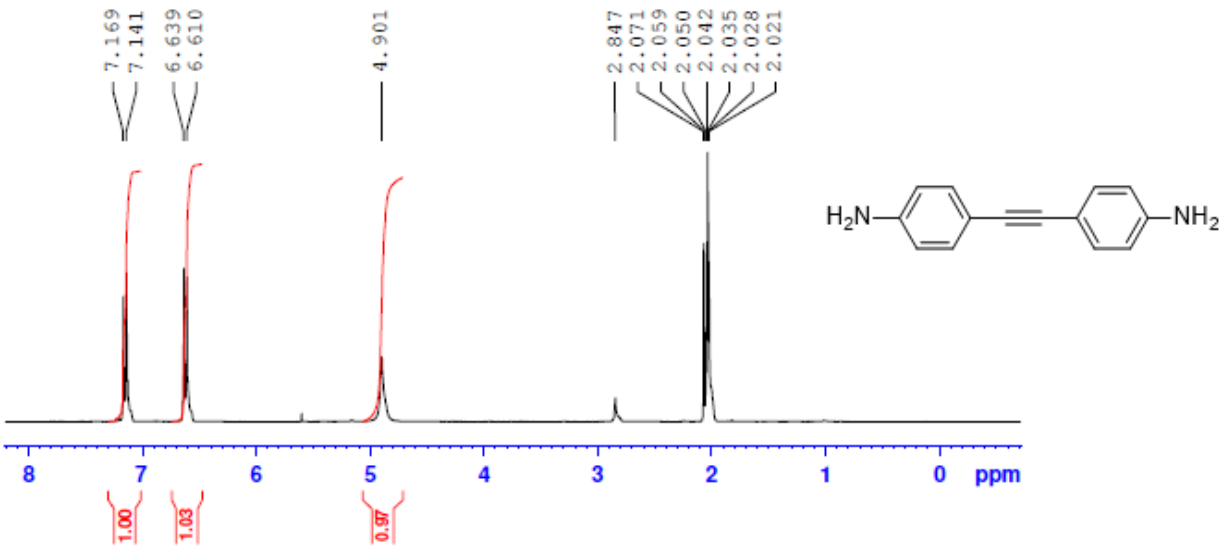
^{1}H and ^{13}C NMR spectra for **Compound 2**



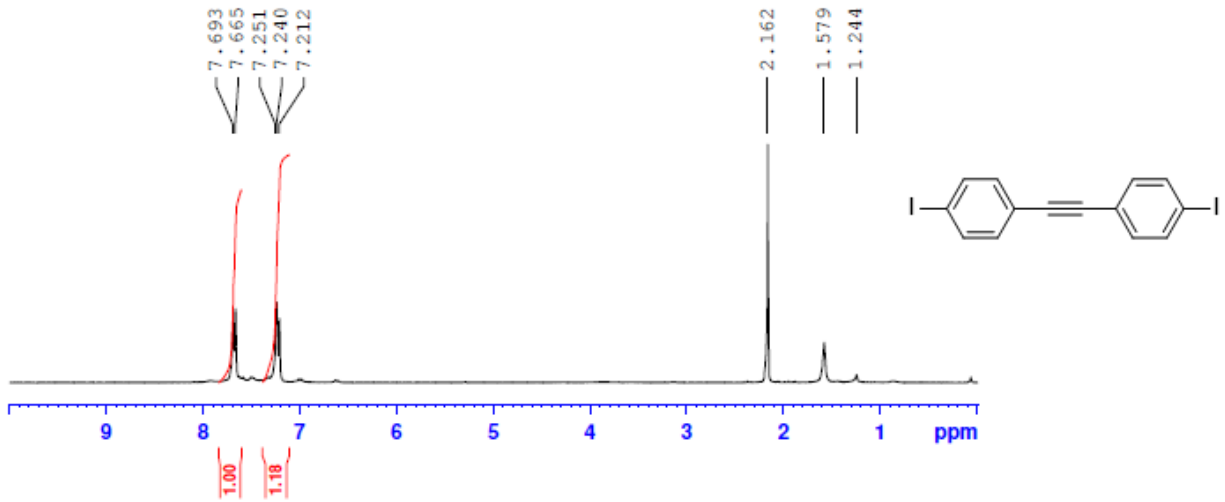
^{1}H NMR spectrum for **Compound 4**



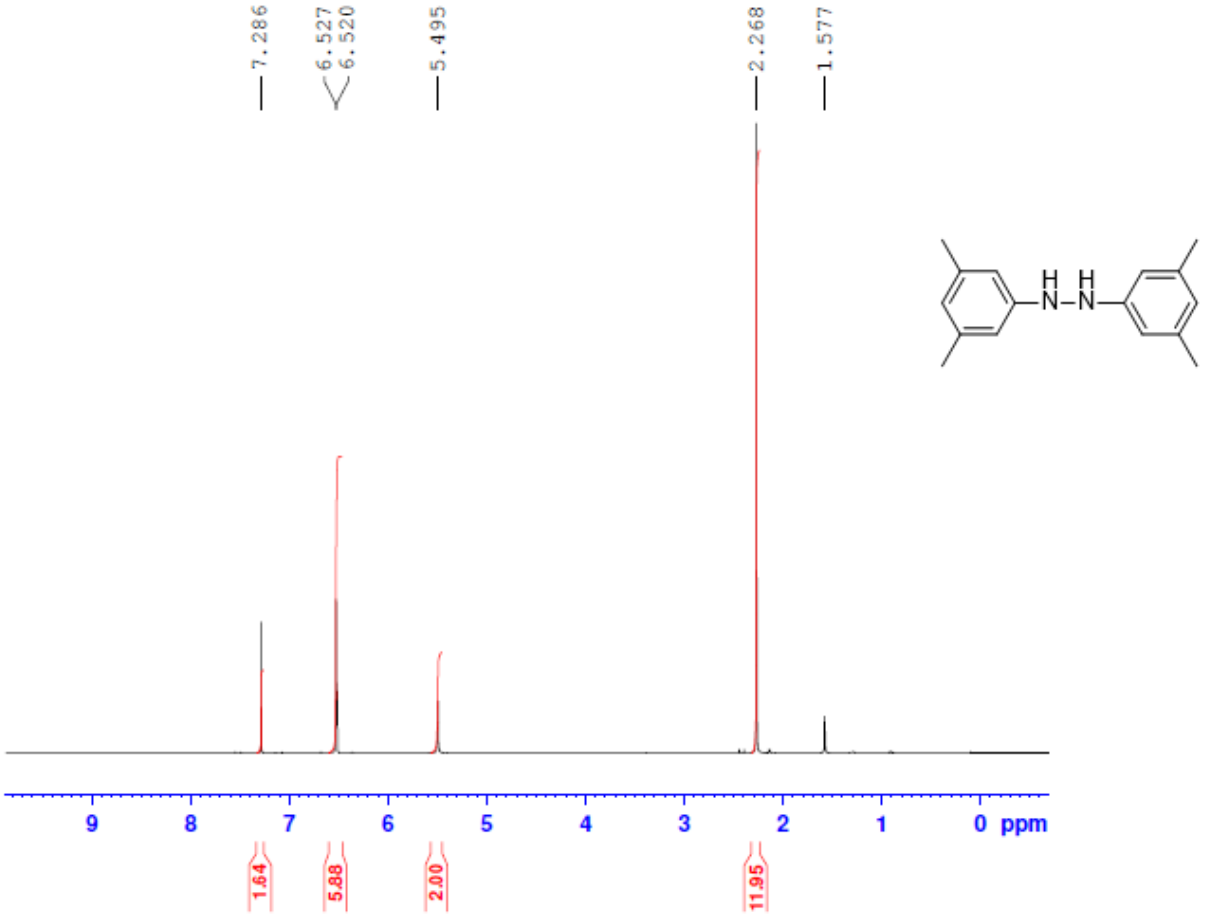
^{1}H NMR spectrum of 4,4'-Diaminotolane (**5**)



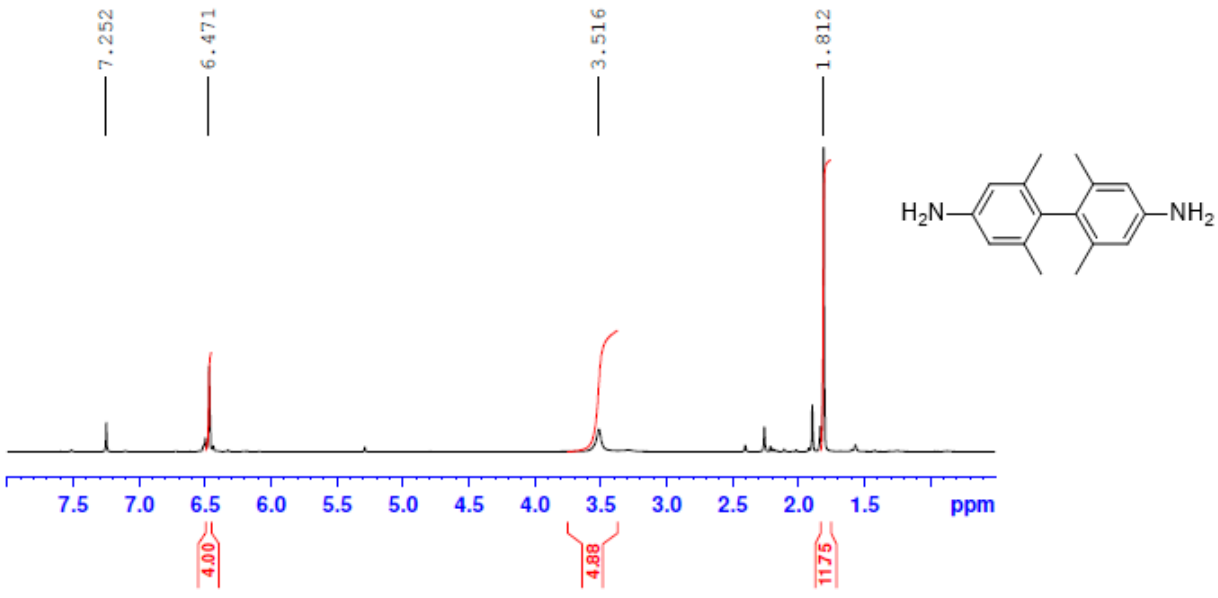
^{1}H NMR spectrum of 4,4'-Diiodotolane (**6**)



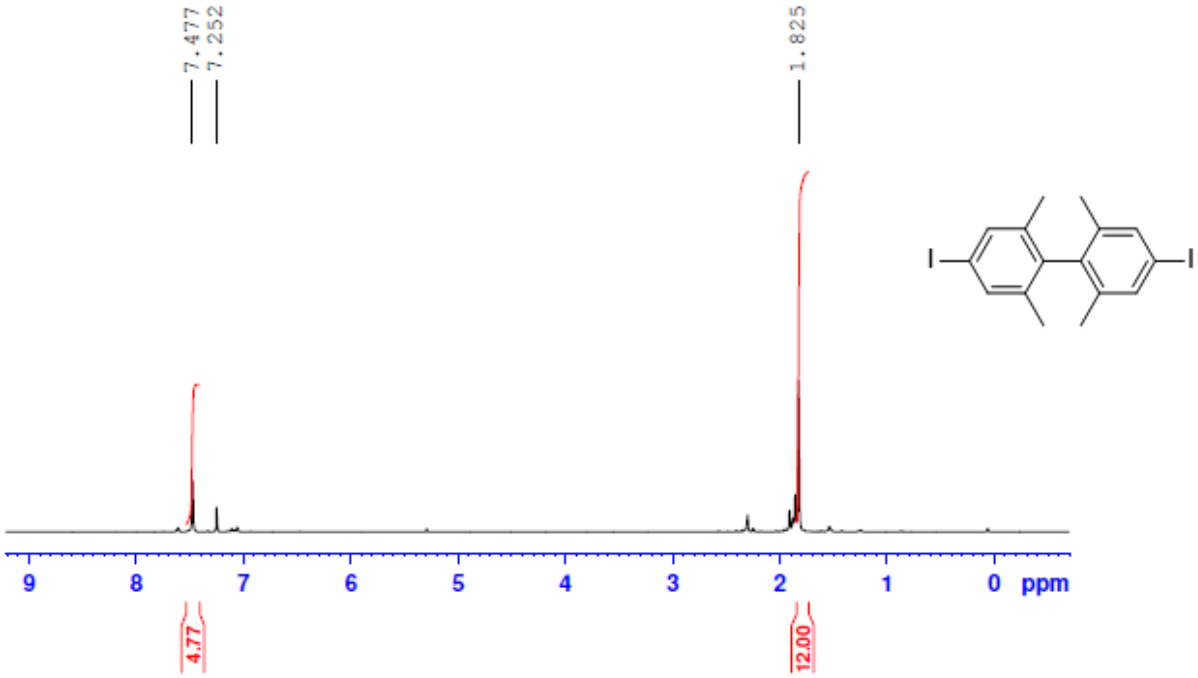
^{1}H NMR spectrum of 3,3',5,5'-Tetramethylphenyl Hydrazine (7)



