Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Multi-Fold Sonogashira Coupling, A New Convenient Approach to Tetraalkynyl Anthracenes with Tunable Photophysical Properties

Khadimul Islam,[a] Himani Narjinari,[a] Akshara Bisarya,[a] Akshai Kumar*[a,b,c]

[a]Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati – 781039, Assam, India.
[b]Centre for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati – 781039, Assam, India.
[c]School of Health Science, Indian Institute of Technology Guwahati, Guwahati-781039, Assam, India

Email id: akshaikumar@iitg.ac.in

Contents **Page No.**

1. Photophysical Properties:

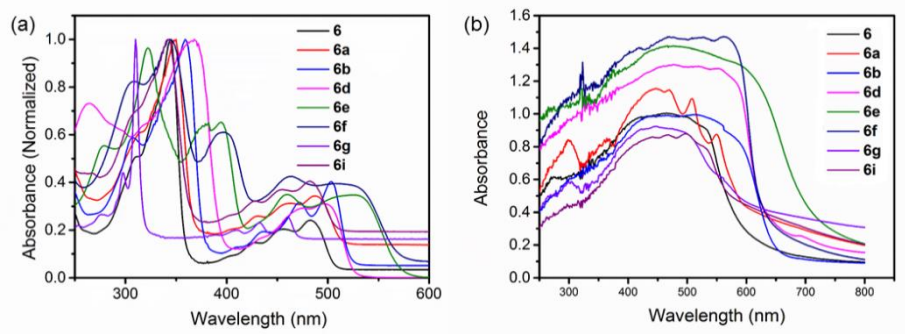


Figure S1. (a) Normalized absorption spectra (293 K, 10^{-5} M) of **6-6i** in $CHCl_3$ (b) Absorption spectra (293 K) of the compounds (**6-6i**) in solid powder state.

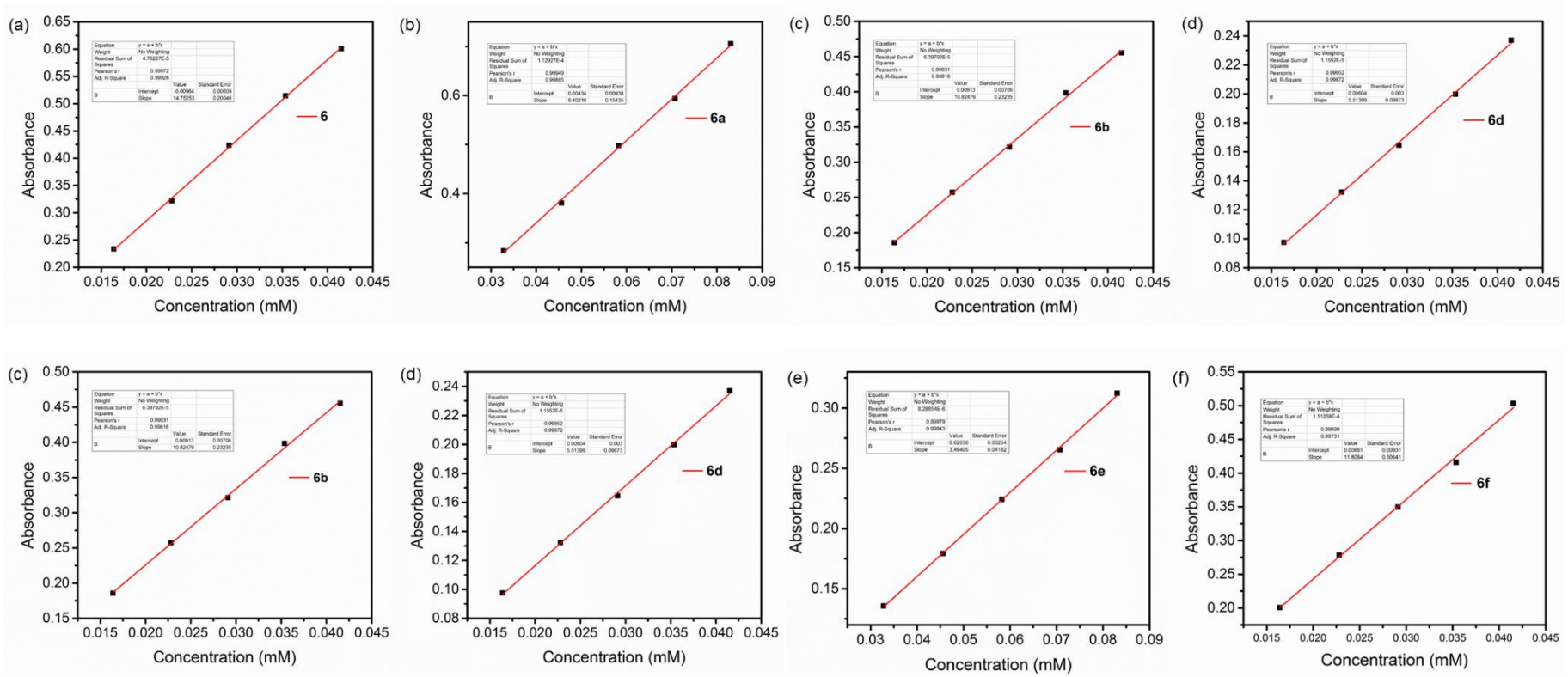


Figure S2. (a-f) Absorbance vs Concentration spectra for the compounds (**6-6f**) in $CHCl_3$.

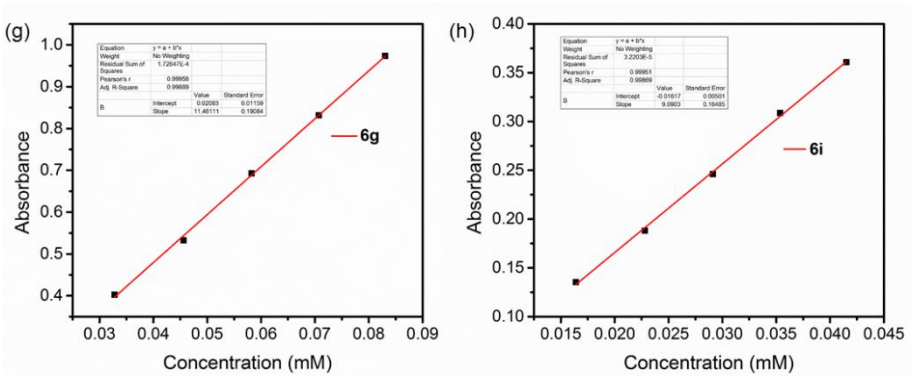


Figure S3. (g-h) Absorbance vs Concentration spectra for the compounds (**6g** & **6i**) in $CHCl_3$.

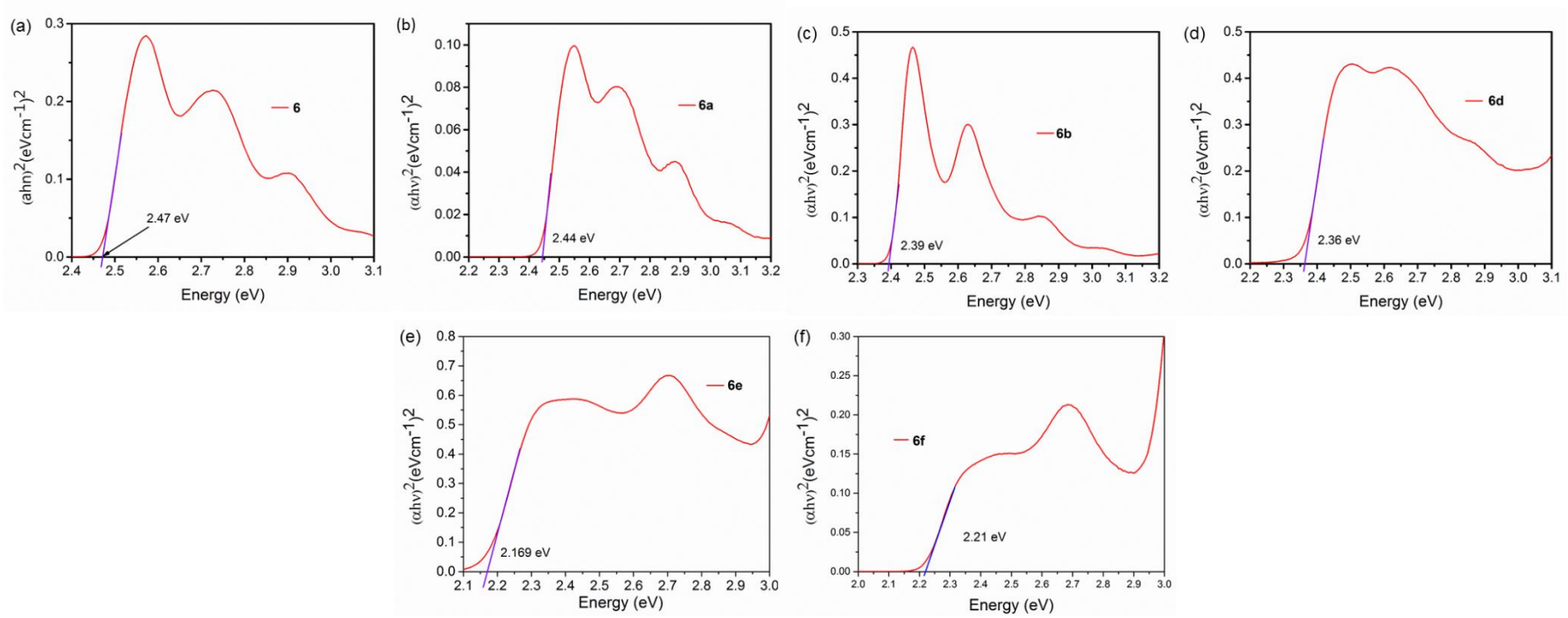


Figure S4. (a-f) Tauc's plot from the Absorption spectra (293 K, 10^{-5} M) of **6**-**6f** in $CHCl_3$ for energy band gap calculation.

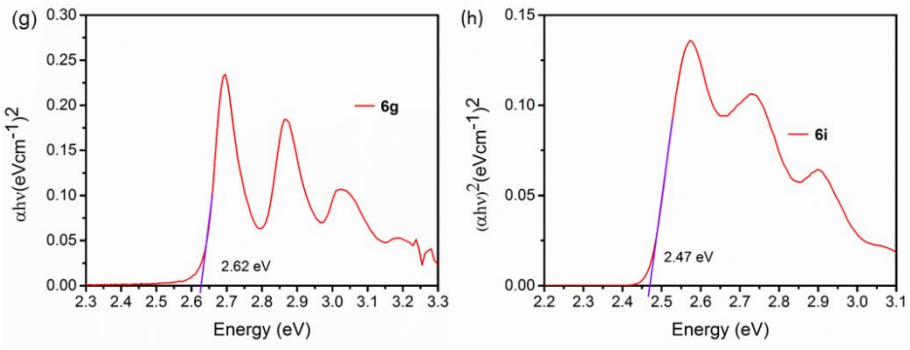


Figure S5. (g-h) Tauc's plot from the Absorption spectra (293 K, 10^{-5} M) of **6g** & **6i** in $CHCl_3$ for energy band gap calculation.

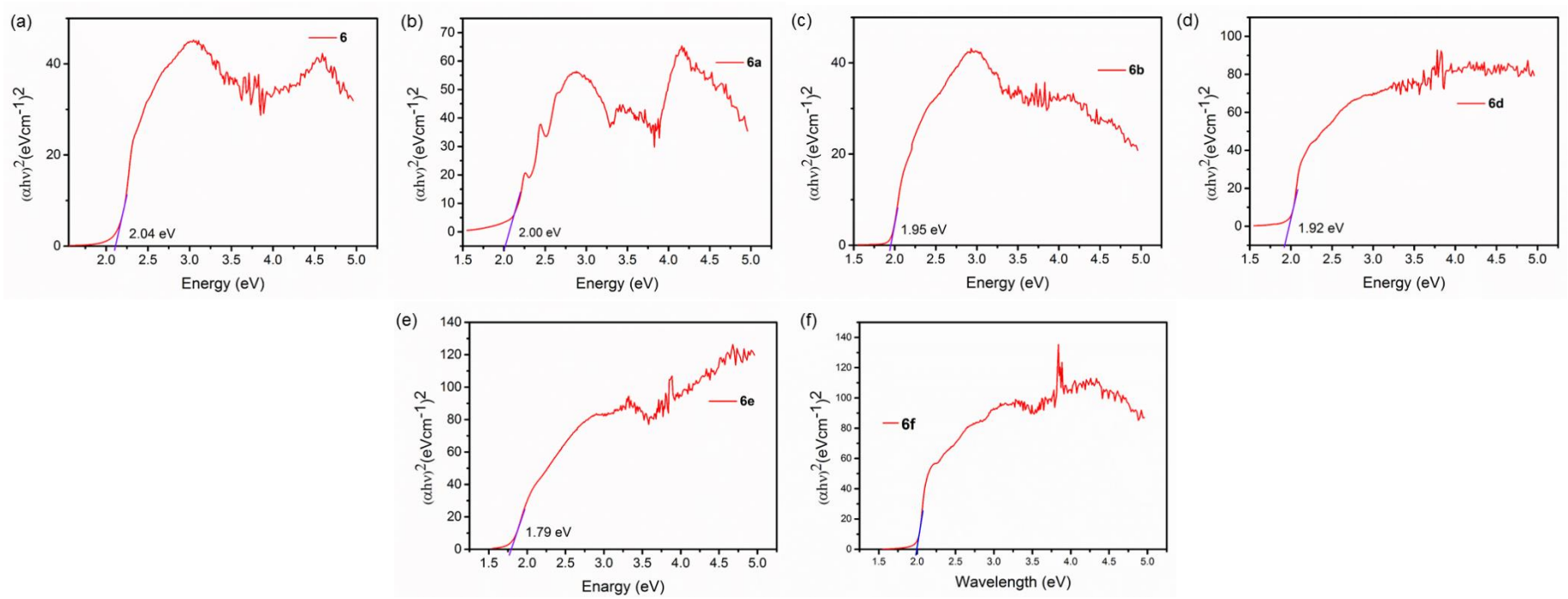


Figure S6. (a-f) Tauc's plot from the Absorption spectra of **6-6f** in solid powder state for energy band gap calculation.

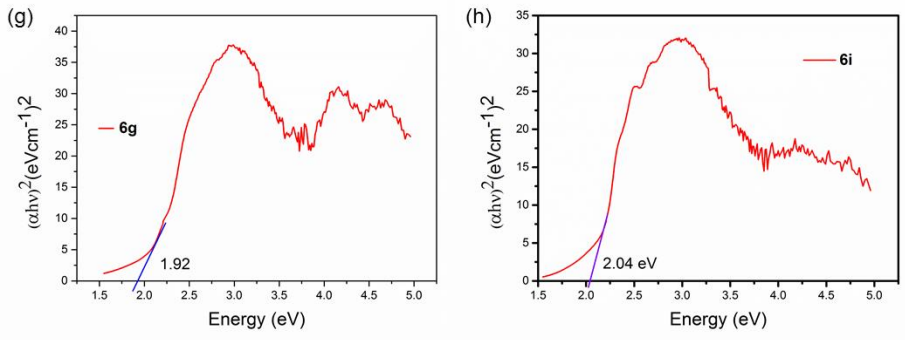


Figure S7. (g-h) Tauc's plot from the Absorption spectra of **6g** & **6i** in solid powder state for energy band gap calculation.

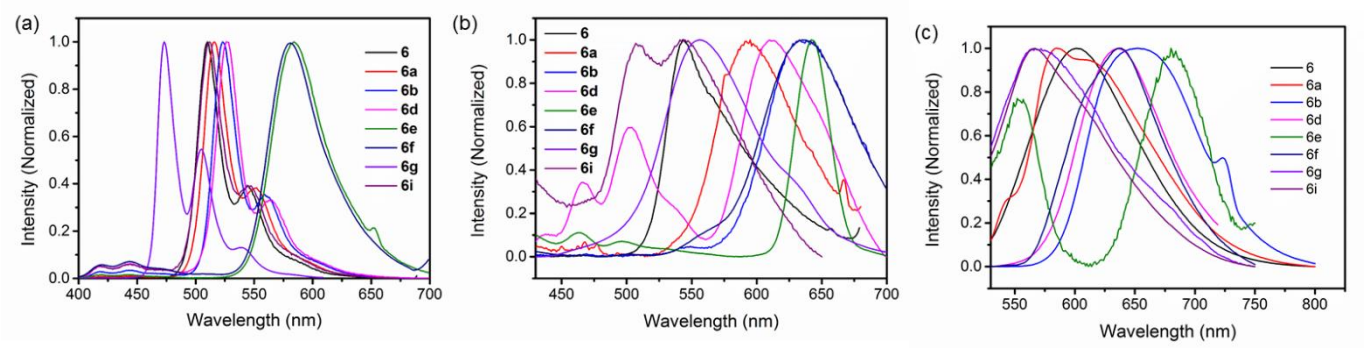


Figure S8. Normalized emission spectra in (a) solution ($CHCl_3$, 293 K, 10^{-6} M), (b) thin-film, and (c) solid powder state for the compounds (**6-6i**).

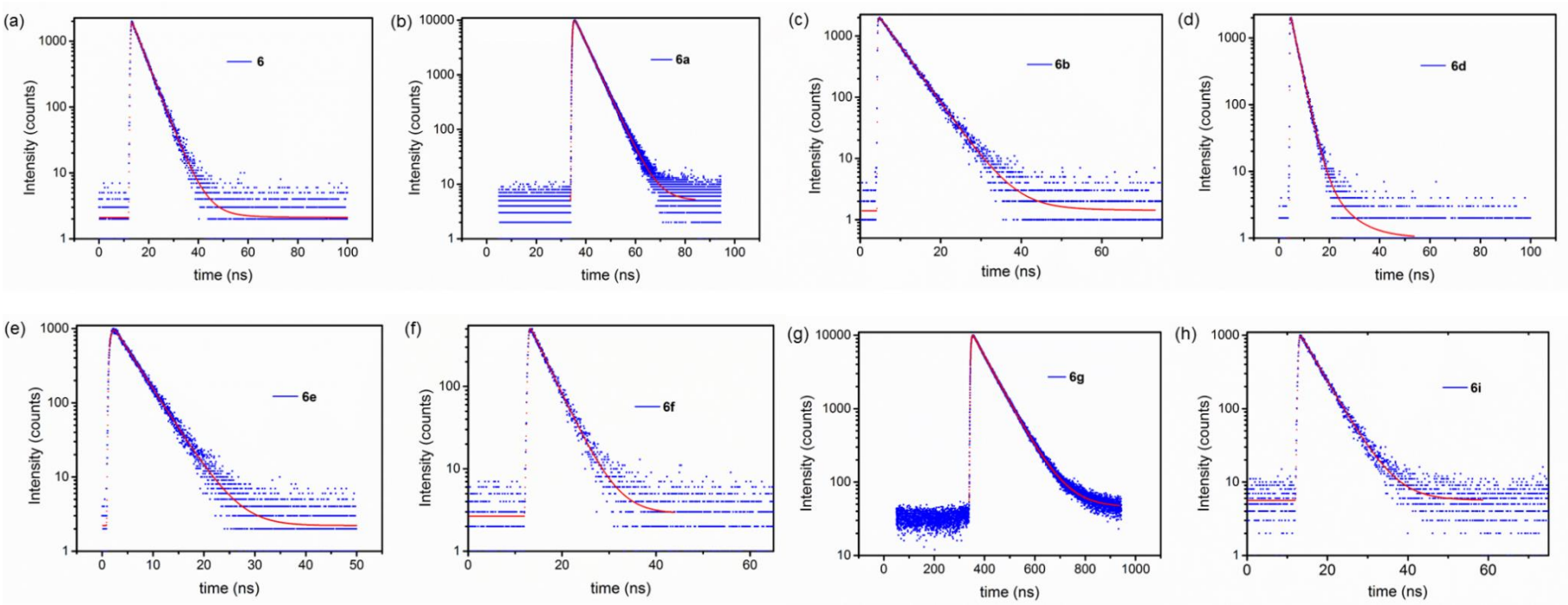


Figure S9. Time-resolved Photoluminescence spectra for the compounds **6-6i**.

Table S1: Time-resolved Photoluminescence data.

Compound	B_1 (%)	τ_1 (ns)	τ_1^2 (ns)	B_2 (%)	τ_2 (ns)	τ_2^2 (ns)	τ_{av} (ns)
6	99.738	4.434	19.660	0.262	15.825	250.43	4.54
6a	25.995	0.192	0.037	74.005	4.423	19.57	4.36
6b	99.824	4.714	22.222	0.176	19.922	396.886	4.83
6d	96.829	2.392	5.722	3.171	8.069	65.109	2.96
6e	96.989	4.085	16.687	3.011	6.246	39.013	4.18
6f	0	0	0	100	3.559	12.666	3.56
6g	36.844	0.327	0.107	63.156	6.879	47.323	6.70
6i	99.877	4.562	20.812	0.123	31.450	989.103	4.79

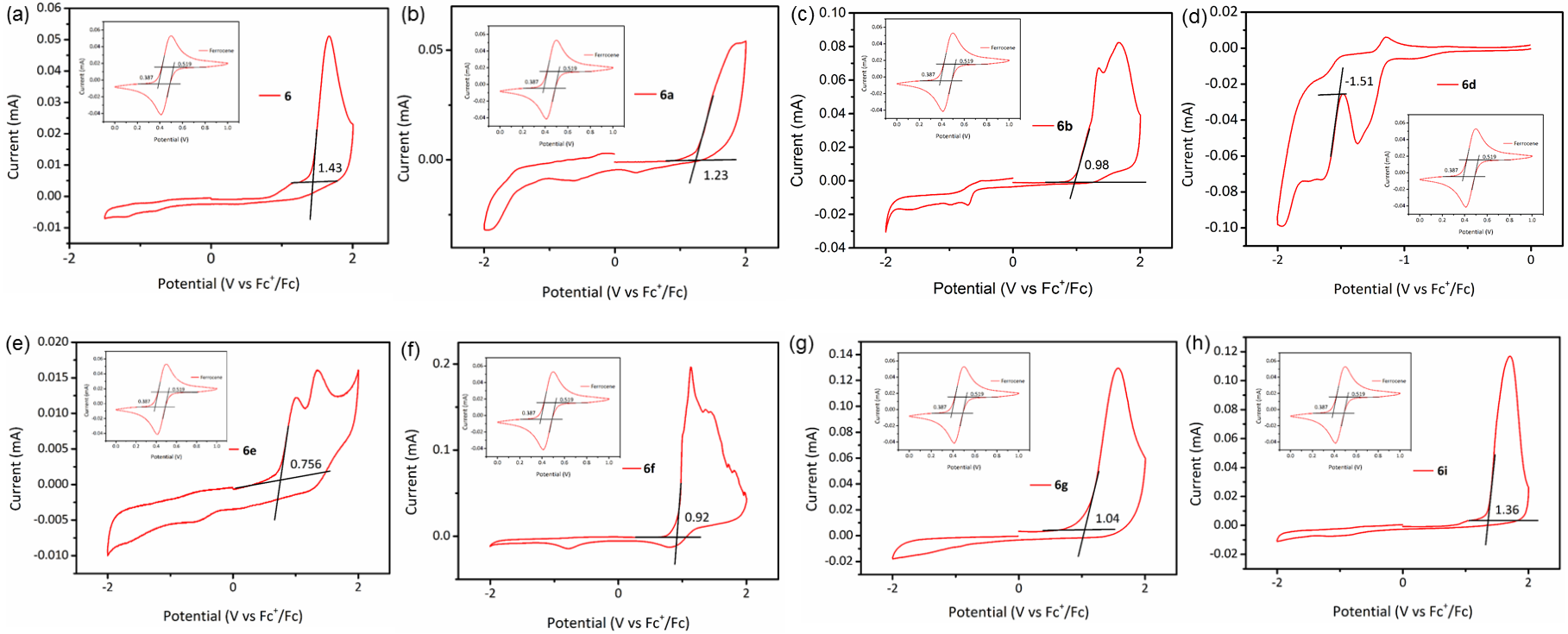


Figure S10. Current vs Potential curve for the compounds **6-6i.**During cyclic voltammetry analysis; glassy carbon was used as working electrode, platinum wire was used as counter electrode, Ag/AgCl was used as reference electrode with acetonitrile as solvent. Scan rate is in 50 mV/s.

Scan direction:

6; Start voltage = 0.0 V, end voltage = 0.0 V, maximum voltage = +2V, minimum voltage = -1.5 V,

6a, **6b**, **6e**, and **6f**; Start voltage = 0.0 V, end voltage = 0.0 V, maximum voltage = +2 V, minimum voltage = -2 V,

6d; Start voltage = 0.0 V, end voltage = 0.0 V, maximum voltage = 0.0 V, minimum voltage = -2 V.

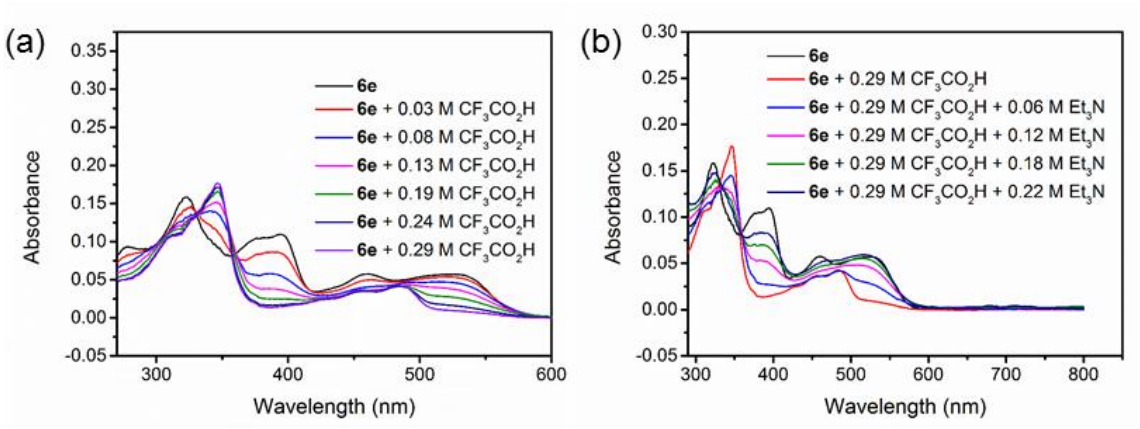


Figure S11. a) Titration of the **6e** (c = 1 x 10^{-5} M) by CF_3COOH in absorption spectra (b) titration of the **6e** by CF_3COOH and Et_3N in absorption spectra

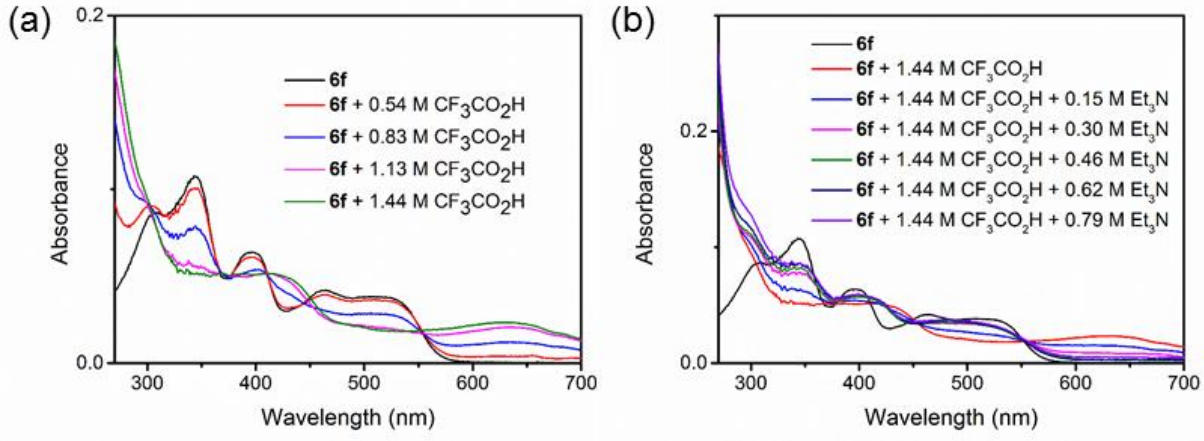


Figure S12. a) Titration of the **6f** (c = 1 x 10^{-5} M) by CF_3COOH in absorption spectra (b) titration of the **6f** by CF_3COOH and Et_3N in absorption spectra

2. X-Ray Crystallographic studies:

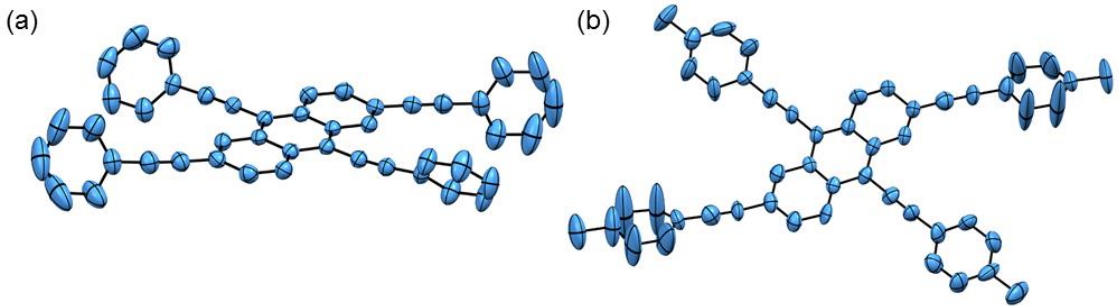


Figure S13. ORTEP diagram of (a) **6** and (b) **6a**.

Table S2. Crystal data for the compounds (**6**) and (**6a**):

	6	**6a**
Identification code (CCDC No)	2070944	2070945
Empirical formula	$C_{46}H_{26}$	$C_{50}H_{34}$
Formula weight	578.67	634.77
Temperature/K	296(2)	296(2)
Space group	P21/n	Pc
Crystal system	Monoclinic	Monoclinic
a/Å	9.8457(7)	14.929(3)
b/Å	19.1932(16)	11.922(3)
c/Å	17.0462(14)	10.529(2)
α/°	90.00	90.00
β/°	101.212(2)	92.393(7)
γ/°	90.00	90.00
Volume/$Å^3$	3159.7(4)	1872.3(7)
Z	4	2
ρ_{calc} g/cm^3	1.216	1.126
μ/mm^{-1}	0.069	0.064
F(000)	1208.0	668.0
Crystal size/mm^3	0.28 × 0.26 × 0.24	0.28 × 0.25 × 0.24
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.24 to 50	5.16 to 50
Index ranges	$-11 \le h \le 11$, $-22 \le k \le 22$, $-20 \le l \le 20$	$-17 \le h \le 17$, $-14 \le k \le 14$, $-12 \le l \le 12$
Reflections collected	198842	45579
Independent reflections	5566 [R_{int} = 0.1546, R_{sigma} = N/A]	6588 [R_{int} = 0.1745, R_{sigma} = N/A]
Data/restraints/parameters	5566/0/415	6588/2/455
Goodness-of-fit on F^2	1.056	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0586, wR_2 = 0.1501	R_1 = 0.0836, wR_2 = 0.1984
Final R indexes [all data]	R_1 = 0.0911, wR_2 = 0.1746	R_1 = 0.1812, wR_2 = 0.2604
Largest diff. peak/hole / e $Å^{-3}$	0.13/-0.24	0.24/-0.23

Alert level A of the crystal 6a.
SHFSU01_ALERT_2_A The absolute value of parameter shift to su ratio > 0.20
Absolute value of the parameter shift to su ratio given 0.326
Additional refinement cycles may be required.
PLAT080_ALERT_2_A Maximum Shift/Error ..... 0.33 Why?
PLAT242_ALERT_2_A Low 'MainMol' Ueq as Compared to Neighbors of C47 Check

Author Response:

The crystal quality was very poor. The crystal was grown by multiple times in different possible ways but it decomposed during the data collection, but the reported data is the best than other collected data. These alerts are shown owing to nonconvergent refinement to one carbon in one of the phenyl ring.

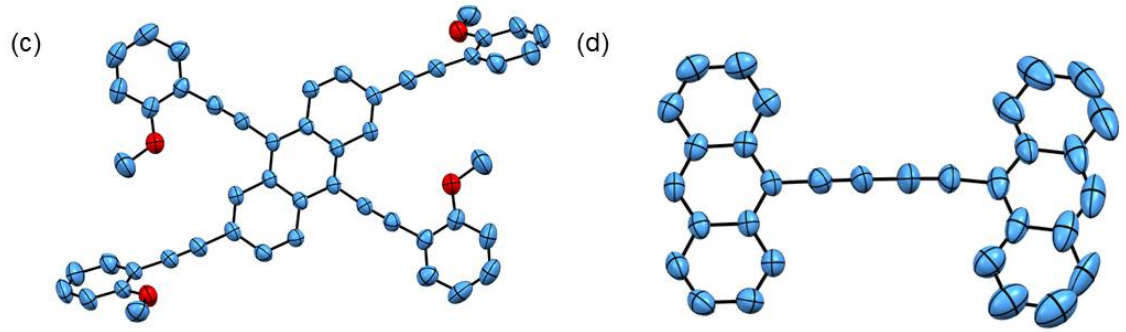


Figure S14. ORTEP diagram of (c) **6b** and (d) **6c´**.

Table S3. Crystal data for compounds (**6b**) and (**6c´**).

