

Direct Palladium Catalyzed Mono- and Diarylation of Diphenyldithienylethenes. A useful method for enhancement of fluorescence intensity and aggregation induced emission effect

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Supporting information

1. Materials and instrumentation

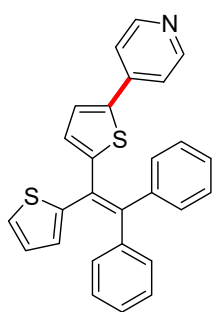
Reagents and solvents were obtained from commercial suppliers and were used without further purification. Column chromatography was carried out using Merck Kieselgel 60 silica gel (particle size: 32-63 Å). Analytical TLC was performed using Merck precoated silica gel 60 F-254 sheets. All the CH activation reactions were carried out under a nitrogen atmosphere. NMR spectroscopic data were acquired on Bruker Avance III spectrometer at 500 MHz for ^1H -NMR and 125 MHz for ^{13}C -NMR. HR-MS spectra were recorded on a 6500 series Q-TOF (Agilent) spectrometer. UV-Vis absorption spectra was measured on the UV-Vis Cary 60-Agilent spectrometer. Fluorescence spectra were recorded on Perkin Elmer FL 8500 spectrometer.

2. General procedure for the CH arylated reaction

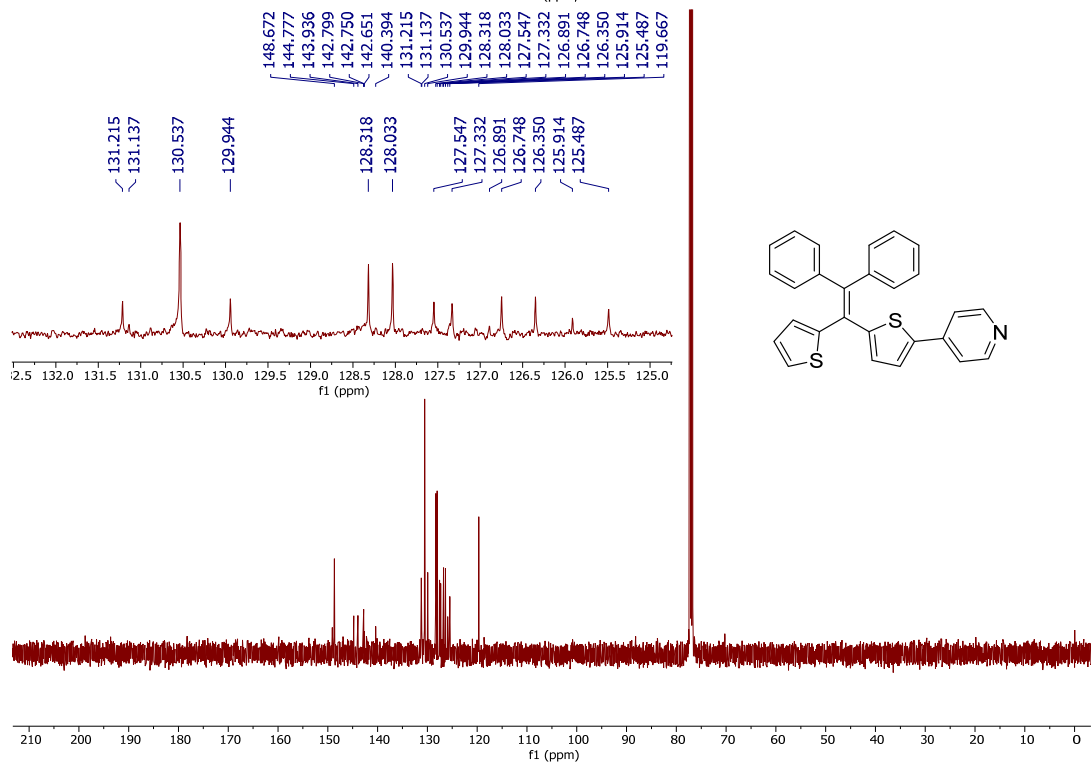
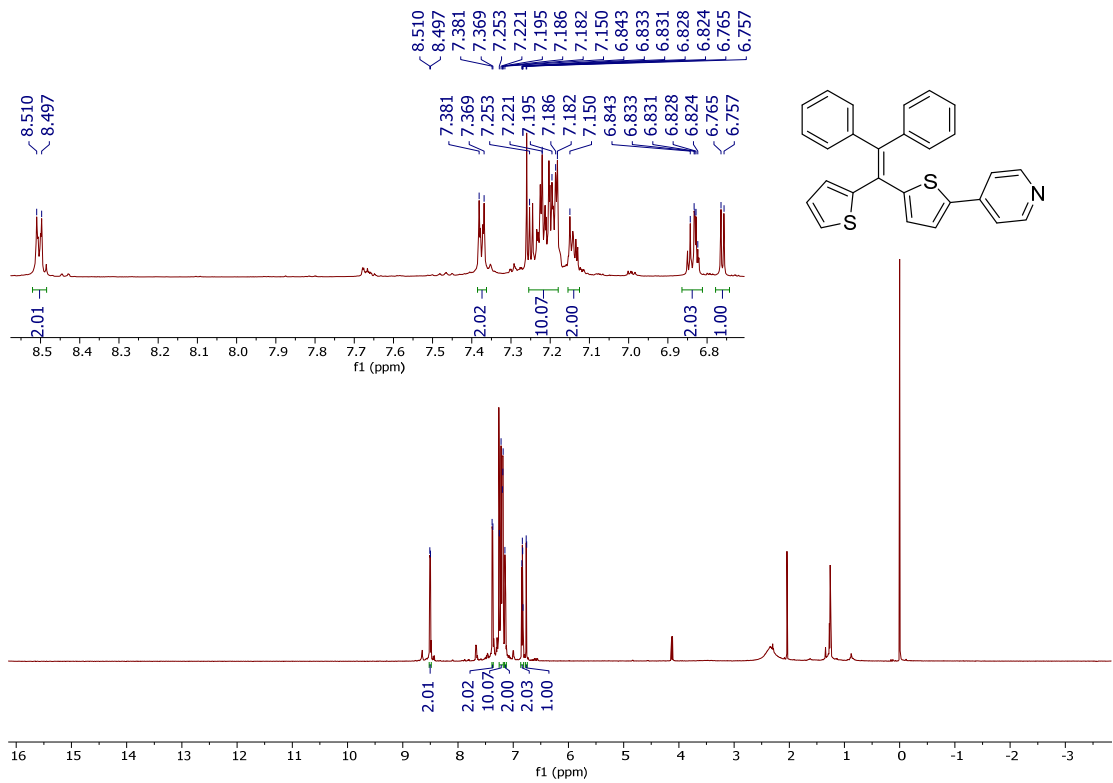
A suspension of DPDTE (69 mg, 0.2 mmol, 1.0 eq), $\text{Pd}(\text{OAc})_2$ (1.0 mg, 0.006 mmol, 0.03 eq), KOAc (58 mg, 0.6 mmol, 3.0 eq), and 4-arylbromide (0.5 eq for monoarylation and 5.0 eq for diarylation) in degassed DMAc (5.0 mL) was stirred at 120 °C for 14h under nitrogen atmosphere. The insoluble impurities were filtered, and the combined filtrates were washed with water (3 x 30 mL) and dried over anhydrous Na_2SO_4 . The solvent was evaporated *in vacuo* to give a crude residue which was purified by column chromatography on silica gel (*n*-hexane) to give pure monoarylated (**2a-f**) and diarylated products (**3a-i**).

3. Characterization of arylated compounds

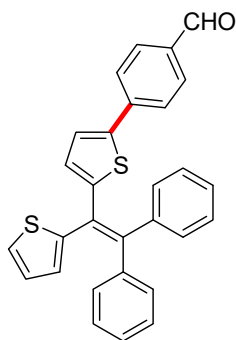
1-(2-(pyridine-4-yl)thien-5-yl)-1-thien-5-yl-2,2-diphenylethene (**2a**)



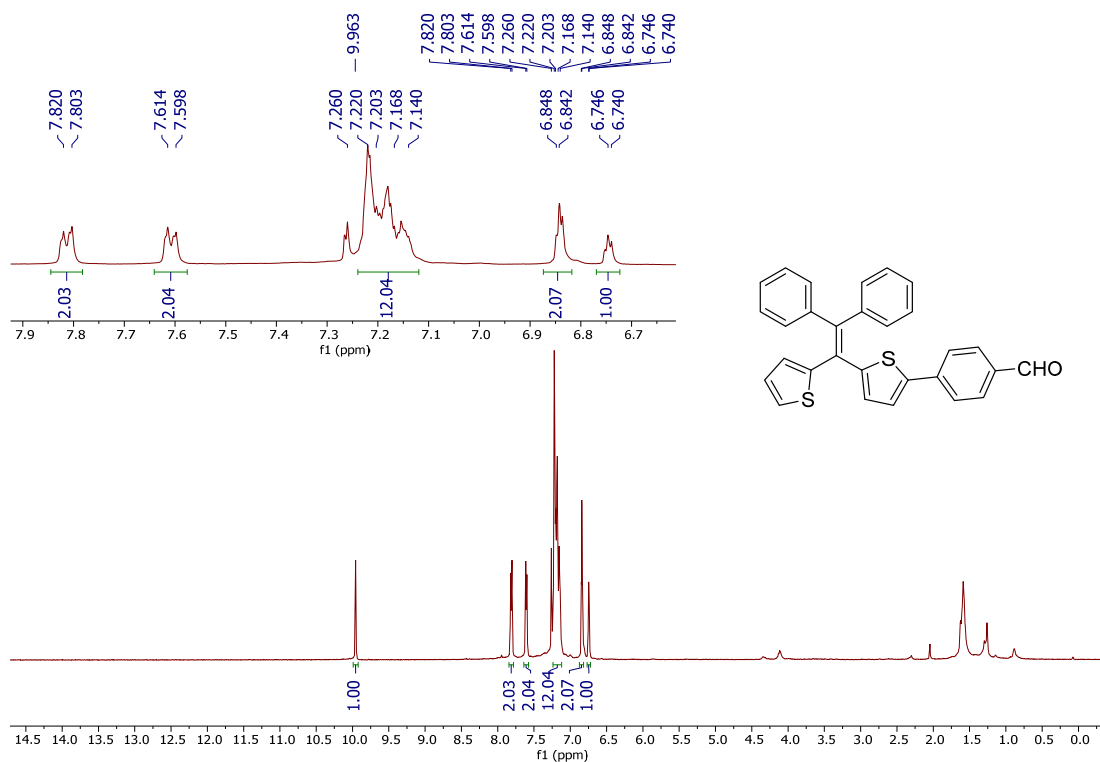
2a (40 mg, 48 %), yellow solid. ^1H -NMR δ_{H} (500 MHz, CDCl_3 , δ ppm): δ 8.50 (2H, *d*, J = 6.5 Hz), δ 7.38 (2H, *d*, J = 6.0 Hz), δ 7.25-7.18 (10H, *m*), δ 7.15-7.13 (2H, *m*), δ 6.84-6.82 (2H, *m*), δ 6.76 (1H, *d*, J = 4.0 Hz); ^{13}C -NMR δ_{C} (125 MHz, CDCl_3 , δ ppm): δ 148.7, 144.8, 143.9, 143.3, 142.8, 142.7, 142.6, 140.4, 131.2, 131.1, 130.5, 129.9, 128.3, 128.0, 127.5, 127.3, 126.9, 126.7, 126.3, 125.9, 125.5, 119.7. HR-MS calcd for $\text{C}_{27}\text{H}_{20}\text{NS}_2$ ($[\text{M}+\text{H}]^+$): 422.1037, found: 422.1039.