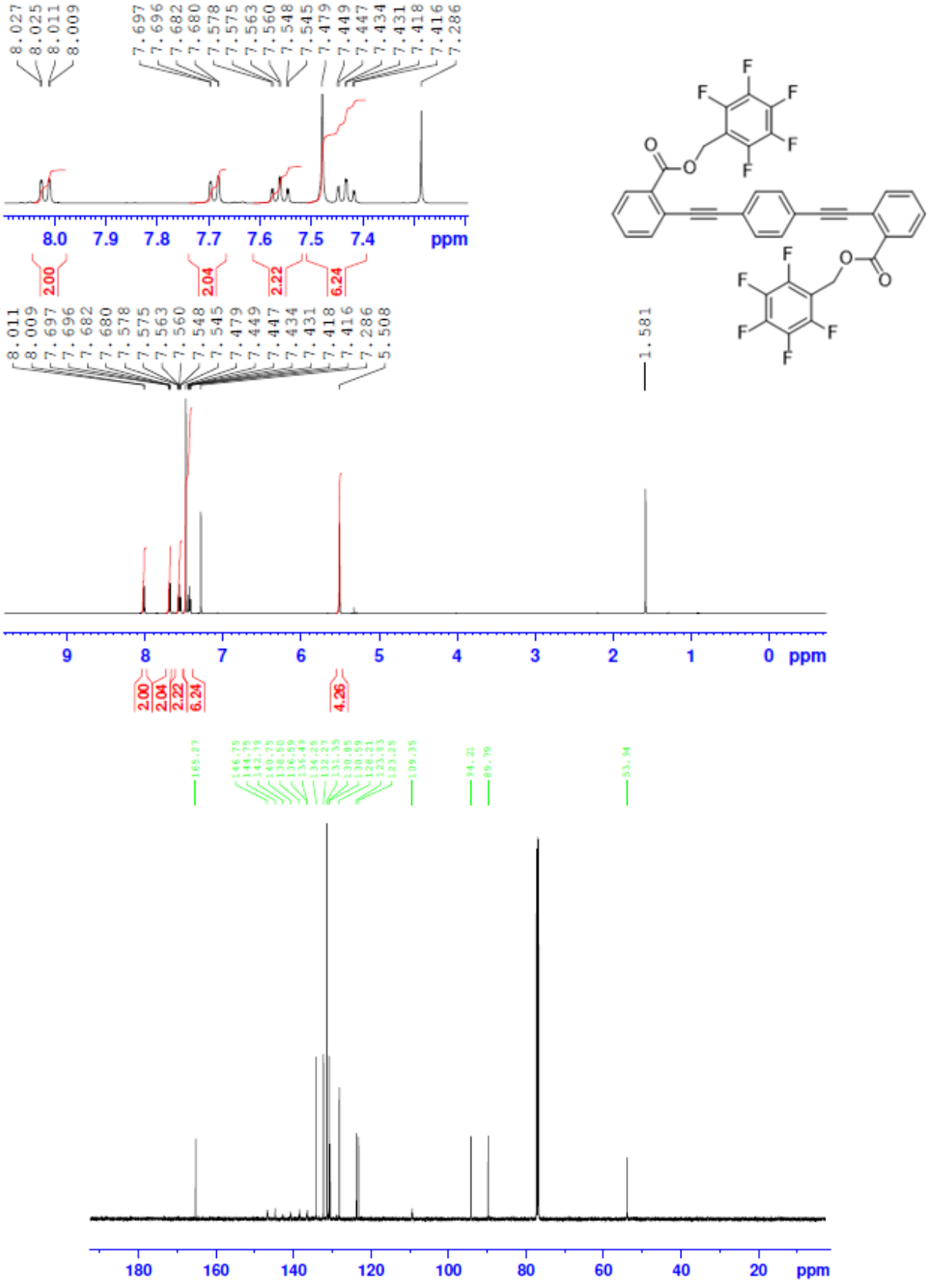
^{1}H NMR spectrum of 4,4'-Diamino-2,2',6,6'-tetramethylbiphenyl (**8**)



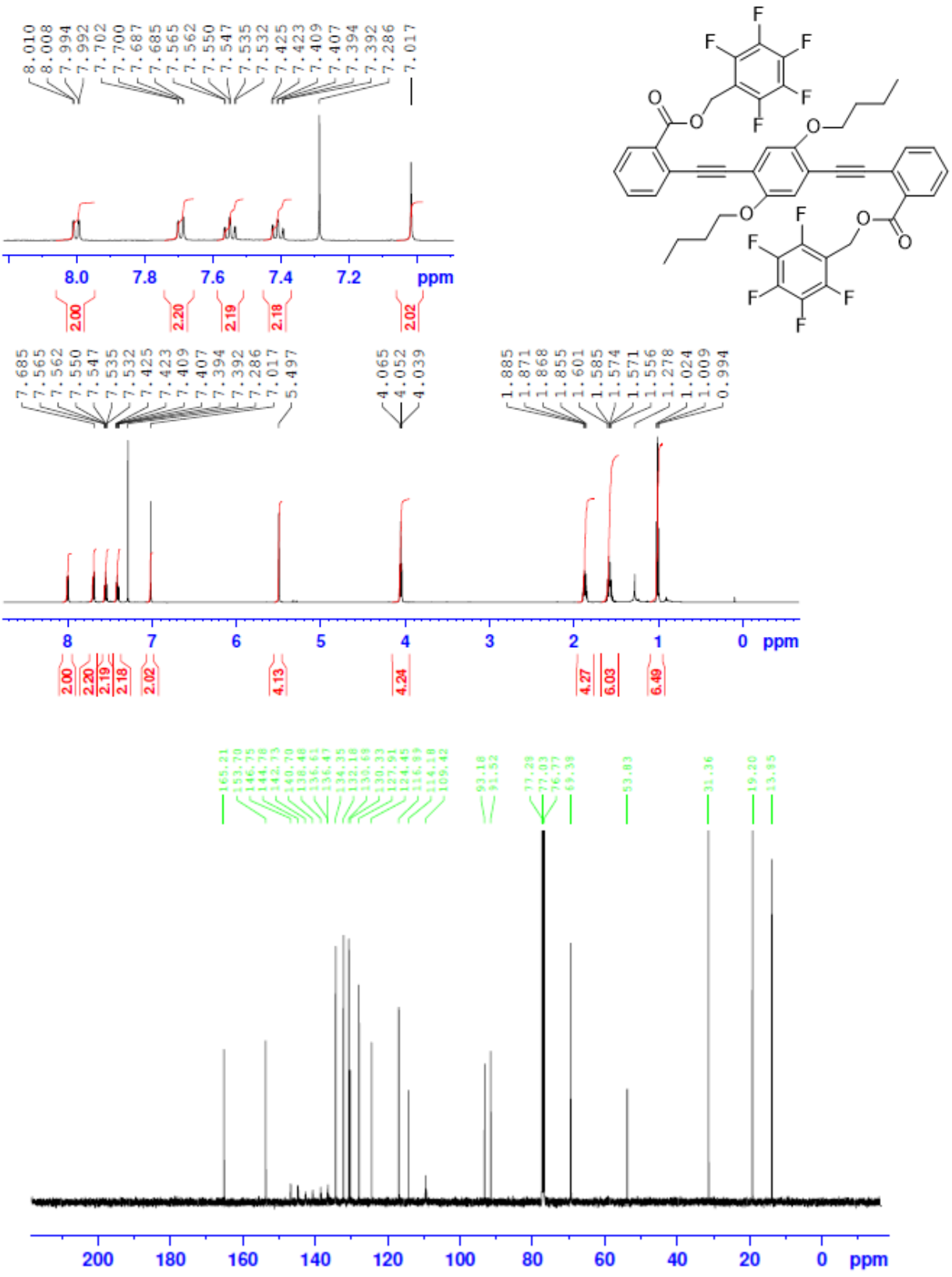
^{1}H NMR spectrum of 4,4'-Diiodo-2,2',6,6'-tetramethylbiphenyl (**9**)



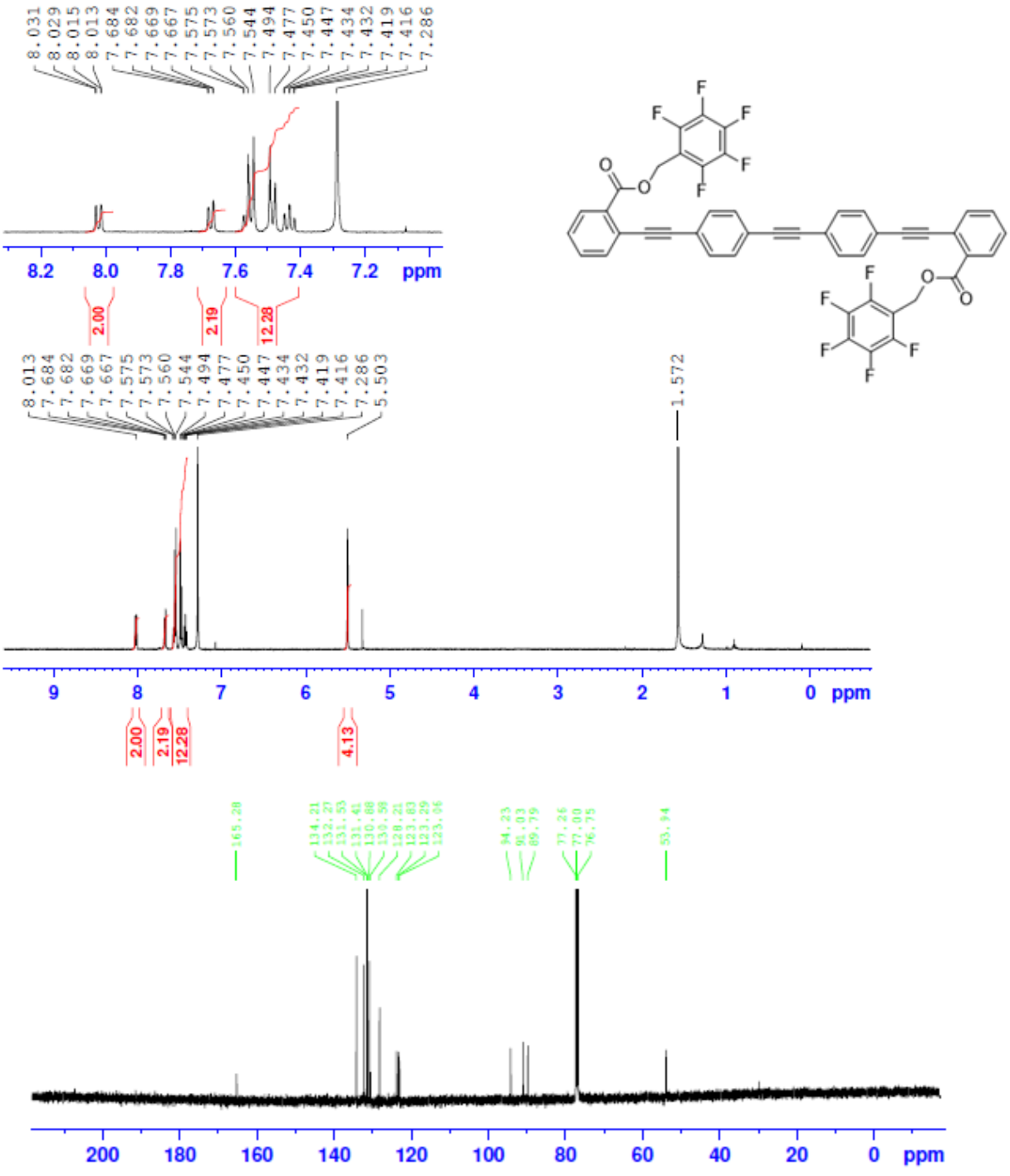
^{1}H and ^{13}C NMR spectra for **3-PE-F5**