	6b	**6c´**
Identification code (CCDC No)	2070946	2086685
Empirical formula	$C_{50}H_{34}O_4$	$C_{32}H_{18}$
Formula weight	698.77	402.46
Temperature/K	296(2)	296(2)
Crystal system	triclinic	orthorhombic
Space group	P-1	P21/n
a/Å	4.6663(5)	11.162(3)
b/Å	14.0000(16)	11.978(3)
c/Å	14.5094(17)	15.916(4)
α/°	75.898(4)	90.00
β/°	83.094(4)	90.00
γ/°	83.357(4)	90.00
Volume/Å^3	908.96(18)	2128.0(9)
Z	1	4
ρcalcg/cm^3	1.254	1.256
μ/mm^{-1}	0.079	0.071
F(000)	354.0	924.0
Crystal size/mm^3	0.28 × 0.25 × 0.23	0.30 × 0.27 × 0.25
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.64 to 50	4.98 to 50
Index ranges	-5 ≤ h ≤ 5, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -18 ≤ l ≤ 17
Reflections collected	22015	12932
Independent reflections	3217 [R_{int} = 0.0933, R_{sigma} = N/A]	3065 [R_{int} = 0.1000, R_{sigma} = N/A]
Data/restraints/parameters	3217/0/246	3065/0/289
Goodness-of-fit on F^2	0.762	0.790
Final R indexes [I>=2σ (I)]	R_1 = 0.0470, wR_2 = 0.1239	R_1 = 0.0719, wR_2 = 0.2009
Final R indexes [all data]	R_1 = 0.0978, wR_2 = 0.1609	R_1 = 0.1641, wR_2 = 0.2674
Largest diff. peak/hole / e Å^{-3}	0.16/-0.15	0.16/-0.12

Alert level A of the crystal 6c´.

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low. 0.815 Why?

Author Response:

The completeness was low due to weak diffraction quality of the crystal.

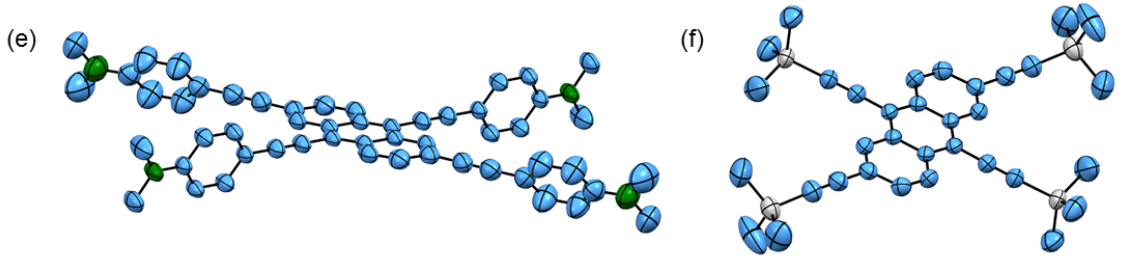


Figure S15. ORTEP diagram of (e) **6e** and (f) **6g**.

Table S4. Crystal data for compounds (**6e**) and (**6g**).

	6e	**6g**
Identification code (CCDC No)	2070947	2070948
Empirical formula	$C_{54}H_{60}N_4$	$C_{34}H_{42}Si_4$
Formula weight	765.105	563.054
Temperature/K	296.15	296.15
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	9.2771(9)	6.0741(8)
b/Å	9.6139(8)	11.2759(16)
c/Å	14.3349(14)	14.146(2)
α/°	71.119(3)	99.128(5)
β/°	86.812(4)	96.304(5)
γ/°	61.782(3)	105.017(4)
Volume/$Å^3$	1058.66(18)	912.3(2)
Z	1	1
ρcalcg/cm^3	1.200	1.025
μ/mm^{-1}	0.070	0.182
F(000)	412.1	302.4
Crystal size/mm^3	0.29 × 0.26 × 0.24	0.28 × 0.26 × 0.24
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.98 to 50	3.82 to 50
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-18 \le l \le 18$	$-8 \le h \le 8$, $-14 \le k \le 15$, $-18 \le l \le 18$
Reflections collected	31337	32125
Independent reflections	3727 [R_{int} = 0.1317, R_{sigma} = 0.0930]	3212 [R_{int} = 0.0810, R_{sigma} = 0.0558]
Data/restraints/parameters	3727/0/266	3212/0/178
Goodness-of-fit on F^2	0.874	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0562, wR_2 = 0.1554	R_1 = 0.0437, wR_2 = 0.1168
Final R indexes [all data]	R_1 = 0.1111, wR_2 = 0.1949	R_1 = 0.0662, wR_2 = 0.1280
Largest diff. peak/hole / e $Å^{-3}$	0.21/-0.23	0.21/-0.22

3. NMR and MALDI spectra

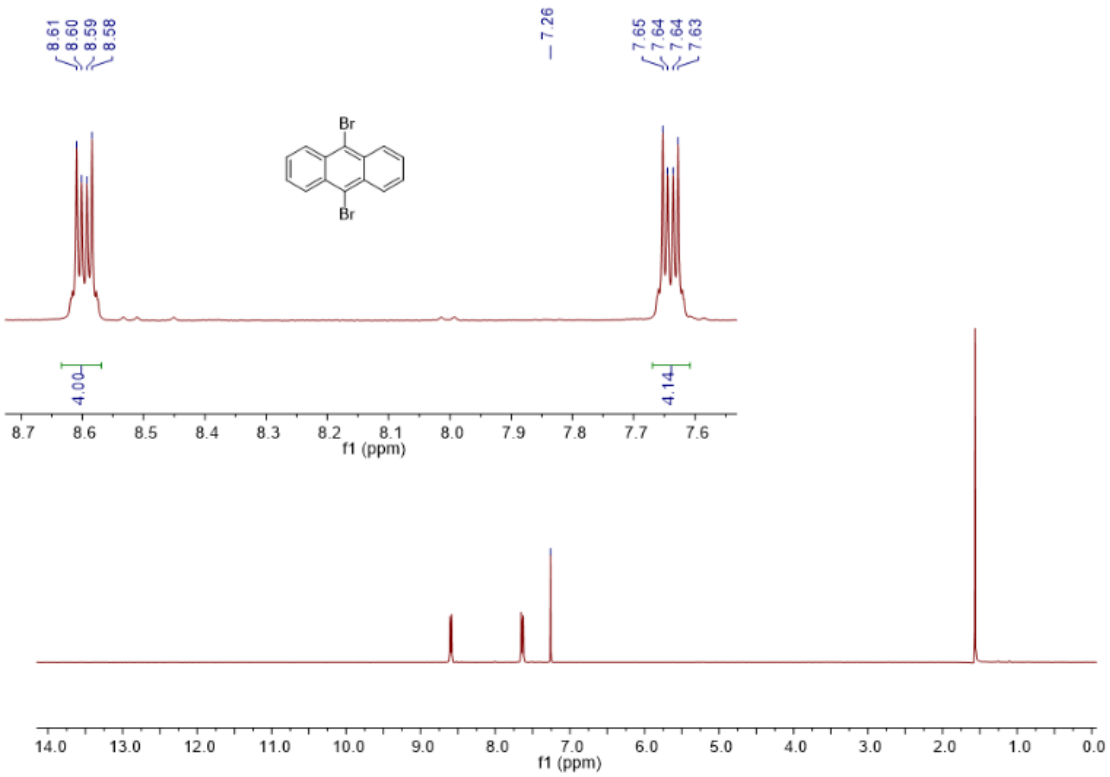


Figure S16. ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$).

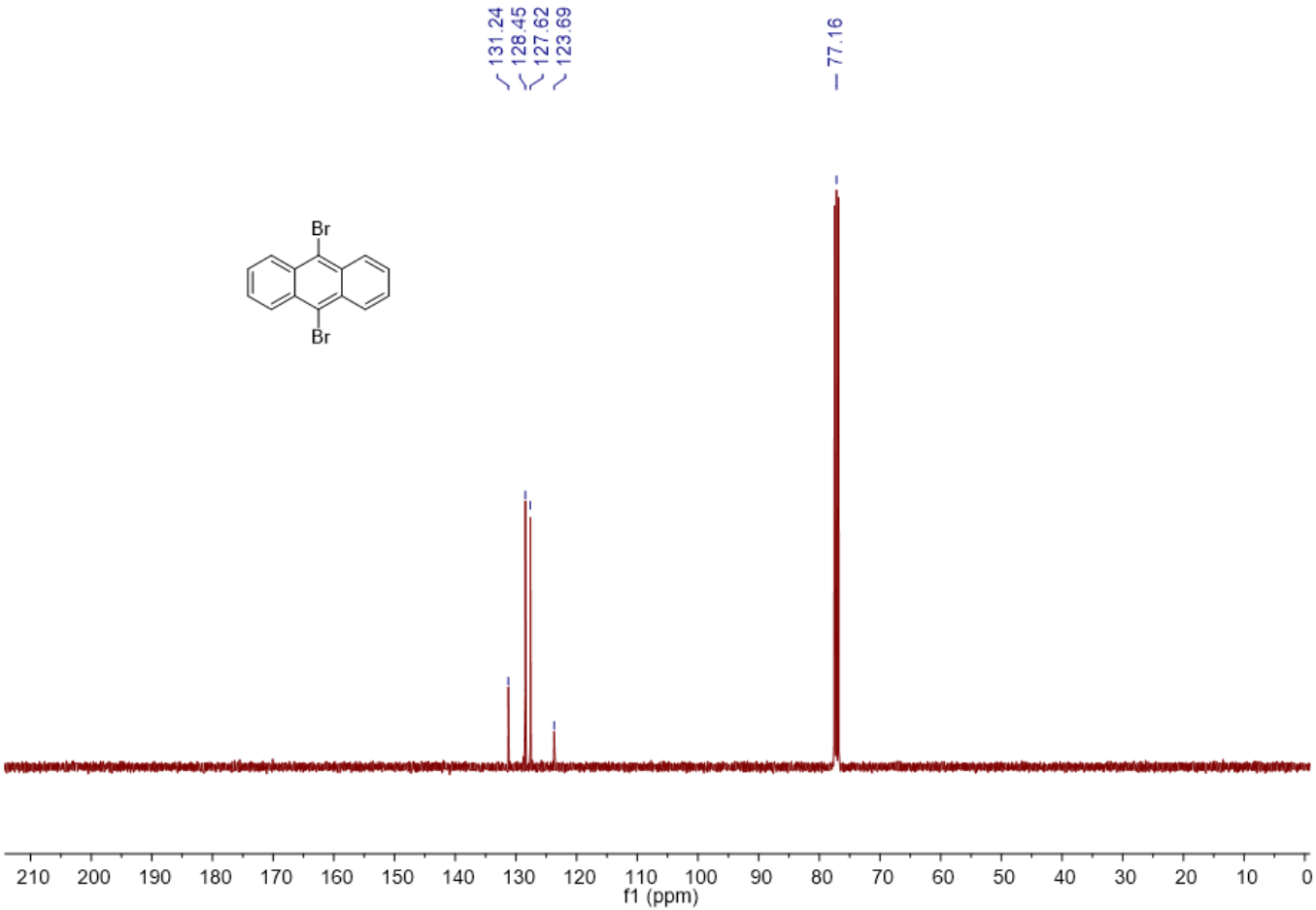


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **2** (101 MHz, $CDCl_3$).

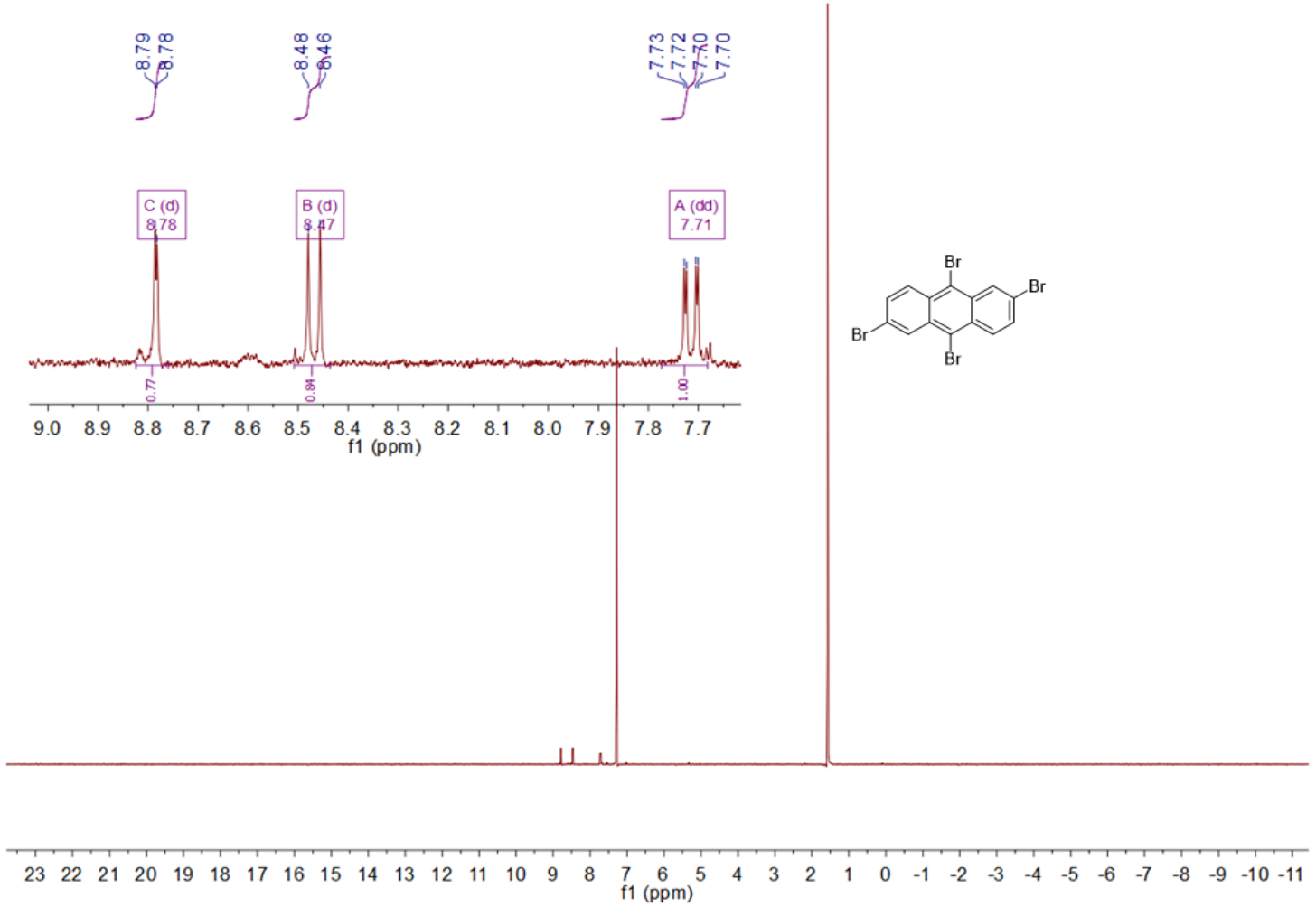


Figure S18. ^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$).

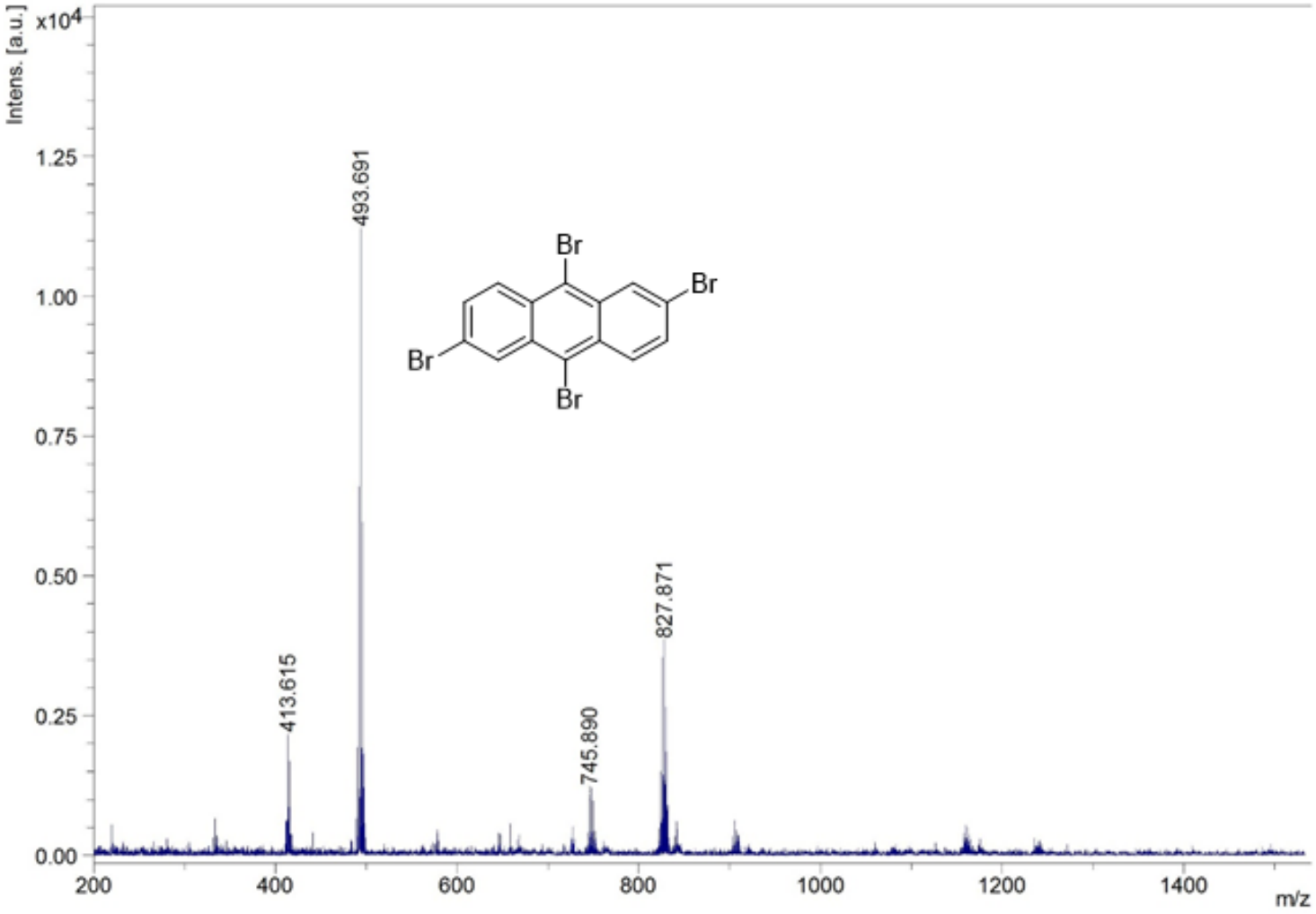


Figure S19. MALDI spectrum of **3**.

.

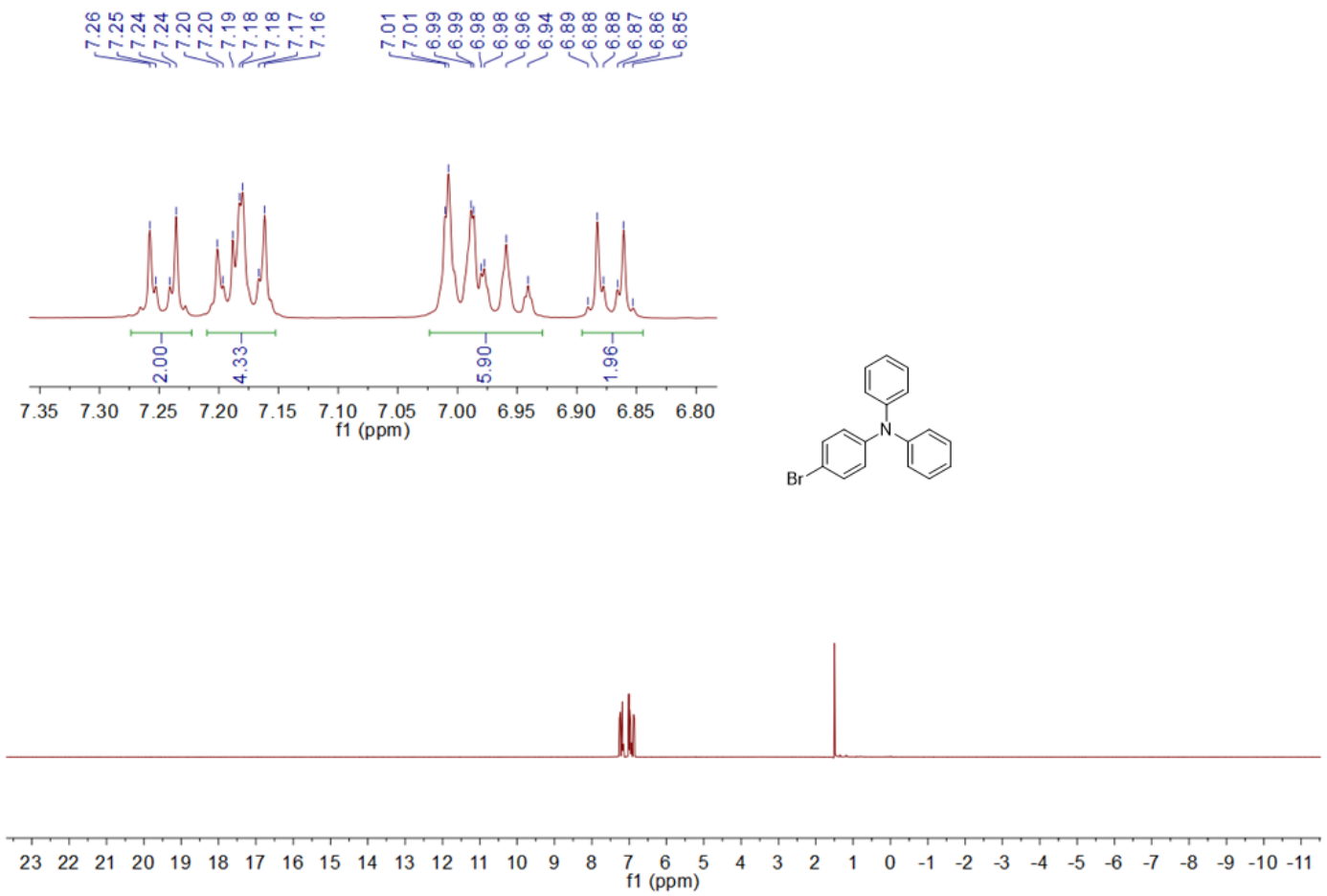


Figure S20. ^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$).

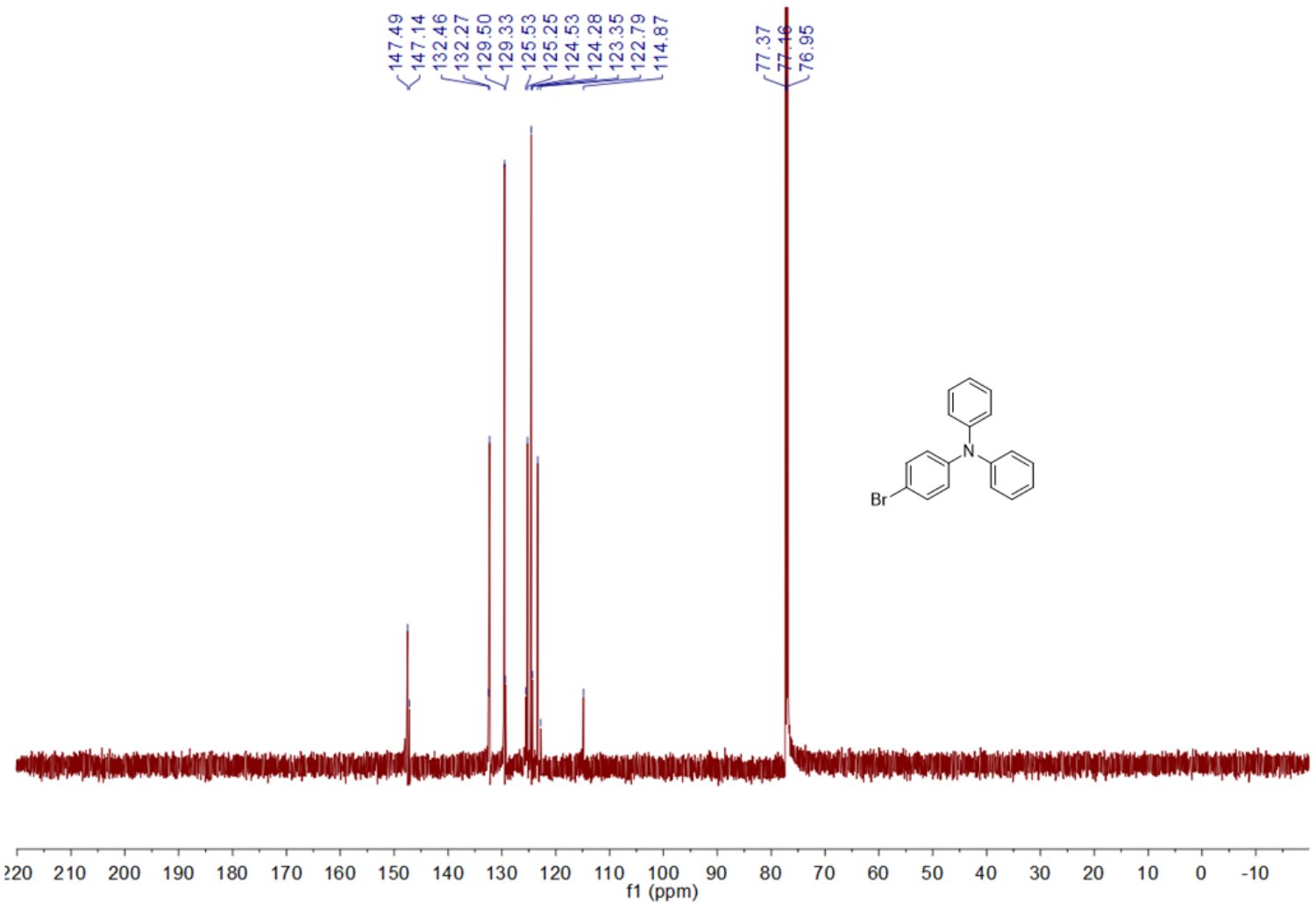


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **7** (151 MHz, $CDCl_3$)

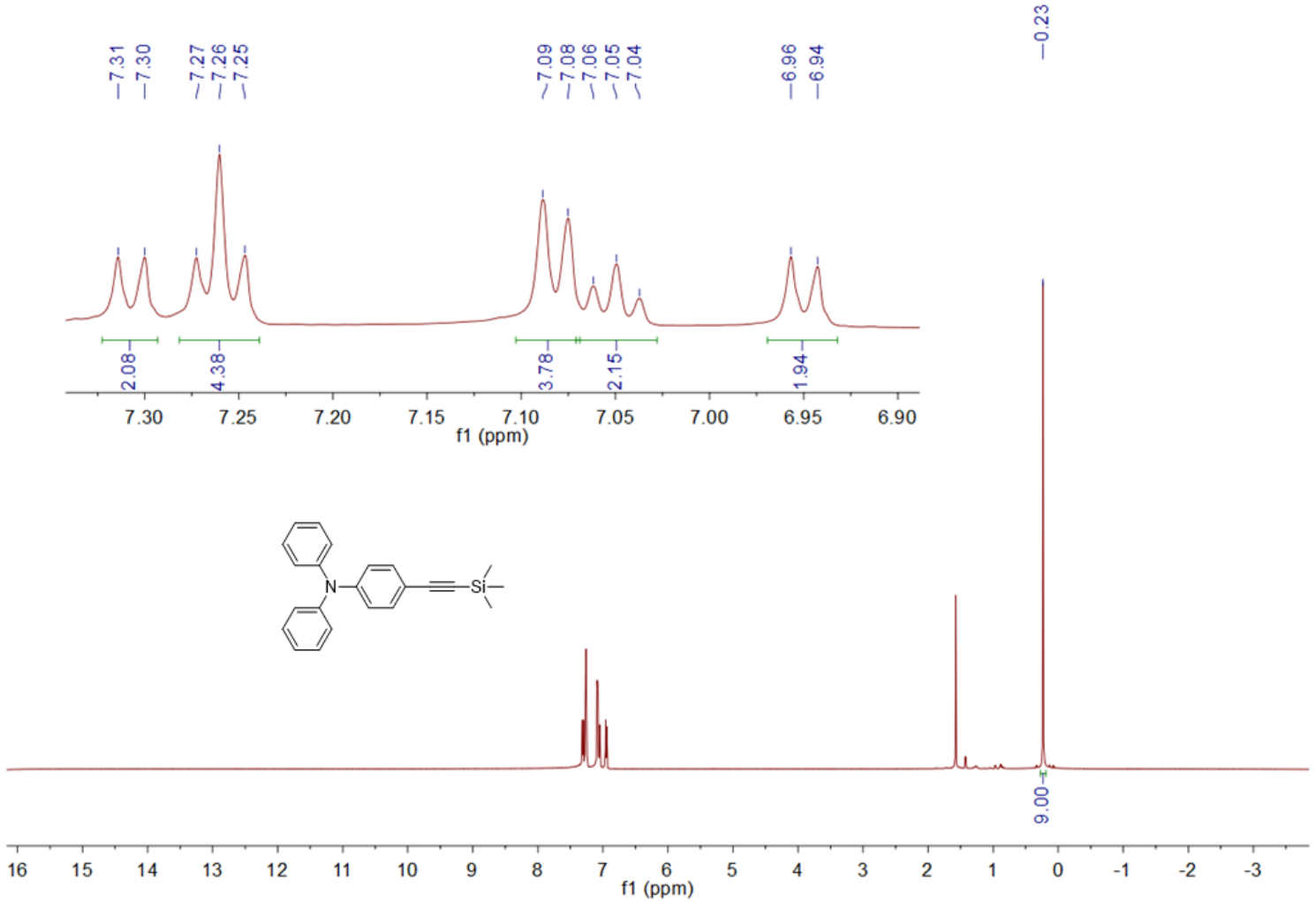


Figure S22. ^{1}H NMR spectrum of **8** (600 MHz, $CDCl_3$).