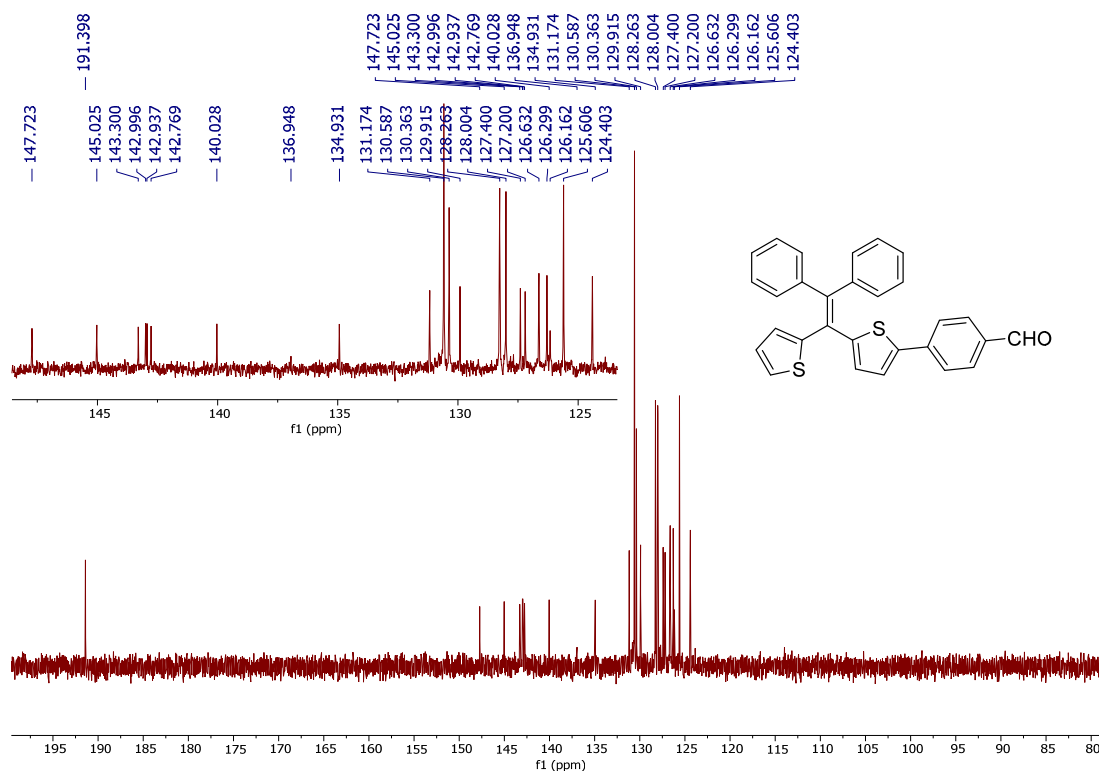


1-(2-(4-formylphenyl)thien-5-yl)-1-thien-5-yl-2,2-diphenylethene (2b)

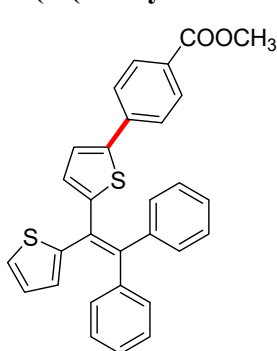


2b (44 mg, 49 %), yellow solid. $^1\text{H-NMR}$ δ_{H} (500 MHz, CDCl_3 , δ ppm): δ 9.96 (1H, *s*), δ 7.81 (2H, *d*, $J = 8.5$ Hz), δ 7.60 (2H, *d*, $J = 8.0$ Hz), δ 7.26-7.14 (12H, *m*), δ 6.84 (2H, *d*, $J = 3.0$ Hz), δ 6.74 (1H, *d*, $J = 3.5$ Hz); $^{13}\text{C-NMR}$ δ_{C} (125 MHz, CDCl_3 , δ ppm): δ 191.4, 147.7, 145.0, 143.3, 143.0, 142.9, 142.8, 140.0, 134.9, 131.2, 130.6, 130.4, 129.9, 128.3, 128.0, 127.4, 127.2, 126.6, 126.3, 126.2, 125.7, 124.4. HR-MS calcd for $\text{C}_{29}\text{H}_{21}\text{OS}_2$ ($[\text{M}+\text{H}]^+$): 449.1034, found: 449.1064.

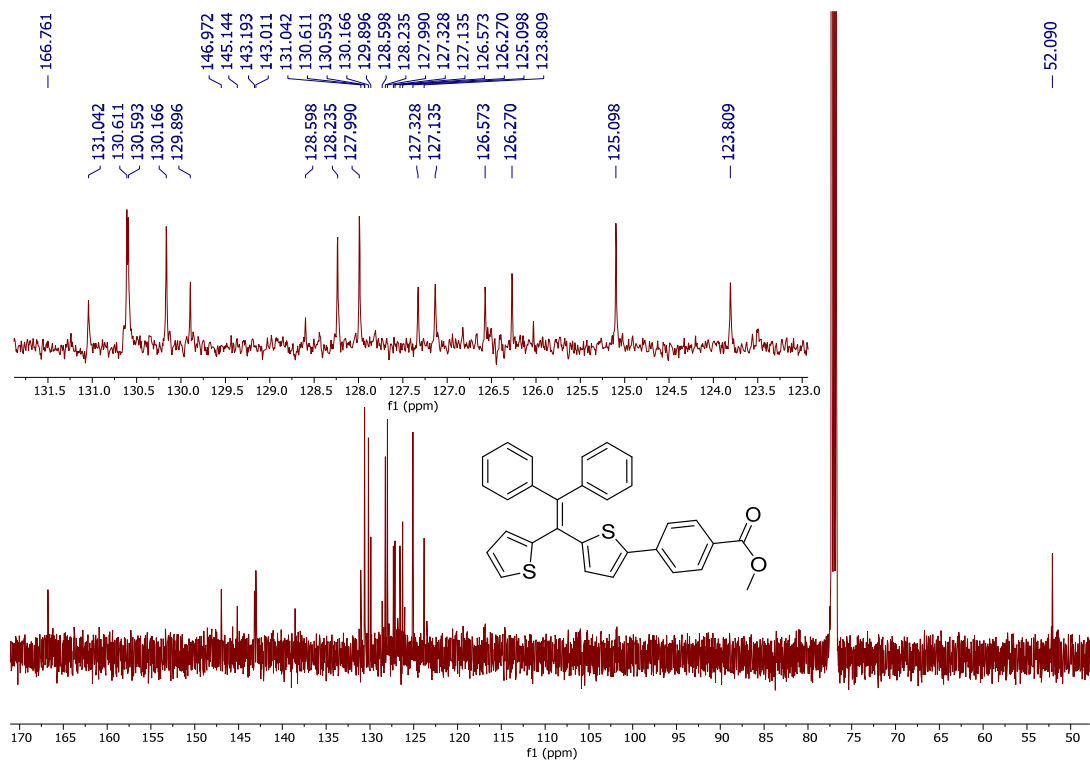
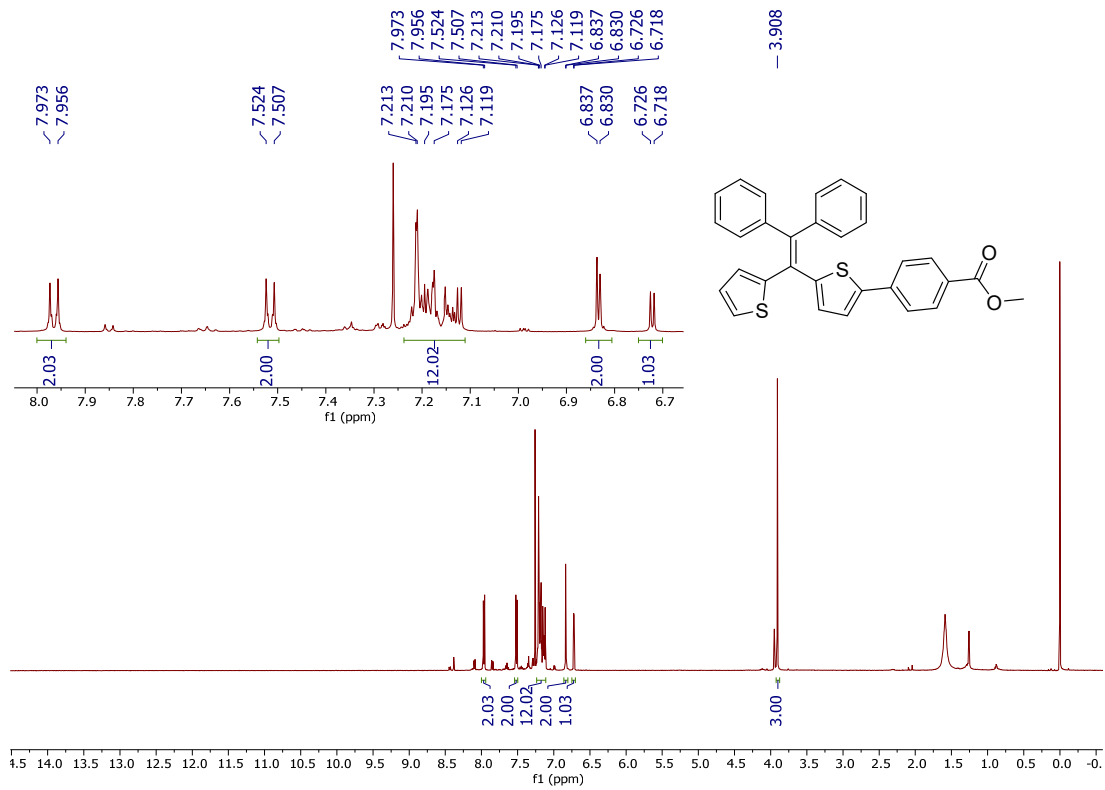




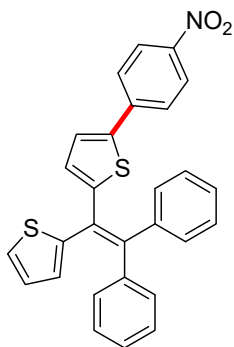
1-(2-(methyl 4-benzoate)thien-5-yl)-1-thien-5-yl-2,2-diphenylethene (2c)



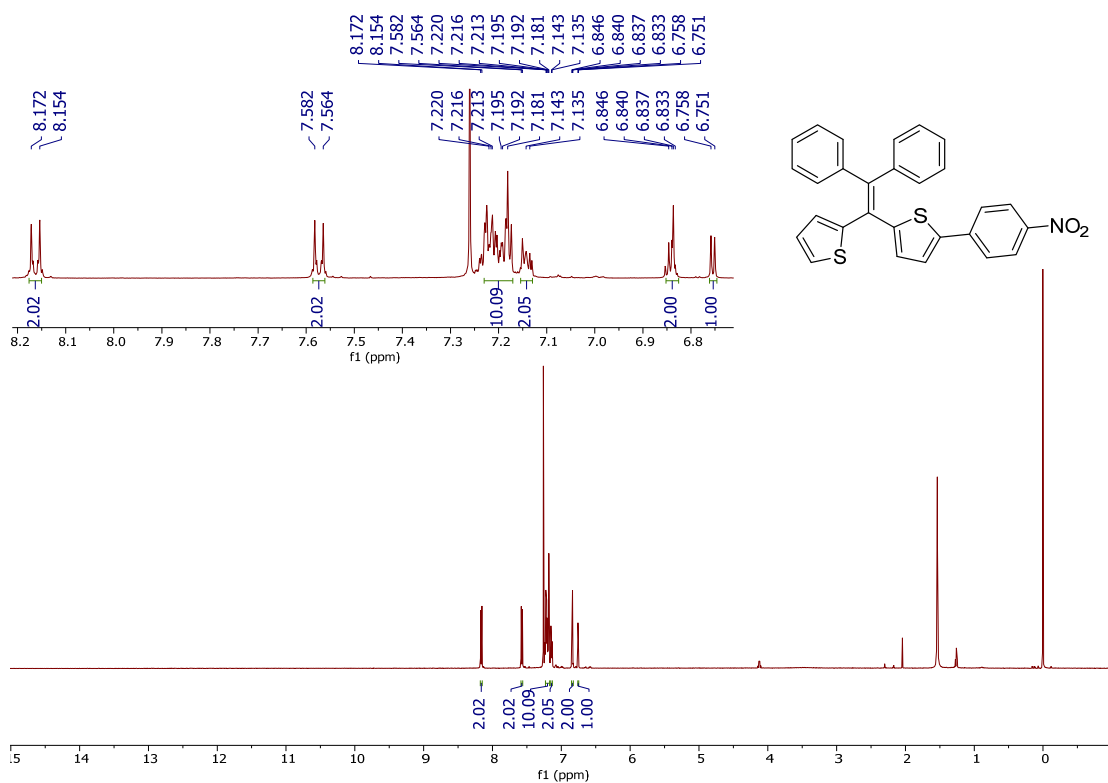
2c (42 mg, 44 %), yellow solid. ¹H-NMR δ_H (500 MHz, CDCl₃, δ ppm): δ 7.96 (2H, *d*, *J* = 8.5 Hz), δ 7.52 (2H, *d*, *J* = 8.5 Hz), δ 7.21-7.12 (12H, *m*), δ 6.83 (2H, *d*, *J* = 3.5 Hz), δ 6.72 (1H, *d*, *J* = 4.0 Hz), δ 3.91 (3H, *s*); ¹³C-NMR δ_C (125 MHz, CDCl₃, δ ppm): δ 166.8, 147.0, 145.1, 143.2, 143.0, 131.0, 130.7, 130.6, 130.2, 129.9, 128.6, 128.2, 128.0, 127.3, 127.1, 126.6, 126.3, 125.1, 123.8, 52.1. HR-MS calcd for C₃₀H₂₃O₂S₂ ([M+H]⁺): 479.1139, found: 479.1136.