^{1}H and ^{13}C NMR spectra for **3-DBPE-F5**

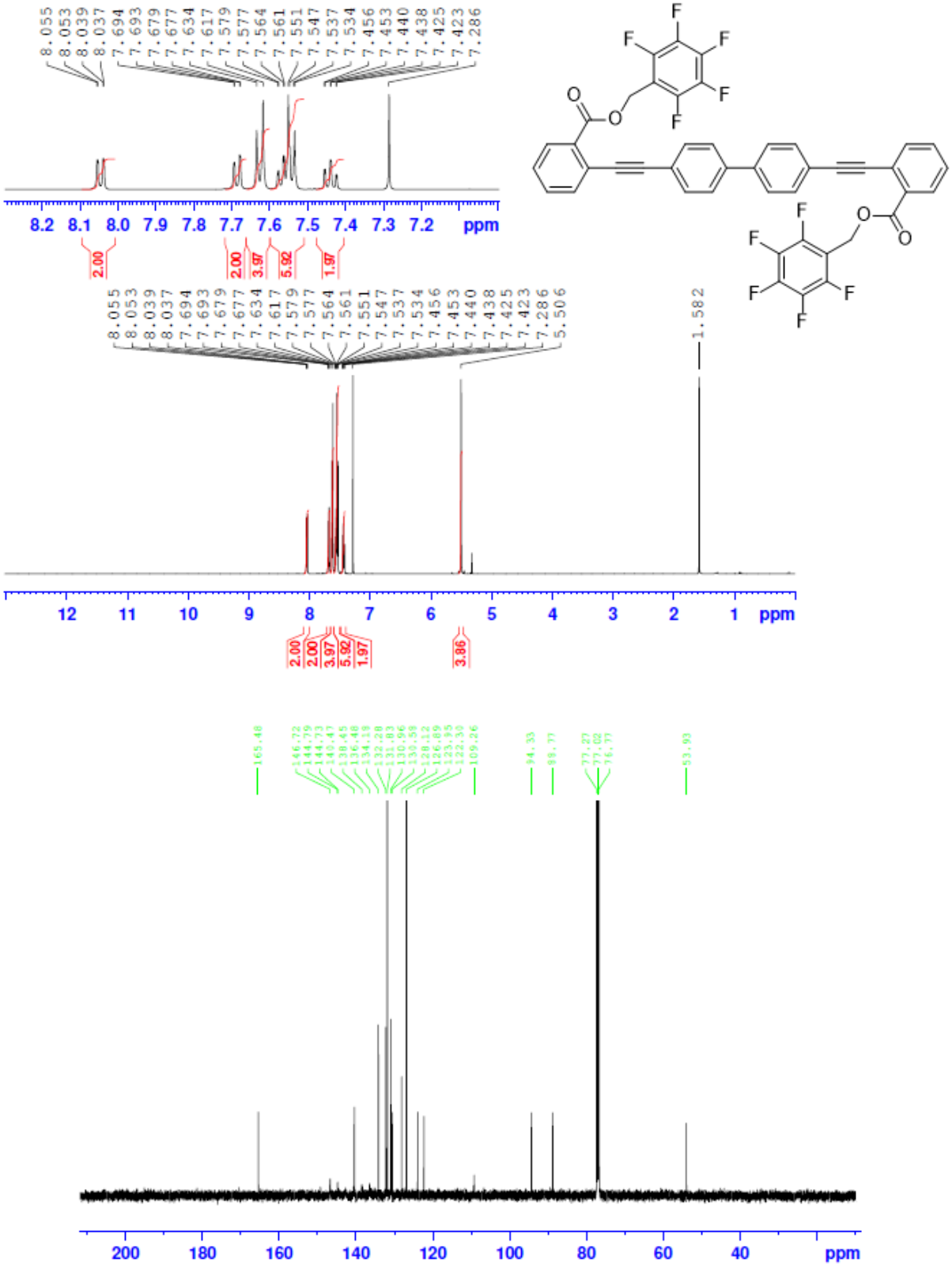


^{1}H and ^{13}C NMR spectra for **4-PE-F5**

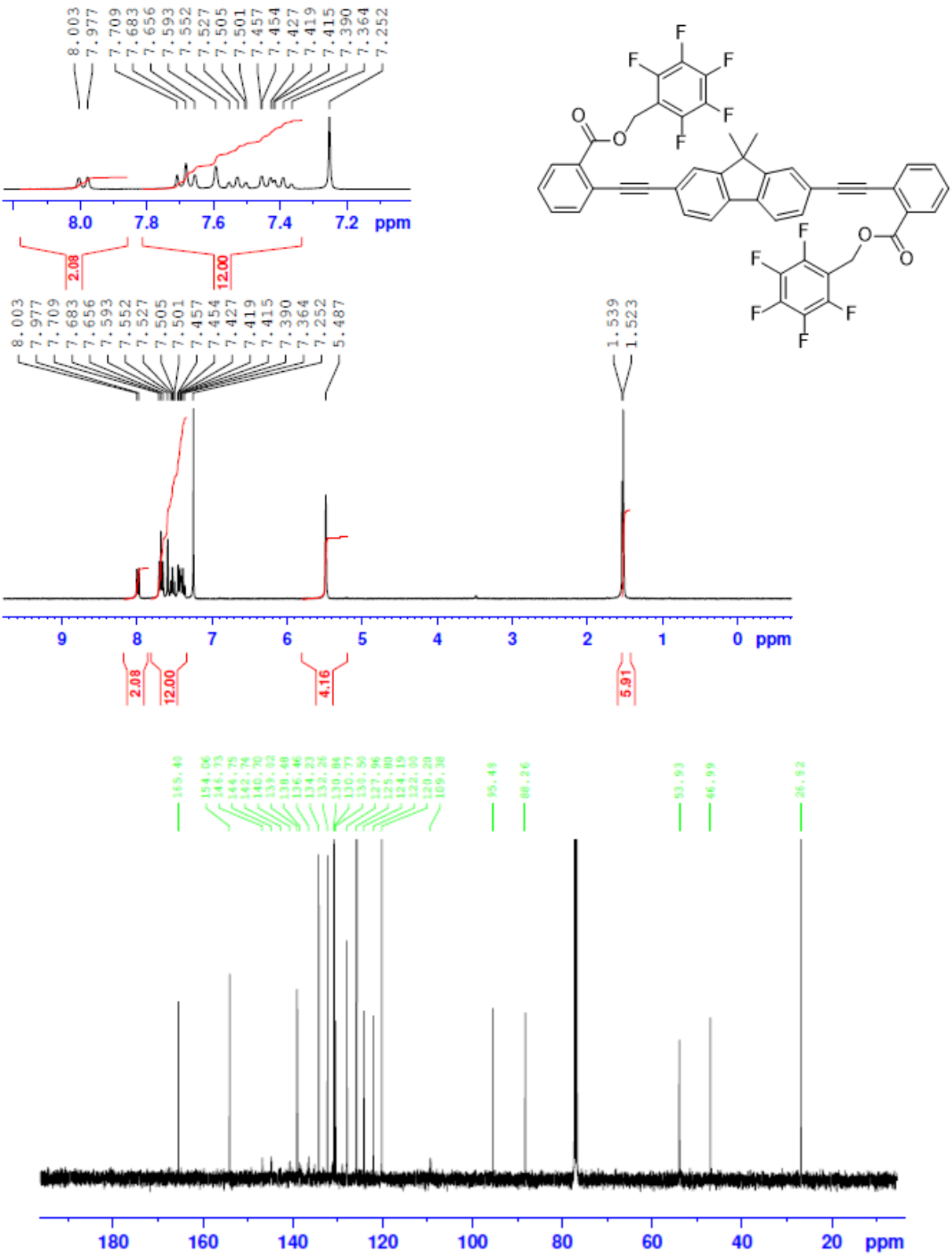


Note: 4-PE-F5 exhibits very poor solubility in most organic NMR solvents

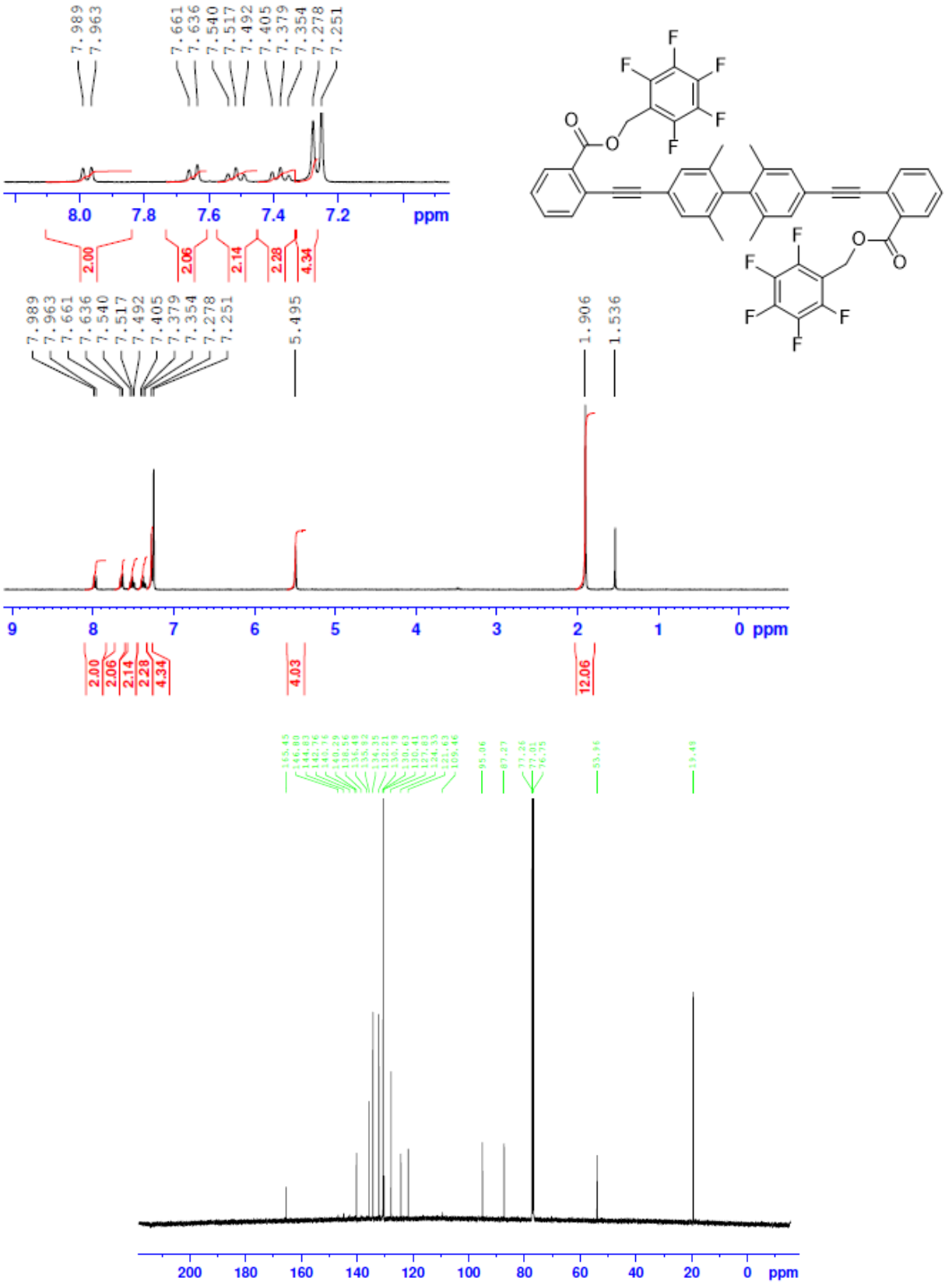
^{1}H and ^{13}C NMR spectra for **4-BP-F5**