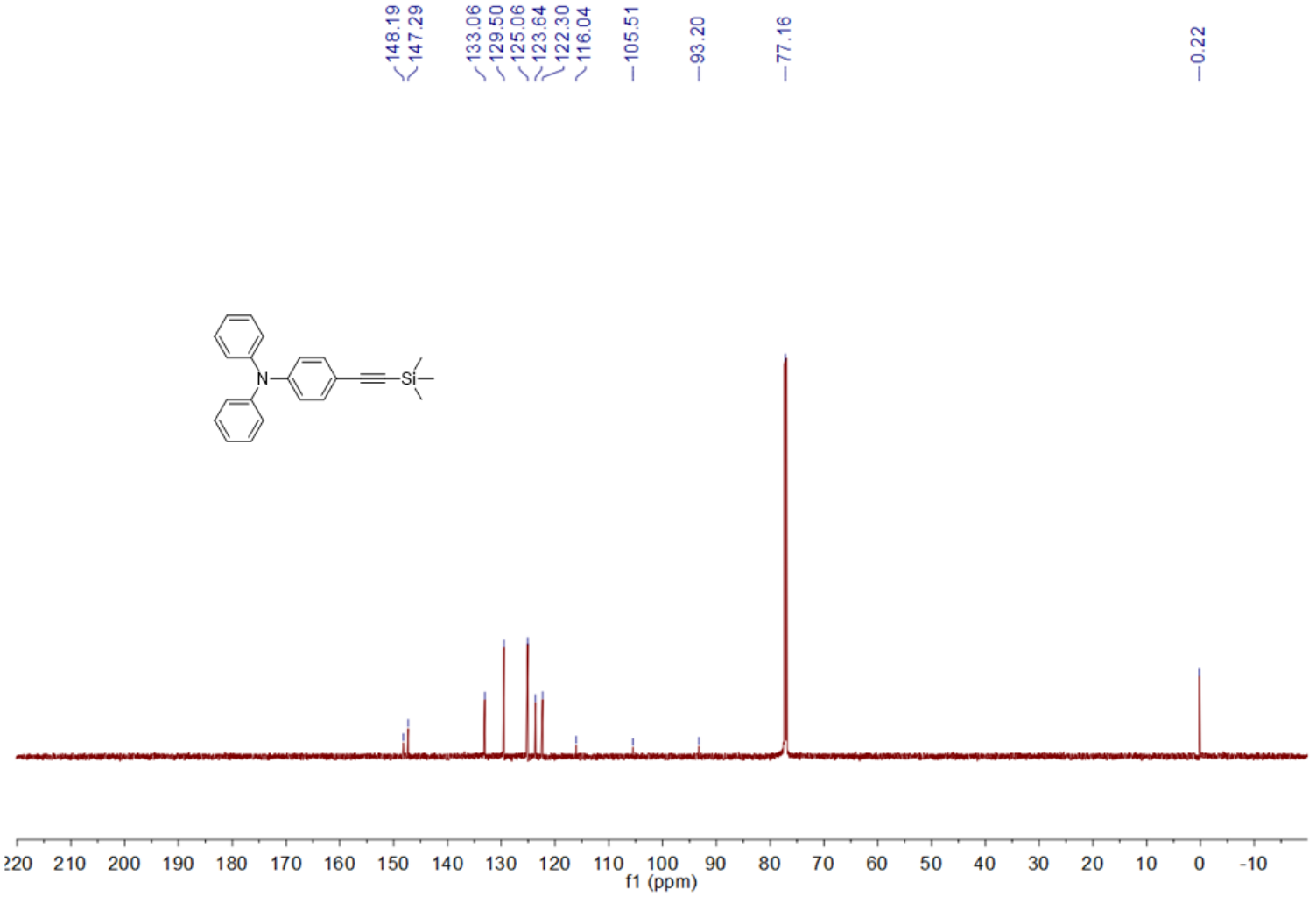


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **8** (151 MHz, $CDCl_3$)

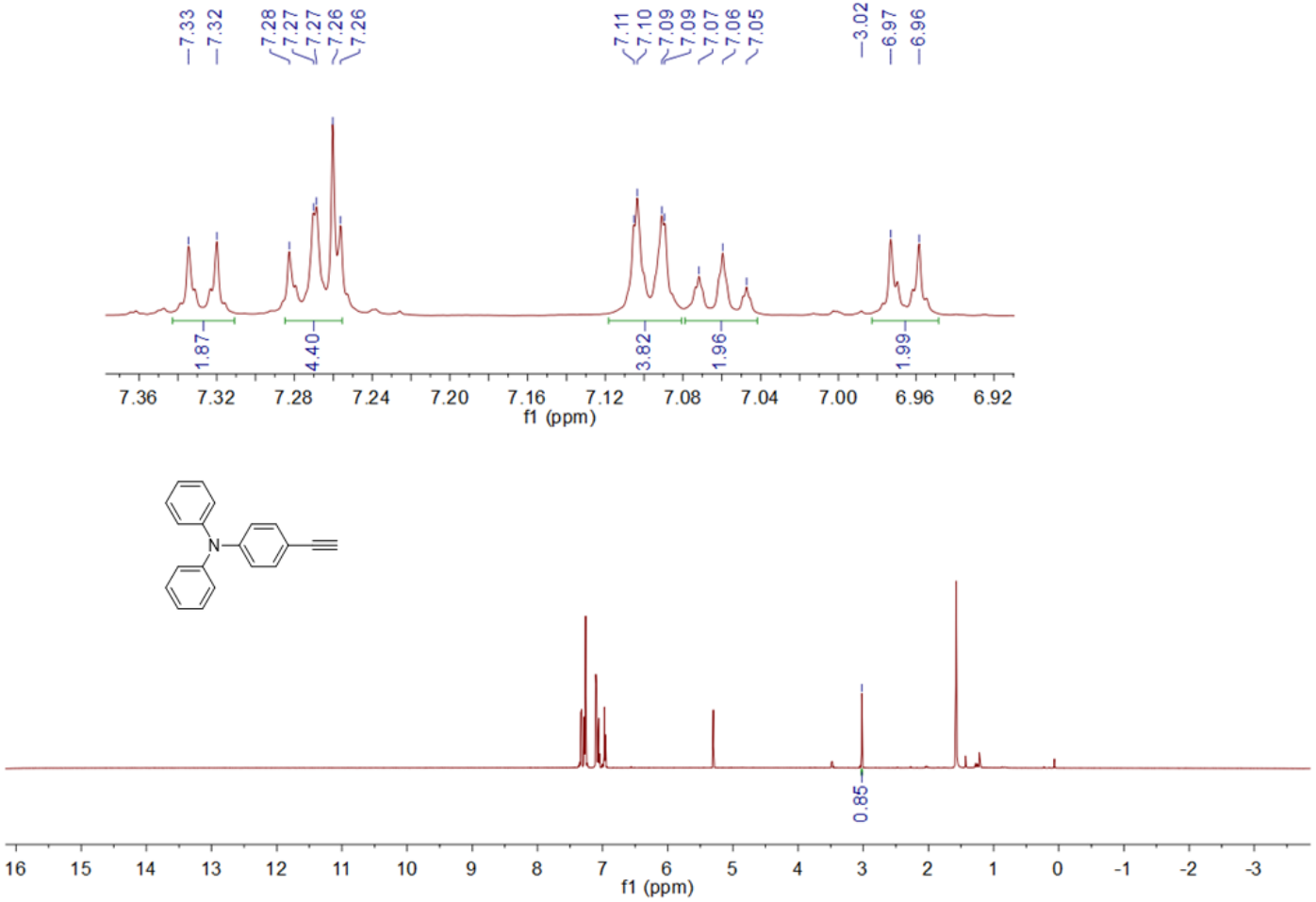


Figure S24. ^{1}H NMR spectrum of **9** (600 MHz, $CDCl_3$).

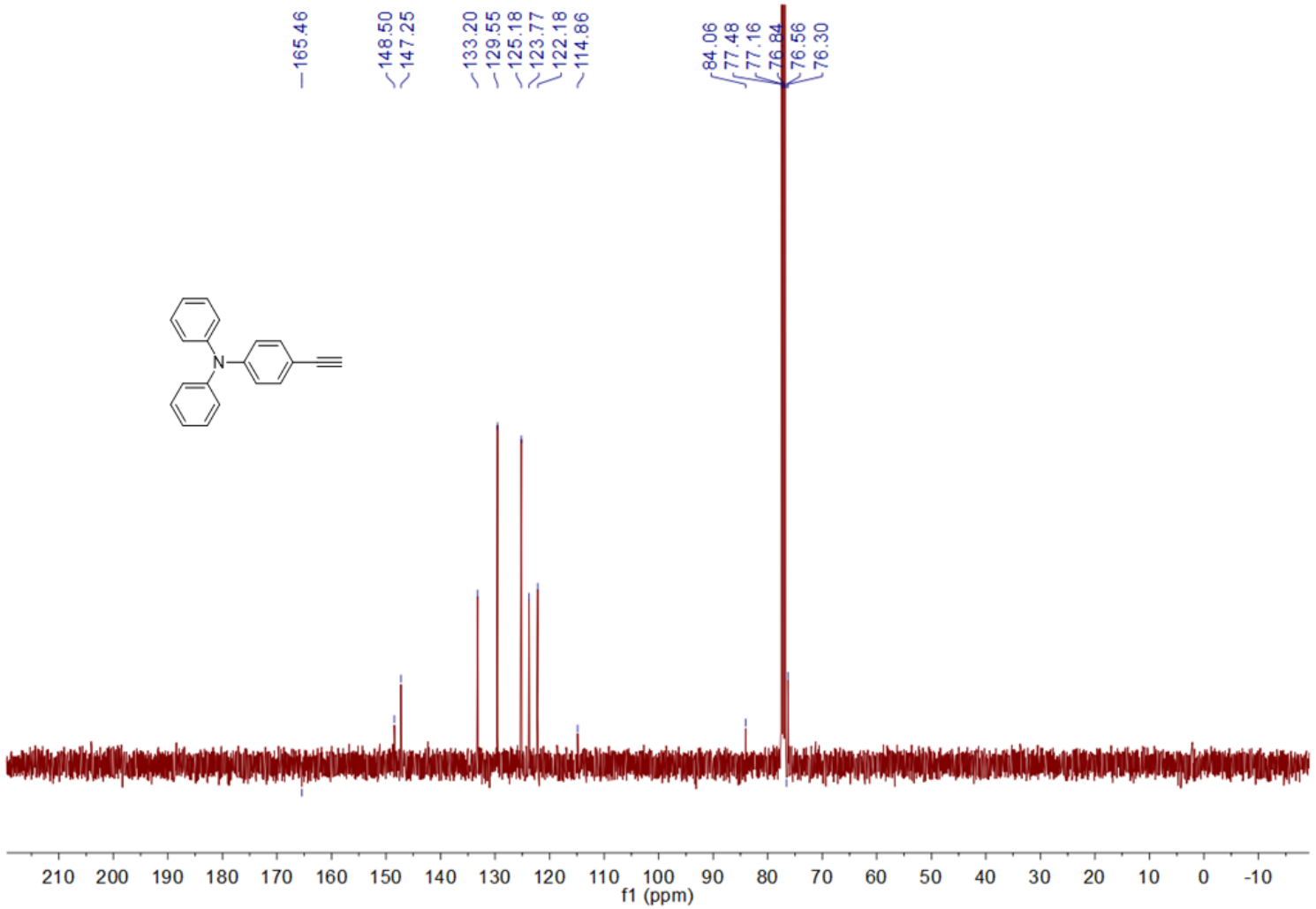


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **9** (101 MHz, $CDCl_3$).

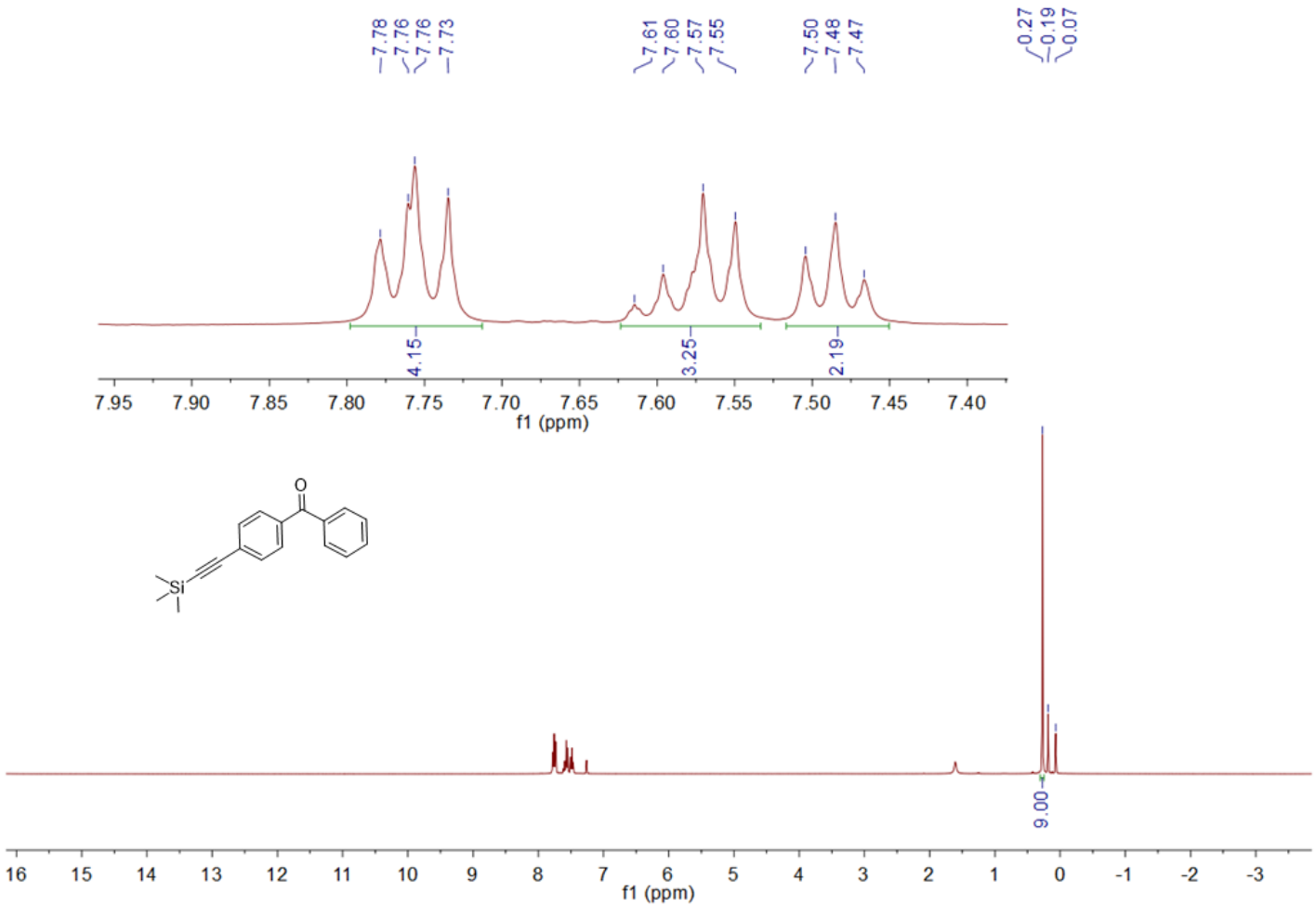


Figure S26. ^{1}H NMR spectrum of **10** (400 MHz, $CDCl_3$).

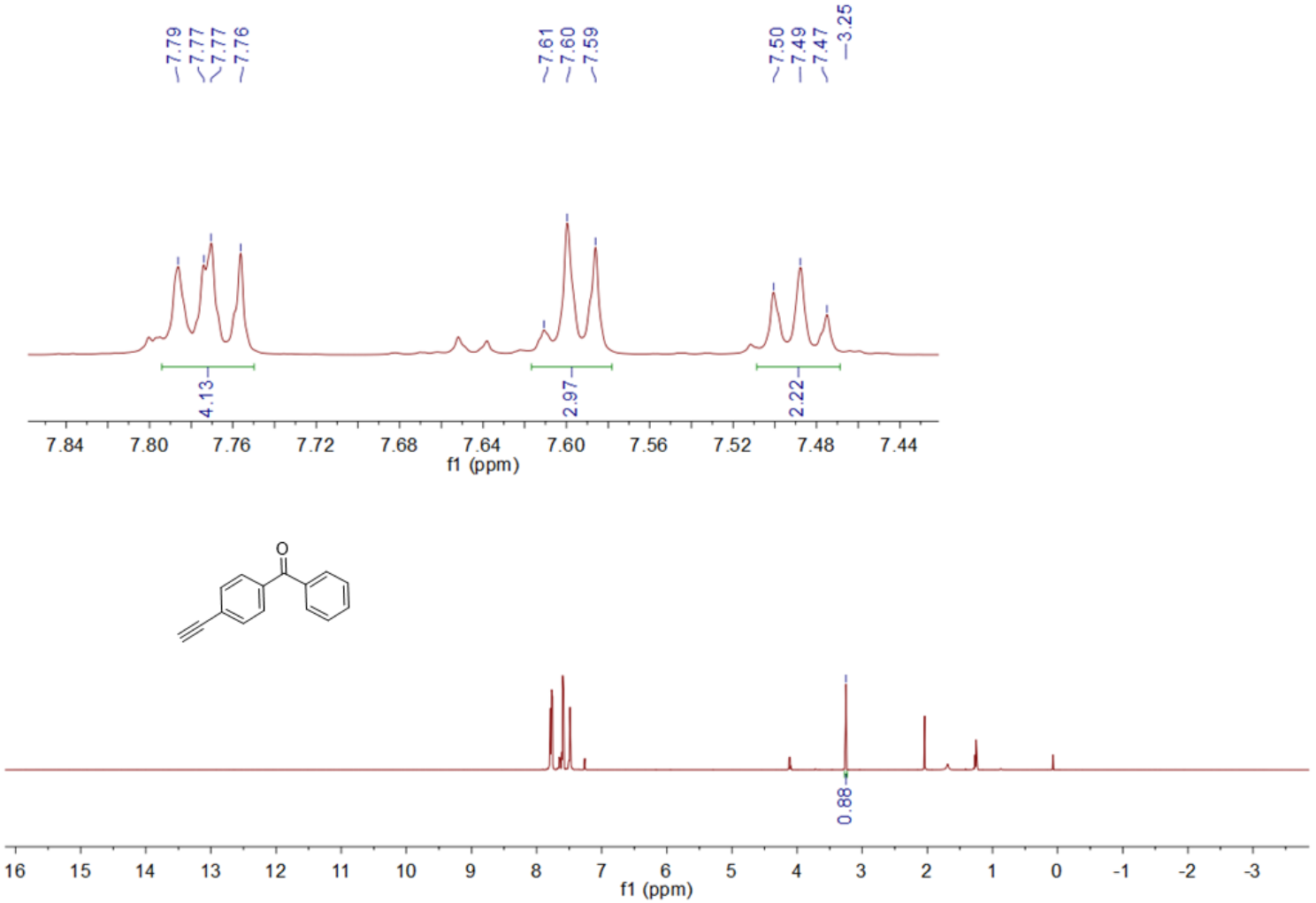


Figure S27. ^{1}H NMR spectrum of **11** (600 MHz, $CDCl_3$).

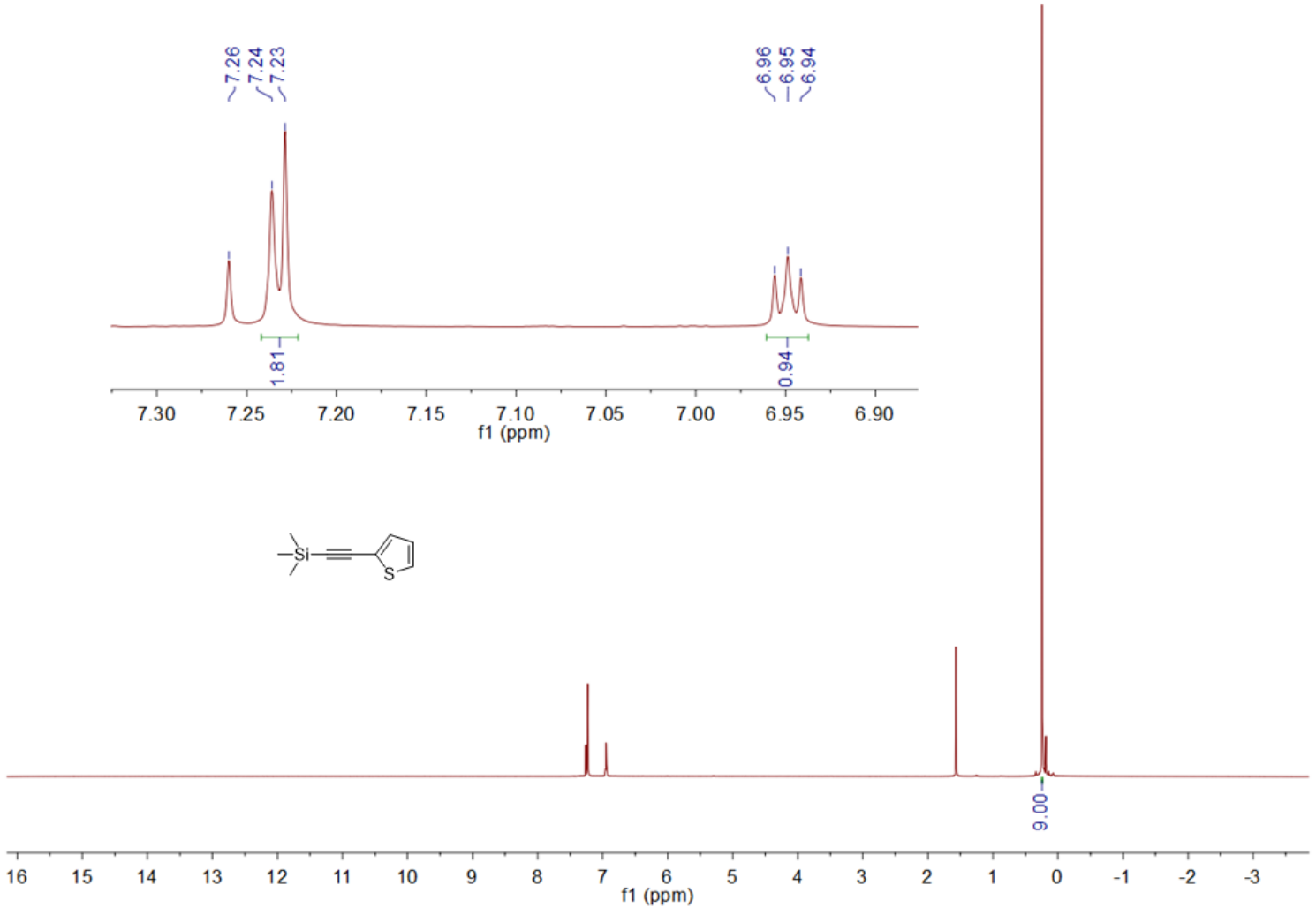


Figure S28. ^{1}H NMR spectrum of **12** (600 MHz, $CDCl_3$).

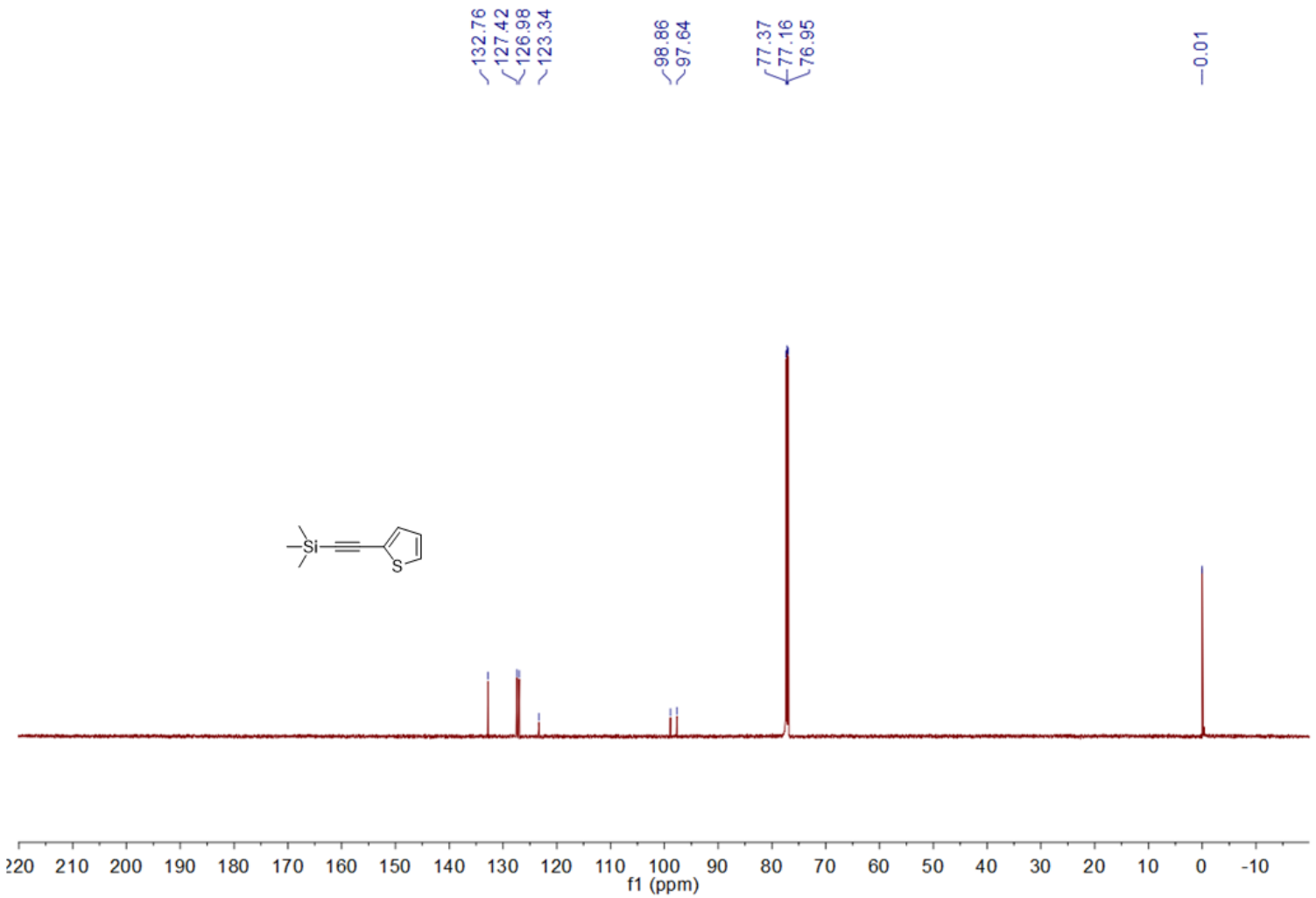


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **12** (151 MHz, $CDCl_3$).

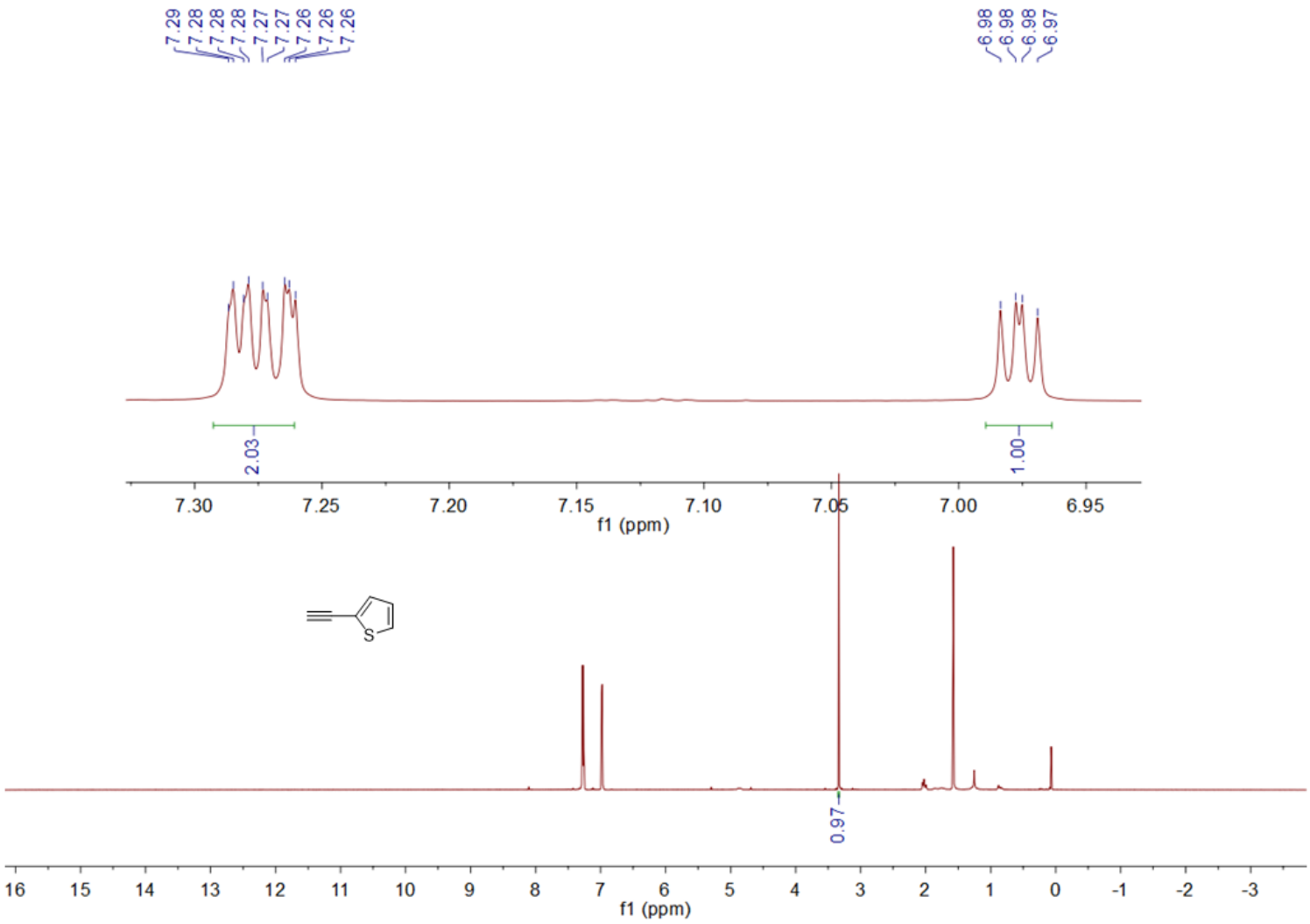


Figure S30. ^{1}H NMR spectrum of **13** (600 MHz, $CDCl_3$).

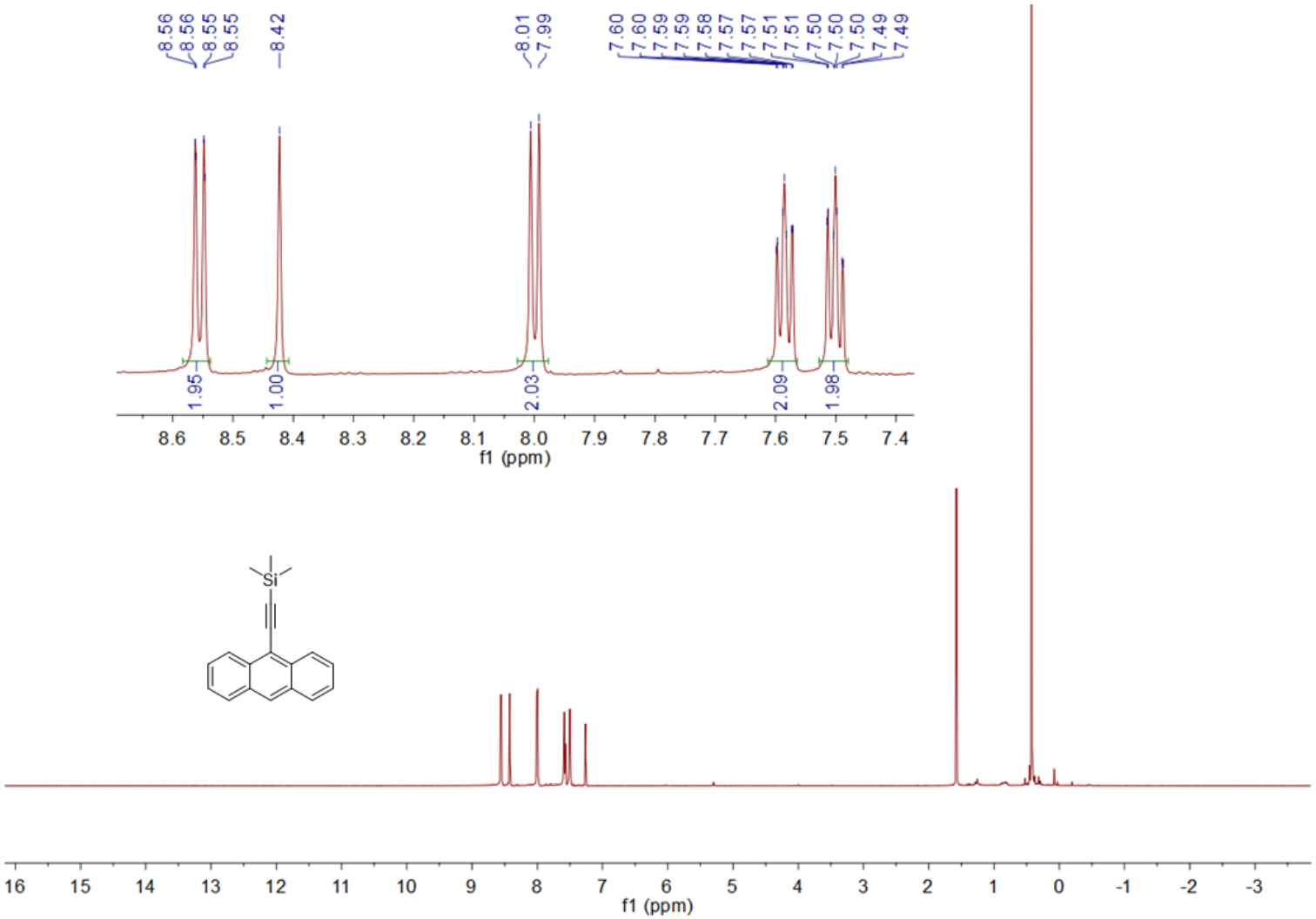


Figure S31. ^{1}H NMR spectrum of **14** (600 MHz, $CDCl_3$).

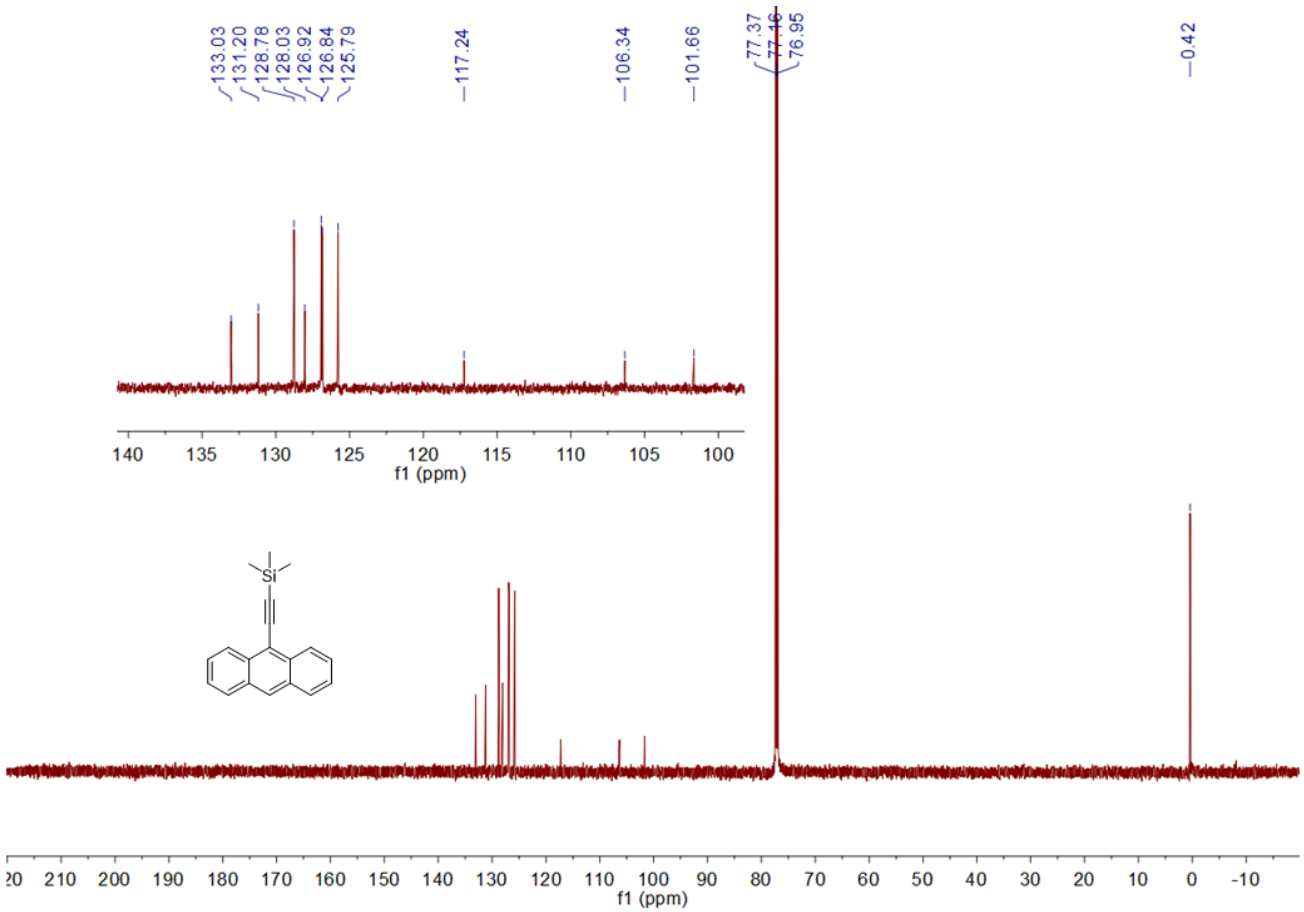


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of **14** (151 MHz, $CDCl_3$).