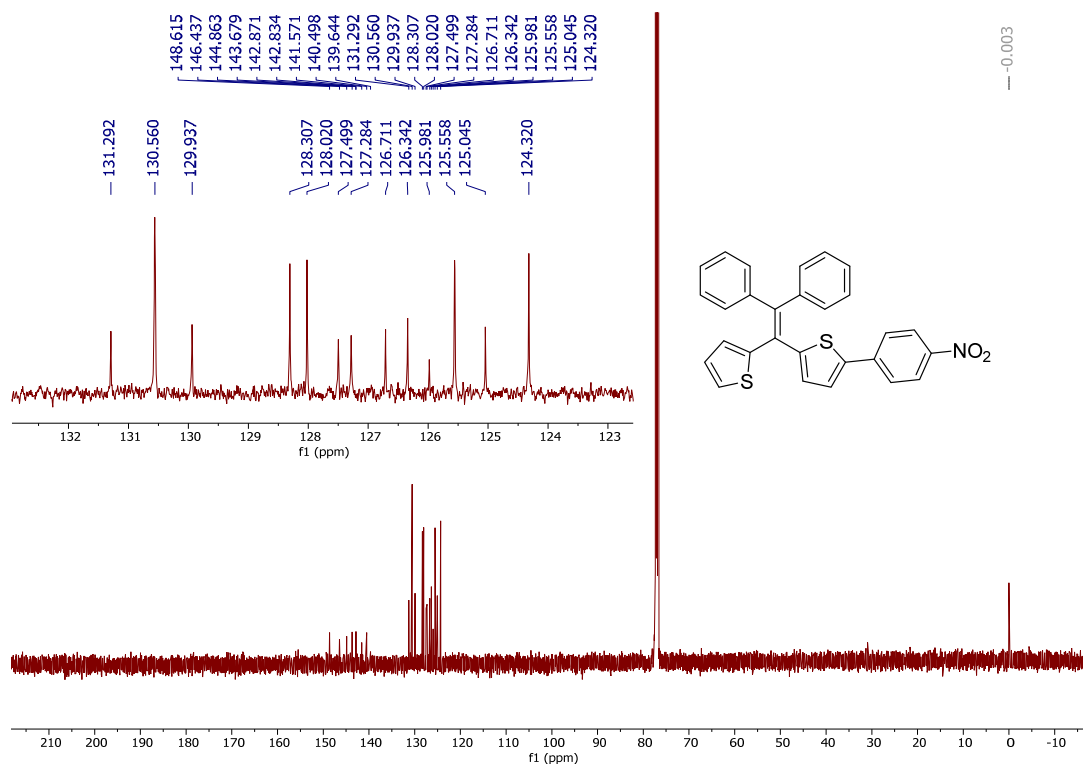


1-(2-(4-nitrophenyl)thien-5-yl)-1-thien-5-yl-2,2-diphenylethene (2d)

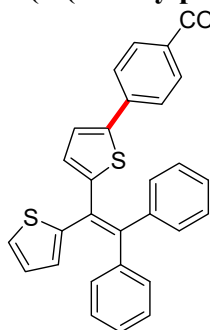


2d (44 mg, 47 %), orange solid. $^1\text{H-NMR}$ δ_{H} (500 MHz, CDCl_3 , δ ppm): δ 8.16 (2H, *d*, $J = 9.0$ Hz), δ 7.57 (2H, *d*, $J = 9.0$ Hz), δ 7.22-7.17 (10H, *m*), δ 7.14 (2H, *m*), δ 6.85-6.84 (2H, *m*), δ 6.75 (1H, *d*, $J = 3.5$ Hz); $^{13}\text{C-NMR}$ δ_{C} (125 MHz, CDCl_3 , δ ppm): δ 148.6, 146.4, 144.9, 143.7, 142.9, 142.8, 141.6, 140.5, 139.6, 131.3, 130.6, 129.9, 128.3, 128.0, 127.5, 127.3, 126.7, 126.3, 126.0, 125.6, 125.0, 124.3. HR-MS calcd for $\text{C}_{28}\text{H}_{19}\text{NO}_2\text{S}_2$ ($[\text{M}]^+$): 465.0857, found: 465.0822.

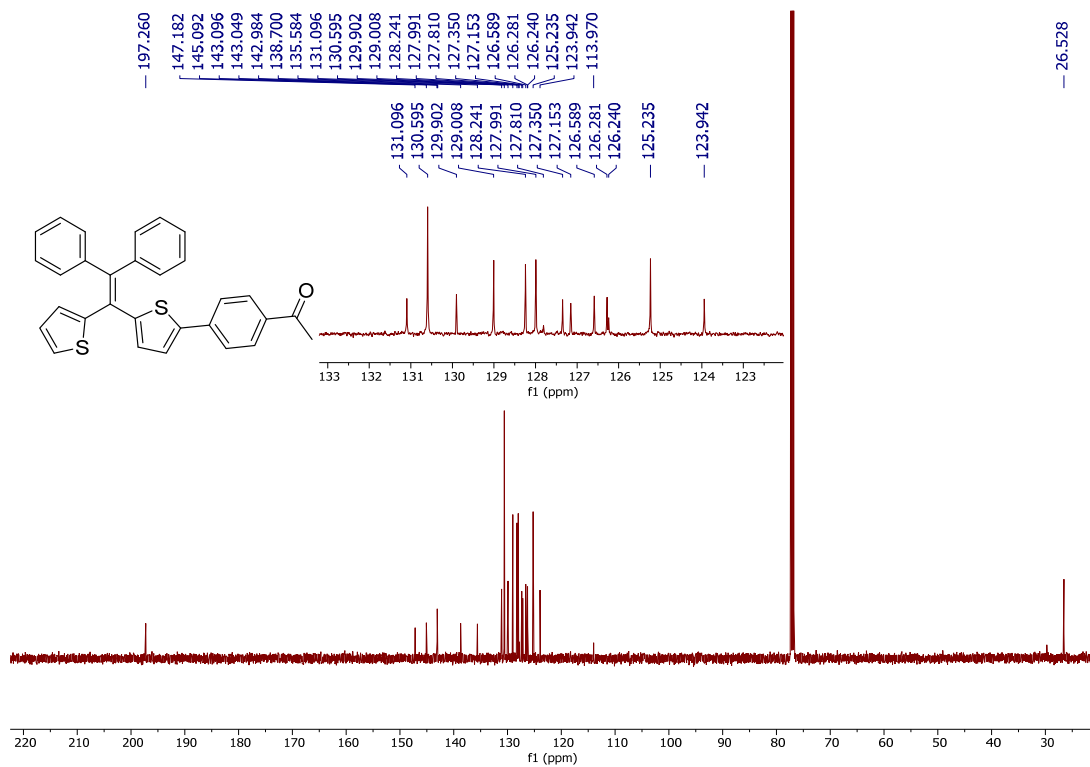
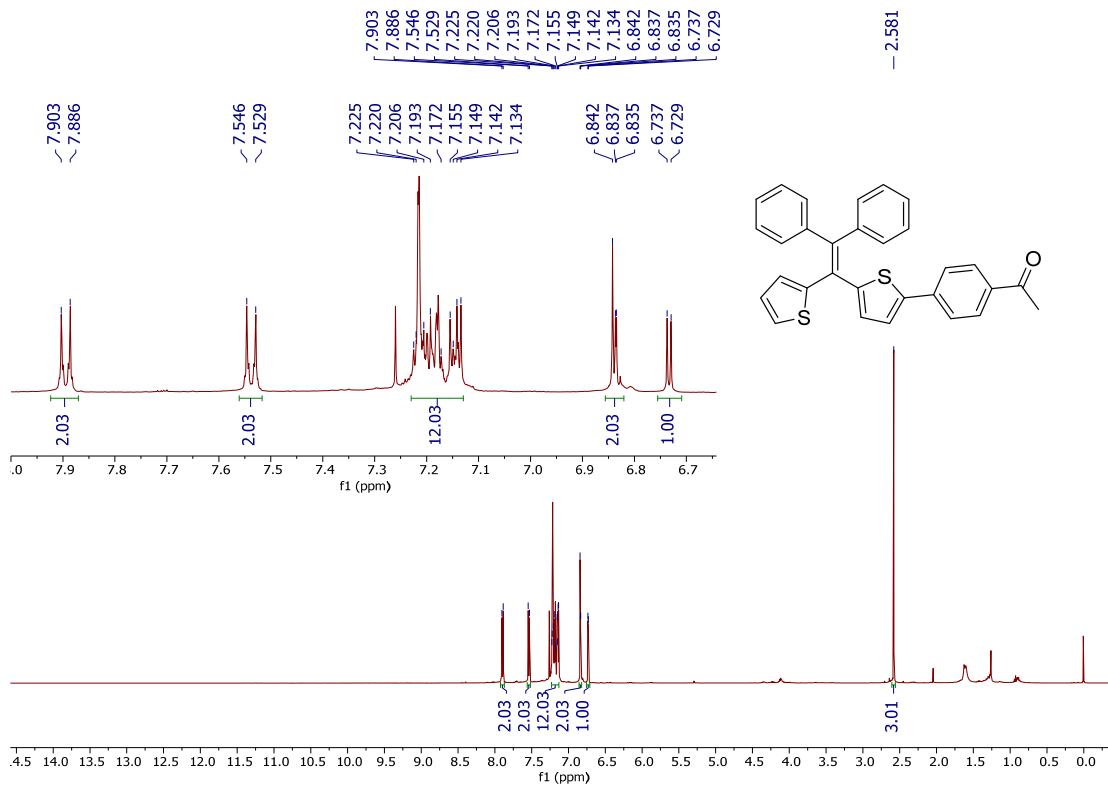




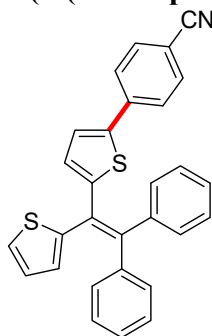
1-(2-(4-acetylphenyl)thien-5-yl)-1-thien-5-yl-2,2-diphenylethene (2e)