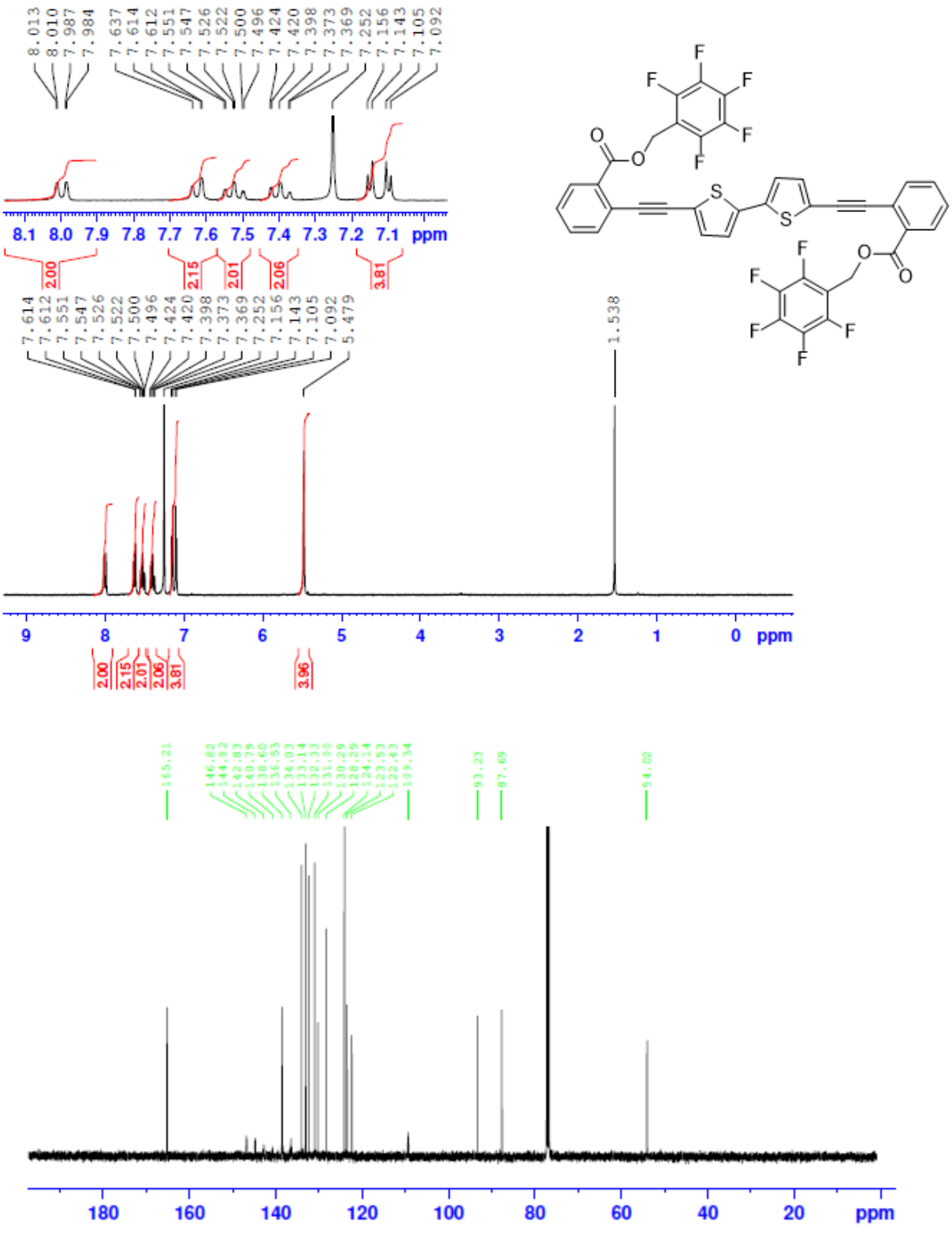
^{1}H and ^{13}C NMR spectra for **4-DMF-F5**



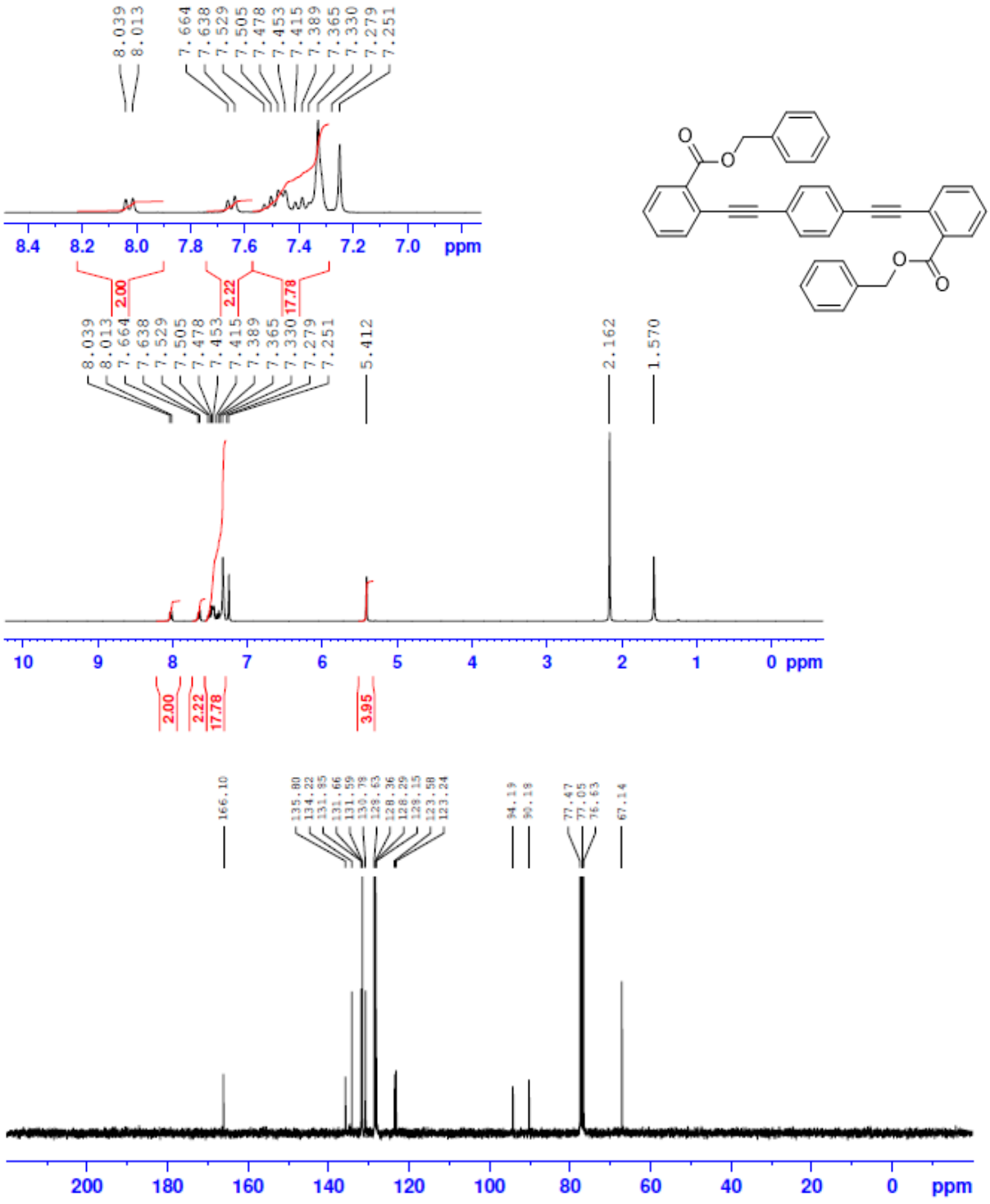
^{1}H and ^{13}C NMR spectra for **4-TMBP-F5**



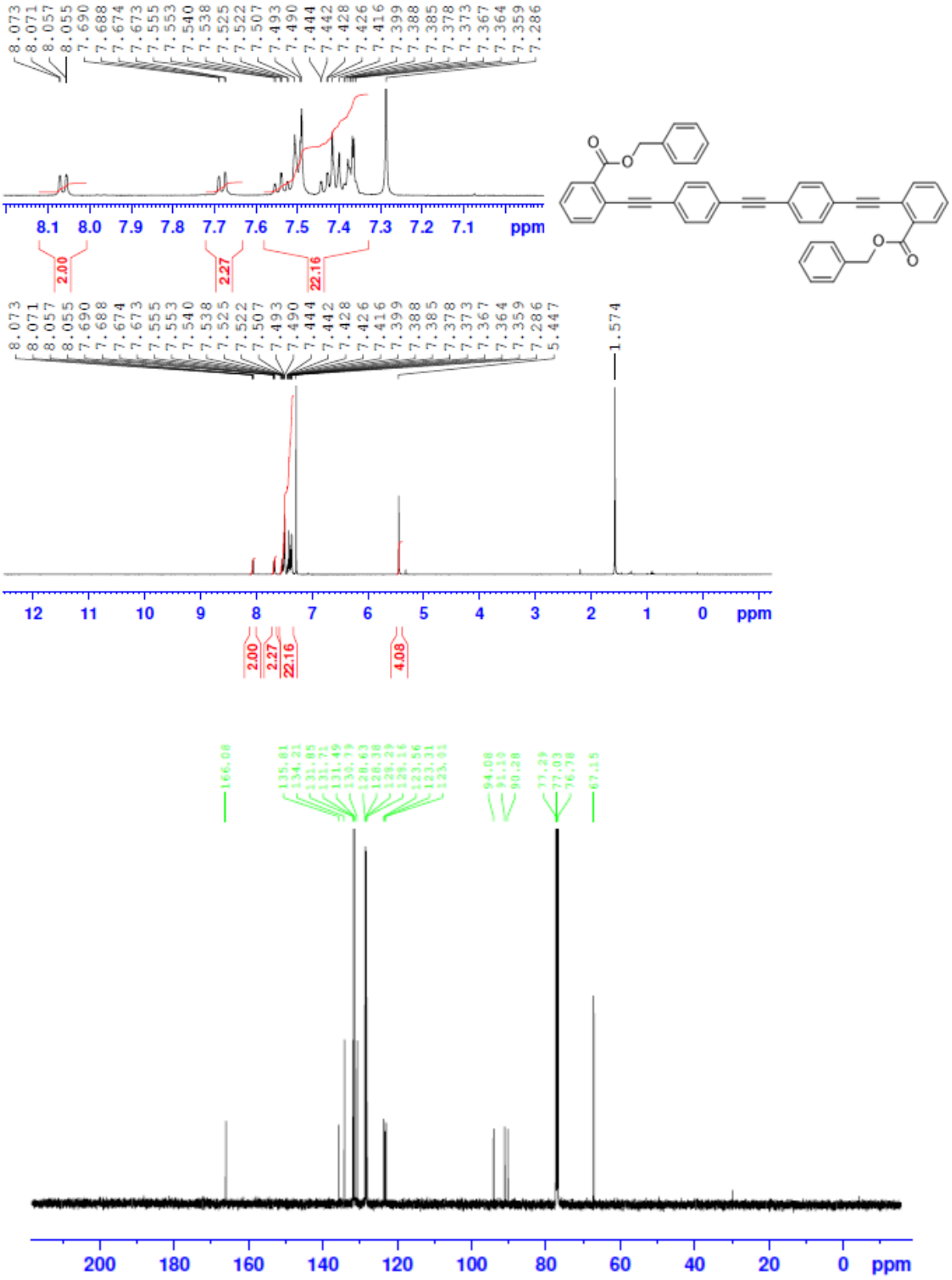
^{1}H and ^{13}C NMR spectra for **4-BT-F5**



^{1}H and ^{13}C NMR spectra for **3-PE-H5**



^{1}H and ^{13}C NMR spectra for **4-PE-H5**



Crystal data and structure refinement for **3-PE-F5**.