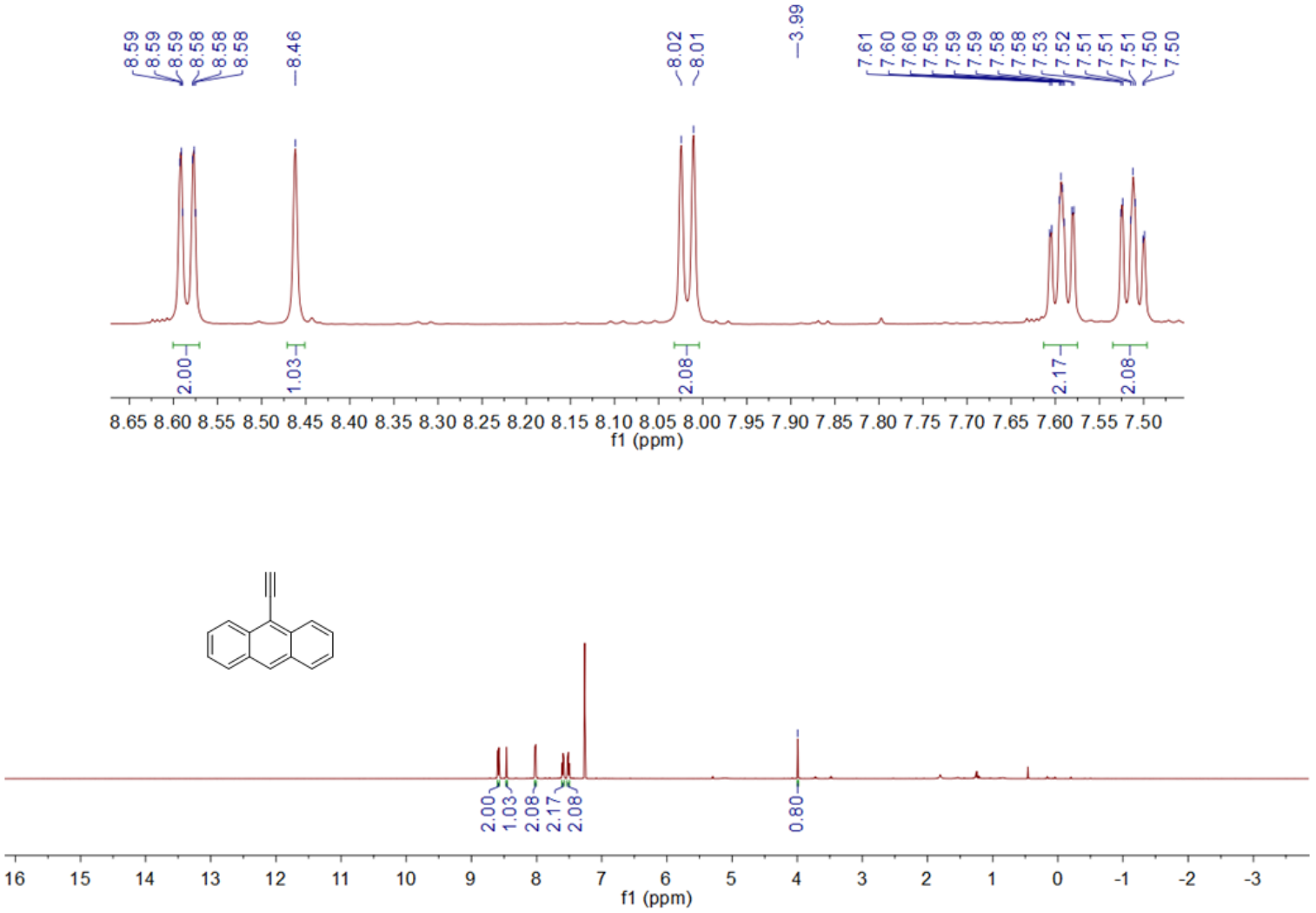


Figure S33. ^{1}H NMR spectrum of **15** (600 MHz, $CDCl_3$).

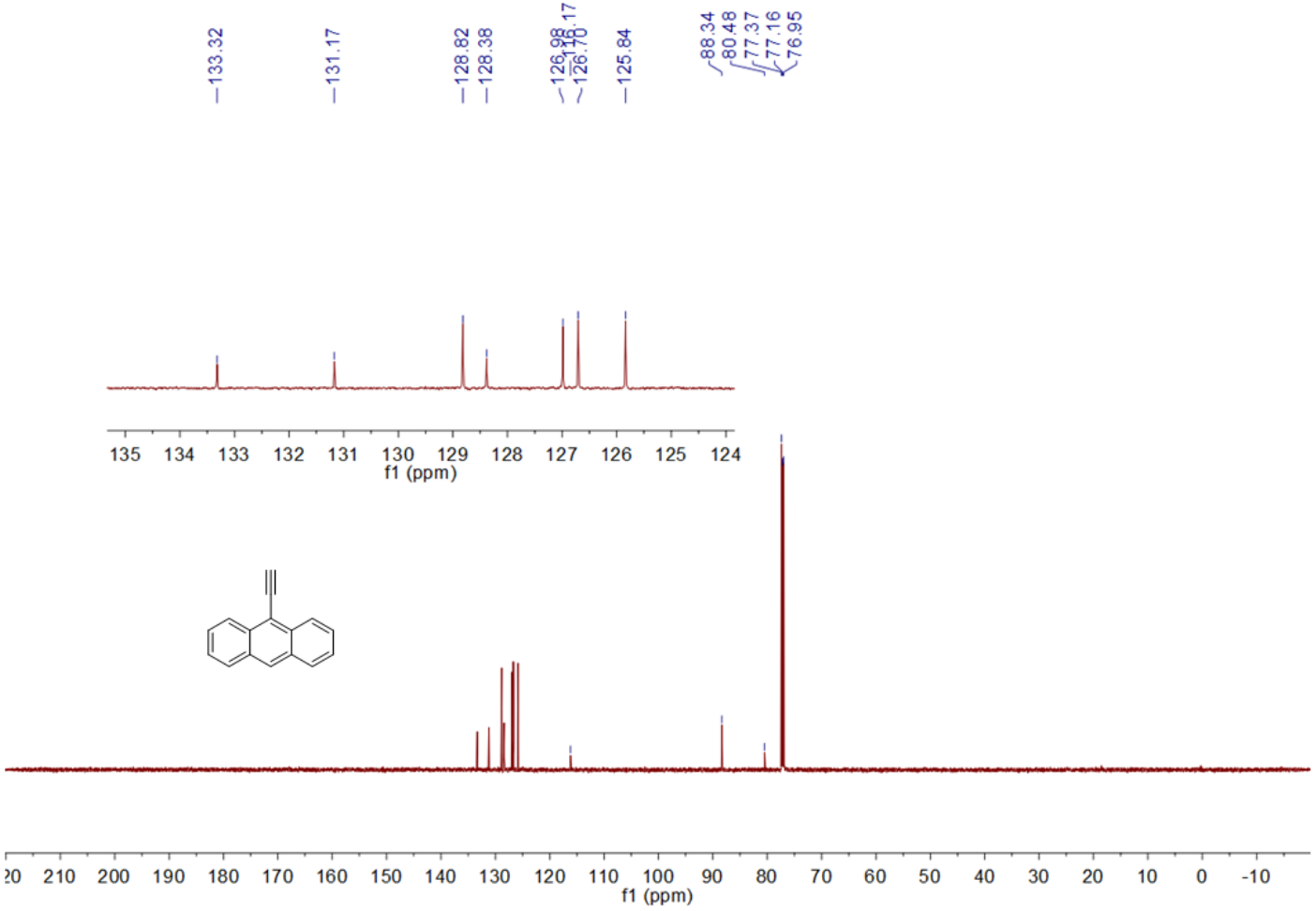


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of **15** (151 MHz, $CDCl_3$).

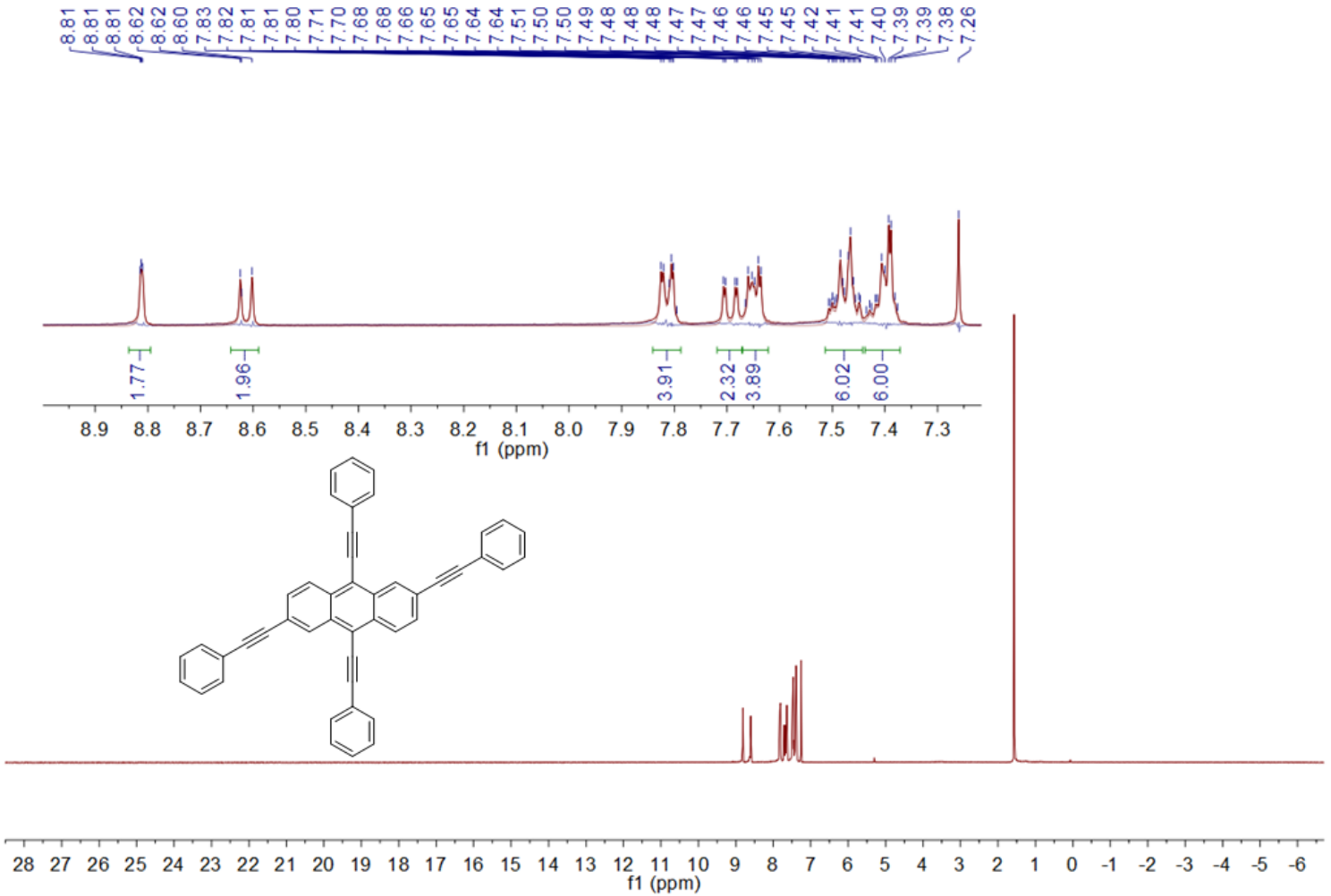


Figure S35. ^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$).

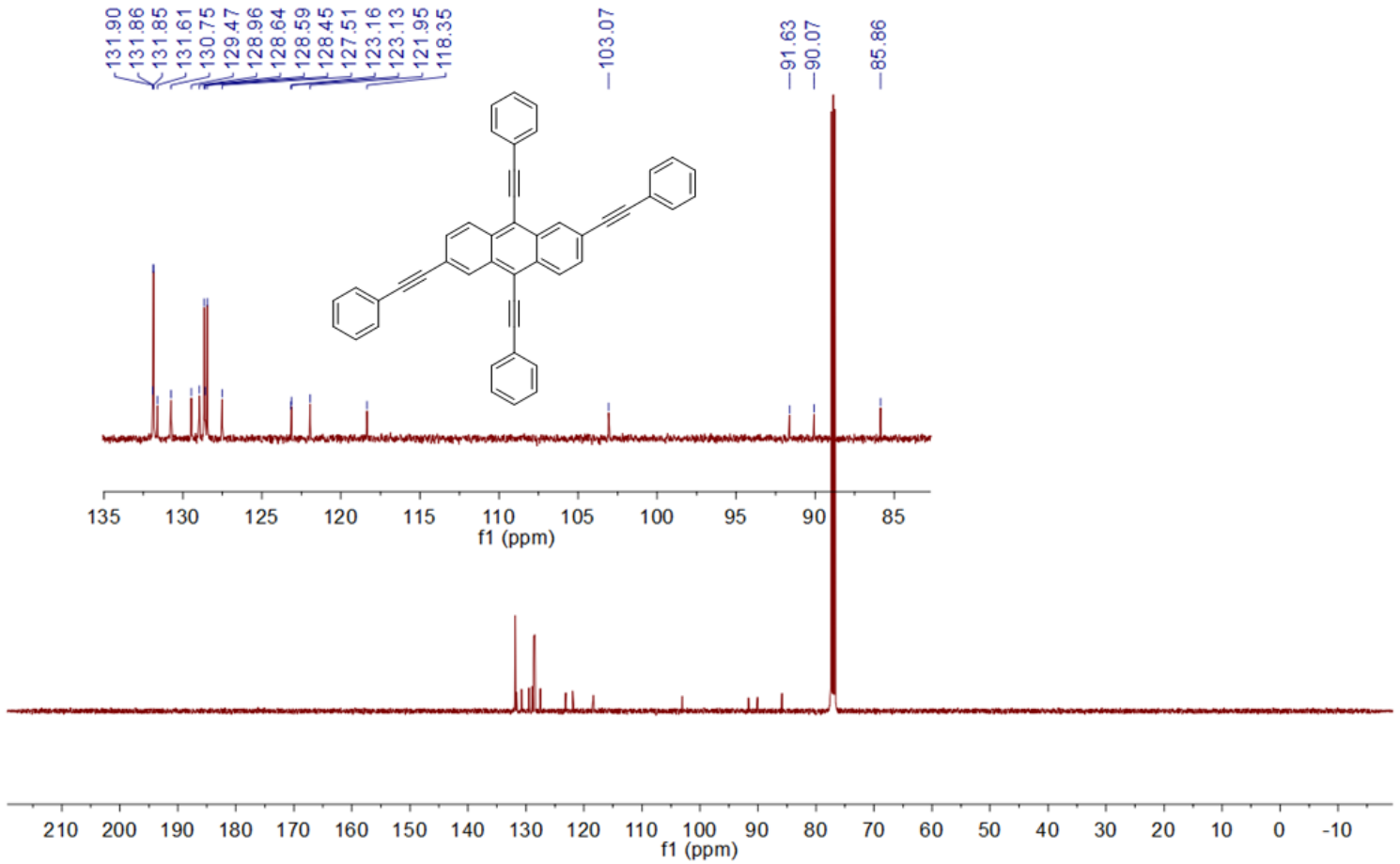


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of **6** (101 MHz, $CDCl_3$).

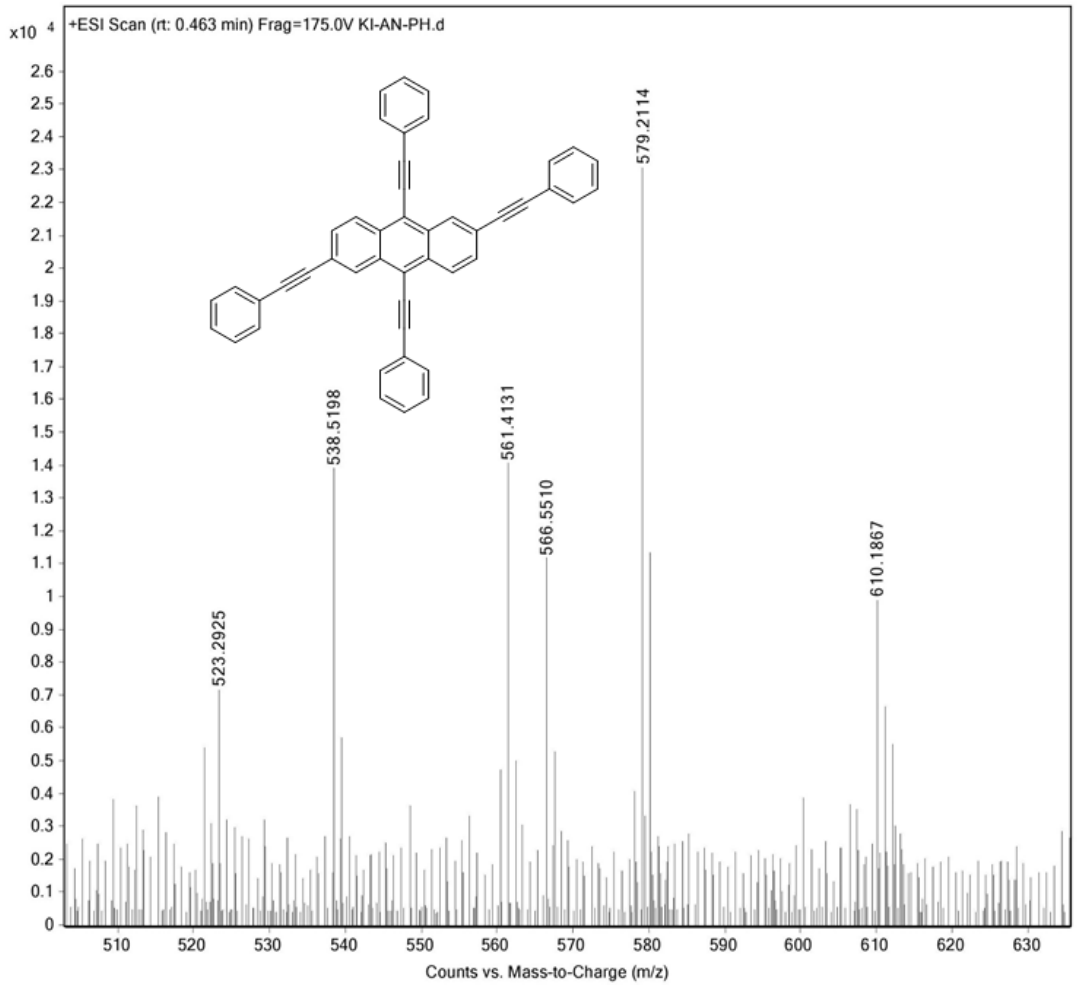


Figure S37. HRMS spectrum of **6**.

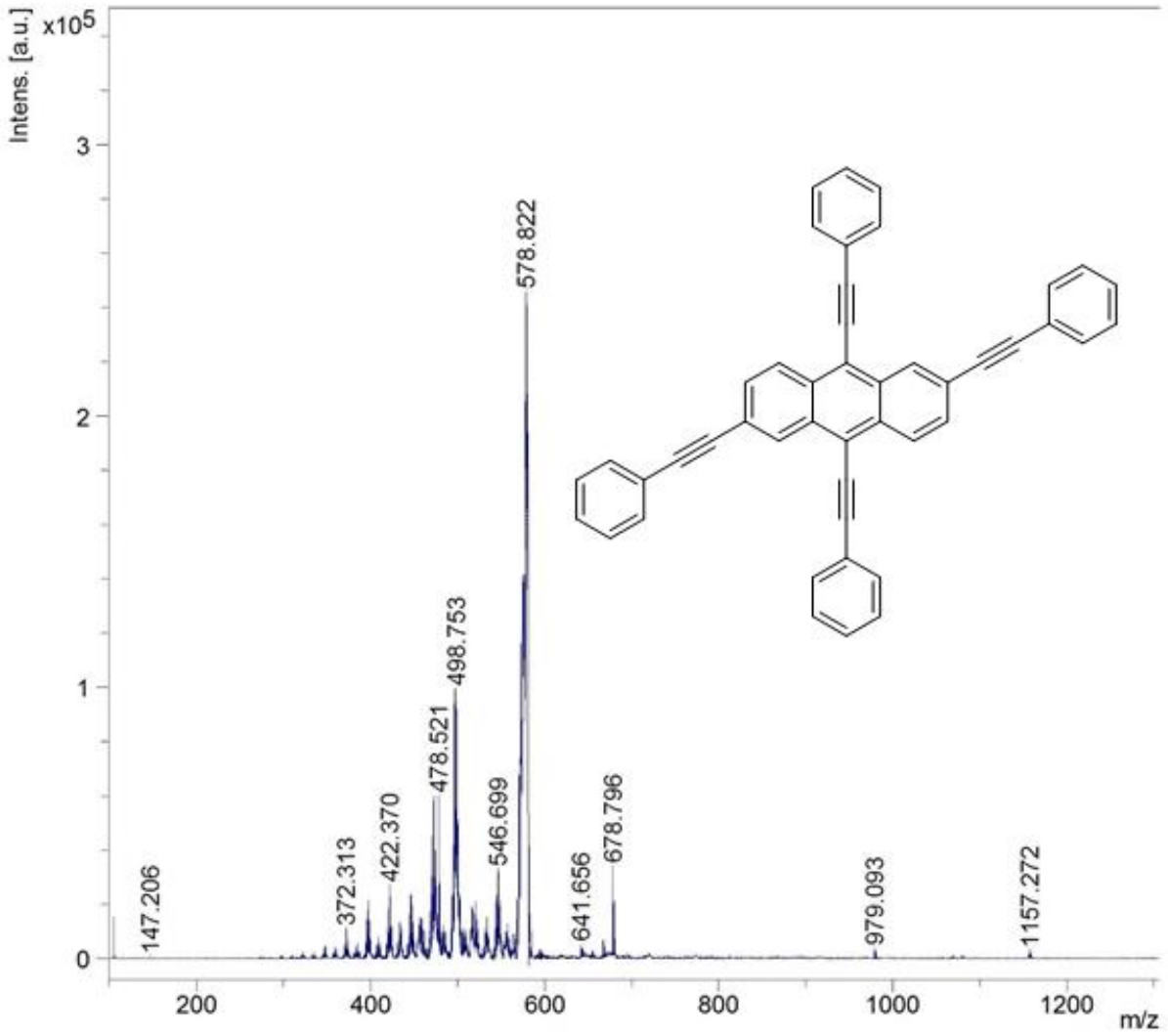
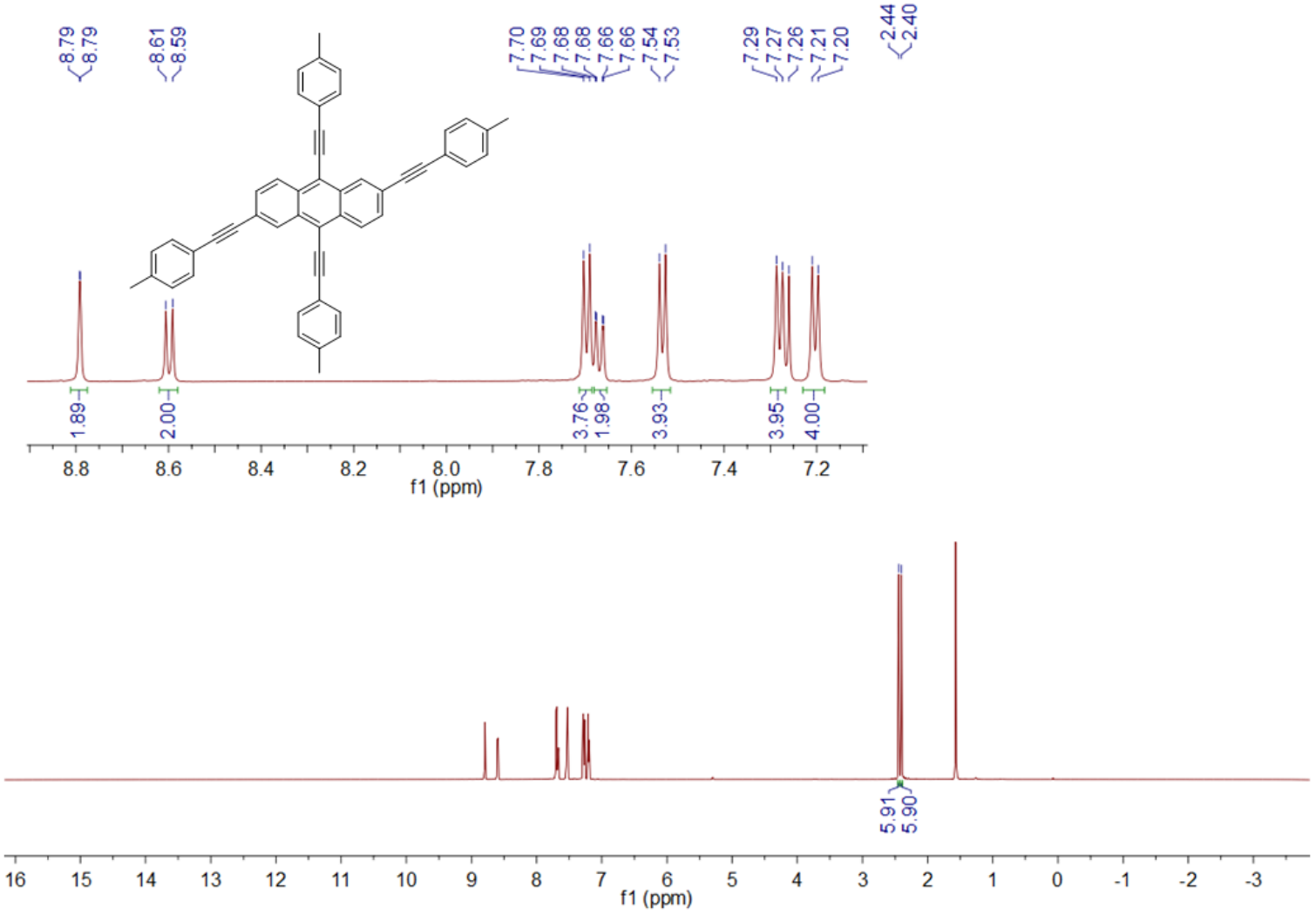


Figure S38. MALDI spectrum of **6**.



.

Figure S39. ^{1}H NMR spectrum of **6a** (400 MHz, $CDCl_3$).

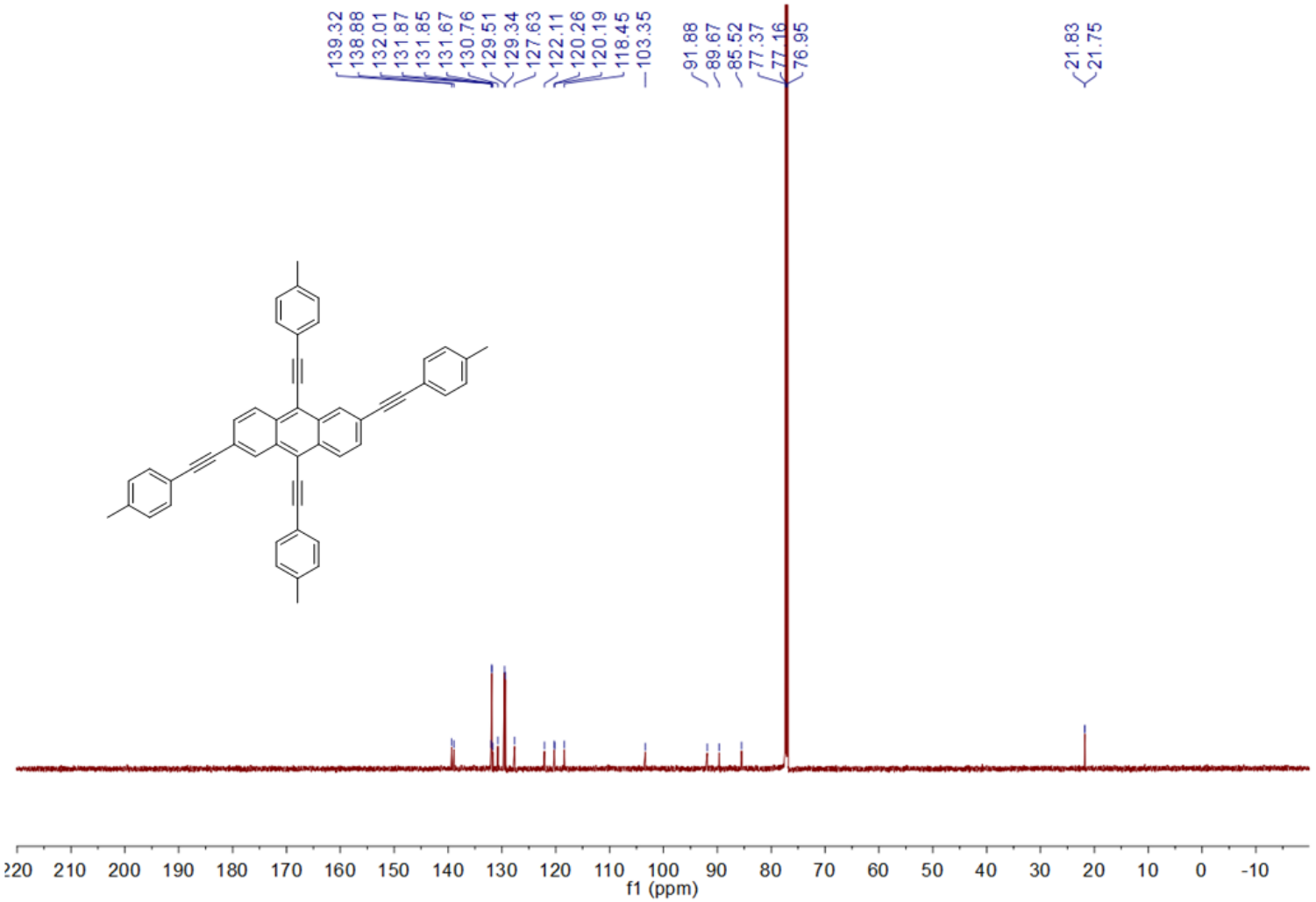


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of **6a** (151 MHz, $CDCl_3$).

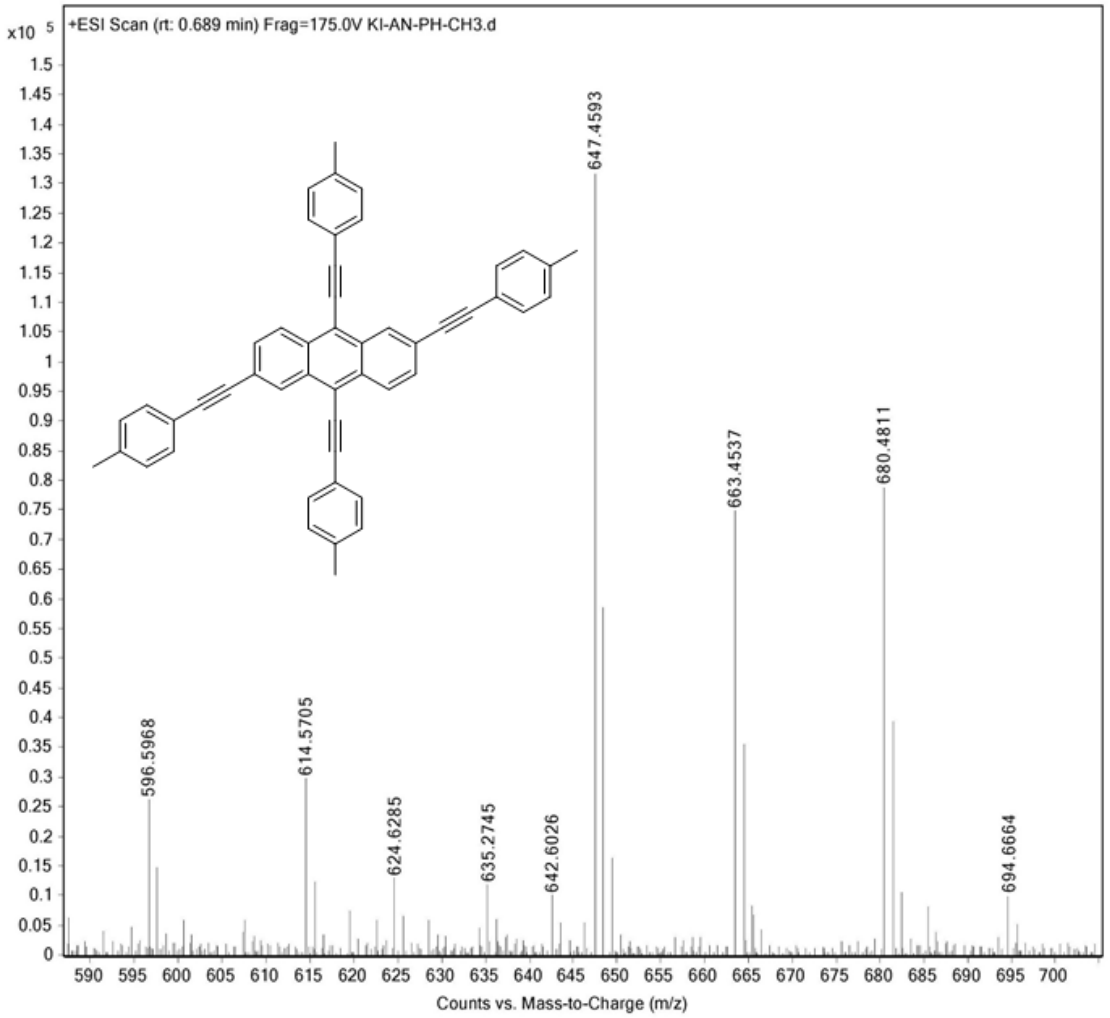


Figure S41. HRMS spectrum of **6a**.