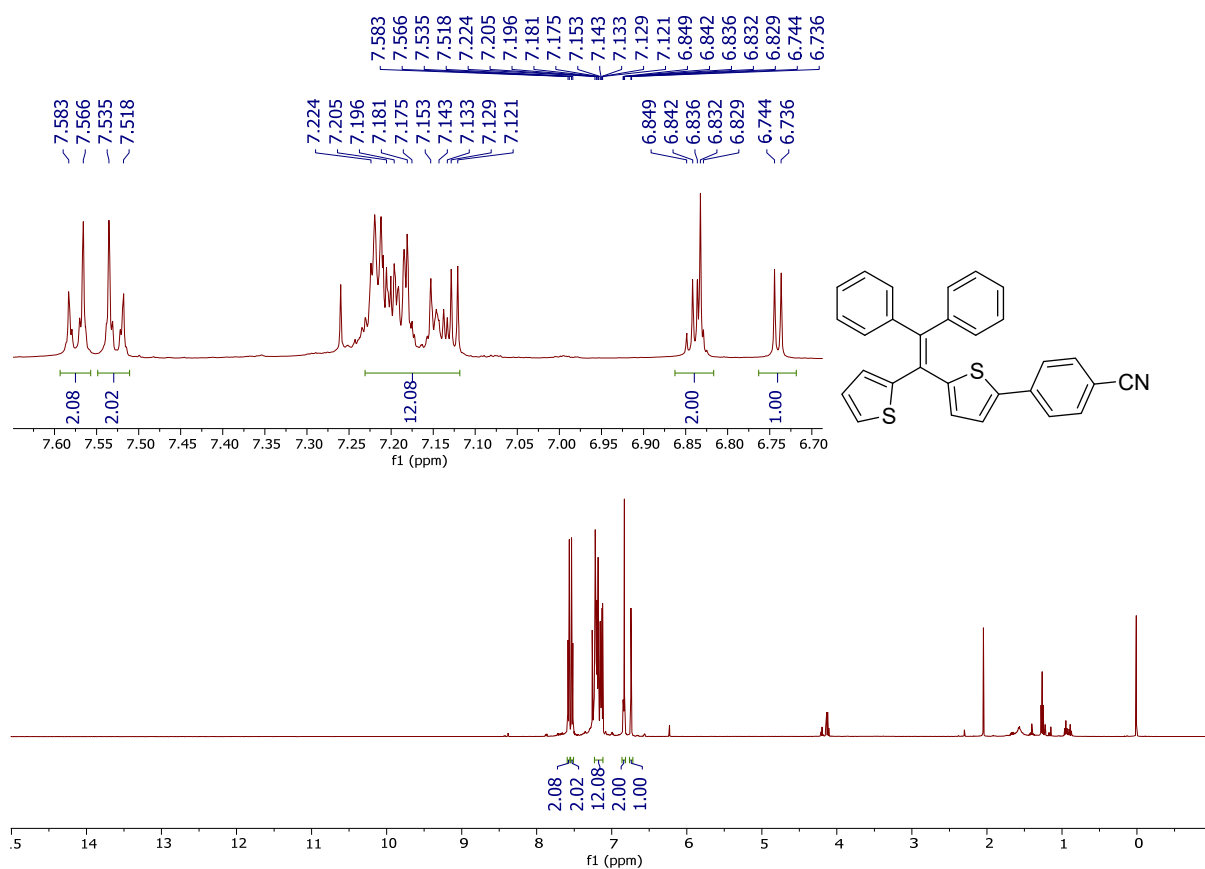
2e (38 mg, 41 %), yellow solid. ¹H-NMR δ_H (500 MHz, CDCl₃, δ ppm): δ 7.89 (2H, *d*, *J* = 8.5 Hz), δ 7.54 (2H, *d*, *J* = 8.5 Hz), δ 7.22-7.13 (12H, *m*), δ 6.84-6.83 (2H, *m*), δ 6.73 (2H, *d*, *J* = 4.0 Hz), δ 2.58 (3H, *s*, -CH₃); ¹³C-NMR δ_C (125 MHz, CDCl₃, δ ppm): δ 197.3, 147.2, 145.1, 143.1, 143.0, 142.9, 138.7, 135.6, 131.1, 130.6, 129.9, 129.0, 128.2, 127.9, 127.8, 127.3, 127.1, 126.6, 126.3, 125.2, 123.9, 26.5. HR-MS calcd for C₃₀H₂₃OS₂ ([M+H]⁺): 463.1190, found: 463.1165.

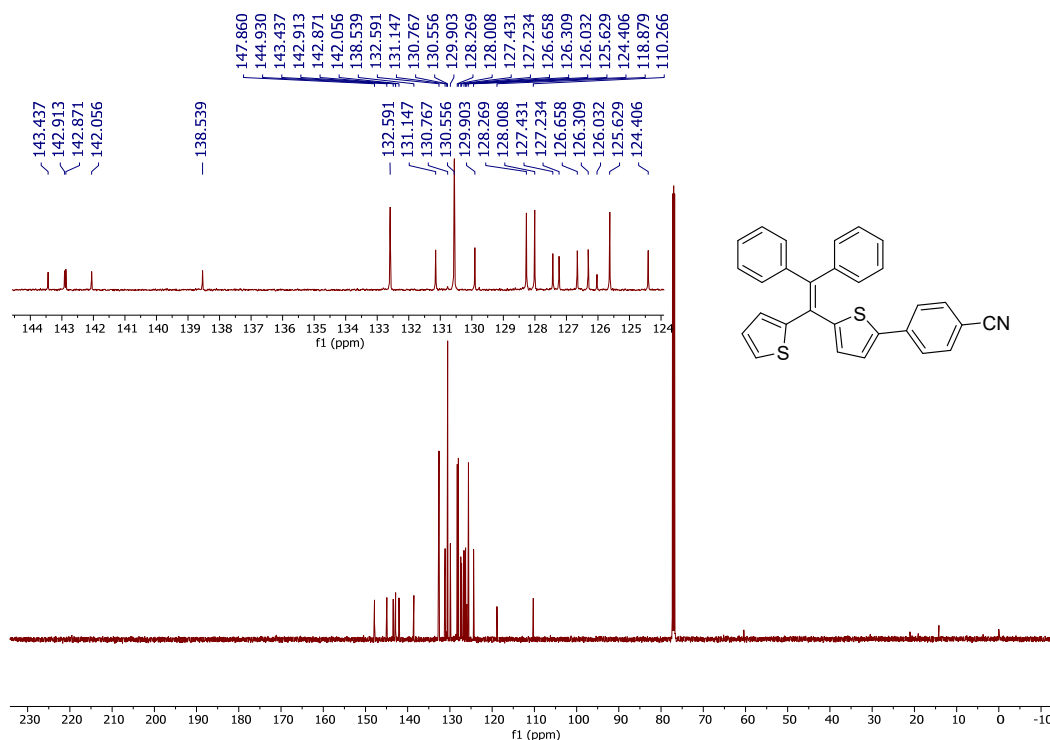


1-(2-(4-nitrilphenyl)thien-5-yl)-1-thien-5-yl-2,2-diphenylethene (2f)

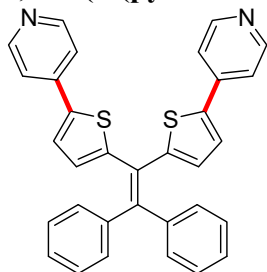


2f (45 mg, 50 %), orange solid. $^1\text{H-NMR}$ δ_{H} (500 MHz, CDCl_3 , δ ppm): δ 7.57 (2H, *d*, J = 8.5 Hz), δ 7.53 (2H, *d*, J = 8.5 Hz), δ 7.22-7.12 (12H, *m*), δ 6.85-6.83 (2H, *m*), δ 6.74 (1H, *d*, J = 4.0 Hz); $^{13}\text{C-NMR}$ δ_{C} (125 MHz, CDCl_3 , δ ppm): δ 147.9, 144.9, 143.4, 142.9, 142.8, 142.1, 138.5, 132.6, 131.1, 130.8, 130.6, 129.9, 129.8, 128.3, 128.0, 127.4, 127.2, 126.7, 126.3, 126.0, 125.6, 124.4, 118.9, 110.3. HR-MS calcd for $\text{C}_{29}\text{H}_{20}\text{NS}_2$ ($[\text{M}+\text{H}]^+$): 446.1037, found: 446.1021.

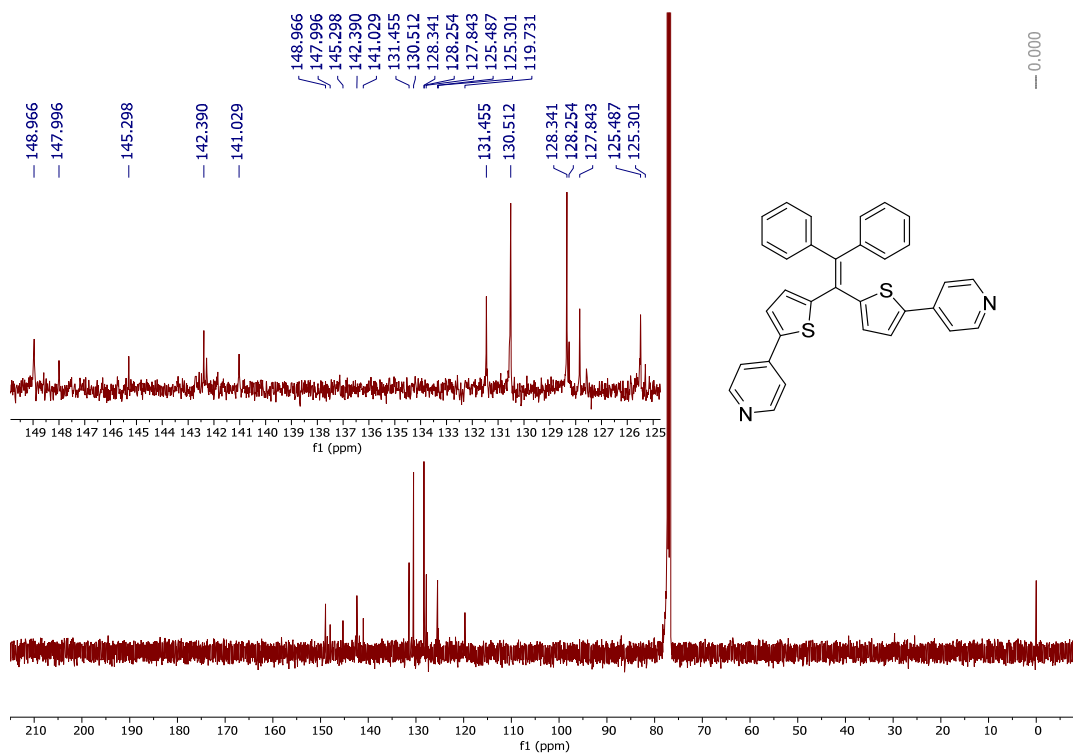
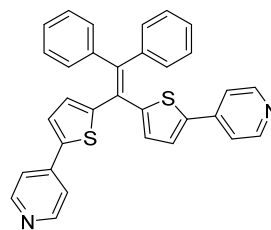
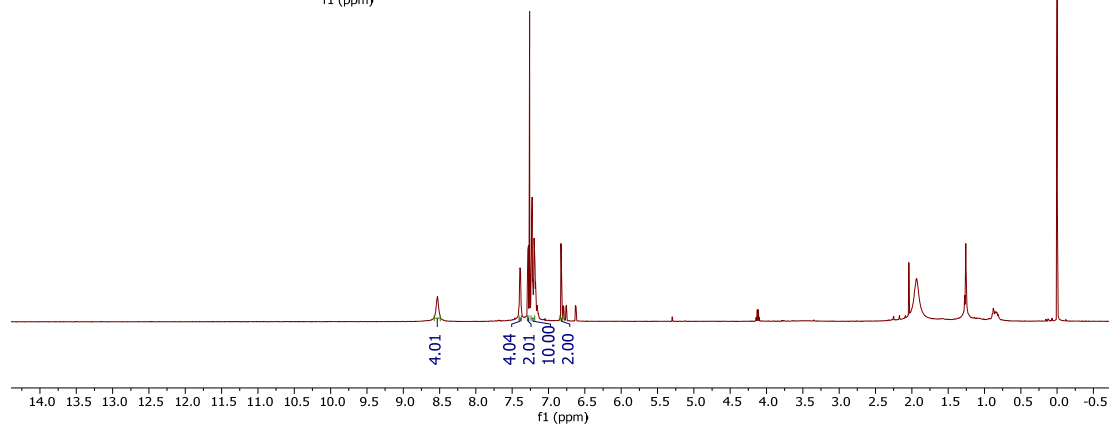
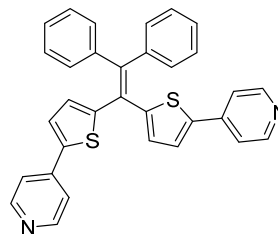
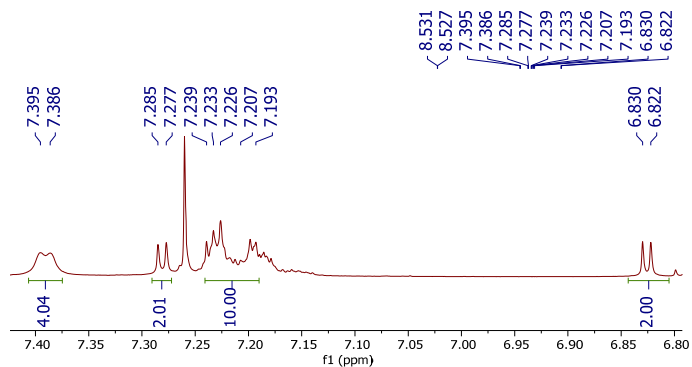