Identification code	WM01105_0m_a	
Empirical formula	C38 H16 F10 O4	
Formula weight	726.51	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.8623(4) Å	α= 77.8230(10)°.
	b = 10.4103(6) Å	β= 80.4870(10)°.
	c = 19.6258(11) Å	γ = 78.4090(10)°.
Volume	1525.47(15) $Å^3$	
Z	2	
Density (calculated)	1.582 Mg/m^3	
Absorption coefficient	0.143 mm^{-1}	
F(000)	732	
Crystal size	0.150 x 0.150 x 0.150 mm^3	
Theta range for data collection	1.070 to 40.337°.	
Index ranges	-14<=h<=14, -18<=k<=18, -35<=l<=35	
Reflections collected	58188	
Independent reflections	19157 [R(int) = 0.0361]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.7479 and 0.702	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19157 / 0 / 469	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0632, wR2 = 0.1445	
R indices (all data)	R1 = 0.1116, wR2 = 0.1695	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.916 and -0.307 $e.Å^{-3}$	

Crystal data and structure refinement for **3-DBPE-F5**

Identification code	WM02113_0m_a	
Empirical formula	C46 H32 F10 O6	
Formula weight	870.71	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.2155(10) Å	α= 90°.
	b = 9.1259(7) Å	β= 90.357(3)°.
	c = 15.7624(12) Å	γ = 90°.
Volume	1901.0(3) $Å^3$	
Z	2	
Density (calculated)	1.521 Mg/m^3	
Absorption coefficient	0.132 mm^{-1}	
F(000)	892	
Crystal size	0.200 x 0.150 x 0.150 mm^3	
Theta range for data collection	2.017 to 30.586°.	
Index ranges	-18<=h<=18, -13<=k<=13, -22<=l<=22	
Reflections collected	86329	
Independent reflections	5823 [R(int) = 0.0294]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.7461 and 0.7231	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5823 / 0 / 281	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.1105	
R indices (all data)	R1 = 0.0490, wR2 = 0.1174	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.616 and -0.202 $e.Å^{-3}$	

Crystal data and structure refinement for **4-PE-F5**.

Identification code	WM0195_0m_a	
Empirical formula	C46 H20 F10 O4	
Formula weight	826.62	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.507(2) Å	α= 98.558(6)°.
	b = 7.869(2) Å	β= 99.414(6)°.
	c = 16.680(5) Å	γ = 106.779(6)°.
Volume	910.4(4) $Å^3$	
Z	1	
Density (calculated)	1.508 Mg/m^3	
Absorption coefficient	0.130 mm^{-1}	
F(000)	418	
Crystal size	0.020 x 0.020 x 0.020 mm^3	
Theta range for data collection	1.265 to 28.954°.	
Index ranges	-10<=h<=10, -10<=k<=10, -22<=l<=22	
Reflections collected	18585	
Independent reflections	4805 [R(int) = 0.0297]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.7458 and 0.6962	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4805 / 0 / 271	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0582, wR2 = 0.1584	
R indices (all data)	R1 = 0.0865, wR2 = 0.1849	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.383 and -0.176 $e.Å^{-3}$	

Crystal data and structure refinement for **4-BP-F5**.

Identification code	WM0173_0m_a	
Empirical formula	C46 H22 Cl6 F10 O4	
Formula weight	1041.10	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.224(4) Å	α= 79.95(4)°.
	b = 10.029(5) Å	β= 77.865(19)°.
	c = 13.383(7) Å	γ = 88.186(19)°.
Volume	1062.5(9) $Å^3$	
Z	1	
Density (calculated)	1.627 Mg/m^3	
Absorption coefficient	0.495 mm^{-1}	
F(000)	464	
Crystal size	0.180 x 0.180 x 0.180 mm^3	
Theta range for data collection	2.062 to 25.841°.	
Index ranges	-10<=h<=10, -12<=k<=12, -16<=l<=16	
Reflections collected	16511	
Independent reflections	4063 [R(int) = 0.0230]	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.7453 and 0.6977	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4063 / 1763 / 653	
Goodness-of-fit on F^2	1.091	
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.1049	
R indices (all data)	R1 = 0.0443, wR2 = 0.1068	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.308 and -0.205 $e.Å^{-3}$	

Crystal data and structure refinement for **4-DMF-F5**

Identification code	WM104_1_0m_a_a_a	
Empirical formula	C47 H24 F10 O4	
Formula weight	842.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.3978(11) Å	α= 108.224(2)°.
	b = 13.2721(12) Å	β= 95.725(2)°.
	c = 14.4774(14) Å	γ = 115.411(2)°.
Volume	1807.7(3) $Å^3$	
Z	2	
Density (calculated)	1.548 Mg/m^3	
Absorption coefficient	0.133 mm^{-1}	
F(000)	856	
Crystal size	0.250 x 0.150 x 0.075 mm^3	
Theta range for data collection	1.539 to 29.550°.	
Index ranges	-15<=h<=15, -18<=k<=18, -20<=l<=20	
Reflections collected	39050	
Independent reflections	10037 [R(int) = 0.0388]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	multi-scan	
Max. and min. transmission	.7459 and .6954	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10037 / 0 / 562	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1212	
R indices (all data)	R1 = 0.0777, wR2 = 0.1427	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.487 and -0.316 $e.Å^{-3}$	

Crystal data and structure refinement for **4-TMBP-F5.**

Identification code	WM0210_1_0m_a	
Empirical formula	C48 H28 F10 O4	
Formula weight	858.70	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.0511(11) Å	α= 68.452(2)°.
	b = 12.6535(11) Å	β= 76.554(2)°.
	c = 14.0972(12) Å	γ = 74.515(2)°.
Volume	1905.0(3) $Å^3$	
Z	2	
Density (calculated)	1.497 Mg/m^3	
Absorption coefficient	0.128 mm^{-1}	
F(000)	876	
Crystal size	0.150 x 0.150 x 0.100 mm^3	
Theta range for data collection	1.571 to 36.579°.	
Index ranges	-20<=h<=20, -21<=k<=21, -23<=l<=23	
Reflections collected	61842	
Independent reflections	18728 [R(int) = 0.0342]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.7472 and 0.7186	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18728 / 0 / 563	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0532, wR2 = 0.1304	
R indices (all data)	R1 = 0.0869, wR2 = 0.1506	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.692 and -0.249 $e.Å^{-3}$	

Crystal data and structure refinement for **4-BT-F5**.

Identification code	WM0189_1_0ma_a	
Empirical formula	C40 H16 F10 O4 S2	
Formula weight	814.65	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.738(18) Å	α= 90°.
	b = 5.738(6) Å	β= 93.92(2)°.
	c = 16.944(16) Å	γ = 90°.
Volume	1720(3) $Å^3$	
Z	2	
Density (calculated)	1.573 Mg/m^3	
Absorption coefficient	0.253 mm^{-1}	
F(000)	820	
Crystal size	.15 x .15 x .12 mm^3	
Theta range for data collection	1.151 to 23.726°.	
Index ranges	-19<=h<=19, -6<=k<=6, -18<=l<=18	
Reflections collected	13709	
Independent reflections	2174 [R(int) = 0.0391]	
Completeness to theta = 23.726°	83.0 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.7449 and 0.6608	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2174 / 0 / 253	
Goodness-of-fit on F^2	1.216	
Final R indices [I>2sigma(I)]	R1 = 0.0729, wR2 = 0.2434	
R indices (all data)	R1 = 0.0896, wR2 = 0.2683	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.387 and -0.365 $e.Å^{-3}$	

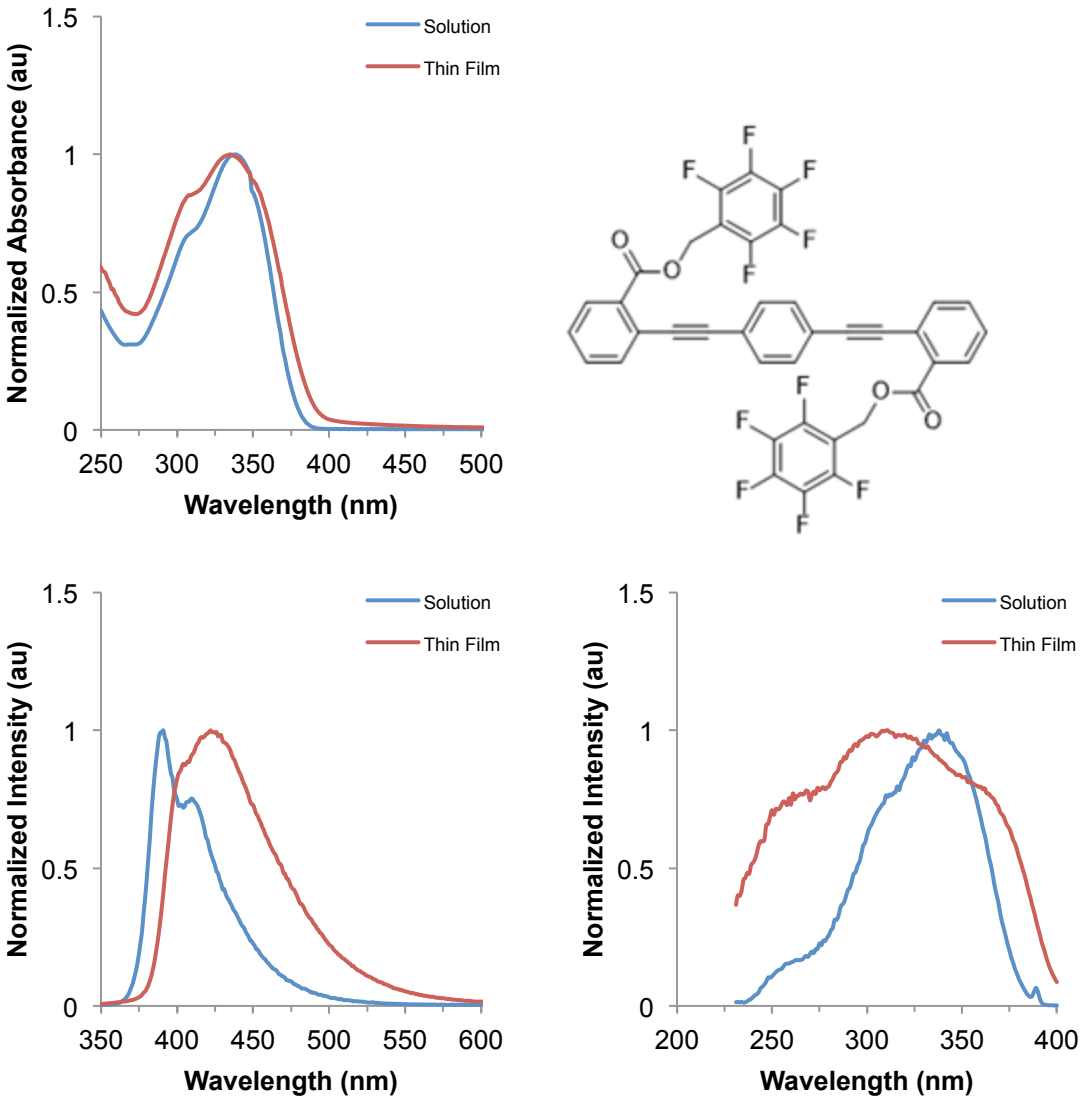
Crystal data and structure refinement for **3-PE-H5.**