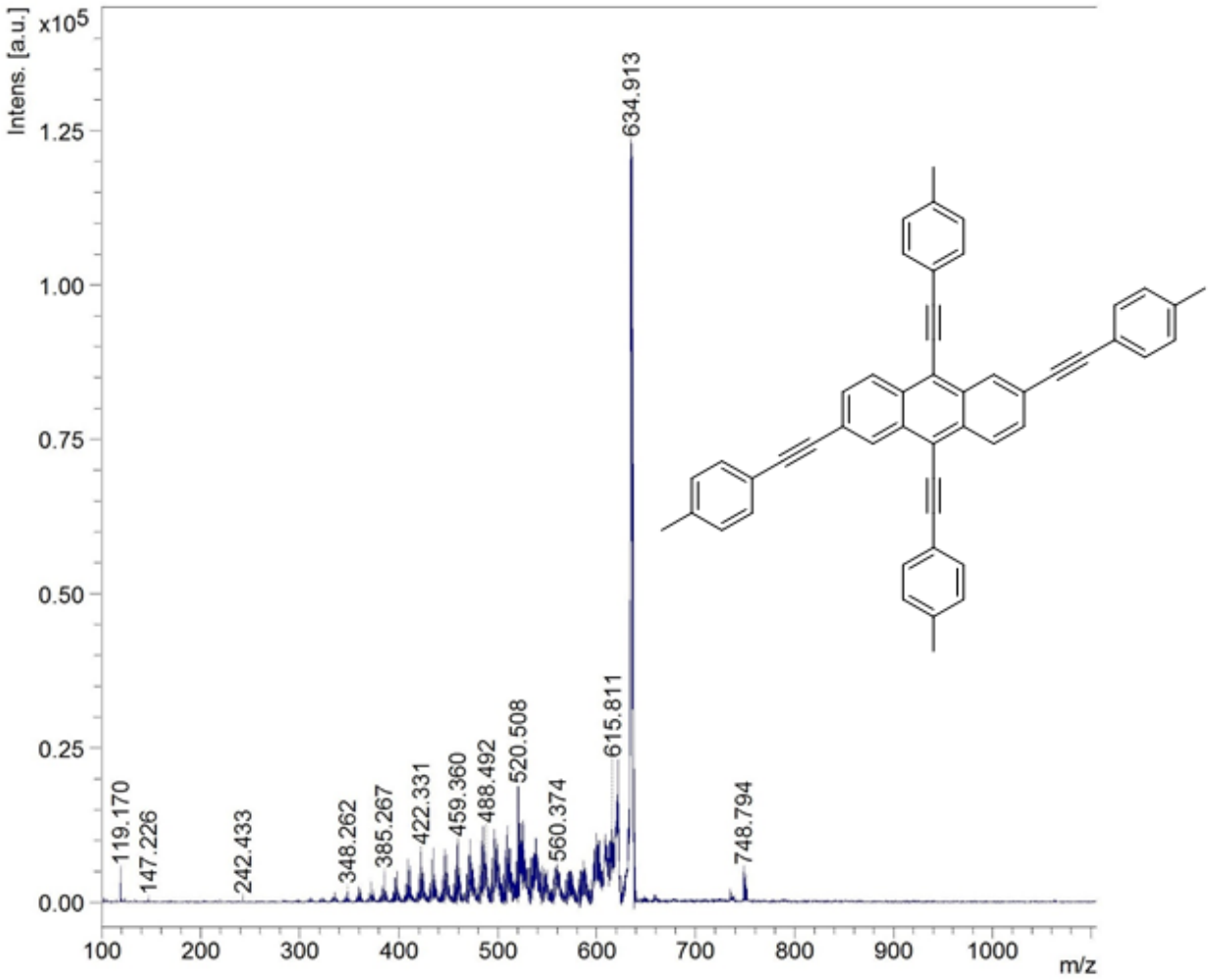


Figure S42. MALDI spectrum of **6a**.

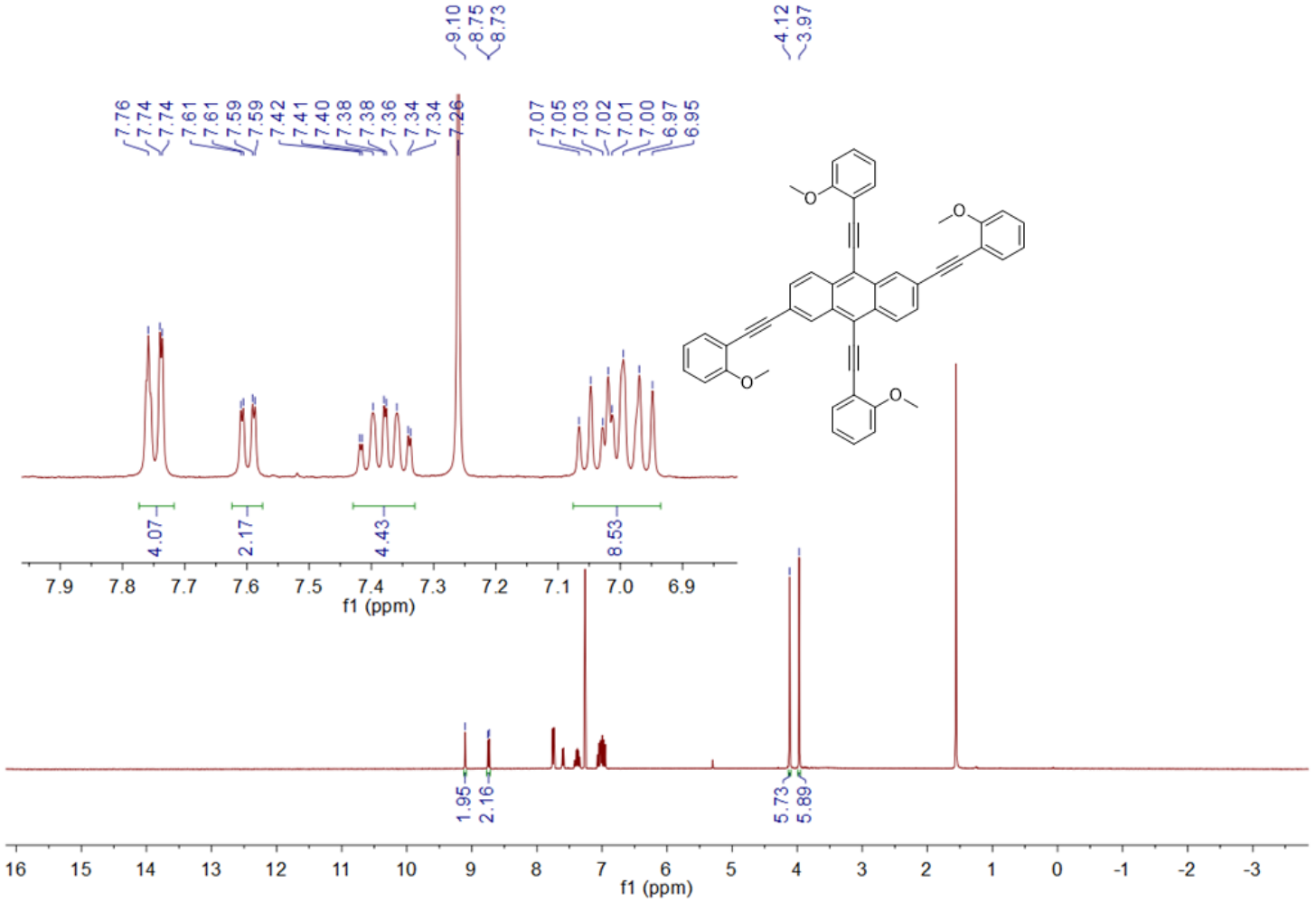


Figure S43. ^{1}H NMR spectrum of **6b** (400 MHz, $CDCl_3$).

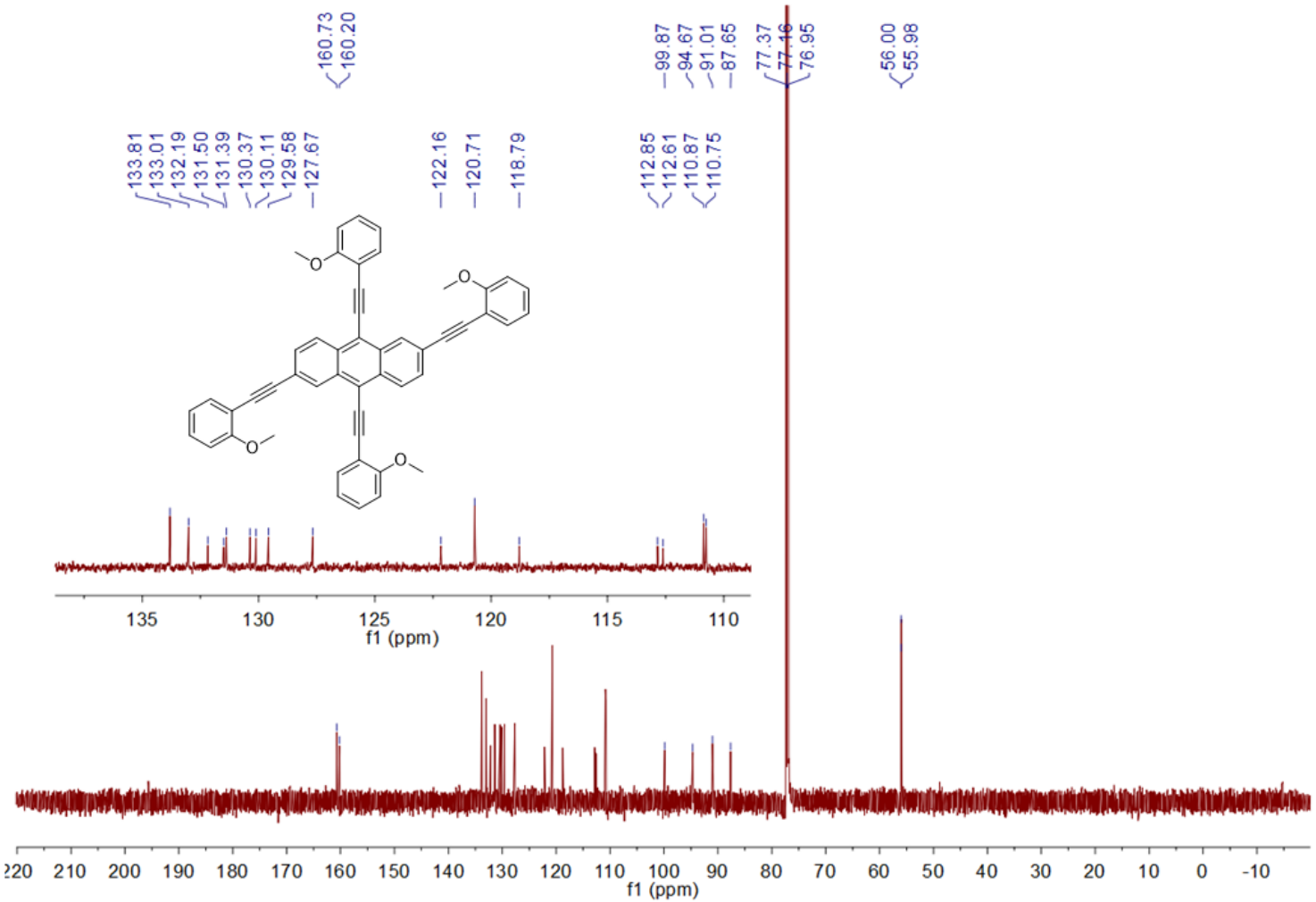


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of **6b** (151 MHz, $CDCl_3$).

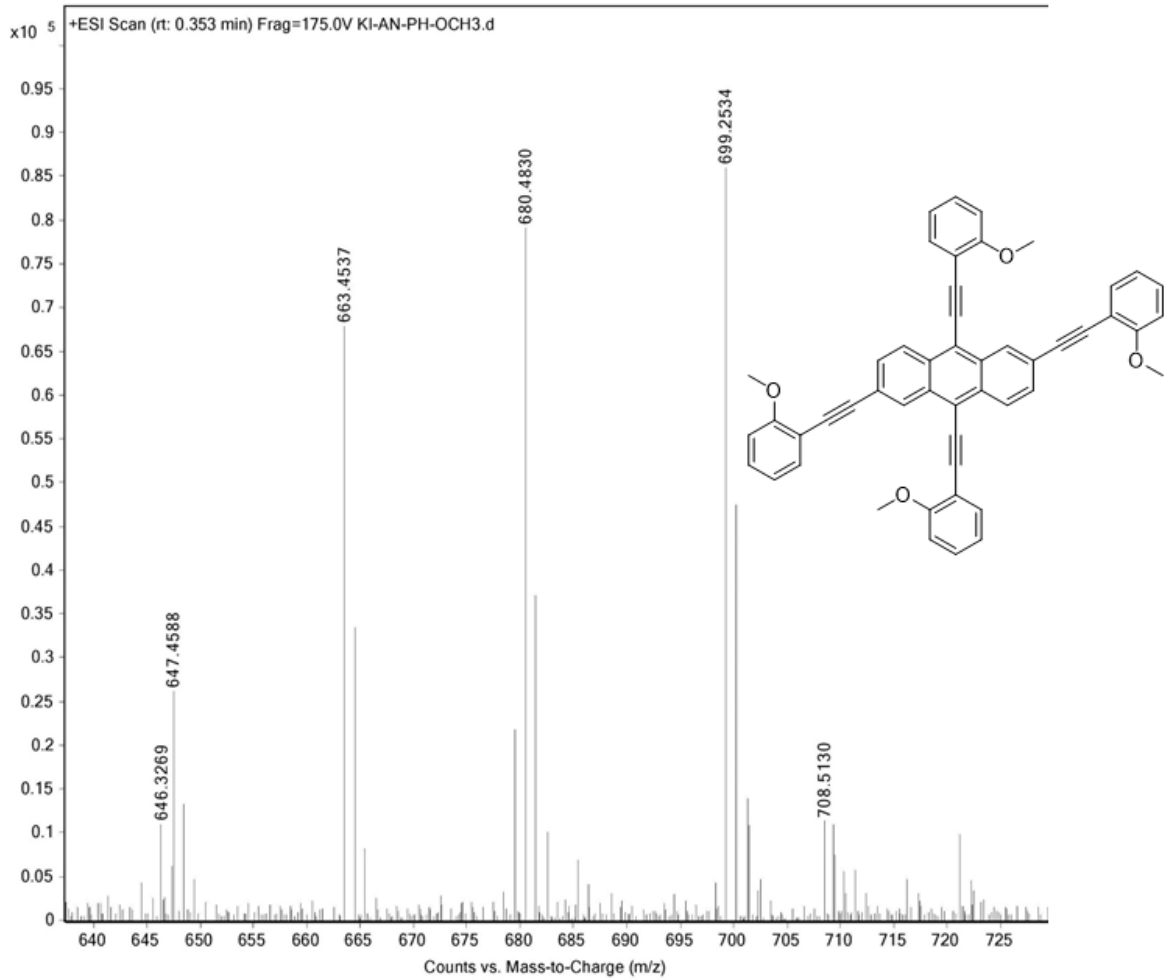


Figure S45. HRMS spectrum of **6b**.

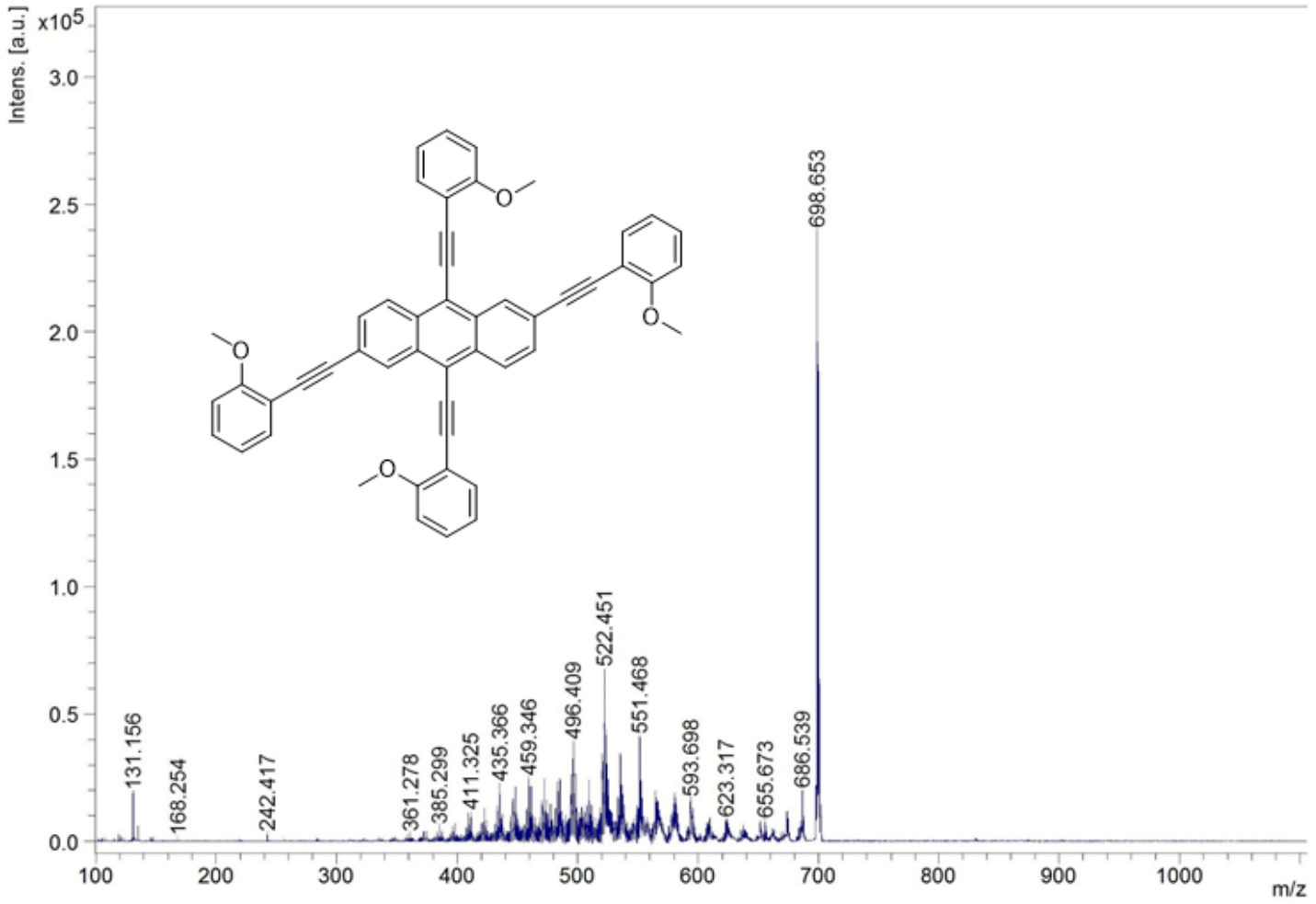


Figure S46. MALDI spectrum of **6b**.

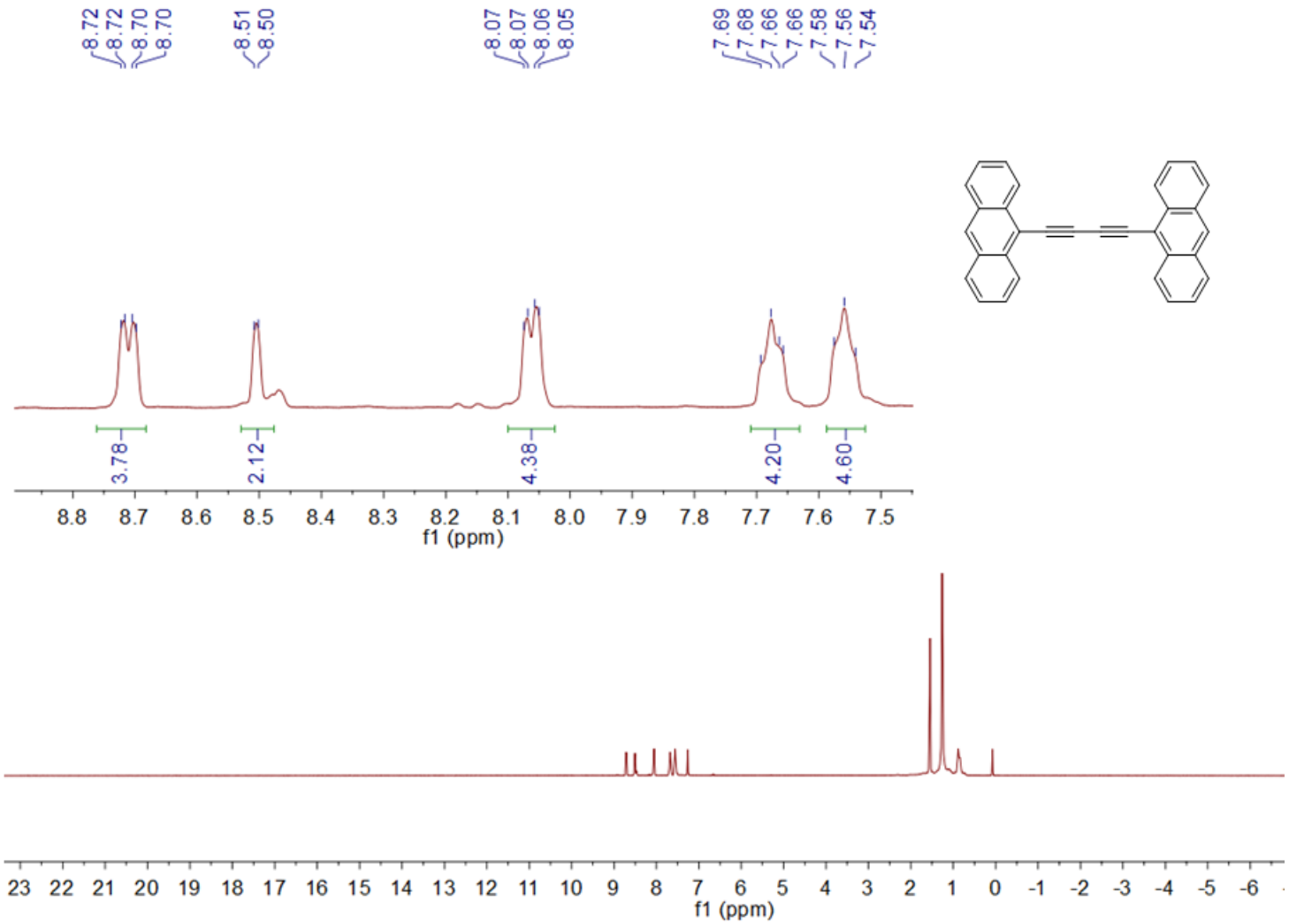


Figure S47. ^{1}H NMR spectrum of **6c´** (500 MHz, $CDCl_3$).

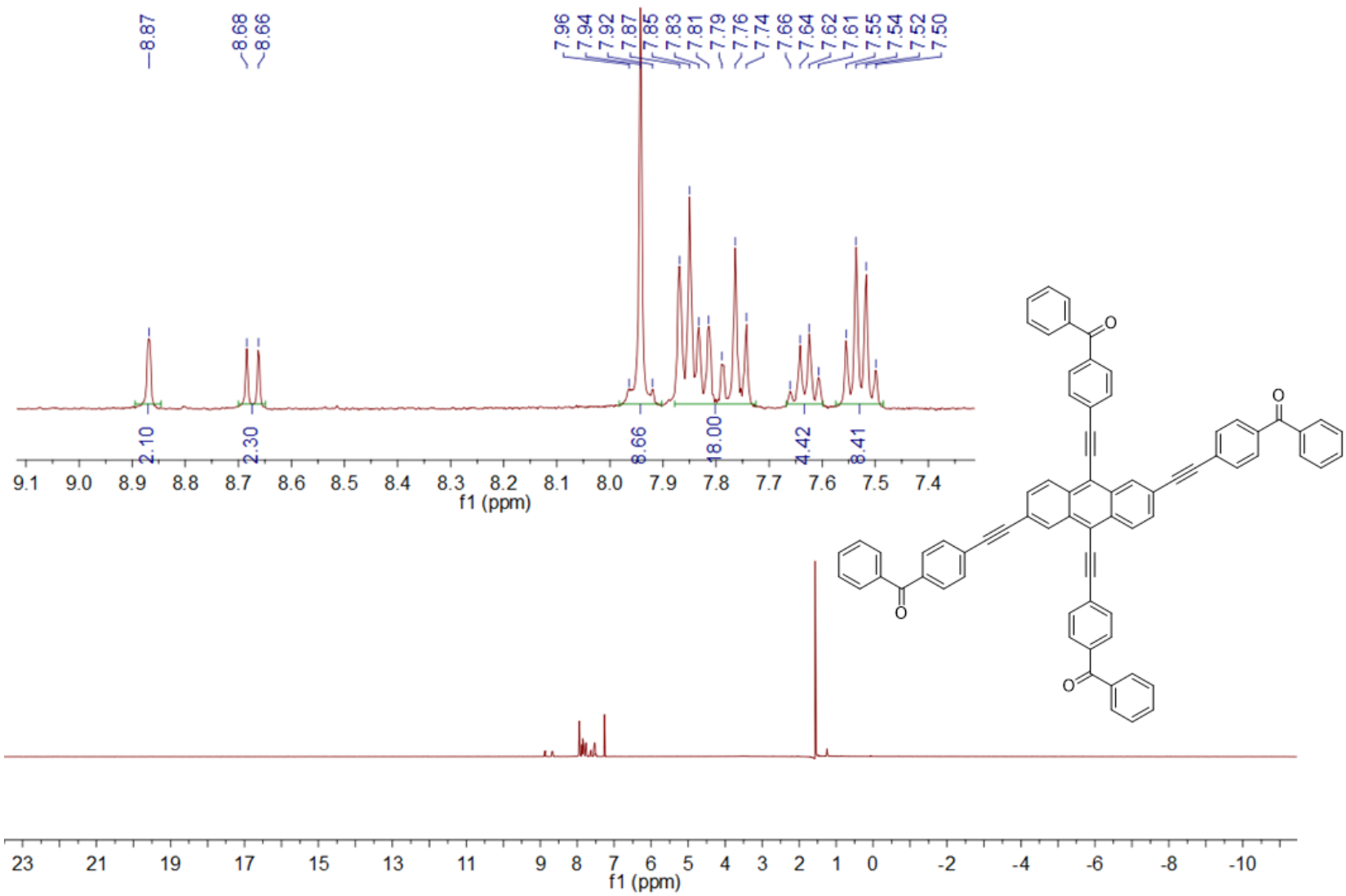


Figure S48. ^{1}H NMR spectrum of **6d** (400 MHz, $CDCl_3$).

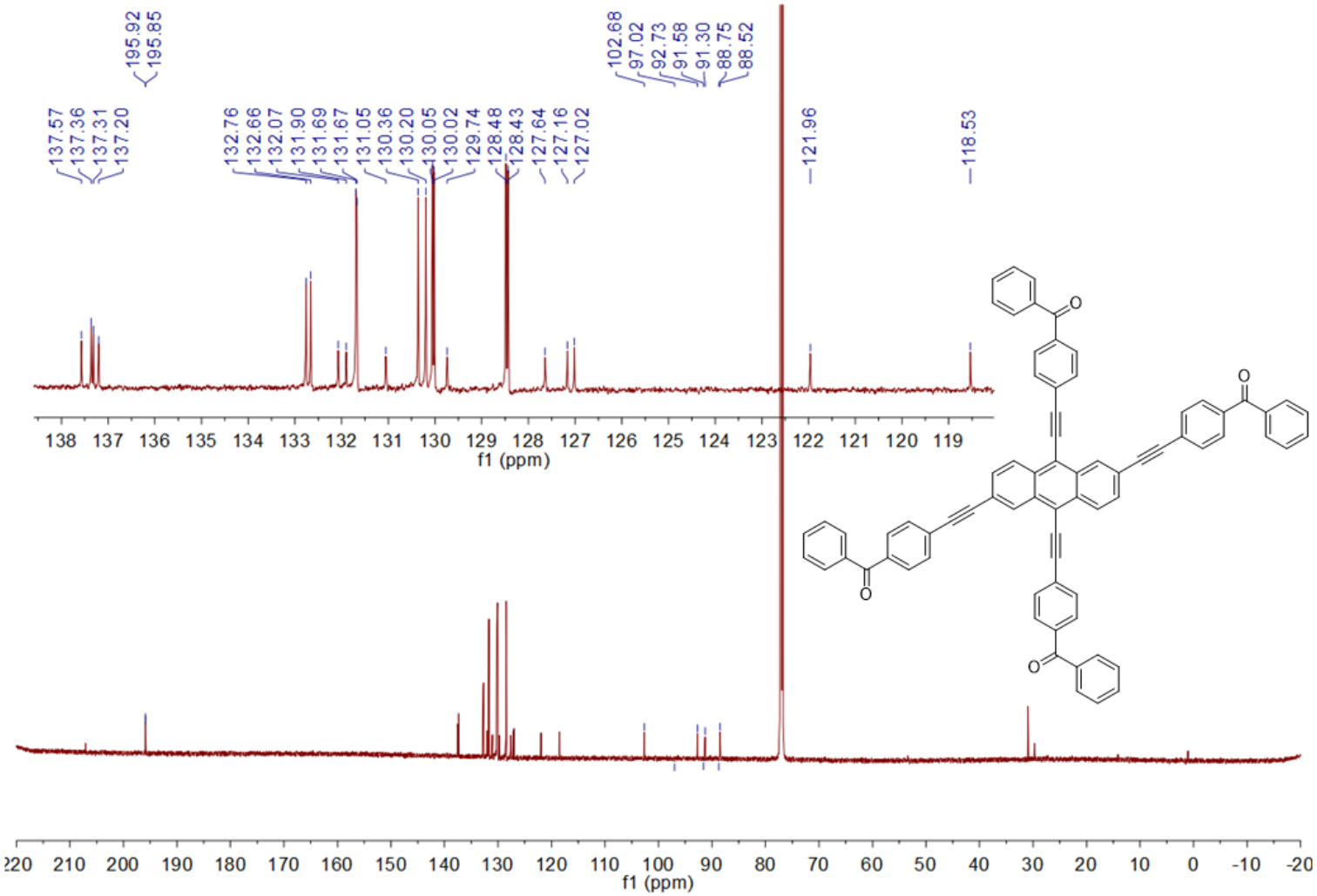


Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum of **6b** (151 MHz, $CDCl_3$).

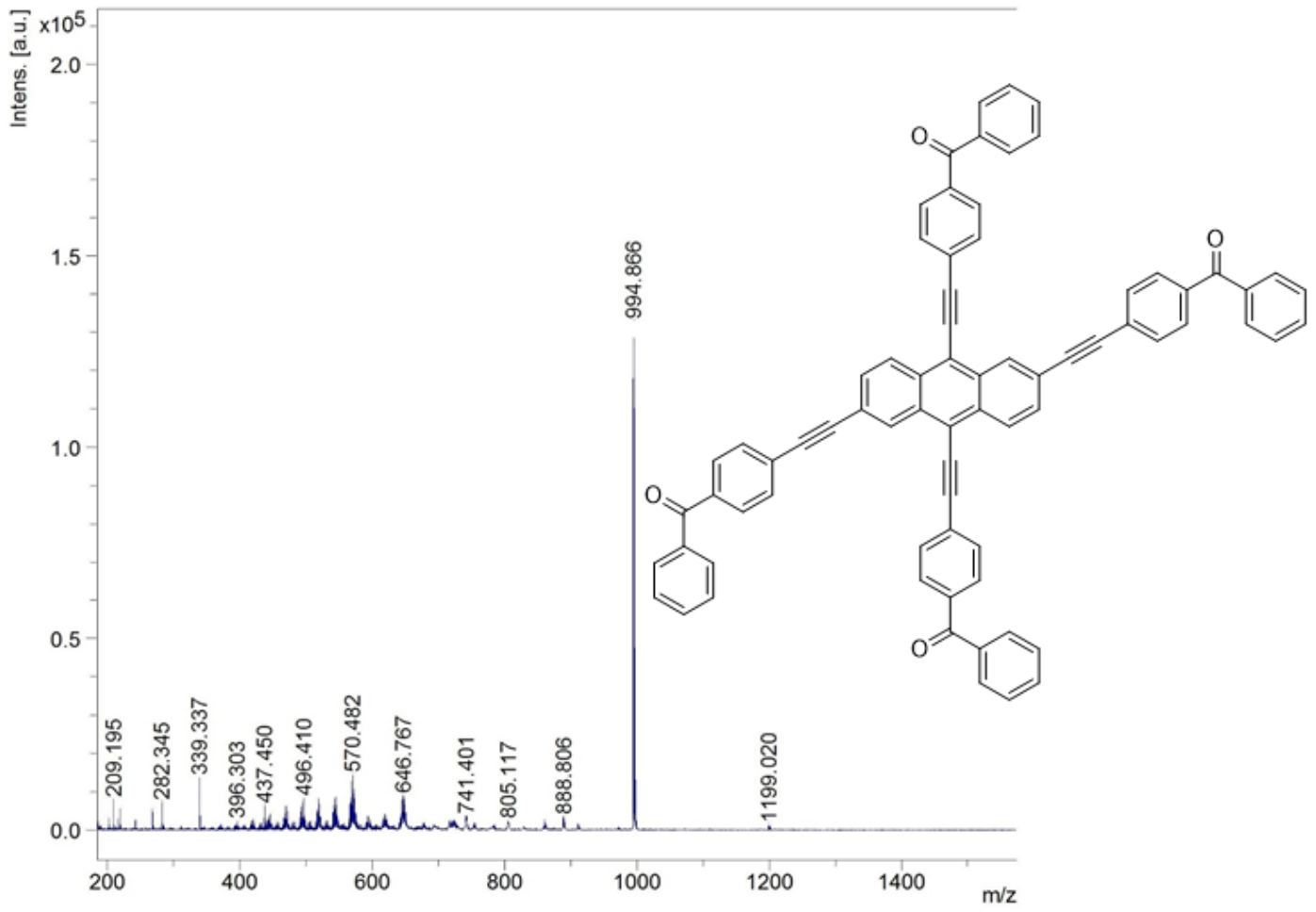


Figure S50. MALDI spectrum of **6d**.