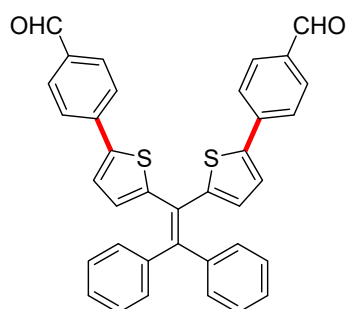
1,1-Di(2-(pyridine-4-yl)thien-5-yl)-2,2-diphenylethene (3a)



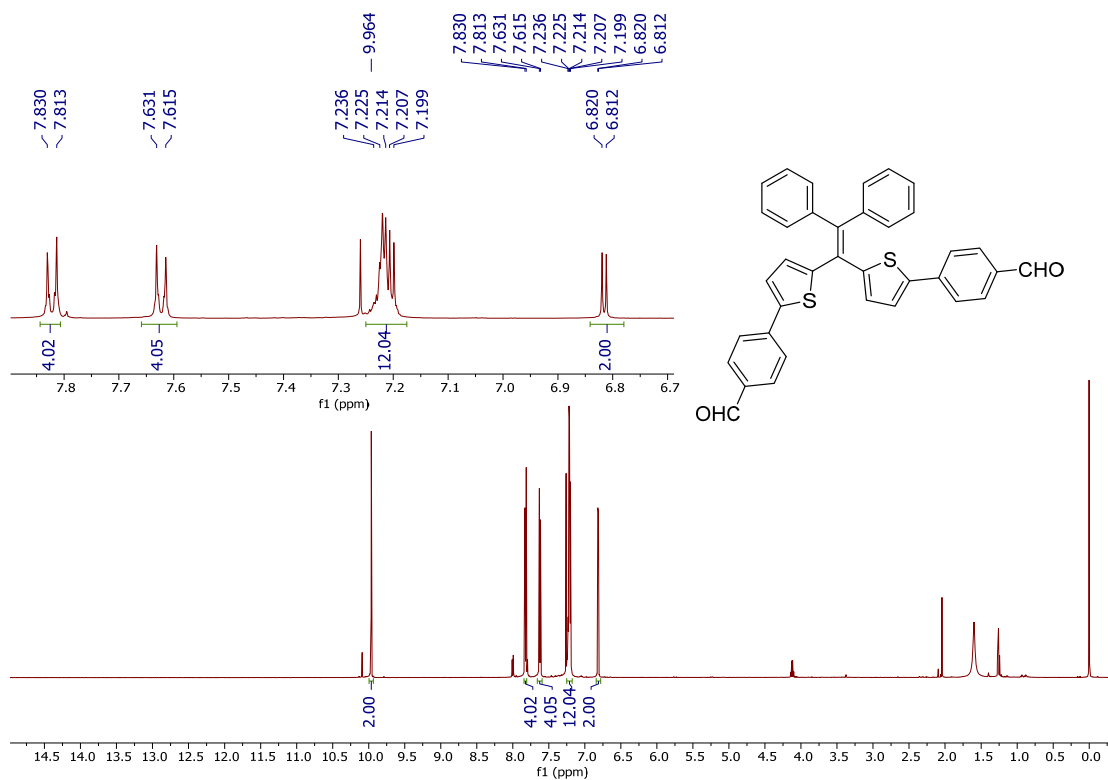
3a (49 mg, 49 %), yellow solid. ¹H-NMR δ_H (500 MHz, CDCl₃, δ ppm): δ 8.53 (4H, *brs*), δ 7.39 (4H, *d*, *J* = 4.5 Hz), δ 7.28 (2H, *d*, *J* = 4.0 Hz), δ 7.23-7.19 (10H, *m*), δ 6.83 (2H, *d*, *J* = 4.0 Hz); ¹³C-NMR δ_C (125 MHz, CDCl₃, δ ppm): δ 149.0, 148.0, 145.3, 142.4, 141.0, 131.5, 130.5, 128.3, 128.2, 127.8, 125.5, 125.3, 119.7. HR-MS calcd for C₃₂H₂₃N₂S₂ ([M+H]⁺): 499.1303, found: 499.1291.

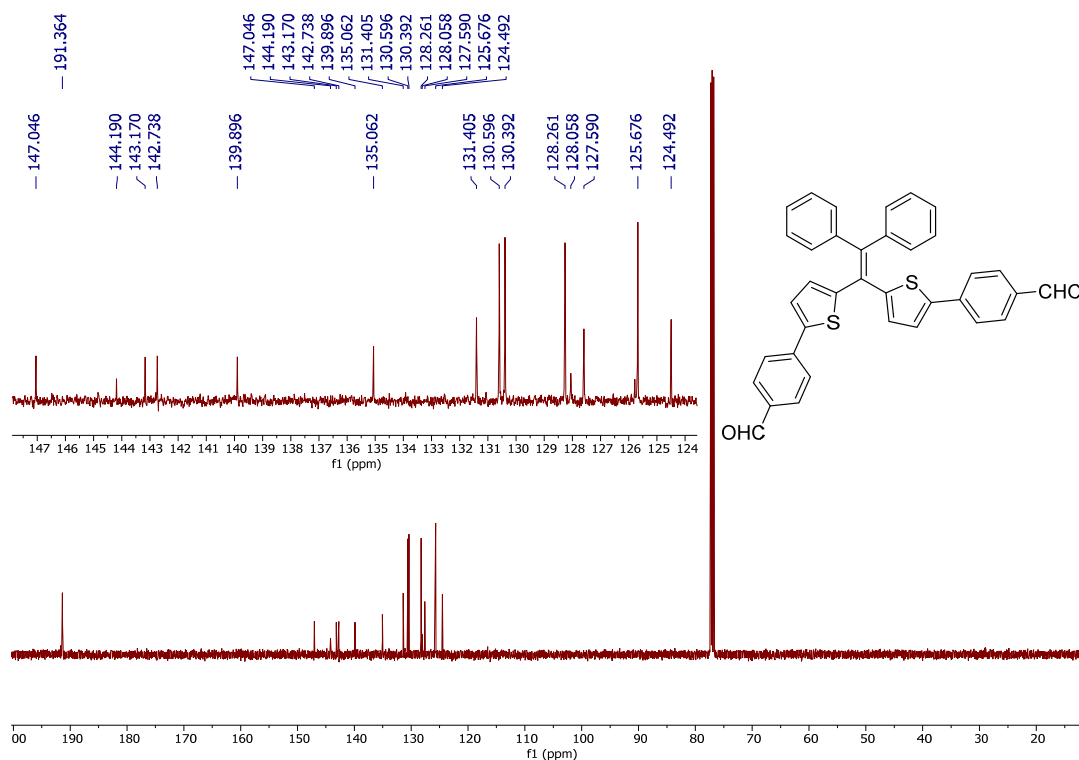


1,1-Di(2-(4-formylphenyl)thien-5-yl)-2,2-diphenylethene (3b)

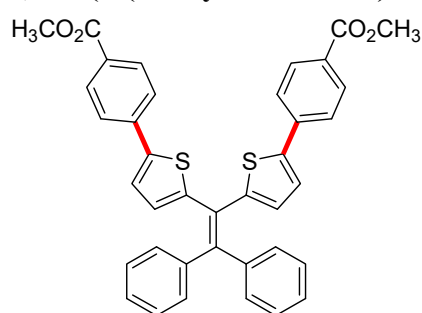


3b (72 mg, 65 %), yellow solid. $^1\text{H-NMR}$ δ_{H} (500 MHz, CDCl_3 , δ ppm): δ 9.96 (2H, s), δ 7.82 (4H, d, $J = 8.5$ Hz), δ 7.62 (4H, d, $J = 8.0$ Hz), δ 7.22-7.21 (12H, m), δ 6.82 (2H, d, $J = 4.0$ Hz); $^{13}\text{C-NMR}$ δ_{C} (125 MHz, CDCl_3 , δ ppm): δ 191.4, 147.0, 144.2, 143.2, 142.7, 139.9, 135.1, 131.4, 130.6, 130.4, 128.3, 128.1, 127.6, 125.7, 124.5. HR-MS calcd for $\text{C}_{36}\text{H}_{25}\text{O}_2\text{S}_2$ ($[\text{M}+\text{H}]^+$): 553.1296, found: 553.1309.

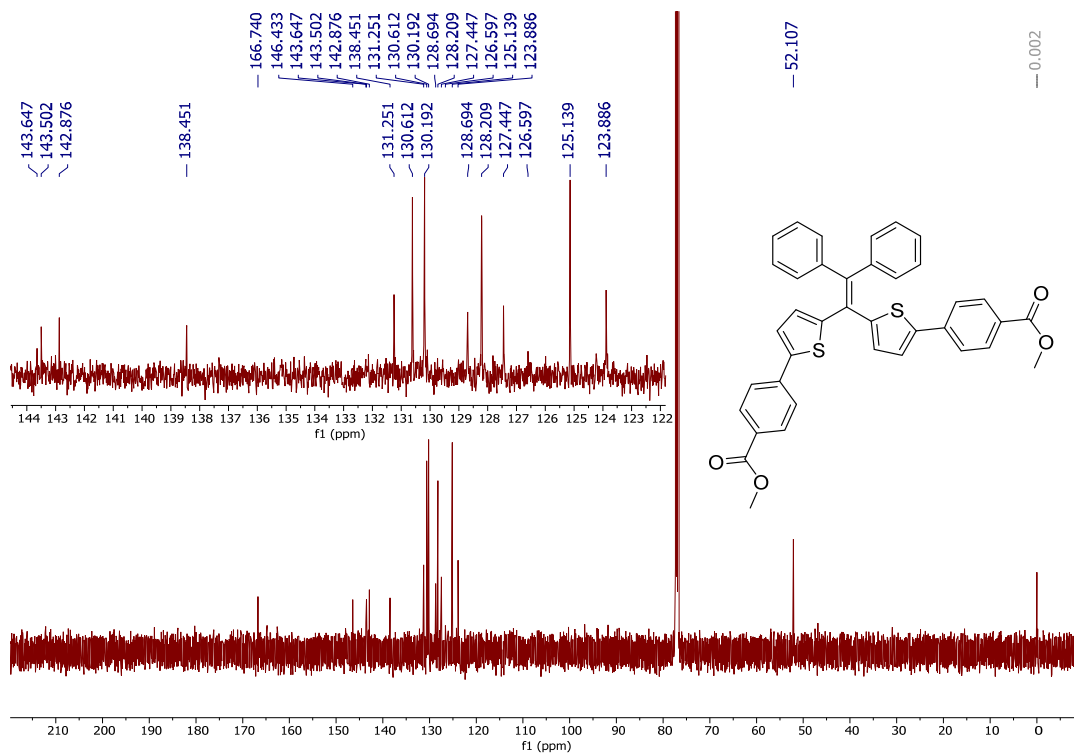
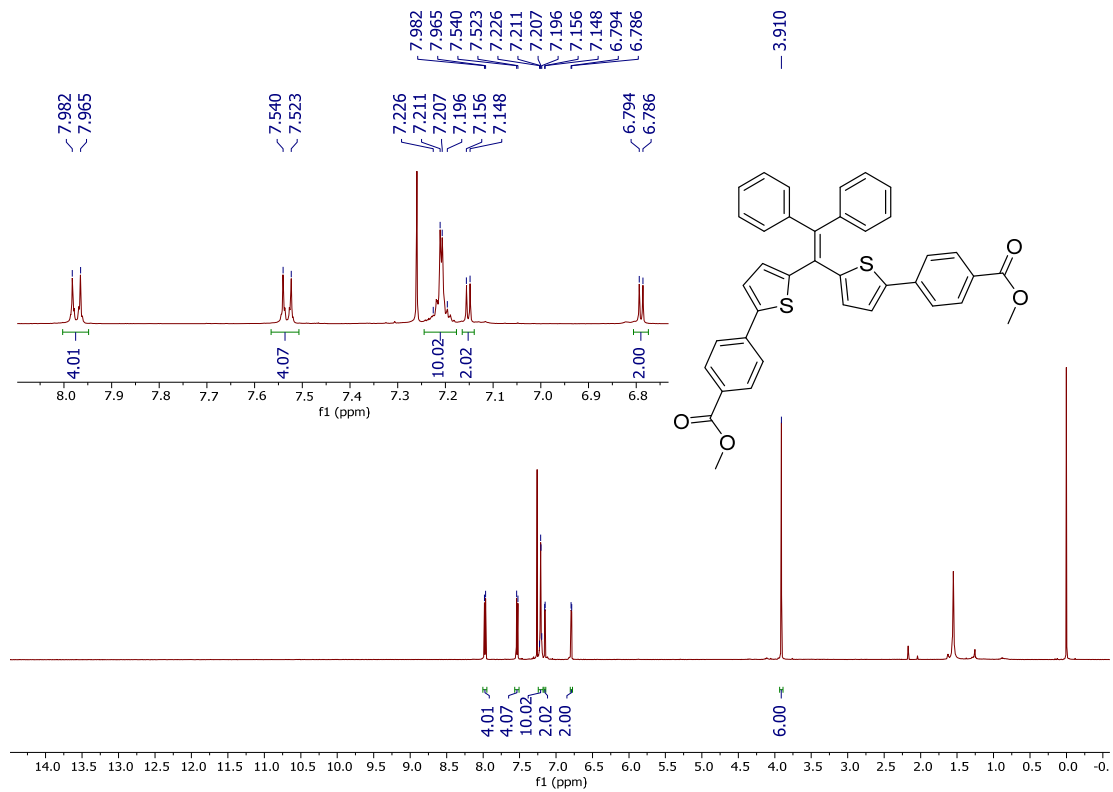