Identification code	WM0133_0M_P1bar_a	
Empirical formula	C38 H26 O4	
Formula weight	546.59	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.7395(8) Å	α= 89.928(2)°.
	b = 9.8000(9) Å	β= 86.471(2)°.
	c = 32.564(3) Å	γ = 89.982(2)°.
Volume	2783.8(4) $Å^3$	
Z	4	
Density (calculated)	1.304 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	1144	
Crystal size	0.200 x 0.150 x 0.150 mm^3	
Theta range for data collection	0.626 to 26.874°.	
Index ranges	-11<=h<=11, -12<=k<=12, -41<=l<=41	
Reflections collected	48402	
Independent reflections	11837 [R(int) = 0.0284]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11837 / 0 / 757	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.1074	
R indices (all data)	R1 = 0.0596, wR2 = 0.1203	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.291 and -0.203 $e.Å^{-3}$	

Crystal data and structure refinement for **4-PE-H5**.

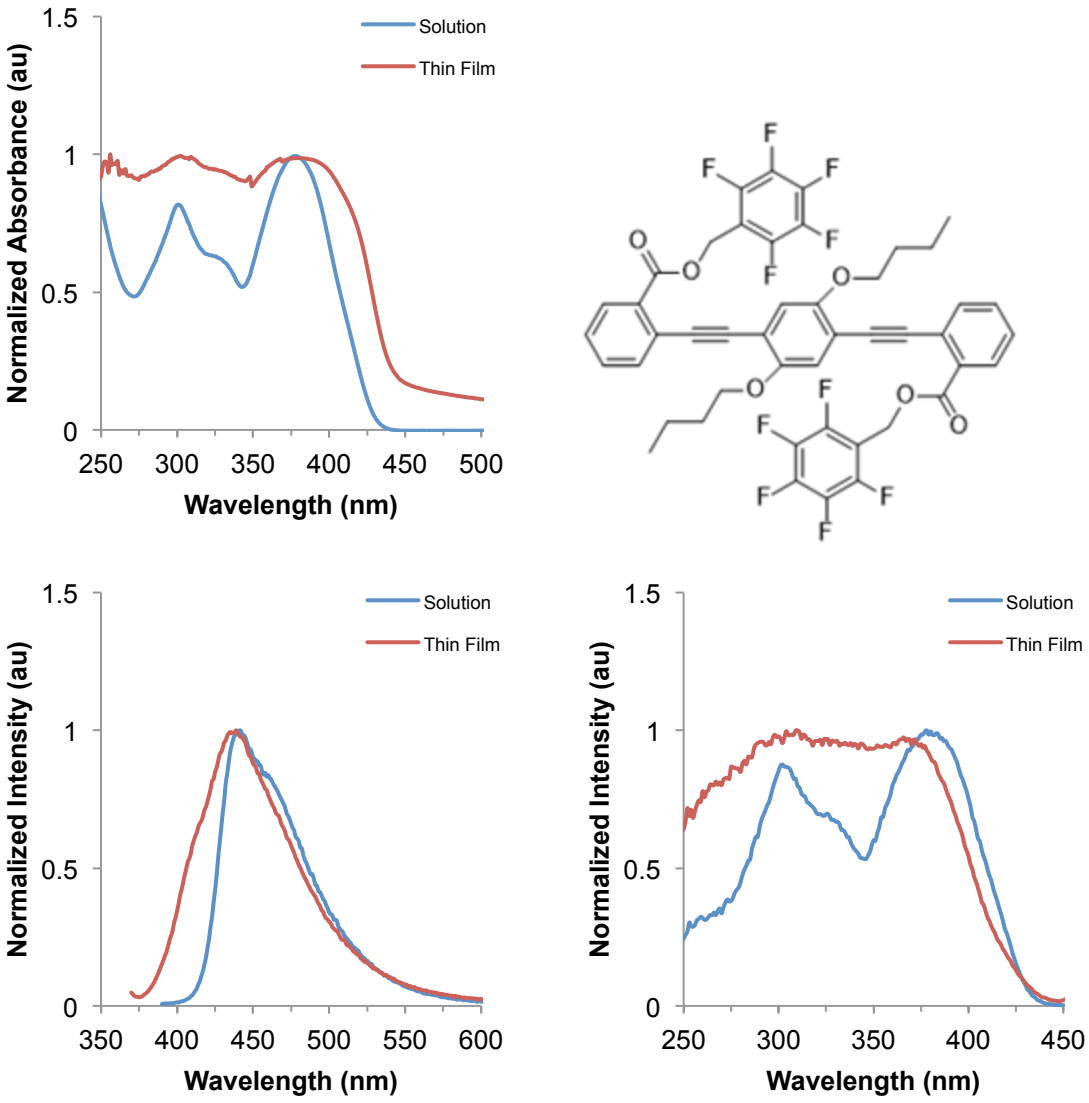
Identification code	X18062	
Empirical formula	C46.84 H30.84 Cl2.52 O4	
Formula weight	746.97	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.1455(7) Å	α= 80.595(2)°.
	b = 9.8705(8) Å	β= 84.255(2)°.
	c = 23.767(2) Å	γ = 88.725(3)°.
Volume	1875.6(3) Å^3	
Z	2	
Density (calculated)	1.323 Mg/m^3	
Absorption coefficient	0.256 mm^{-1}	
F(000)	773	
Crystal size	0.120 x 0.100 x 0.010 mm^3	
Theta range for data collection	2.132 to 30.508°.	
Index ranges	-11<=h<=11, -14<=k<=14, -33<=l<=33	
Reflections collected	59772	
Independent reflections	11450 [R(int) = 0.0509]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.7036	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11450 / 291 / 562	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0548, wR2 = 0.1337	
R indices (all data)	R1 = 0.0924, wR2 = 0.1523	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.401 and -0.334 e.Å^{-3}	

Optical spectroscopy of **3-PE-F5**



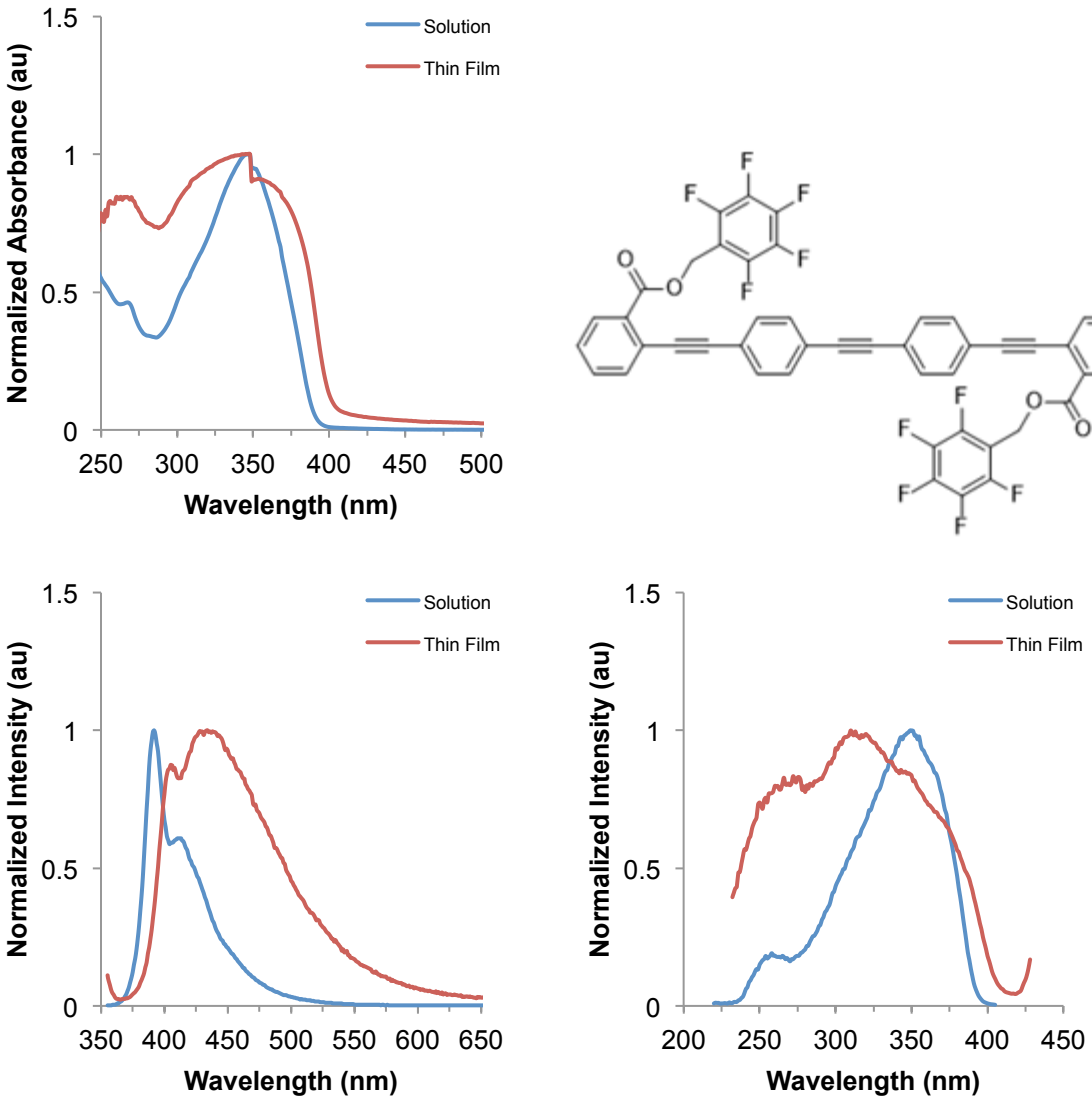
Absorbance (top left), emission (bottom left), and excitation (bottom right) of **3-PE-F5** in solution and as a drop cast thin film.