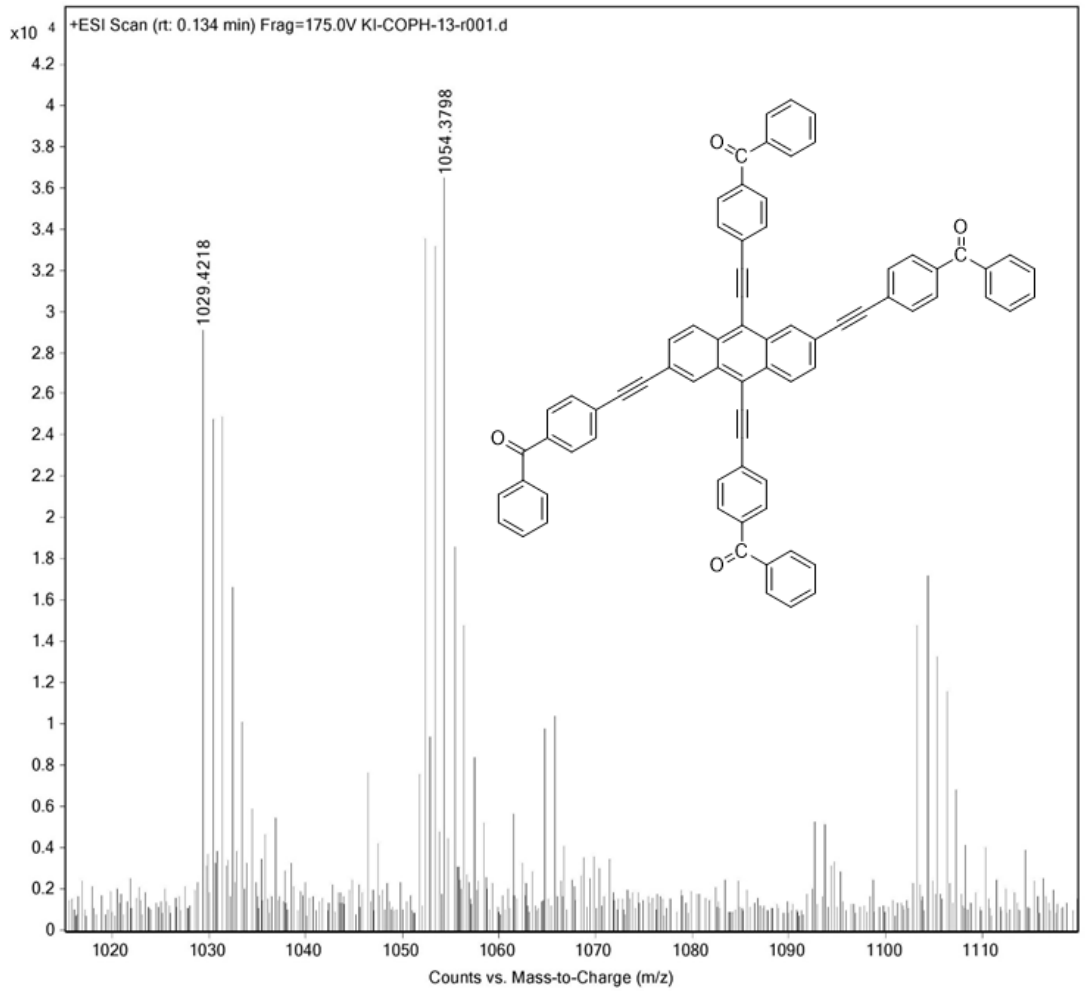


Figure S51. HRMS spectrum of **6d**.

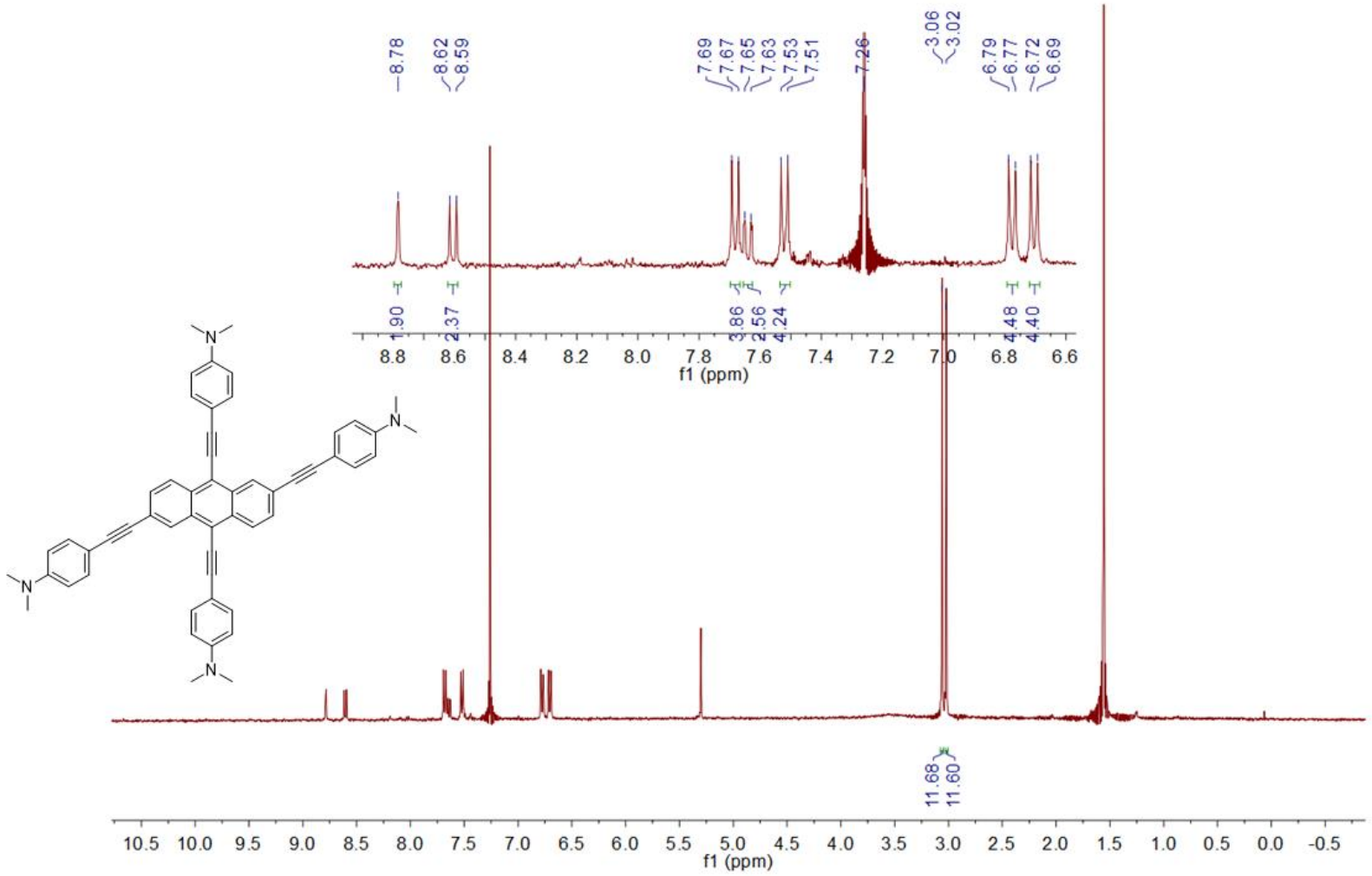


Figure S52. ^{1}H NMR spectrum of **6e** (400 MHz, $CDCl_3$).

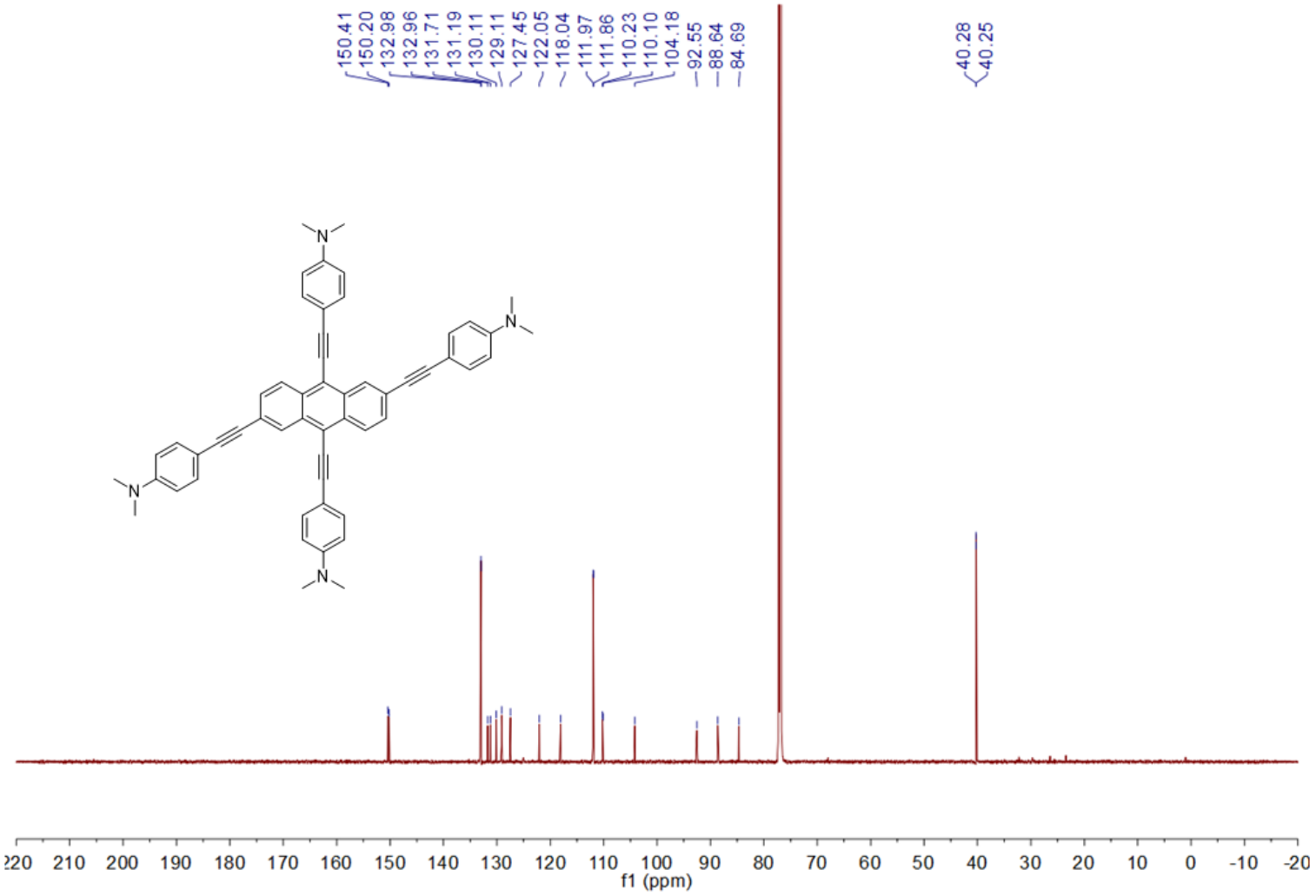


Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum of **6e** (151 MHz, $CDCl_3$).

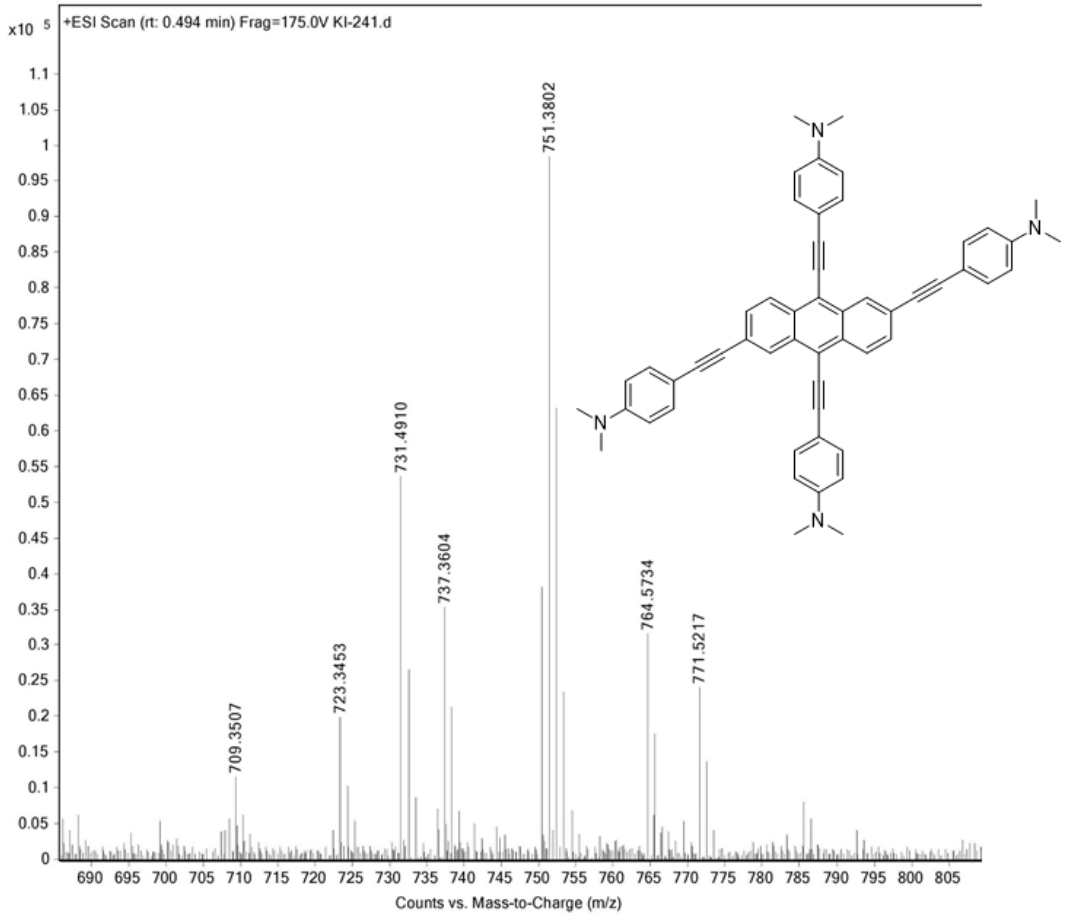


Figure S54. HRMS spectrum of **6e.**

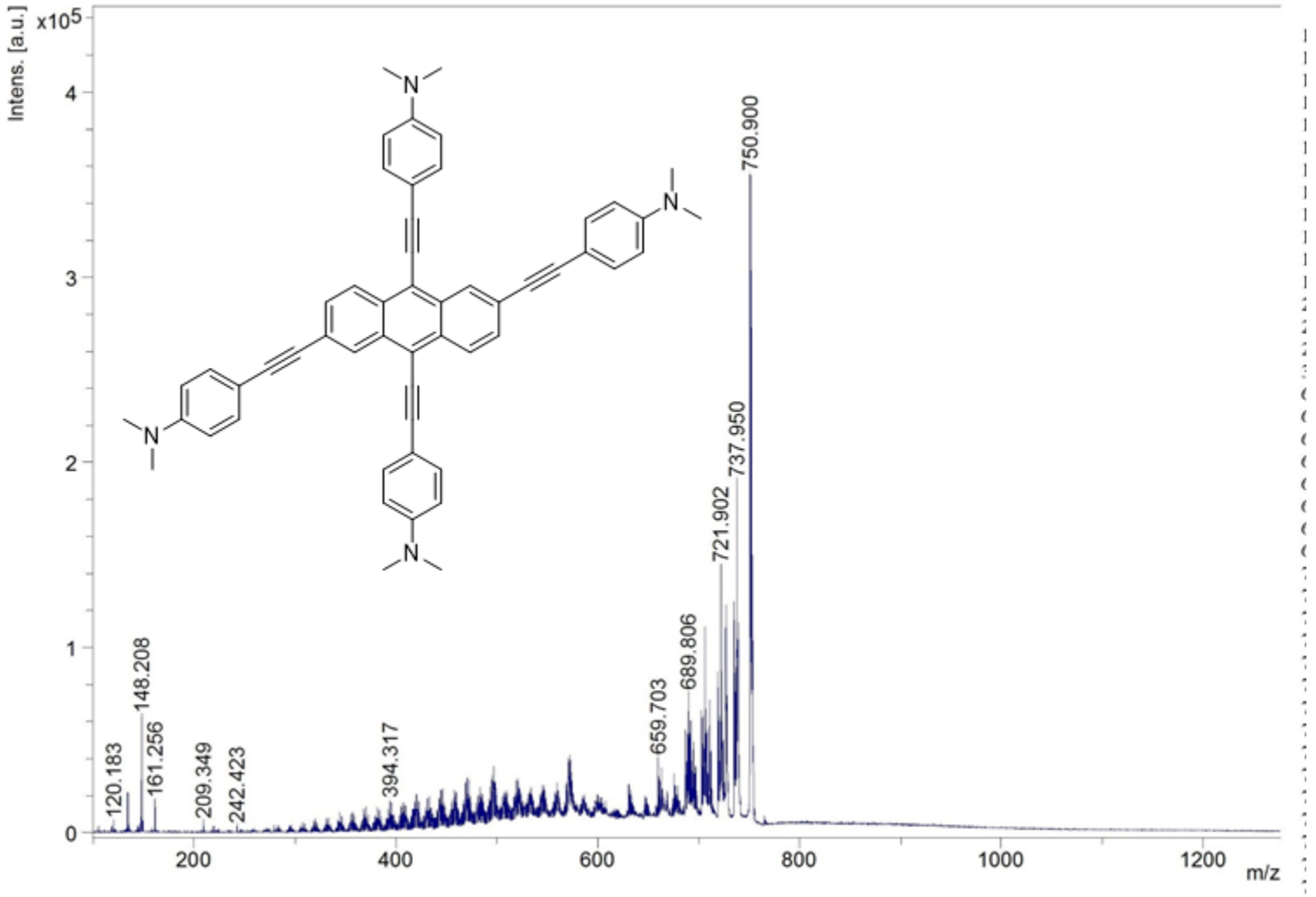


Figure S55. MALDI spectrum of **6e.**

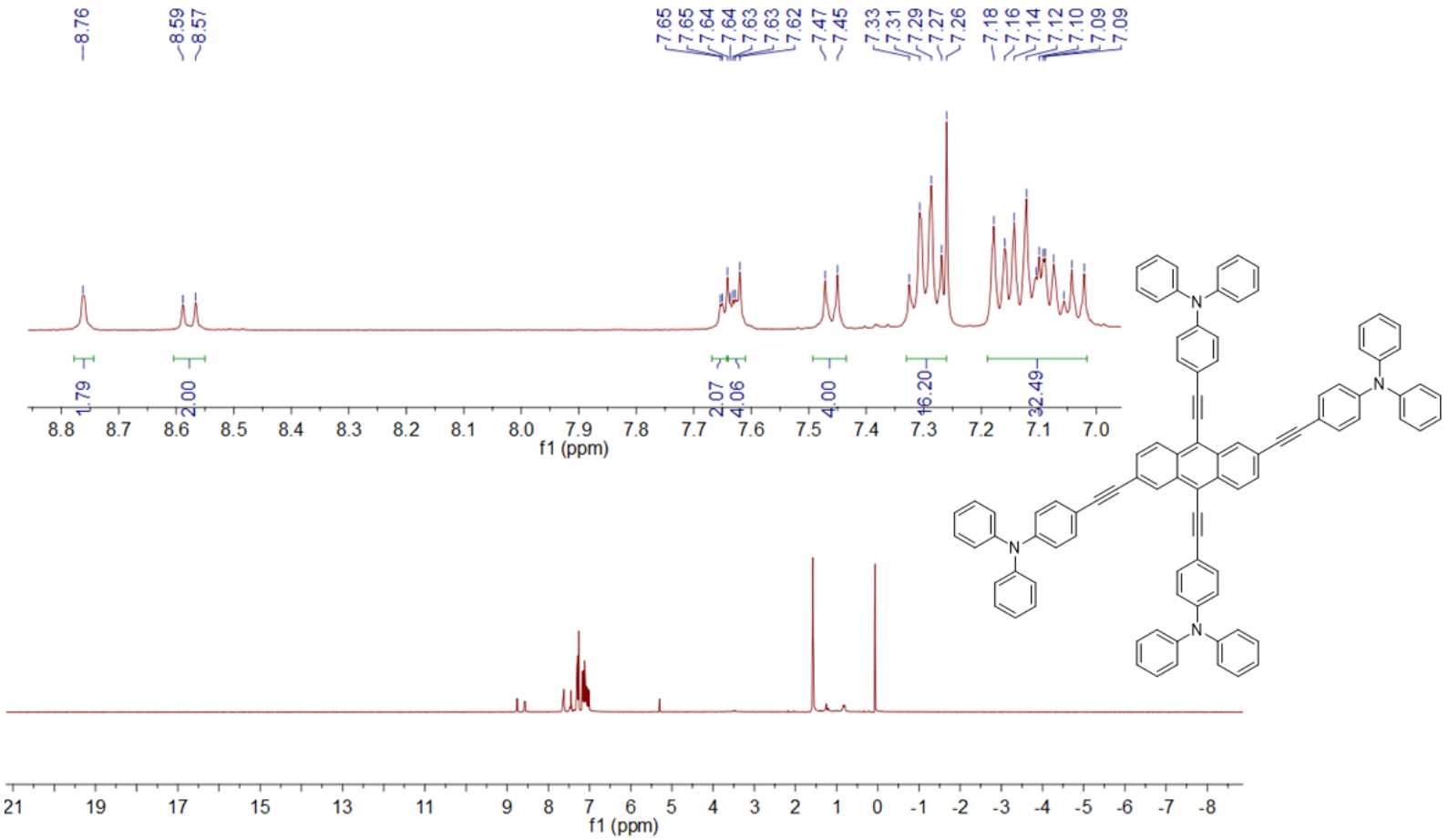


Figure S56. ^{1}H NMR spectrum of **6f** (400 MHz, $CDCl_3$).

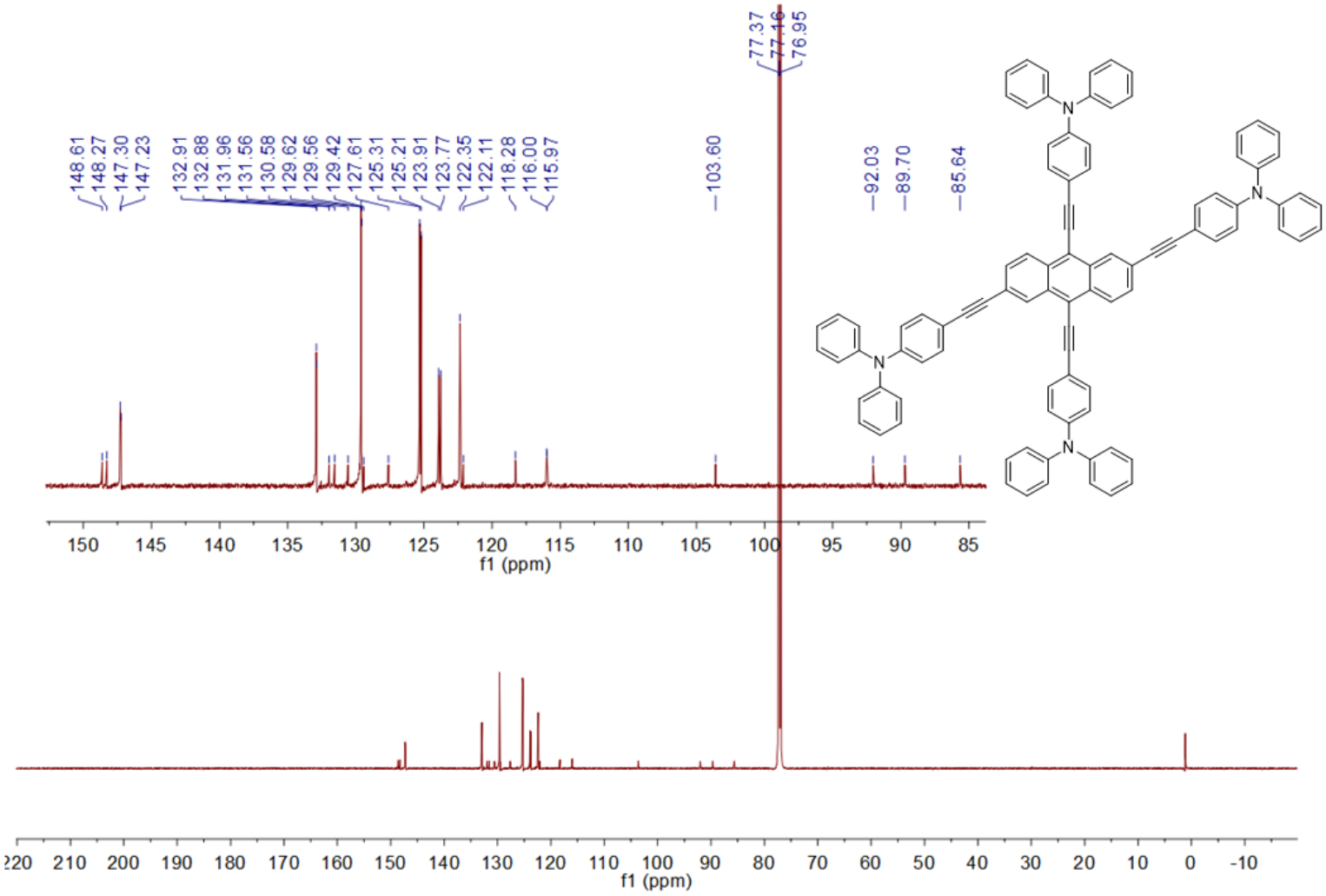


Figure S57. $^{13}C\{^{1}H\}$ NMR spectrum **6f** (151 MHz, $CDCl_3$).

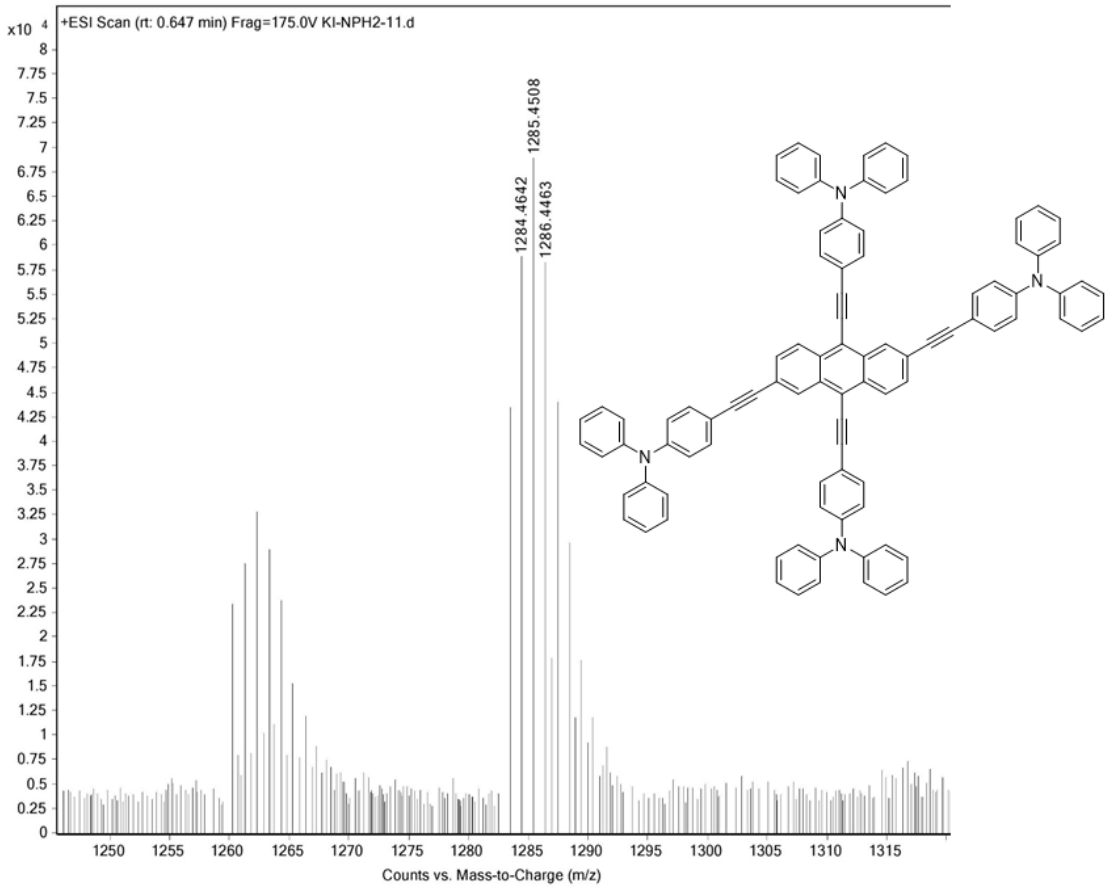


Figure S58. HRMS spectrum of **6f**.