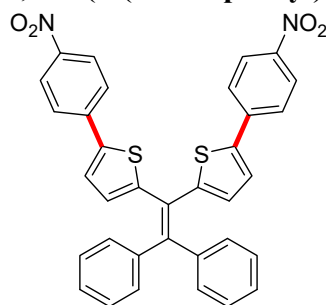


1,1-Di(2-(methyl 4-benzoate)thien-5-yl)-2,2-diphenylethene (3c)

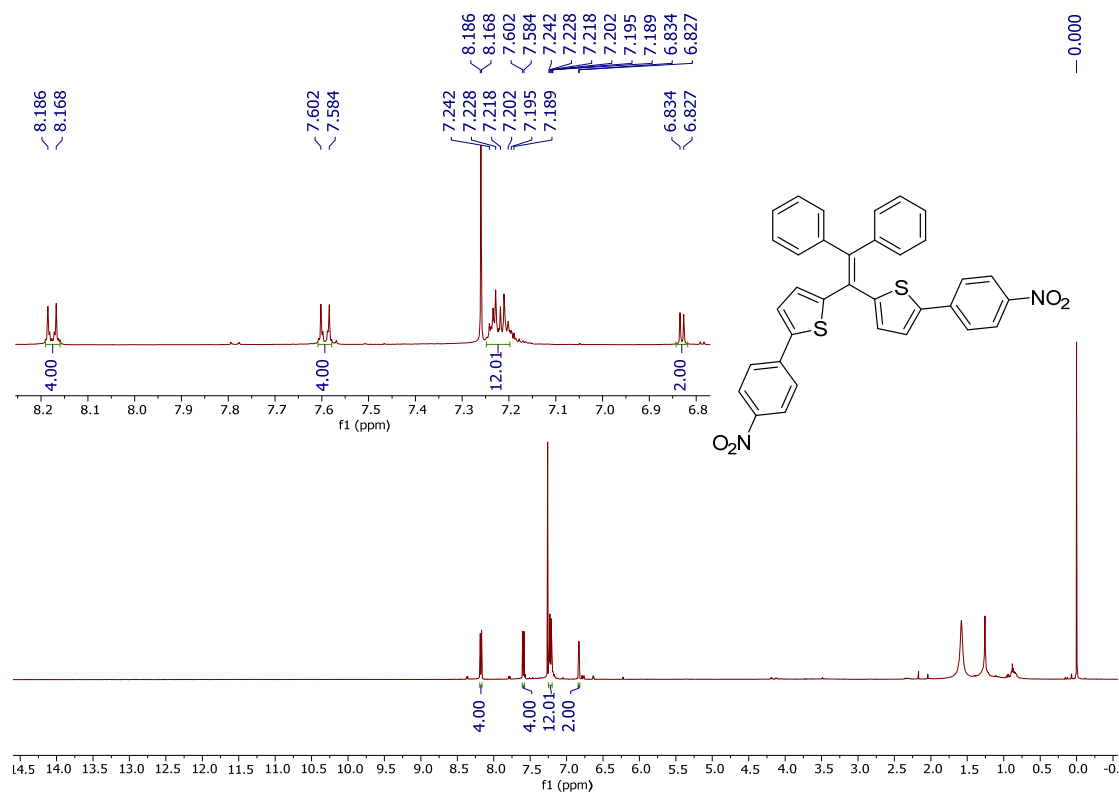


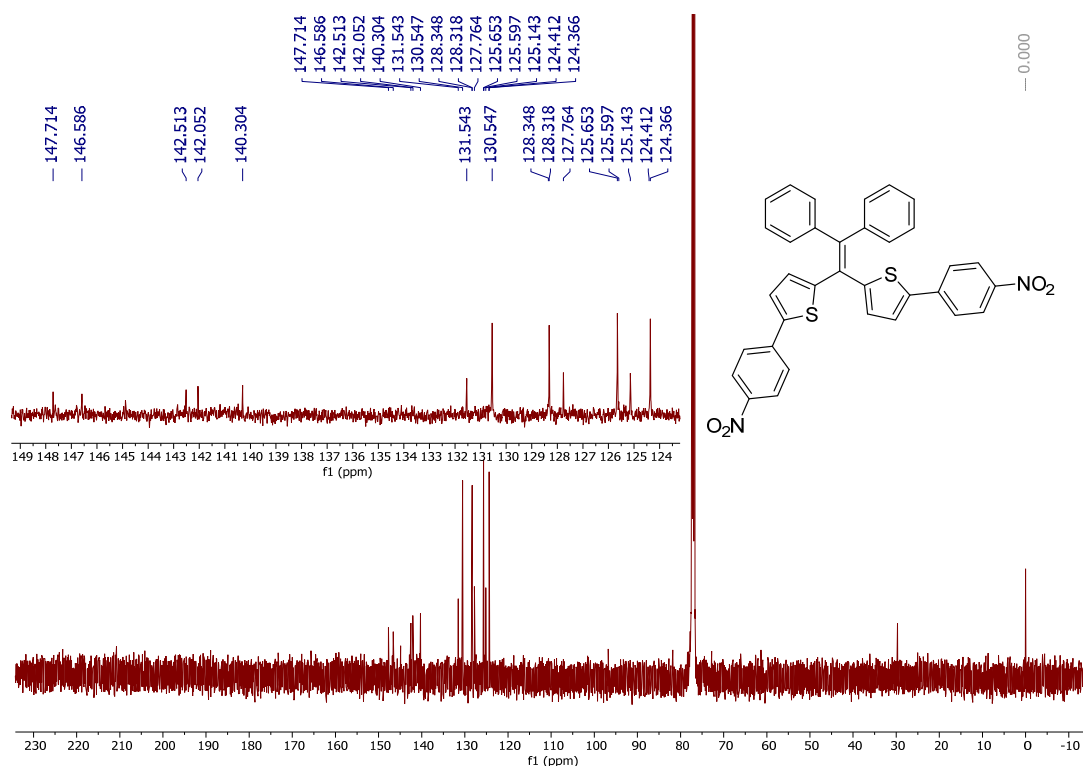
3c (74 mg, 61 %), yellow solid. ¹H-NMR δ_{H} (500 MHz, CDCl₃, δ ppm): δ 7.97 (4H, *d*, *J* = 9.0 Hz), δ 7.53 (4H, *d*, *J* = 9.0 Hz), δ 7.21-7.19 (10H, *m*), δ 7.15 (2H, *d*, *J* = 4.0 Hz), δ 6.79 (2H, *d*, *J* = 4.0 Hz), δ 3.91 (6H, *s*); ¹³C-NMR δ_{C} (125 MHz, CDCl₃, δ ppm): δ 166.7, 146.4, 143.6, 143.5, 142.9, 138.5, 131.3, 130.6, 130.2, 128.7, 128.2, 127.4, 126.6, 125.1, 123.9, 52.1. HR-MS calcd for C₃₈H₂₈O₄S₂ ([M]⁺): 612.1429, found: 612.1421.



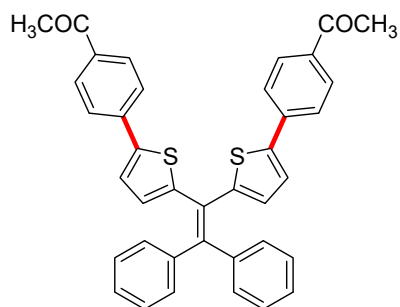
1,1-Di(2-(4-nitrophenyl)thien-5-yl)-2,2-diphenylethene (3d)

3d (73 mg, 62 %), orange solid. $^1\text{H-NMR}$ δ_{H} (500 MHz, CDCl_3 , δ ppm): δ 8.18 (4H, *d*, $J = 9.0$ Hz), δ 7.59 (4H, *d*, $J = 8.0$ Hz), δ 7.24-7.19 (12H, *m*), δ 6.83 (2H, *d*, $J = 3.5$ Hz); $^{13}\text{C-NMR}$ δ_{C} (125 MHz, CDCl_3 , δ ppm): δ 147.7, 147.6, 146.6, 144.9, 142.5, 142.1, 140.3, 131.5, 130.5, 128.3, 127.8, 125.7, 125.6, 125.1, 124.4. HR-MS calcd for $\text{C}_{34}\text{H}_{23}\text{N}_2\text{O}_4\text{S}_2$ ($[\text{M}+\text{H}]^+$): 587.1099, found: 587.1078.

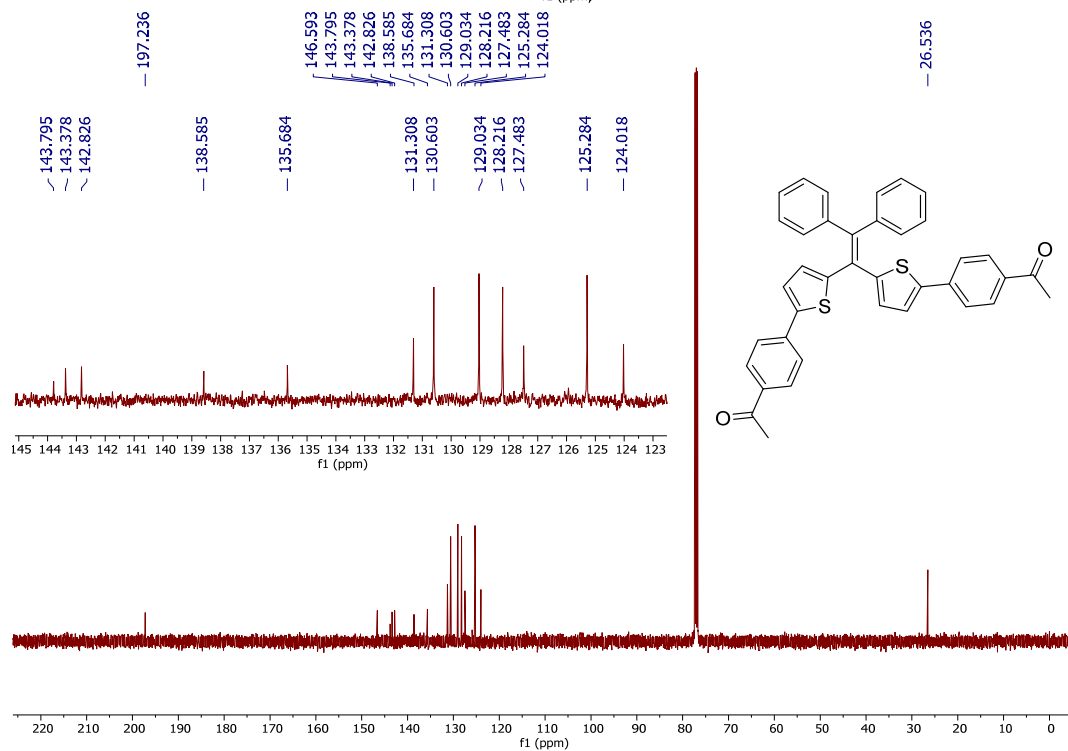
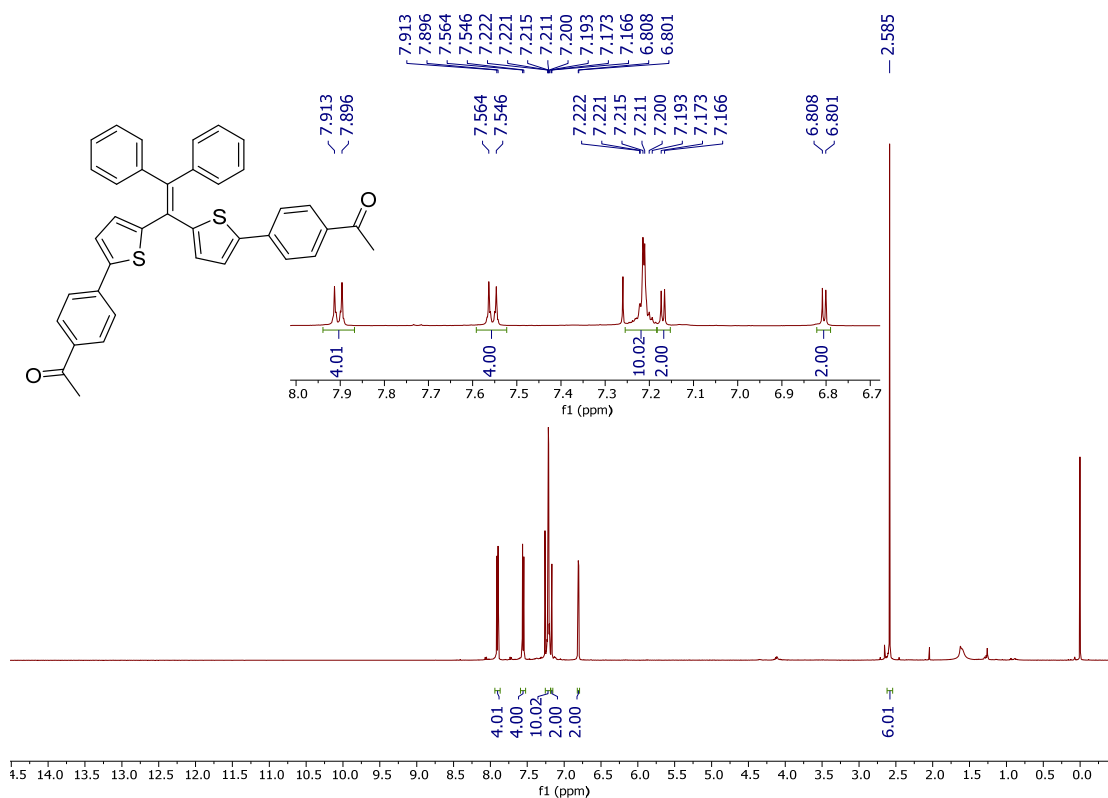