Optical spectroscopy of **3-DBPE-F5**



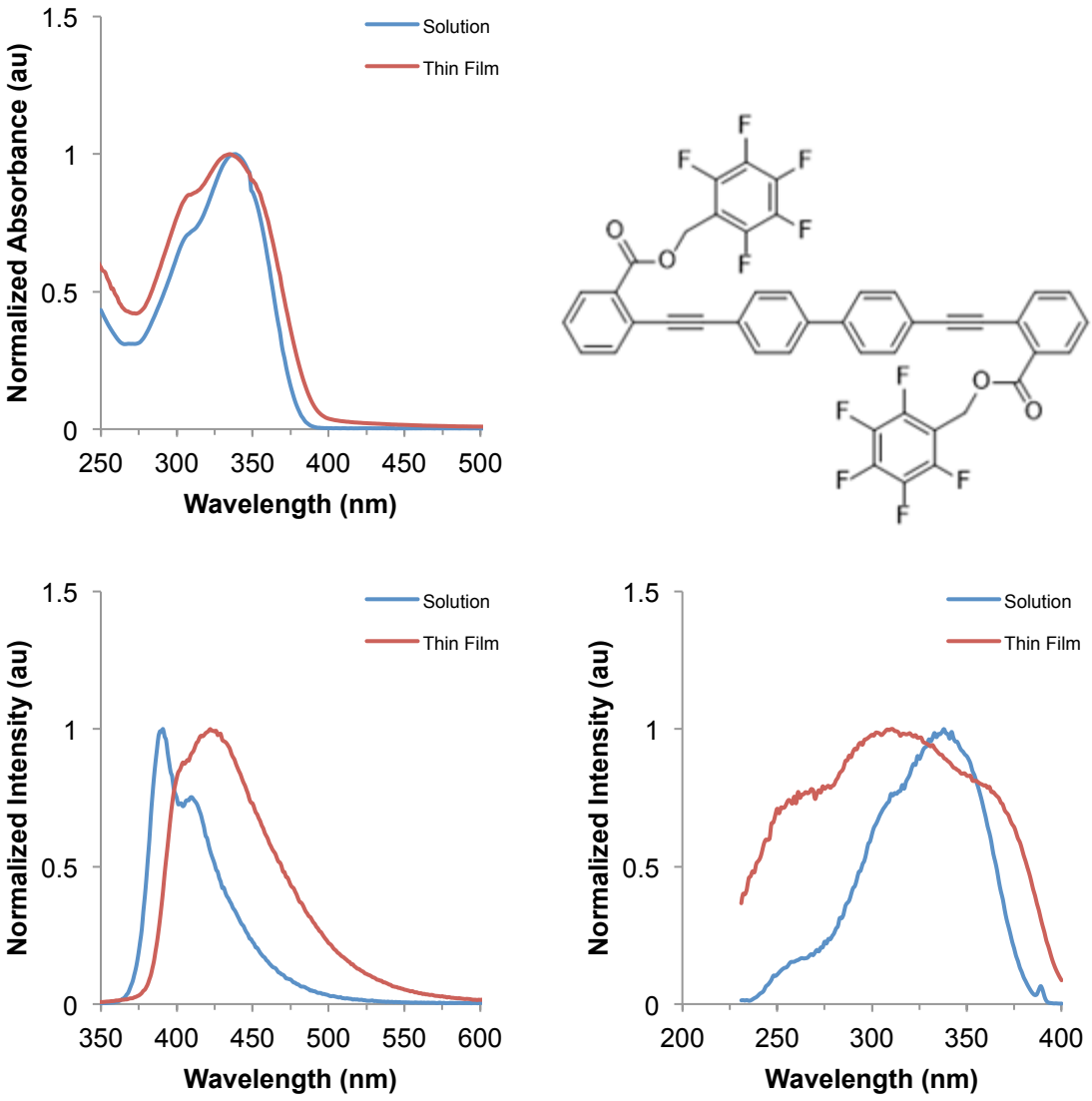
Absorbance (top left), emission (bottom left), and excitation (bottom right) of **3-PE-F5** in solution and as a drop cast thin film.

Optical spectroscopy of **4-PE-F5**



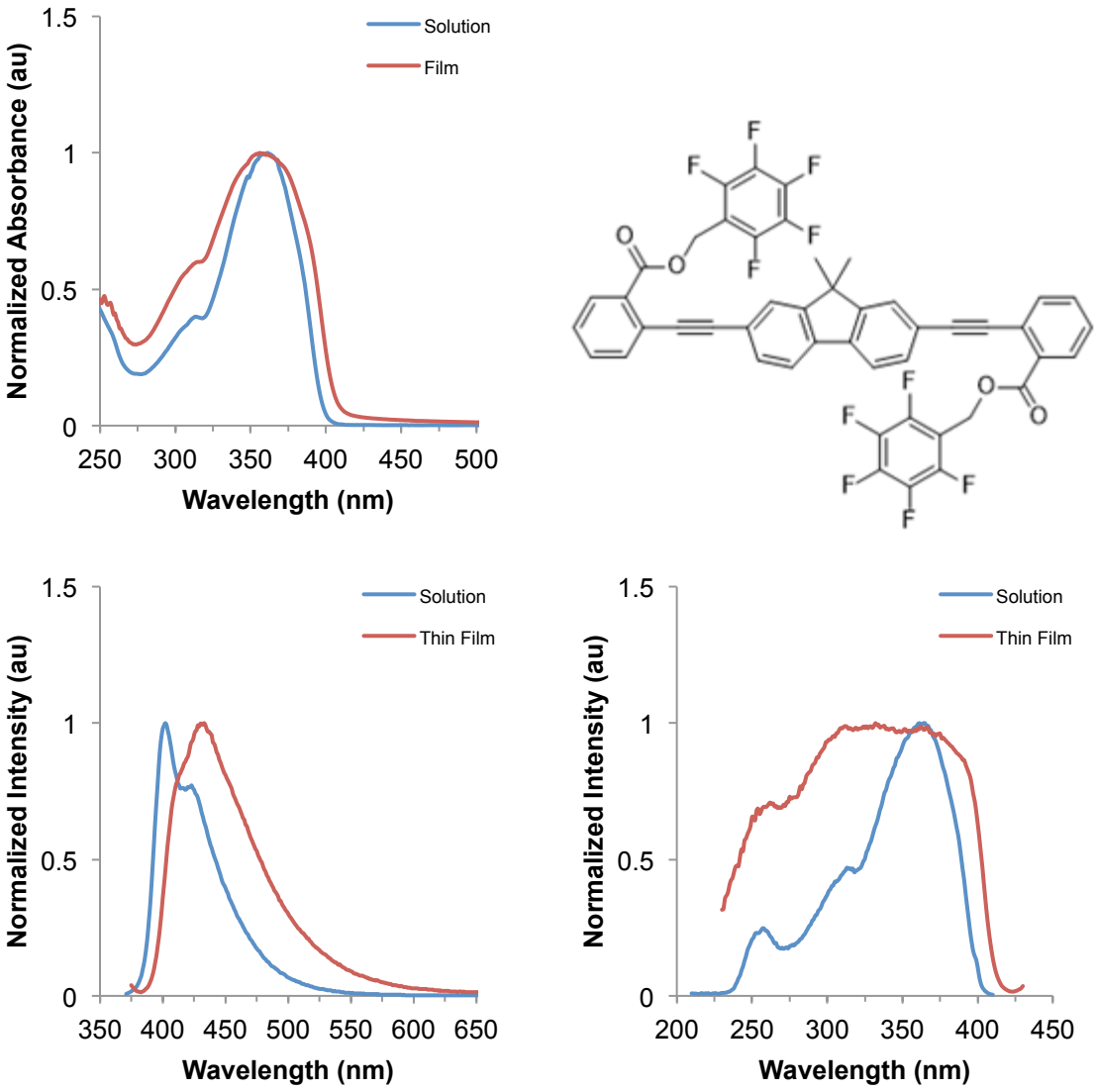
Absorbance (top left), emission (bottom left), and excitation (bottom right) of **4-PE-F5** in solution and as a drop cast thin film.

Optical spectroscopy of **4-BP-F5**



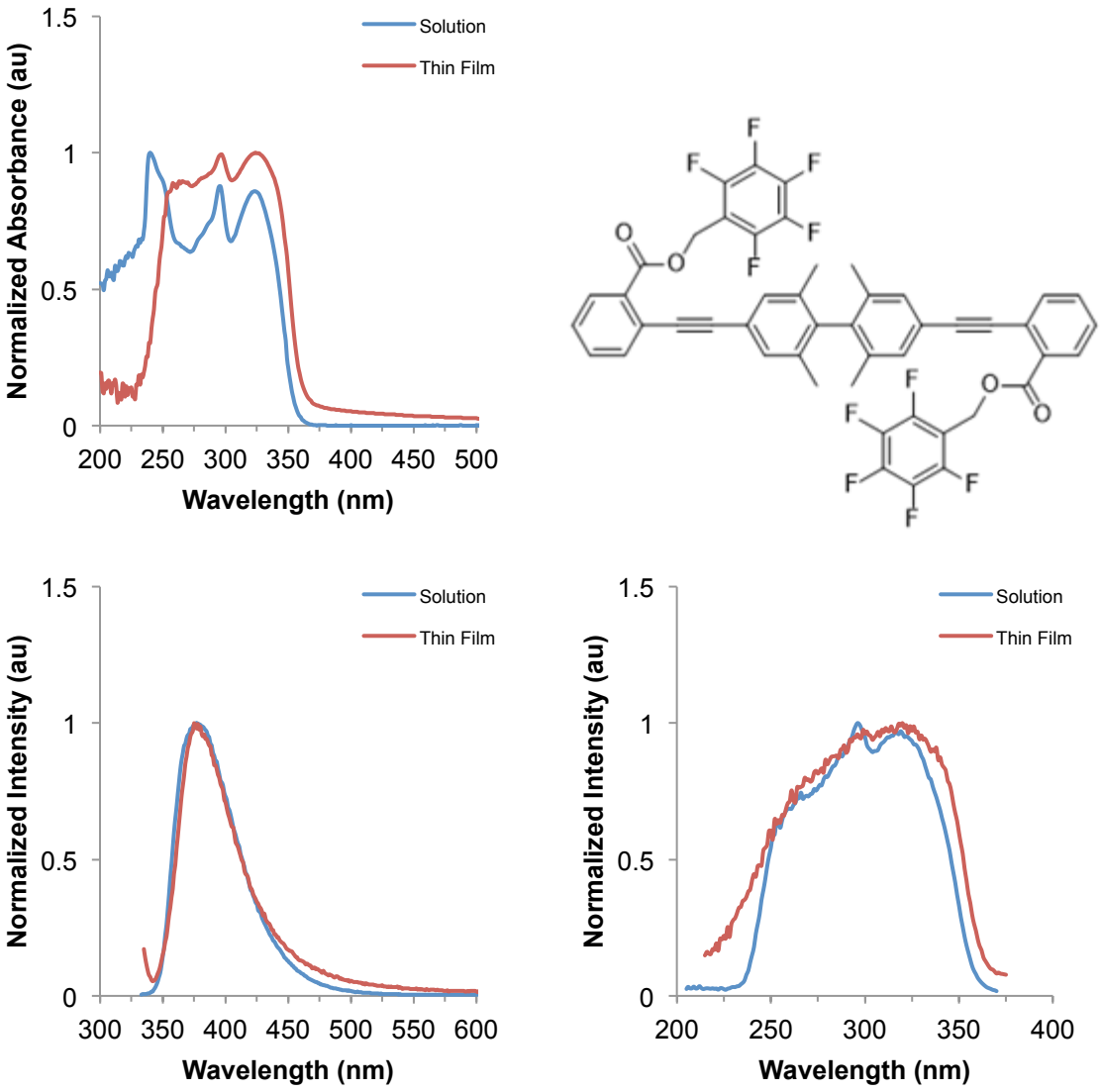
Absorbance (top left), emission (bottom left), and excitation (bottom right) of **4-BP-F5** in solution and as a drop cast thin film.