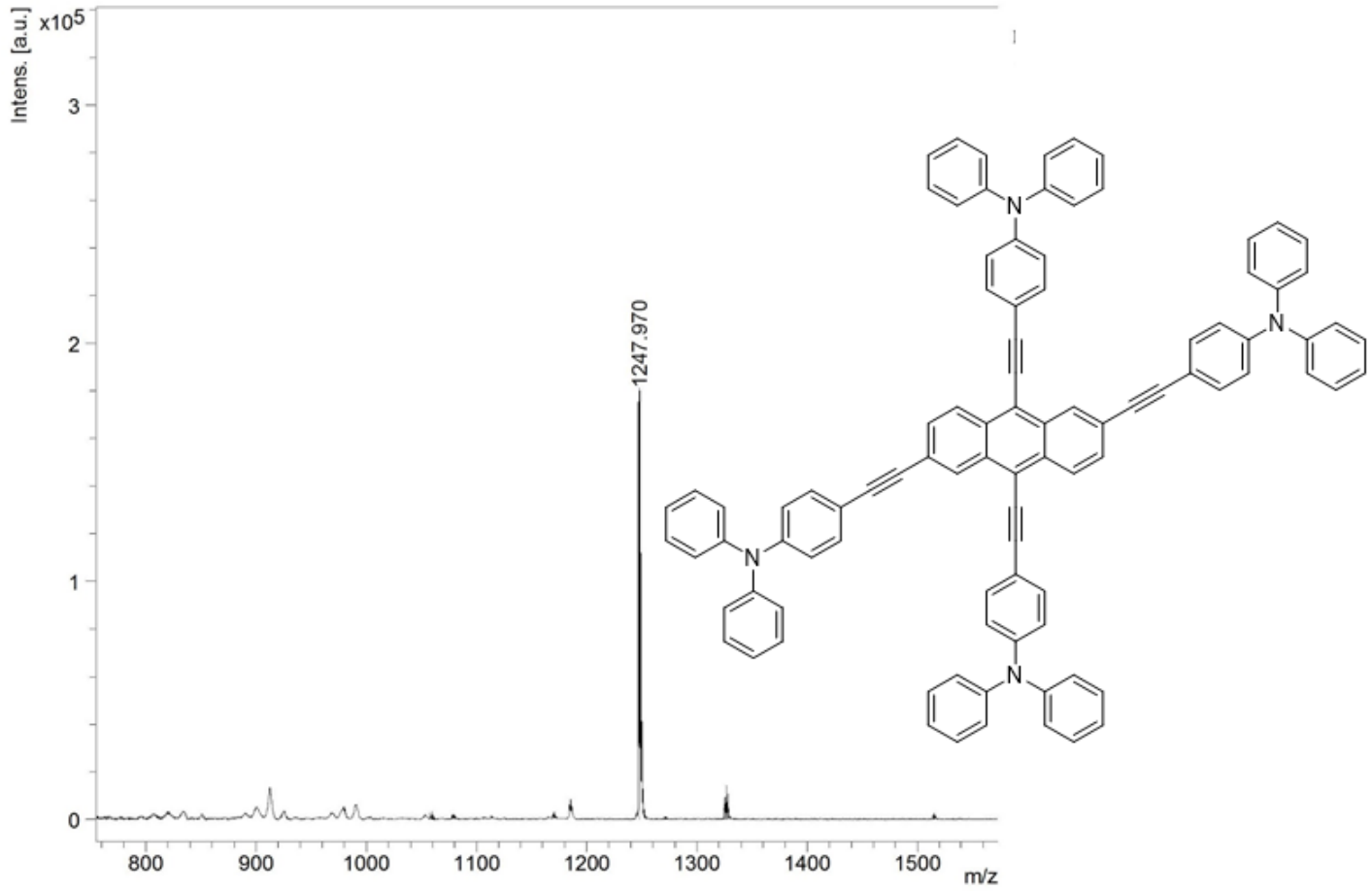


Figure S59. MALDI spectrum **6f**

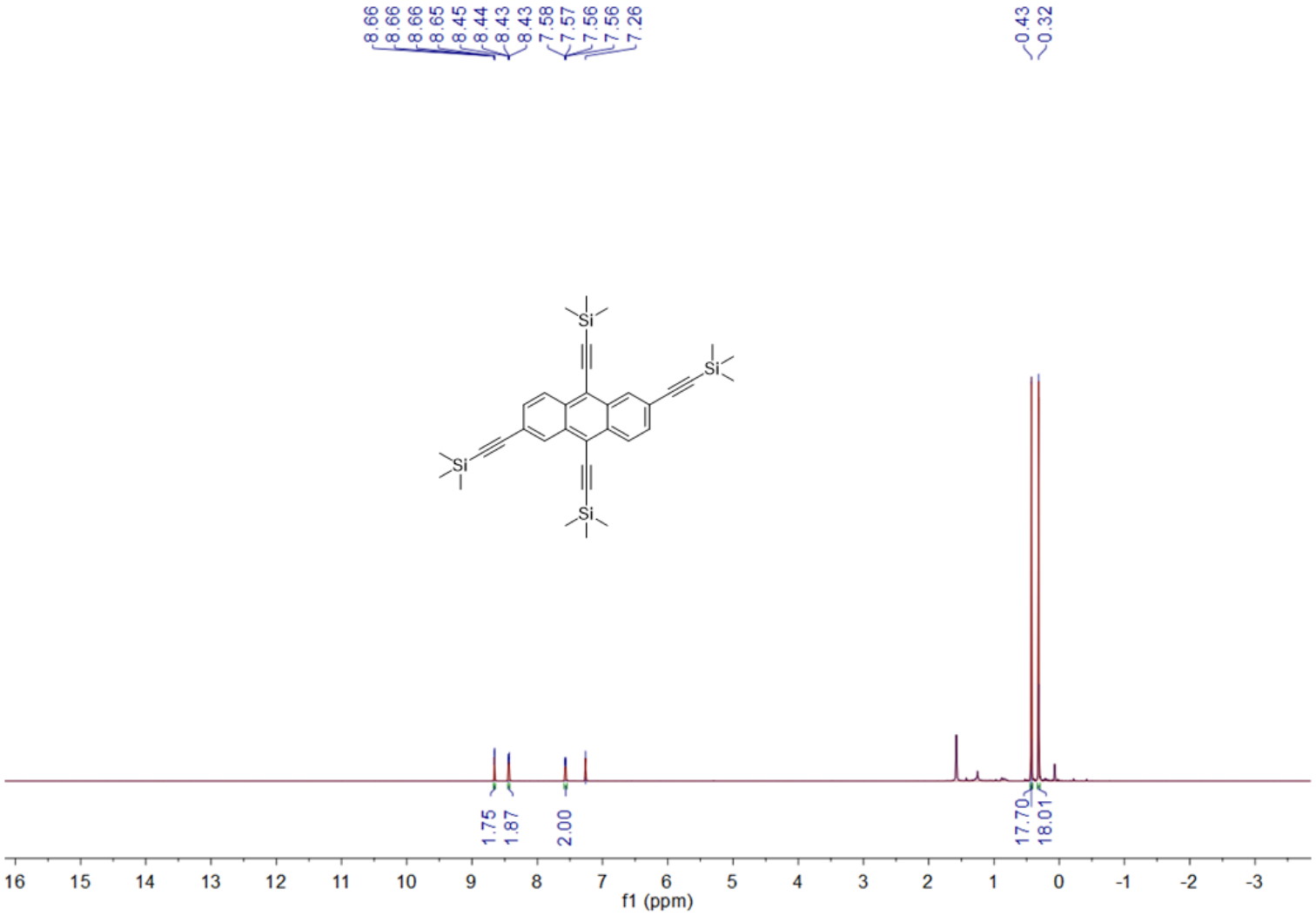


Figure S60. ^{1}H NMR spectrum of **6g** (600 MHz, $CDCl_3$).

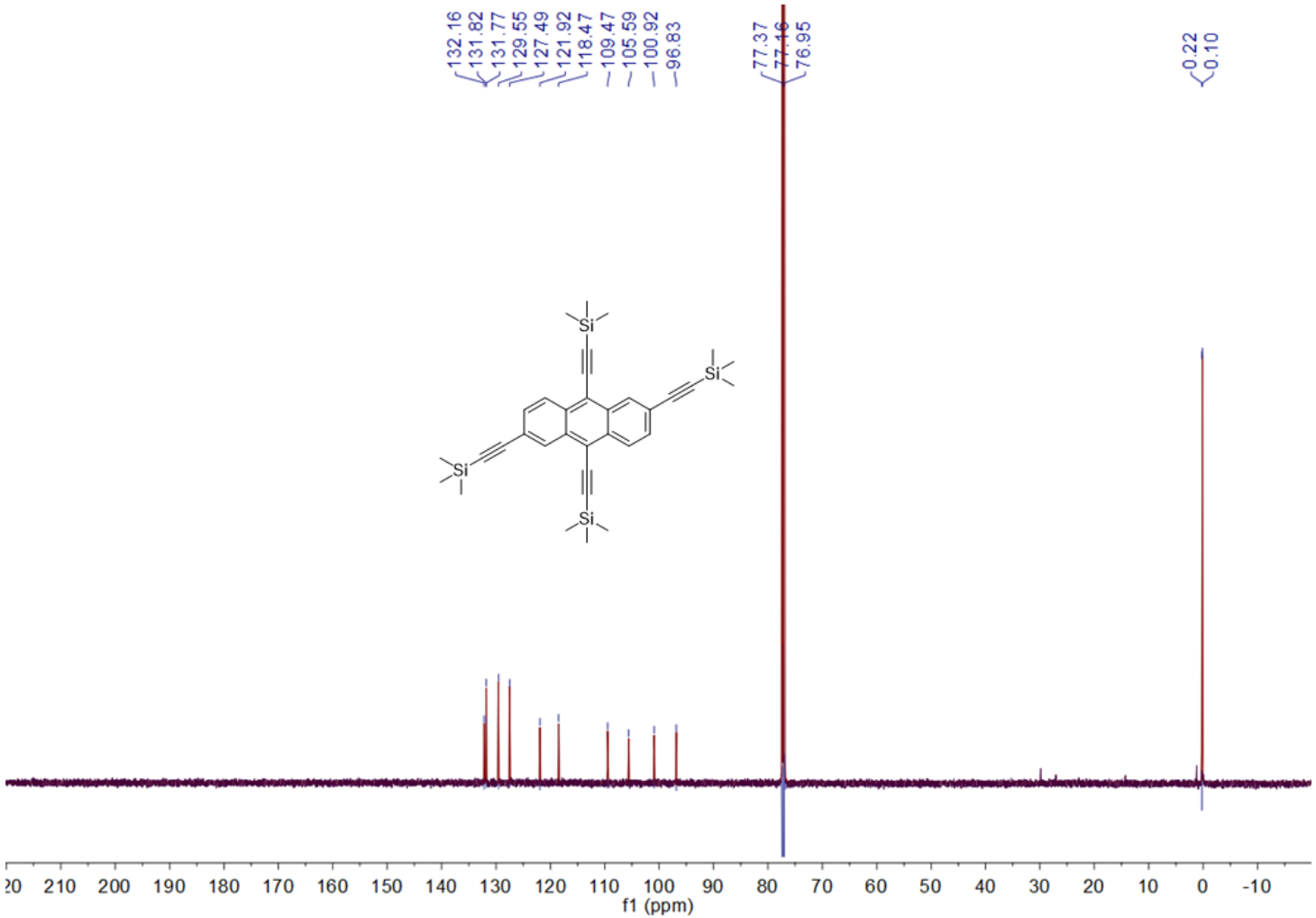


Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum of **6g** (151 MHz, $CDCl_3$).

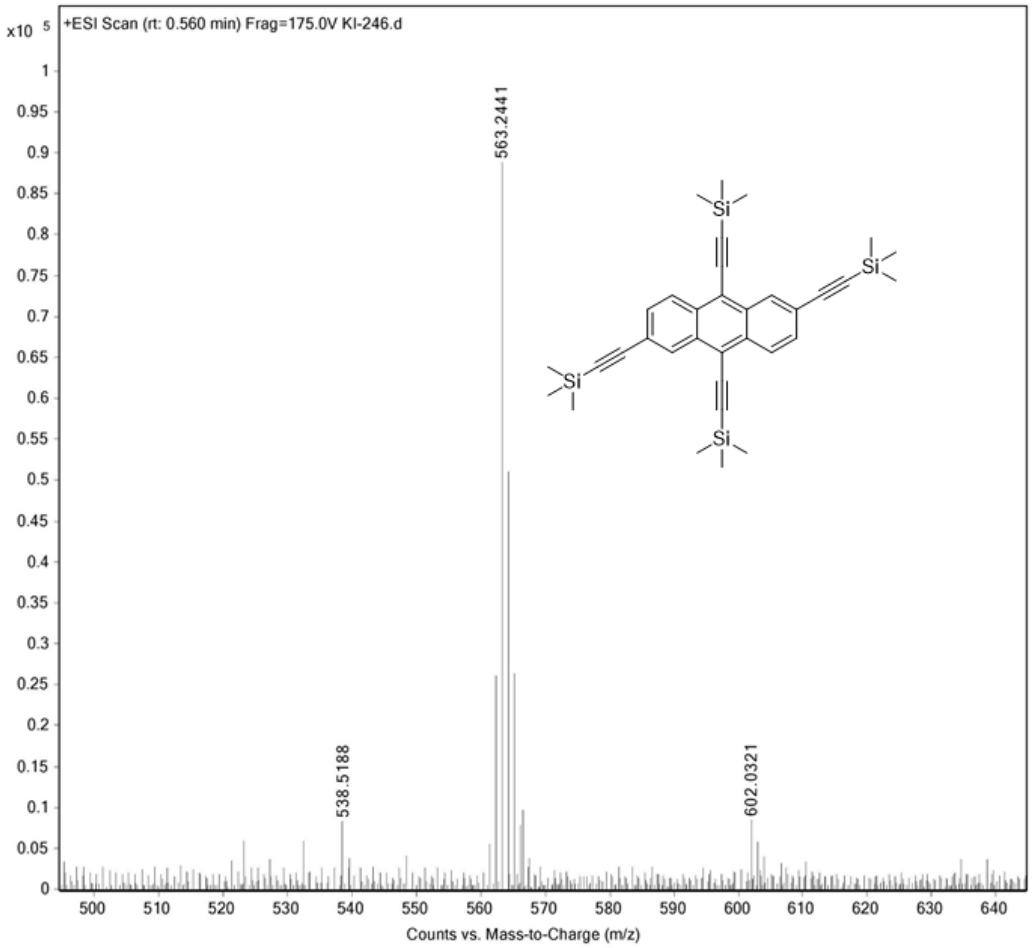


Figure S62. HRMS spectrum of **6g**.

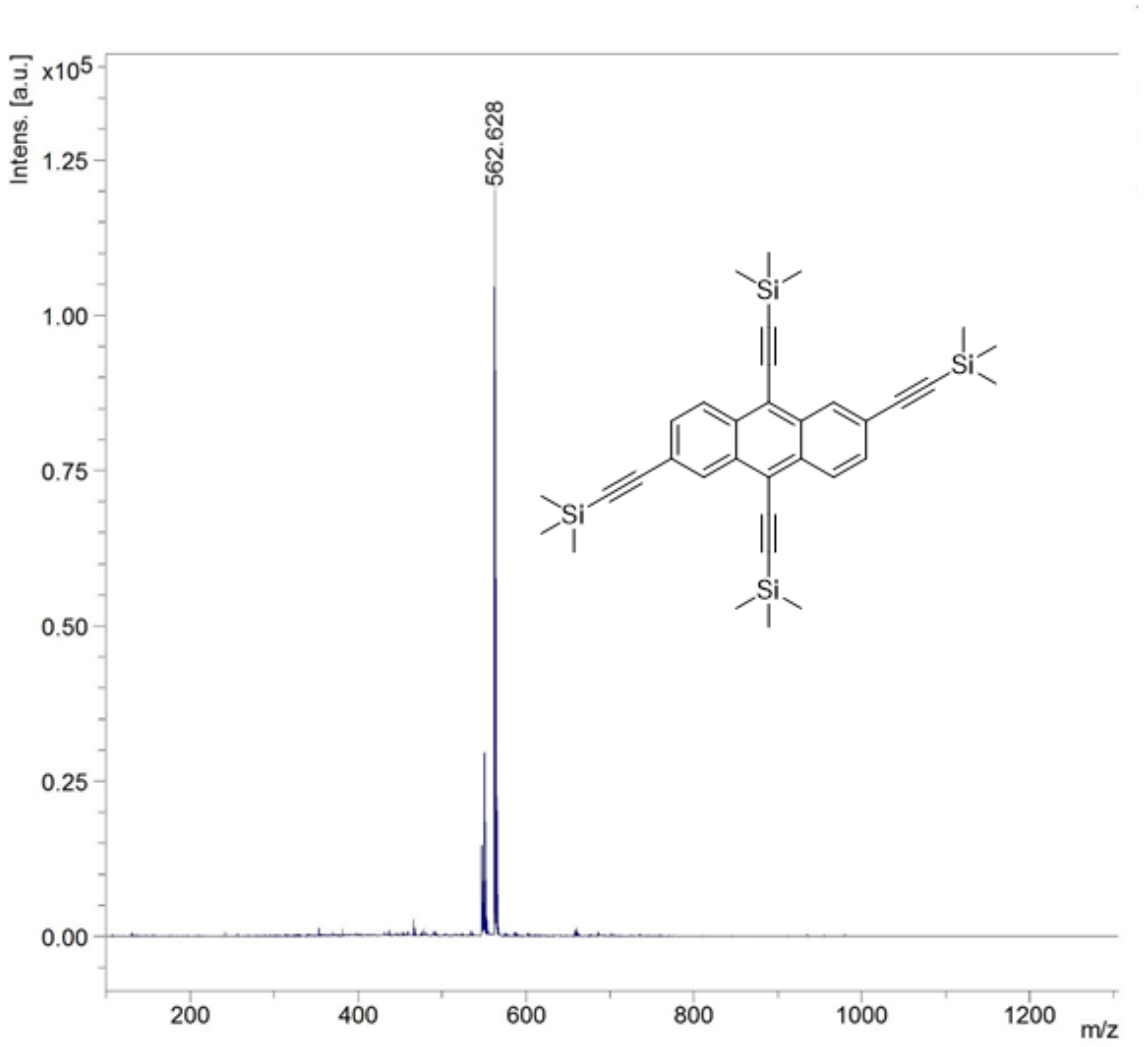


Figure S63. MALDI spectrum of **6g.**

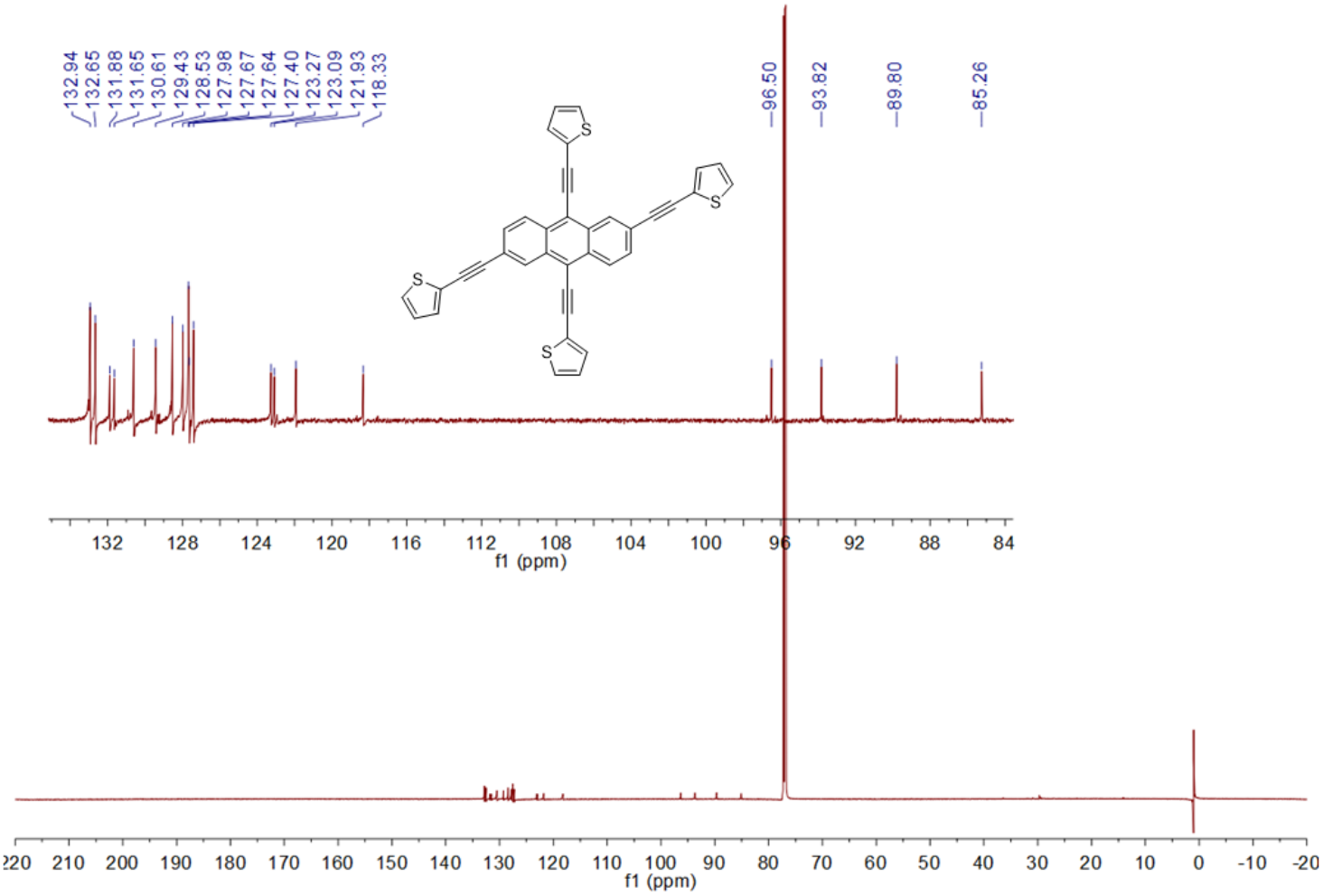


Figure S64. ^{1}H NMR spectrum of **6h** (600 MHz, $CDCl_3$).

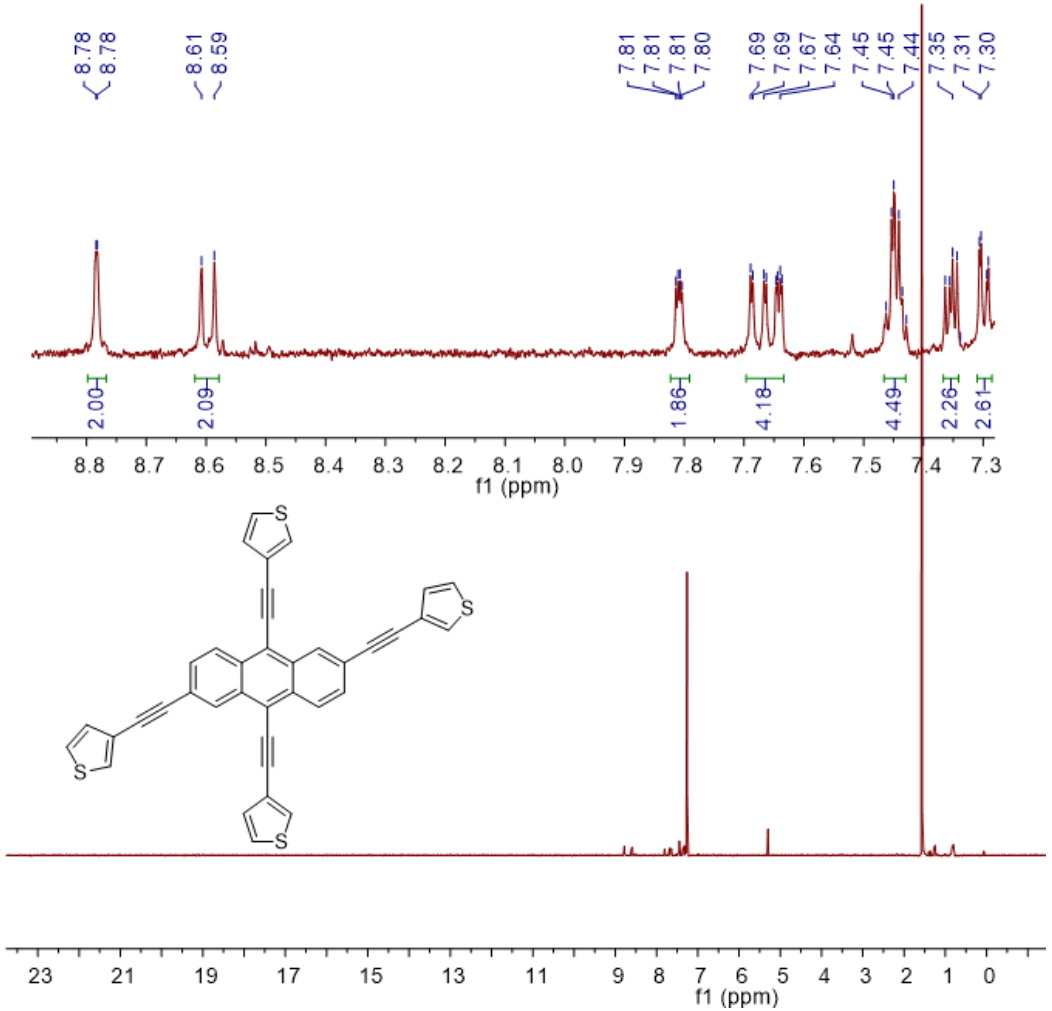


Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum of **6h** (151 MHz, $CDCl_3$).

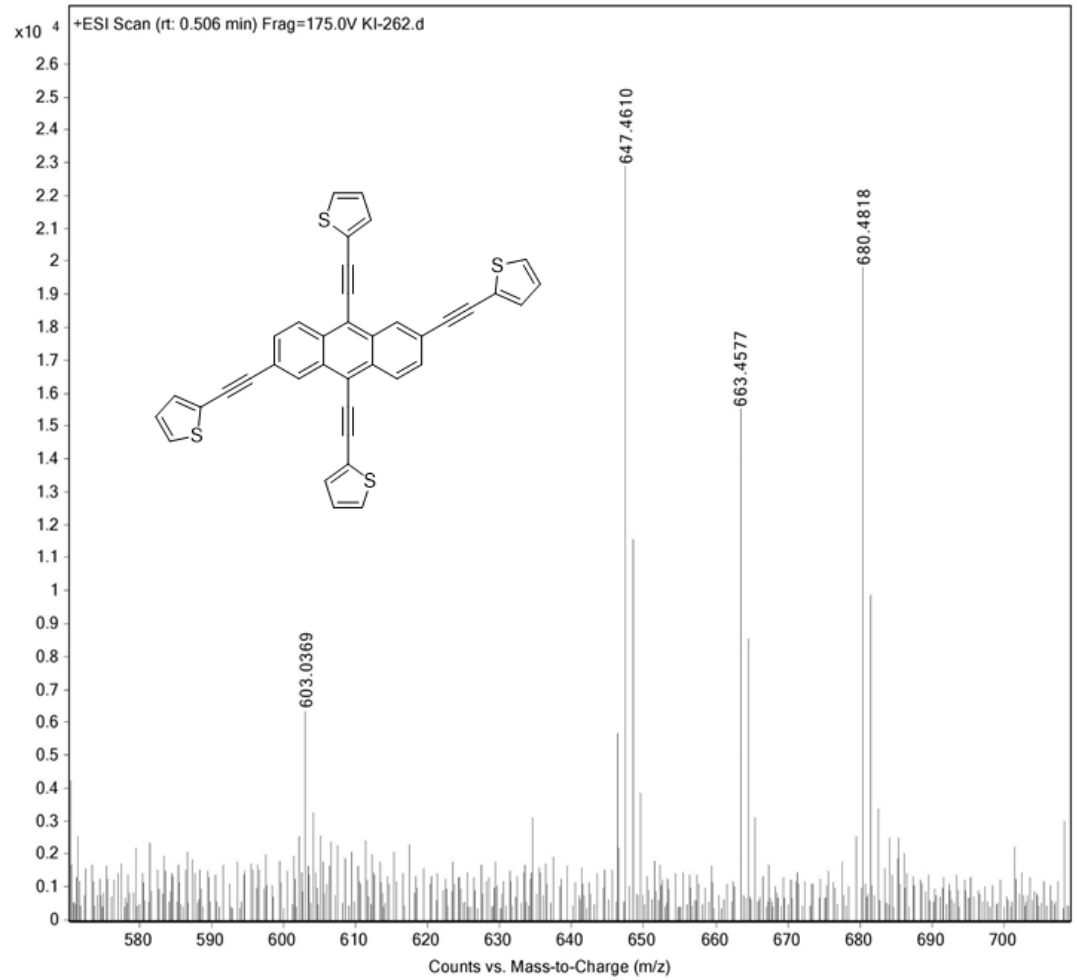


Figure S66. HRMS spectrum of **6h**.

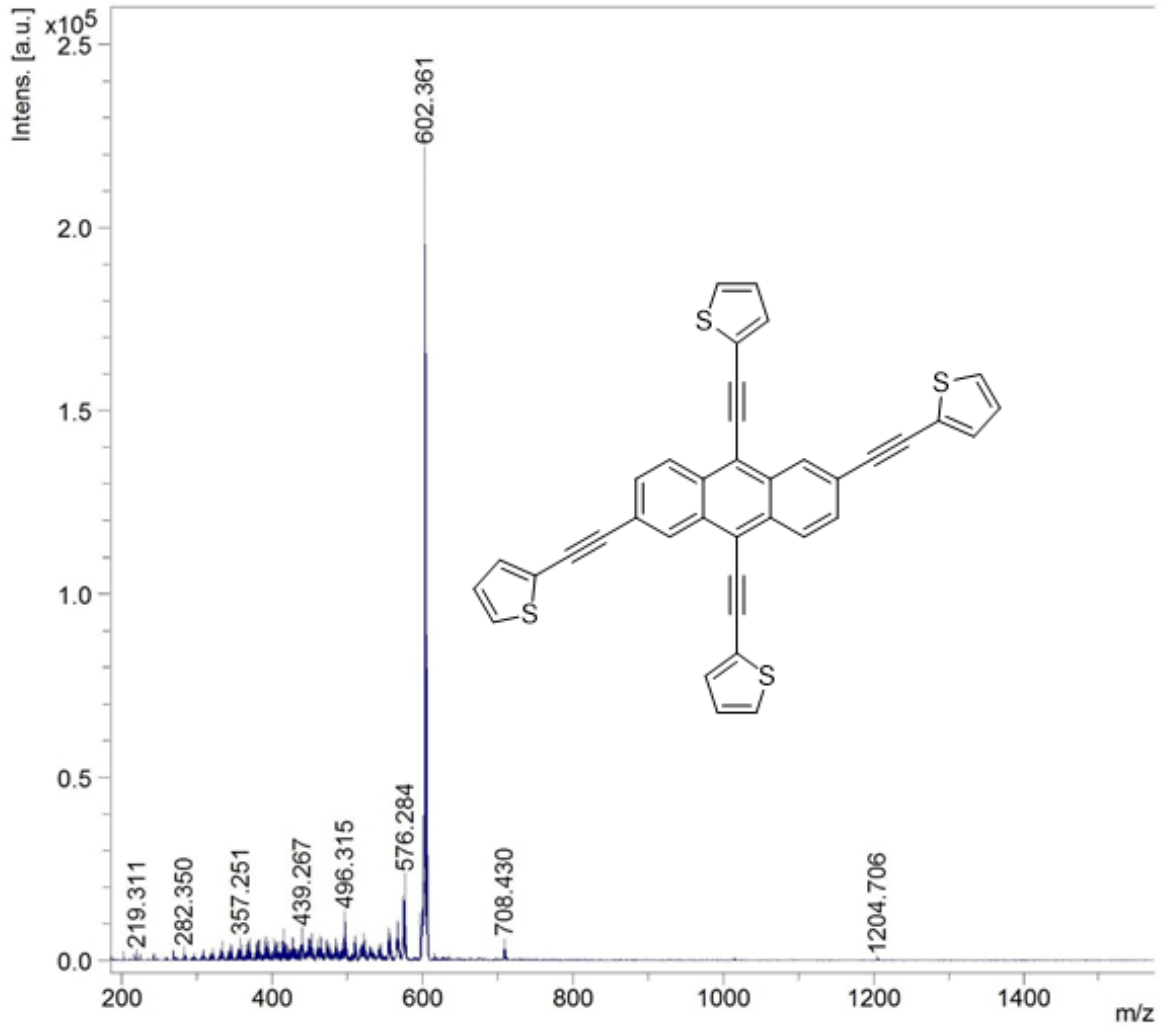


Figure S67. MALDI spectrum of **6h**.

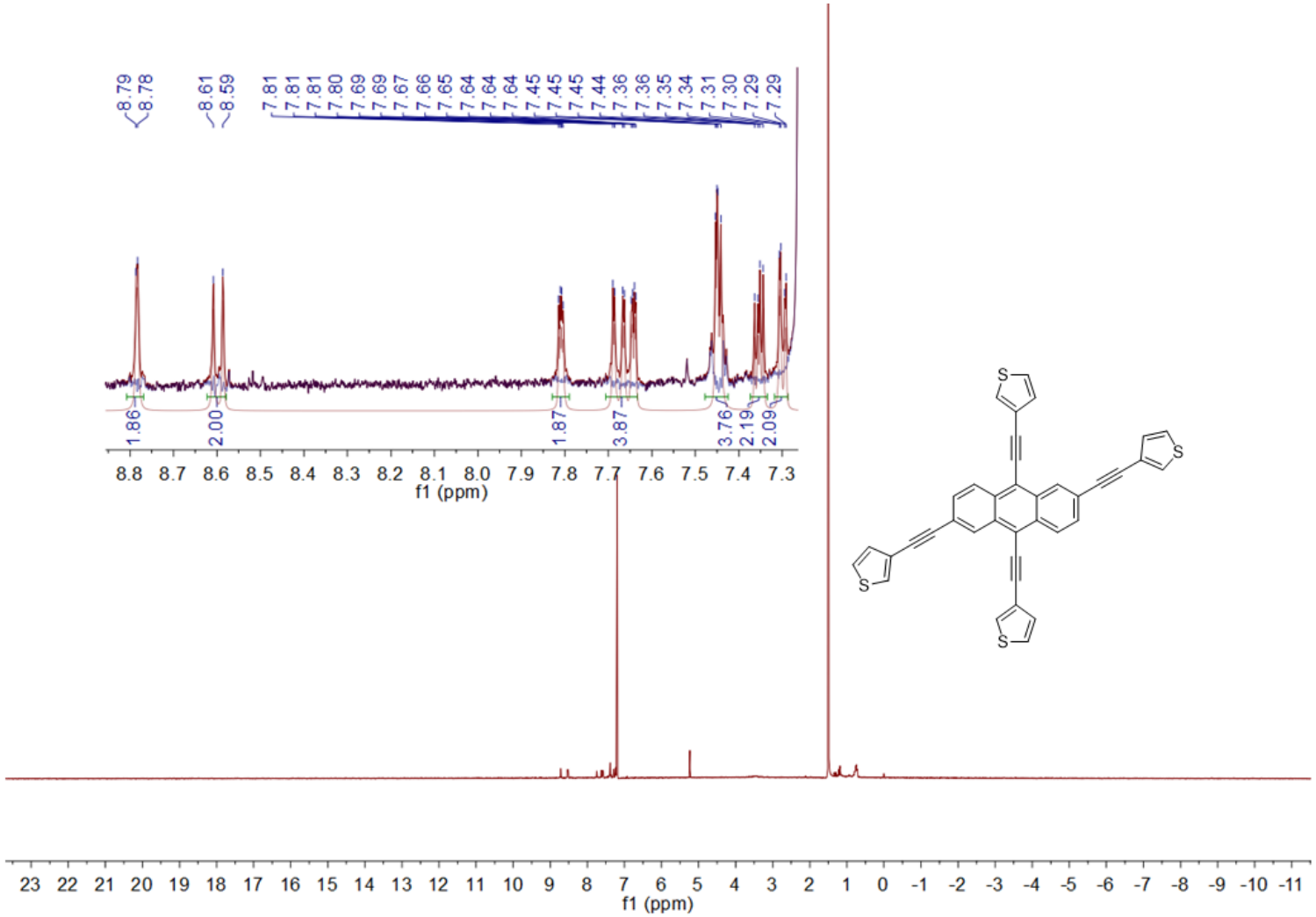


Figure S68 ^{1}H NMR spectrum of **6i** (400 MHz, $CDCl_3$).