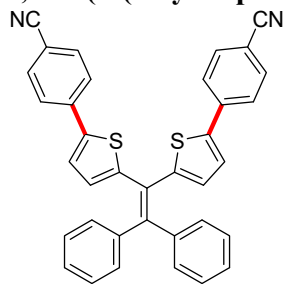
1,1-Di(2-(4-acetylphenyl)thien-5-yl)-2,2-diphenylethene (3e)



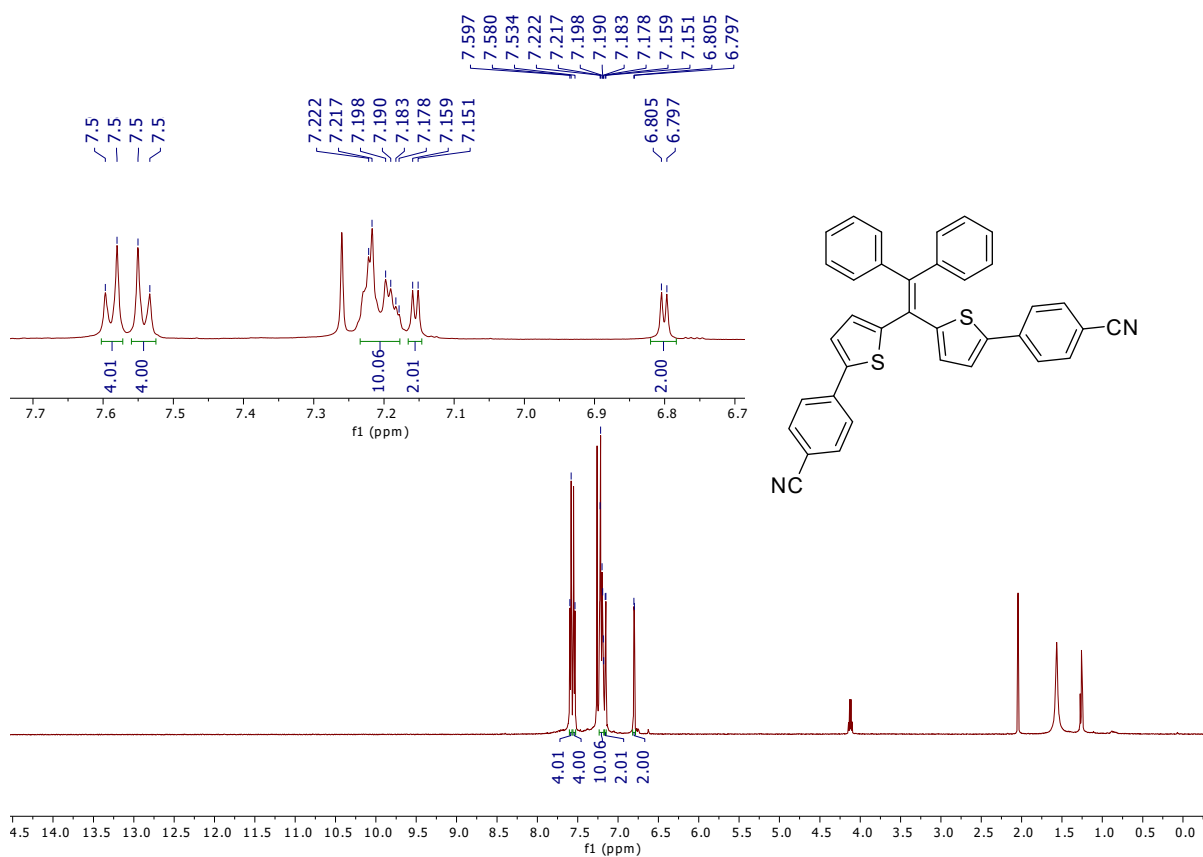
3e (68 mg, 59 %), yellow solid. ¹H-NMR δ_{H} (500 MHz, CDCl₃, δ ppm): δ 7.91 (4H, *d*, *J* = 8.5 Hz), δ 7.56 (4H, *d*, *J* = 8.5 Hz), δ 7.17 (2H, *d*, *J* = 4.0 Hz), δ 7.23-7.19 (10H, *m*), δ 6.80 (2H, *d*, *J* = 4.0 Hz), δ 2.58 (6H, *s*); ¹³C-NMR δ_{C} (125 MHz, CDCl₃, δ ppm): δ 197.2, 146.6, 143.8, 143.4, 142.8, 138.6, 135.7, 131.3, 130.6, 129.0, 128.2, 127.5, 125.3, 124.0, 26.5. HR-MS calcd for C₃₈H₂₈O₂S₂ ([M]⁺): 580.1531, found: 580.1506.

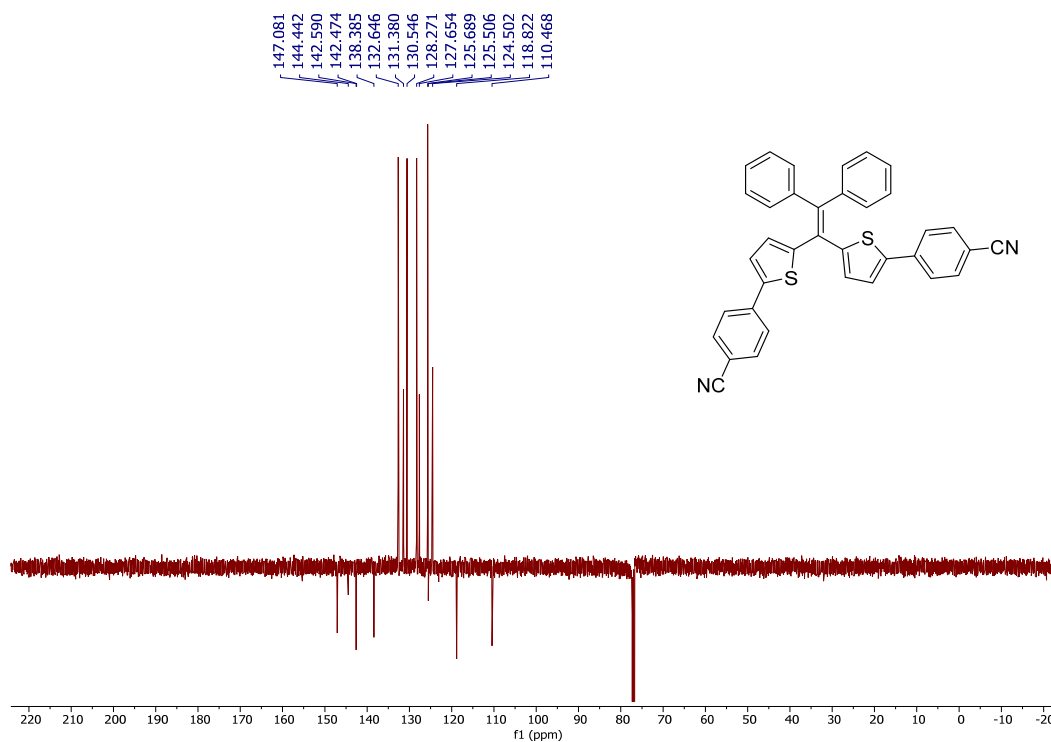


1,1-Di(2-(4-cyanophenyl)thien-5-yl)-2,2-diphenylethene (3f)

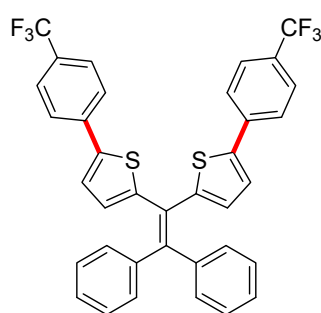


3f (72 mg, 66 %), yellow solid. $^1\text{H-NMR}$ δ_{H} (500 MHz, CDCl_3 , δ ppm): δ 7.59 (4H, *d*, $J = 8.5$ Hz), δ 7.54 (4H, *d*, $J = 8.5$ Hz), δ 7.23-7.19 (10H, *m*), δ 7.16 (2H, *d*, $J = 4.0$ Hz), δ 6.80 (2H, *d*, $J = 4.0$ Hz); $^{13}\text{C-NMR}$ δ_{C} (125 MHz, CDCl_3 , δ ppm): δ 147.1, 144.4, 142.6, 142.5, 138.4, 132.6, 131.4, 130.5, 128.3, 127.7, 125.7, 125.5, 124.5, 118.8, 110.5. HR-MS calcd for $\text{C}_{36}\text{H}_{22}\text{N}_2\text{S}_2$ ($[\text{M}]^+$): 546.1224, found: 546.1218.