Optical spectroscopy of **4-DMF-F5**



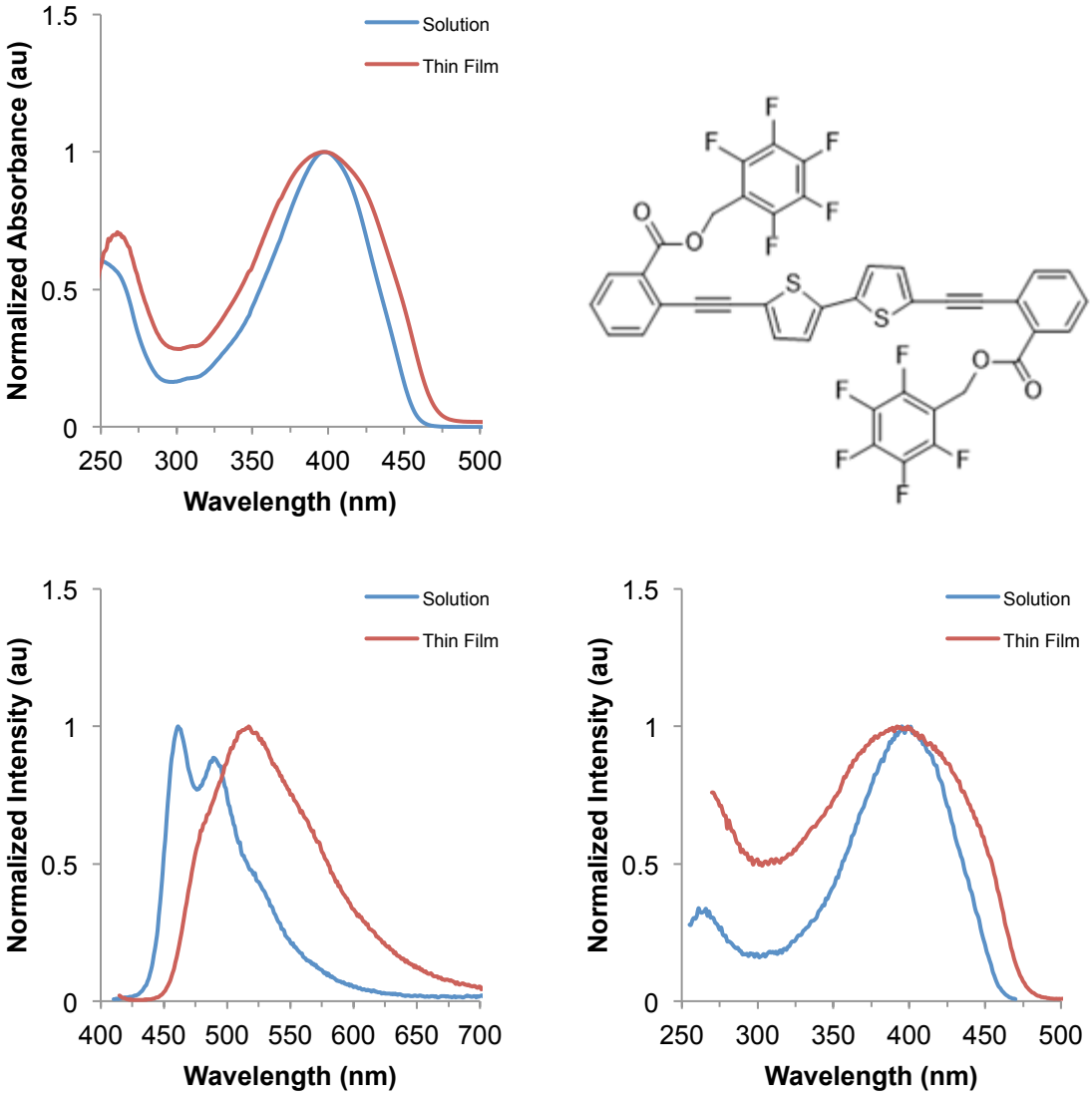
Absorbance (top left), emission (bottom left), and excitation (bottom right) of **4-DMF-F5** in solution and as a drop cast thin film.

Optical spectroscopy of **4-TMBP-F5**



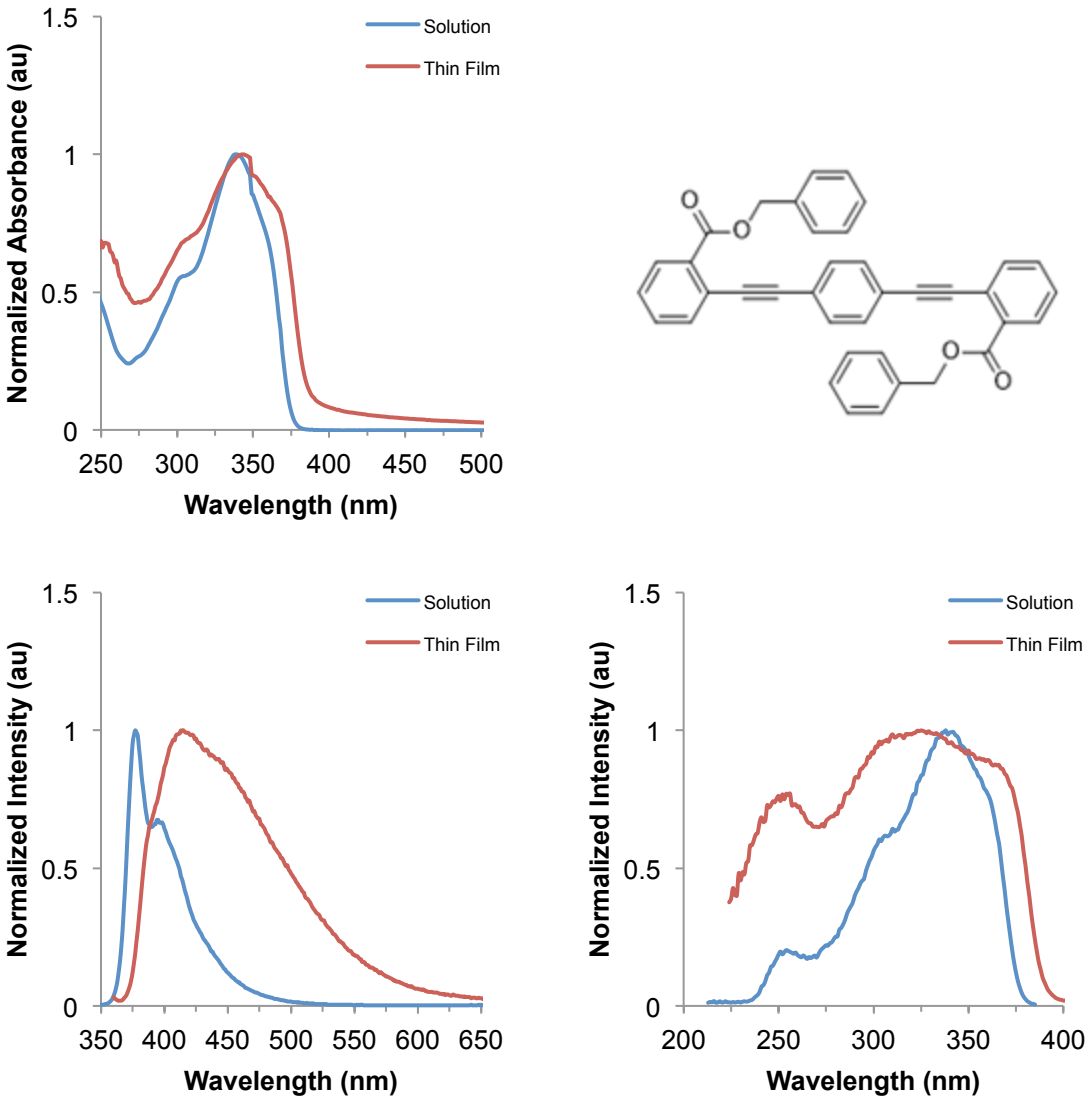
Absorbance (top left), emission (bottom left), and excitation (bottom right) of **4-TMBP-F5** in solution and as a drop cast thin film.

Optical spectroscopy of **4-BT-F5**



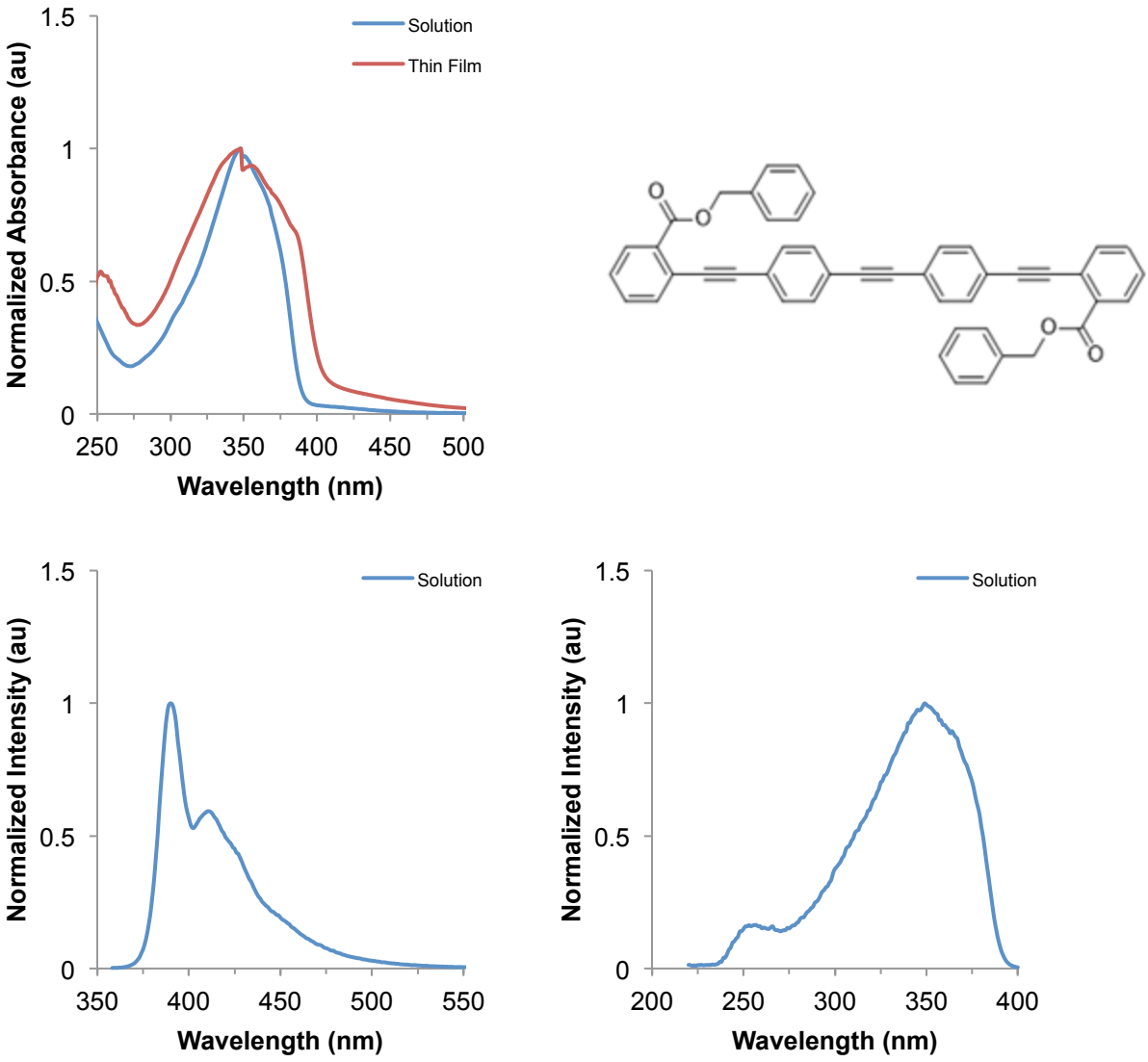
Absorbance (top left), emission (bottom left), and excitation (bottom right) of **4-BT-F5** in solution and as a drop cast thin film.

Optical spectroscopy of **3-PE-H5**



Absorbance (top left), emission (bottom left), and excitation (bottom right) of **3-PE-H5** in solution and as a drop cast thin film.

Optical spectroscopy of **4-PE-H5**



Absorbance (top left), emission (bottom left), and excitation (bottom right) of **3-PE-H5** in solution and as a drop cast thin film (absorbance only).

Quantitative Comparison of Thin Film Fluorescence Emission Spectra of **4-PE-F5** and **4-PE-H5**, acquired in three different positions on each film. The absorbance at the excitation wavelength (345 nm) of these two films was indistinguisable (0.025).