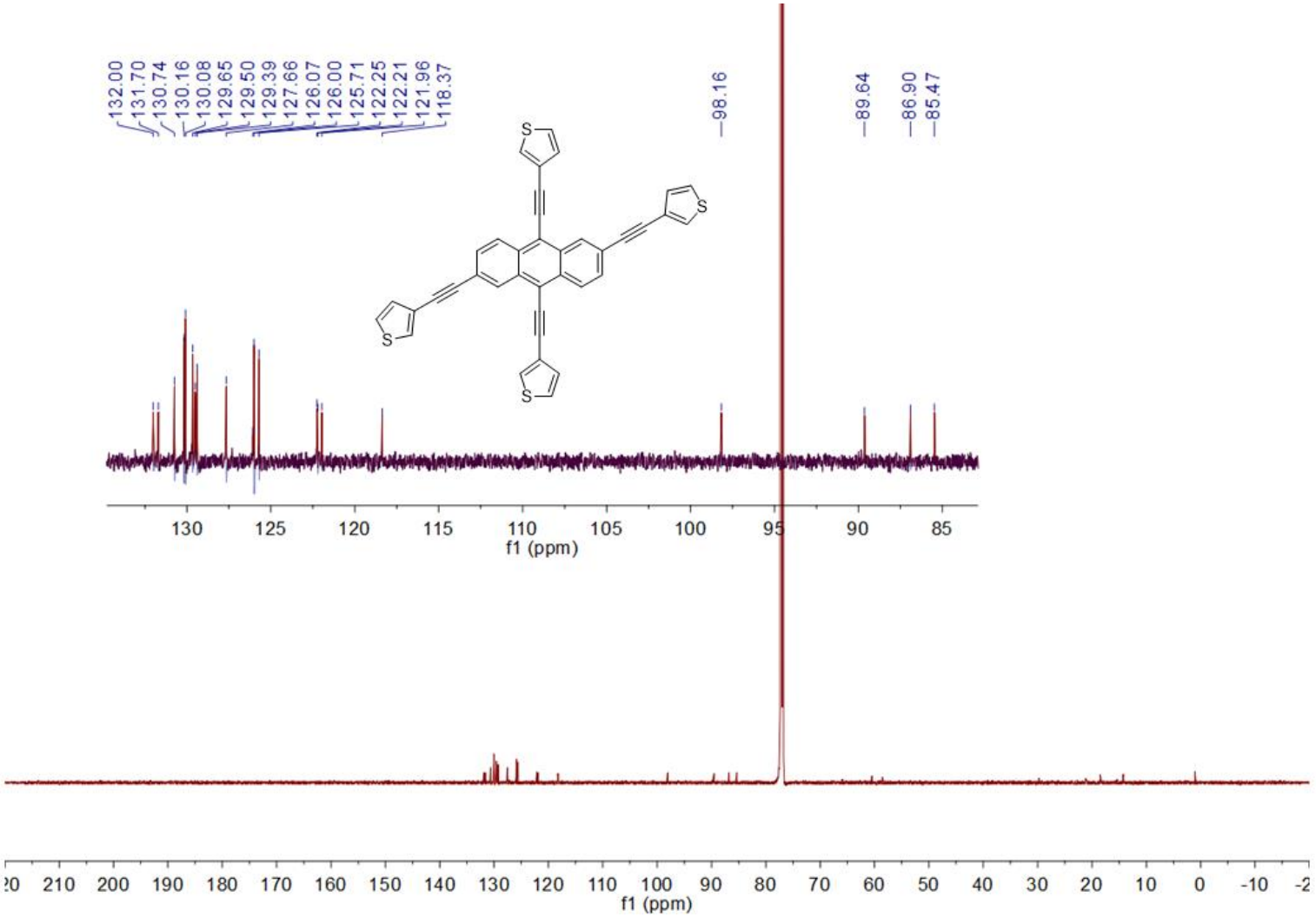


Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum of **6i** (151 MHz, $CDCl_3$).

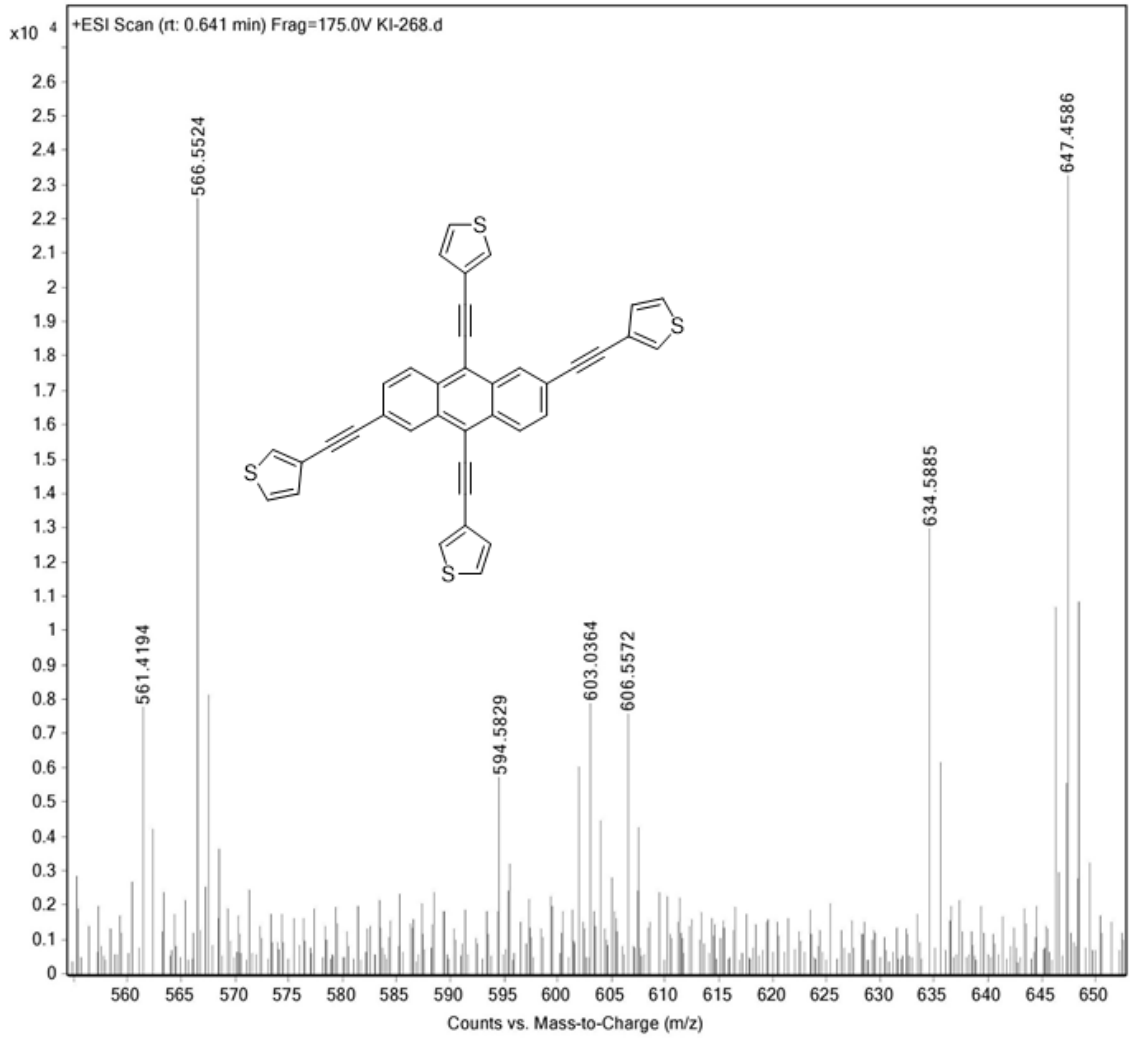


Figure S70. HRMS spectrum of **6i**.

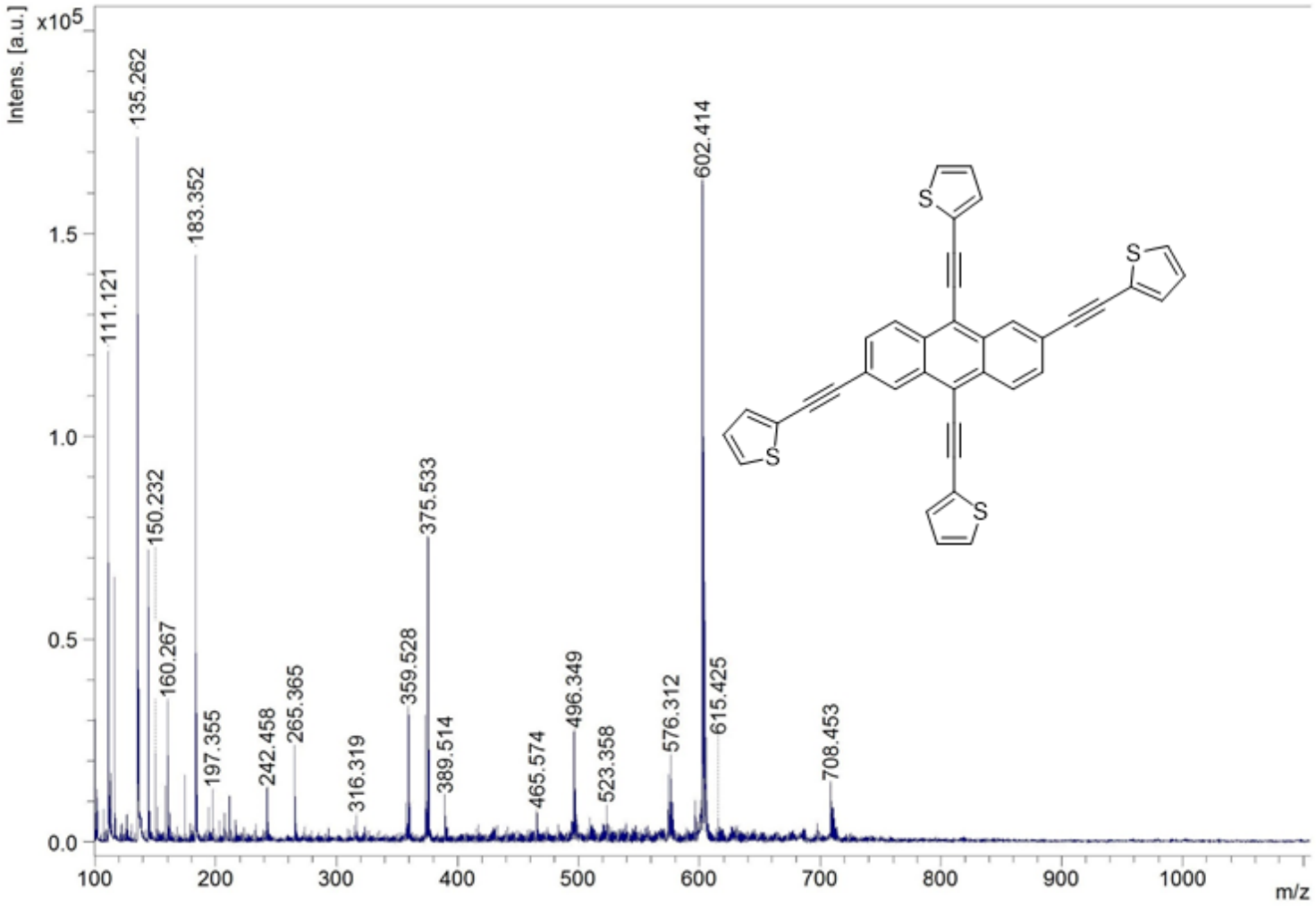


Figure S71. MALDI spectrum of **6i**.

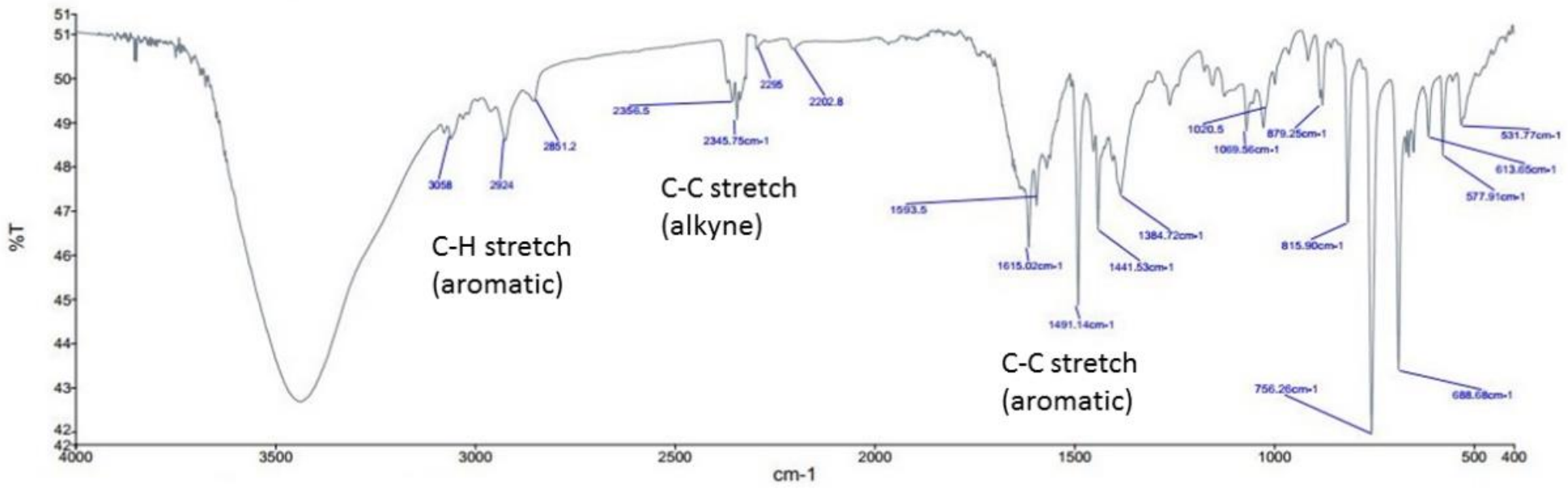


Figure S72. IR spectrum of **6** in KBr pellet.

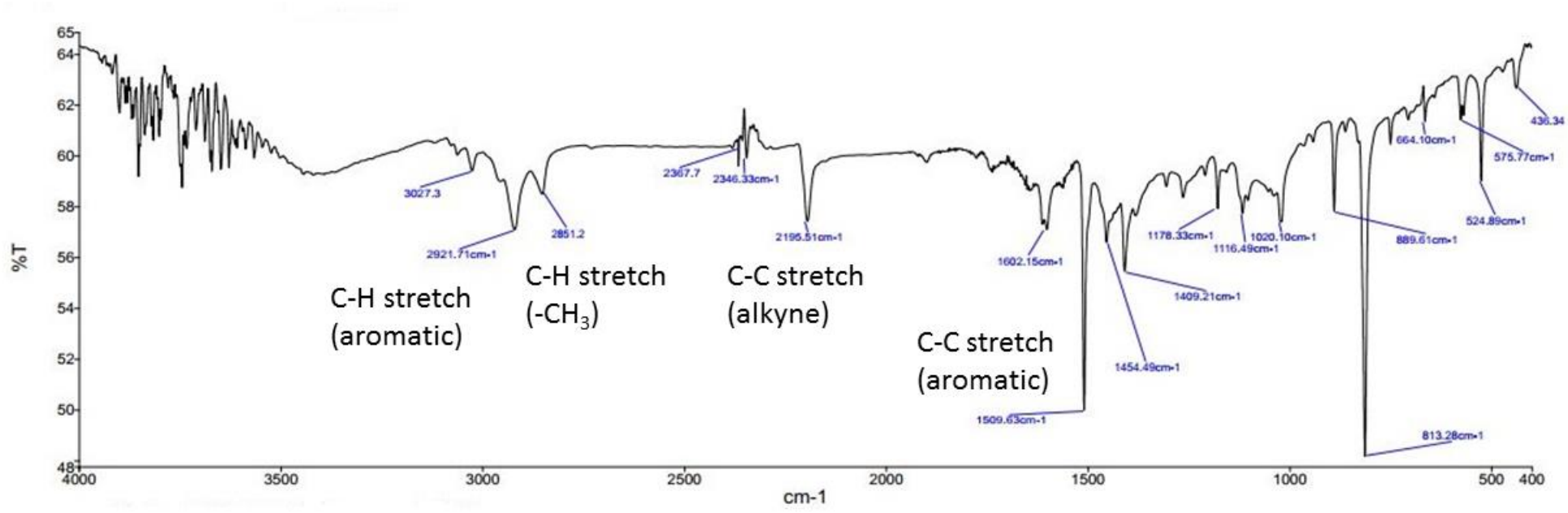


Figure S73. IR spectrum of **6a** in KBr pellet.

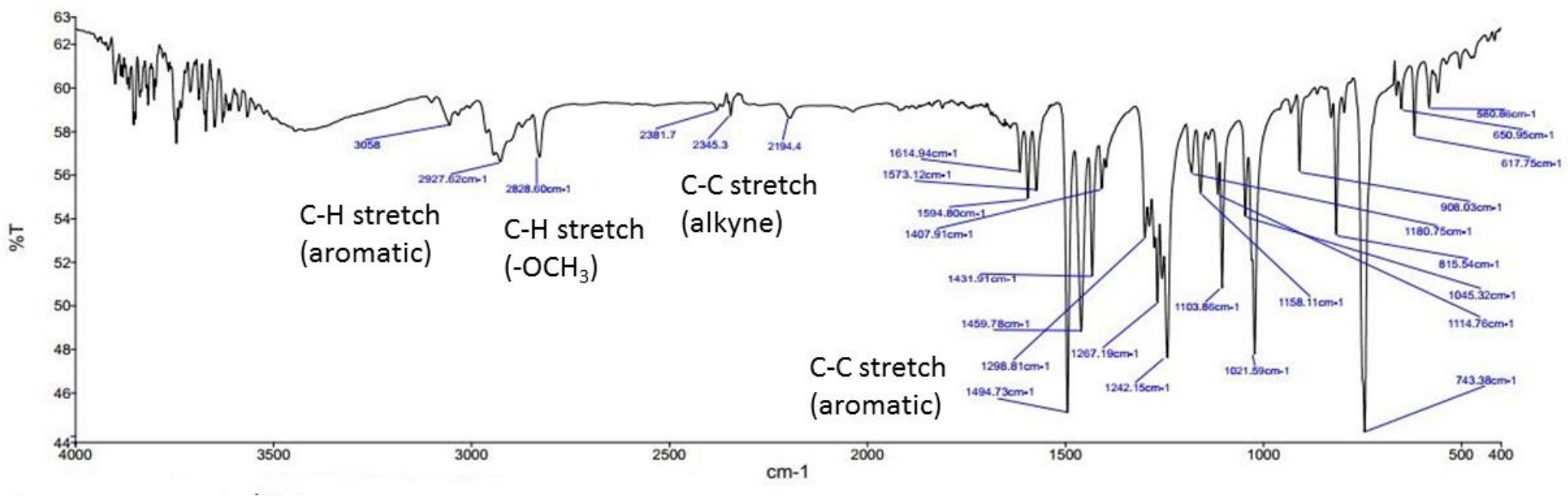


Figure S74. IR spectrum of **6b** in KBr pellet

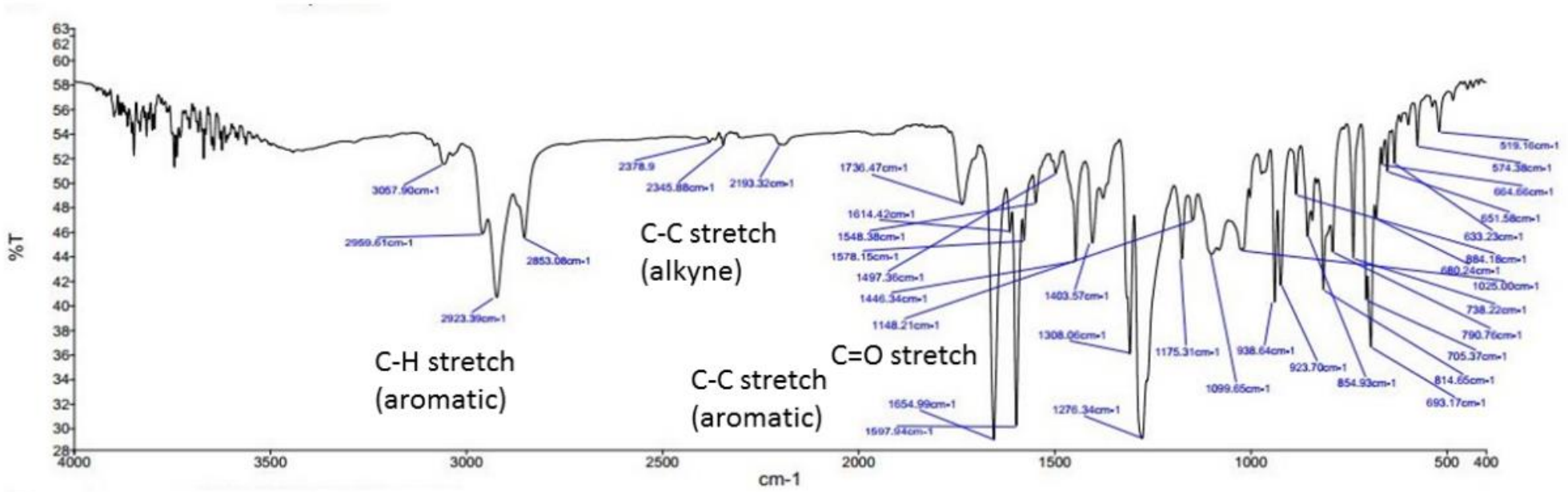


Figure S75. IR spectrum of **6d** in KBr pellet.

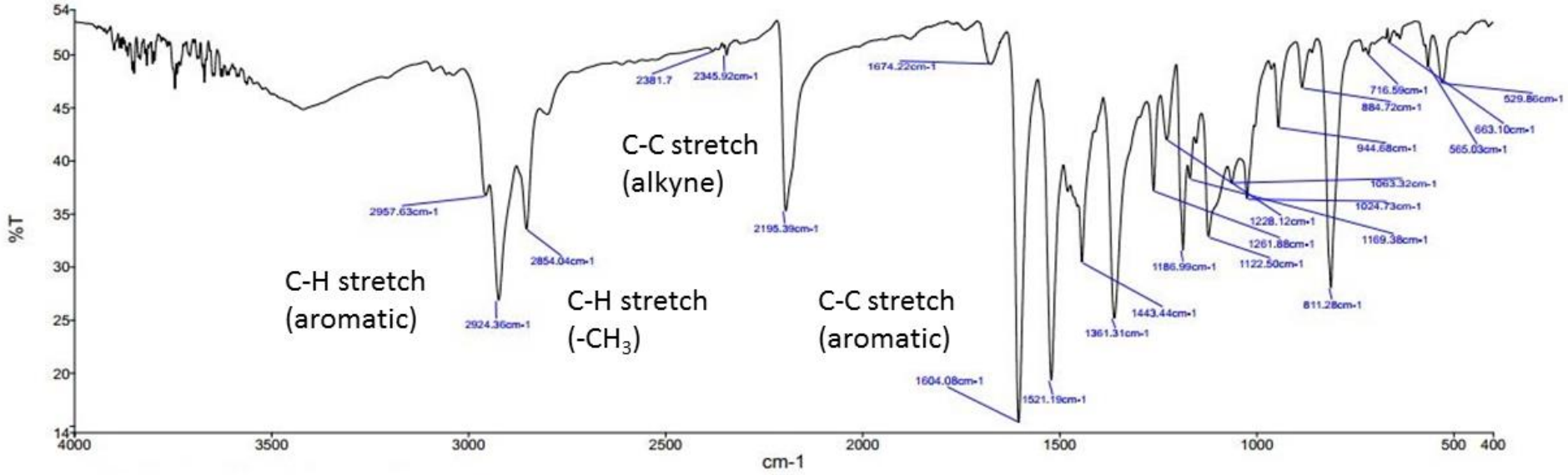


Figure S76. IR spectrum of **6e** in KBr pellet.

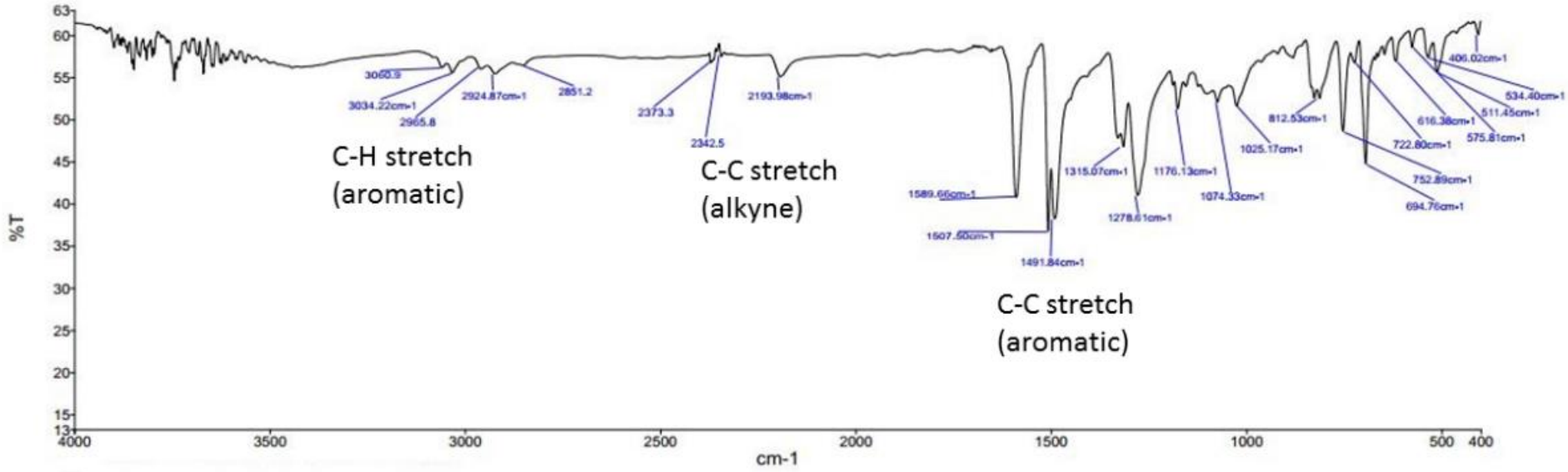


Figure S77. IR spectrum of **6f** in KBr pellet.

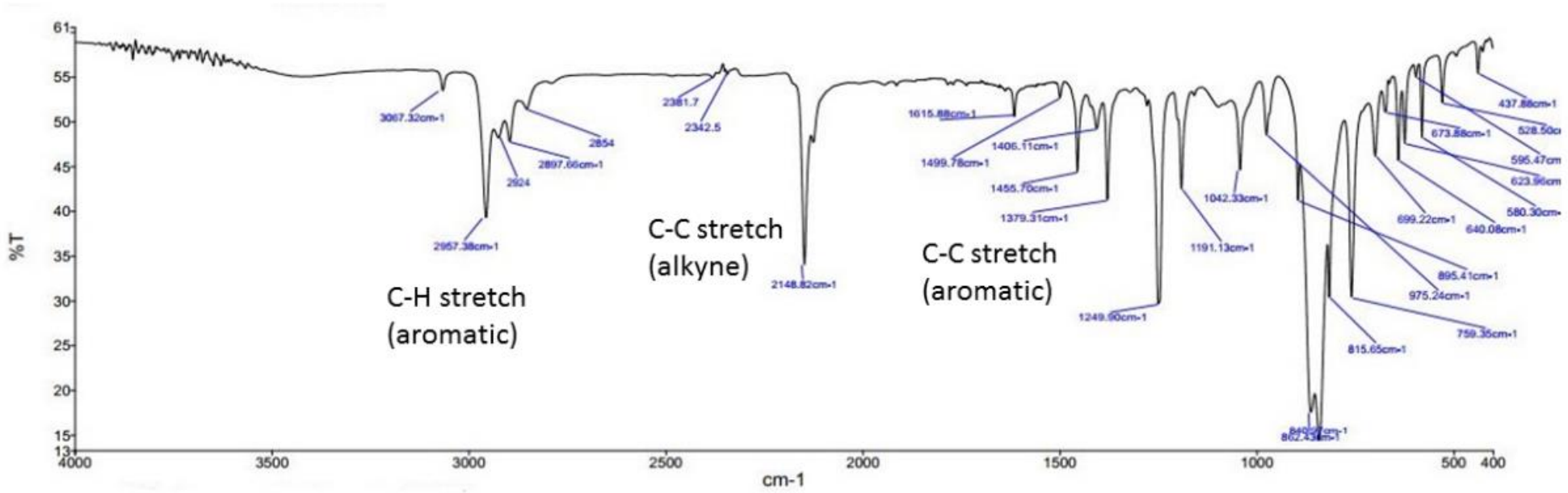


Figure S78. IR spectrum of **6g** in KBr pellet.

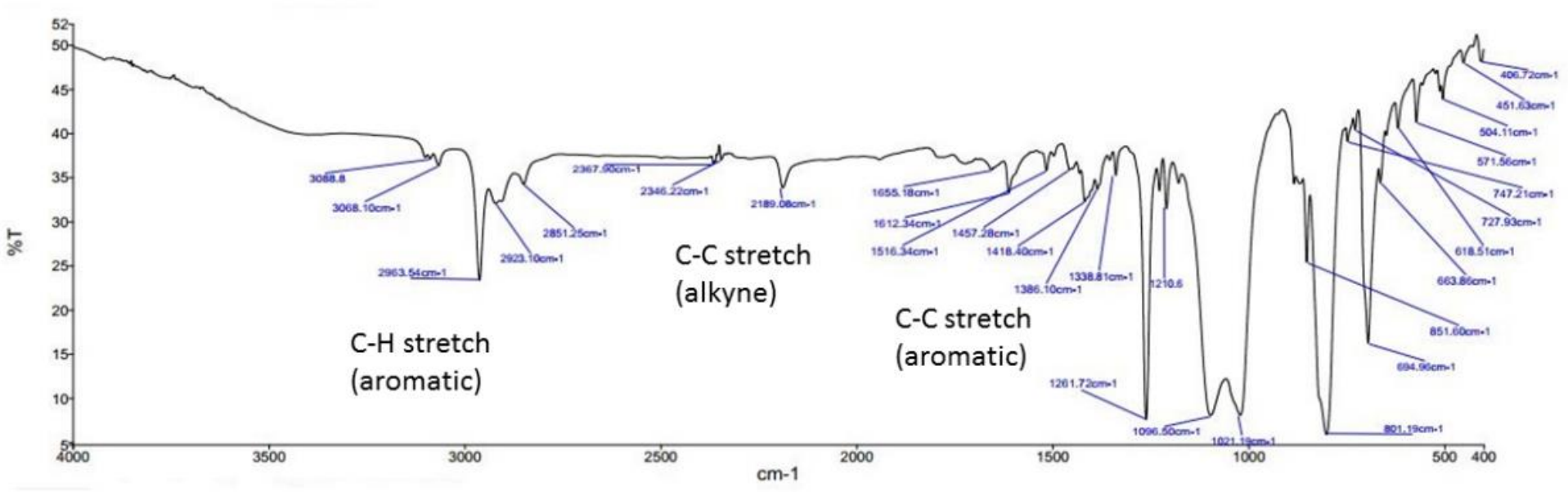


Figure S79. IR spectrum of **6h** in KBr pellet.

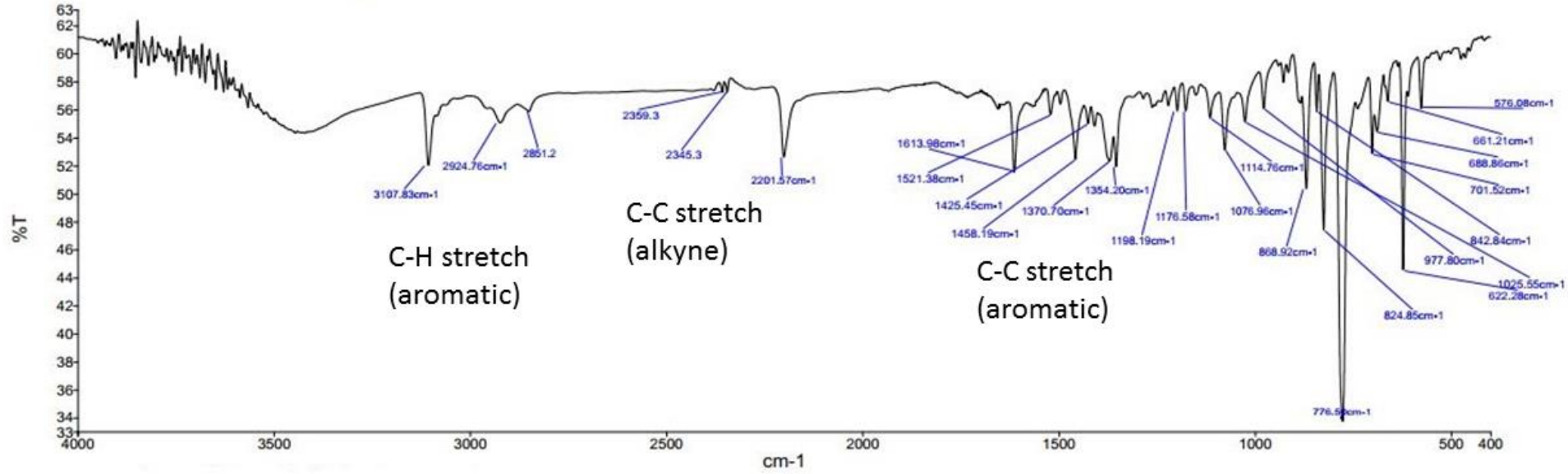


Figure S80. IR spectrum of **6i** in KBr pellet.