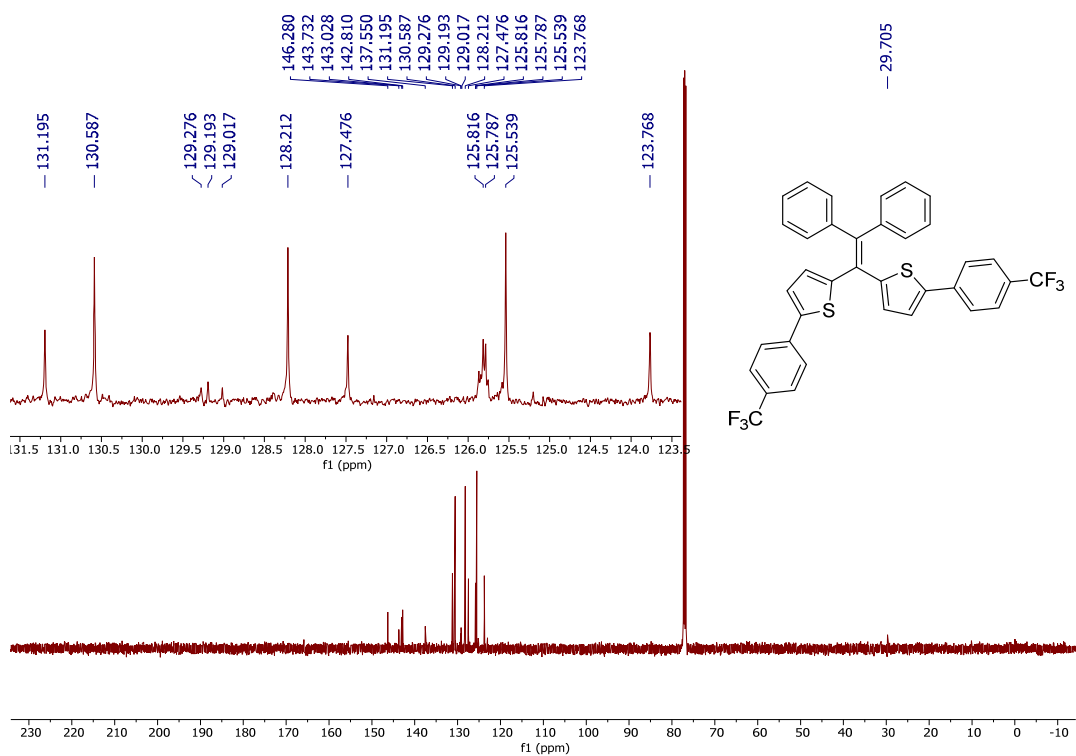
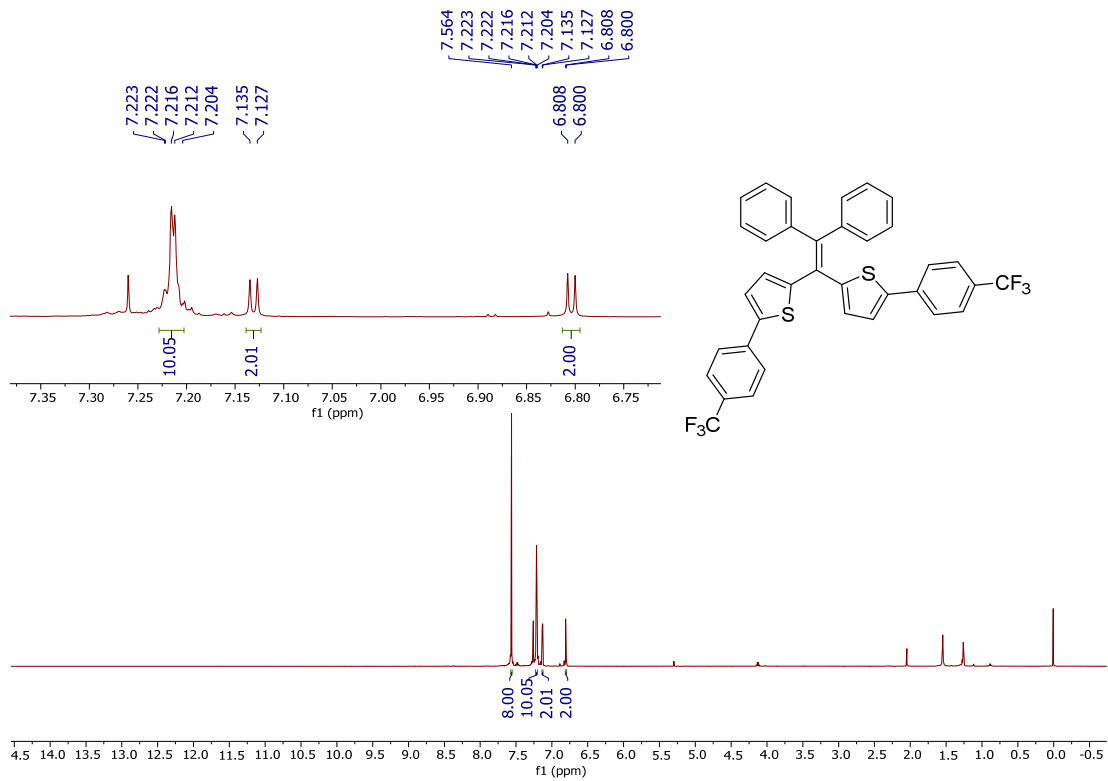




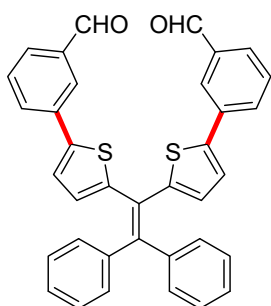
1,1-Di(2-(4-trifluoromethylphenyl)thien-5-yl)-2,2-diphenyl ethene (3g)



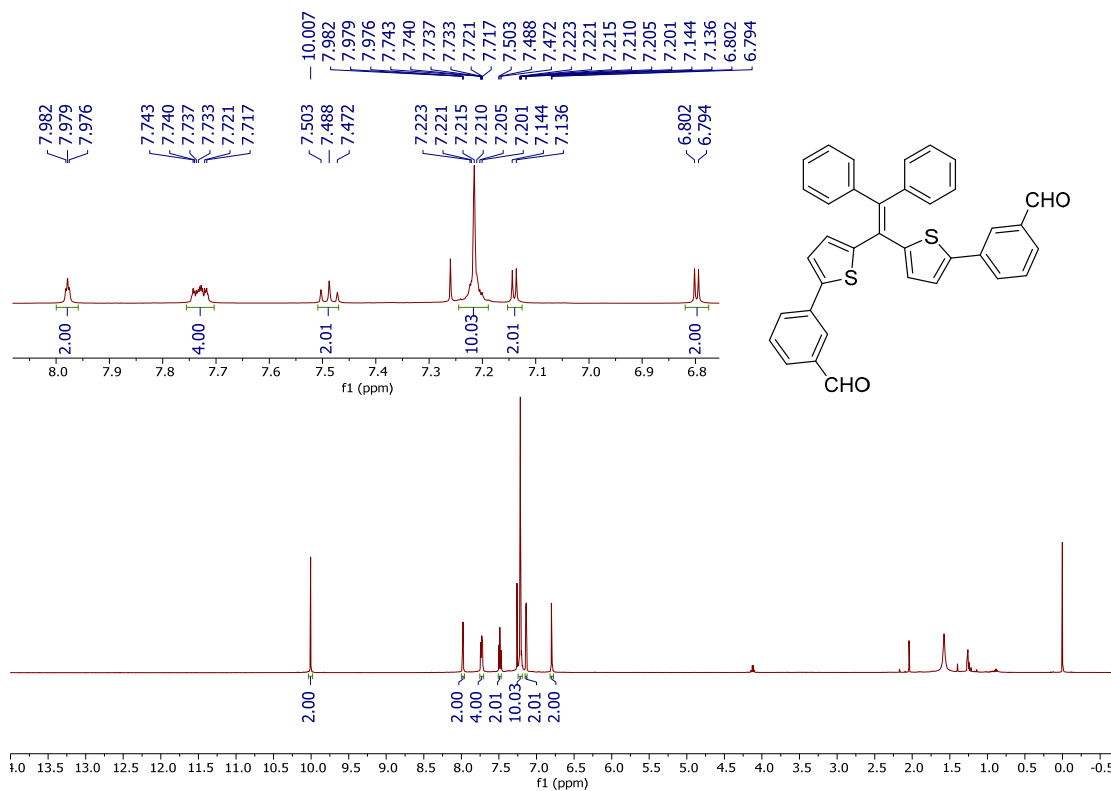
3g (70 mg, 55 %), yellow solid. ¹H-NMR δ_H (500 MHz, CDCl₃, δ ppm): δ 7.56 (8H, *s*), δ 7.22-7.19 (10H, *m*), δ 7.13 (2H, *d*, *J* = 4.0 Hz), 6.80 (2H, *d*, *J* = 4.0 Hz); ¹³C-NMR δ_C (125 MHz, CDCl₃, δ ppm): δ 146.3, 143.7, 143.0, 142.8, 137.6, 131.2, 130.6, 129.3, 129.2, 129.0, 128.2, 127.5, 125.9, 125.8, 125.5, 123.8, 29.3. HR-MS calcd for C₃₆H₂₂F₆S₂ ([M]⁺): 632.1067, found: 632.1065.

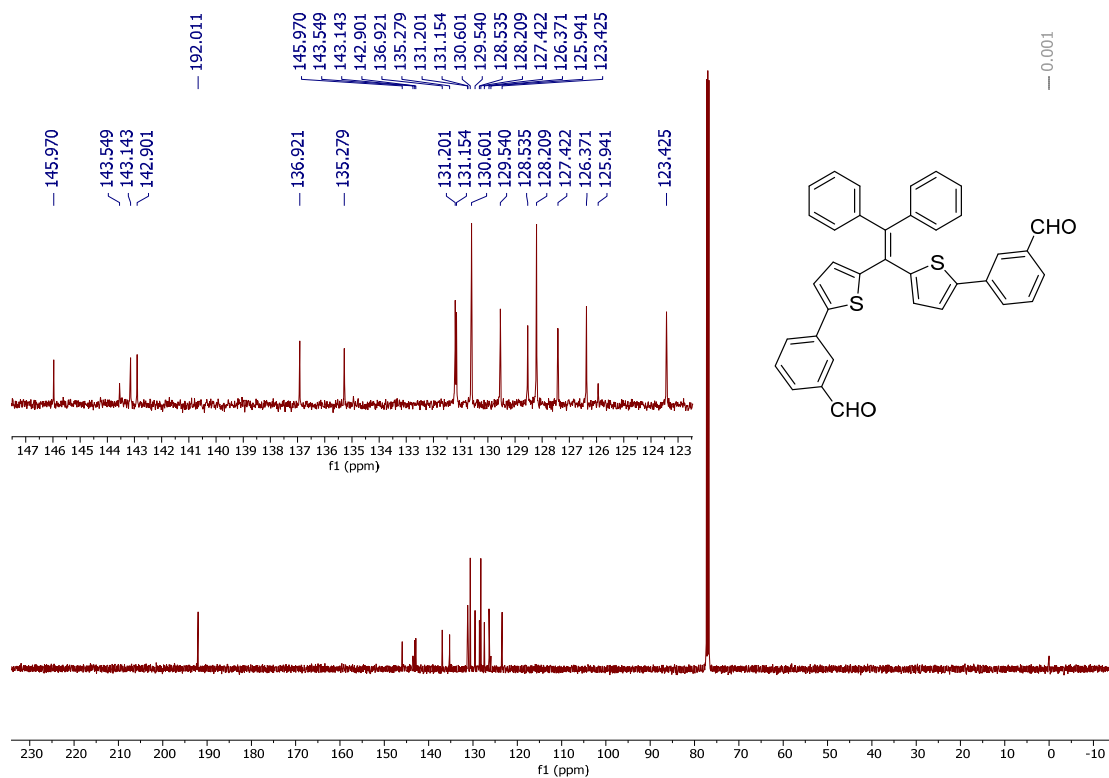


1,1-Di(2-(3-formylphenyl)thien-5-yl)-2,2-diphenyl ethene (3h)

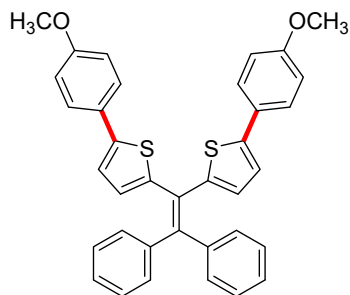


3h (67 mg, 61 %), yellow solid. $^1\text{H-NMR}$ δ_{H} (500 MHz, CDCl_3 , δ ppm): δ 10.01 (2H, *s*), δ 7.98 (2H, *t*), δ 7.74-7.72 (4H, *m*), δ 7.49 (2H, *t*, $J=7.5$ Hz), δ 7.22-7.20 (10H, *m*), δ 7.14 (2H, *d*, $J=4.0$ Hz), δ 6.80 (2H, *d*, $J=4.0$ Hz); $^{13}\text{C-NMR}$ δ_{C} (125 MHz, CDCl_3 , δ ppm): δ 192.0, 146.0, 143.5, 143.1, 142.9, 136.9, 135.3, 131.2, 131.1, 130.6, 129.5, 128.5, 128.2, 127.4, 126.4, 125.9, 123.4. HR-MS calcd for $\text{C}_{36}\text{H}_{24}\text{O}_2\text{S}_2$ ($[\text{M}]^+$): 552.1218, found: 552.1181.

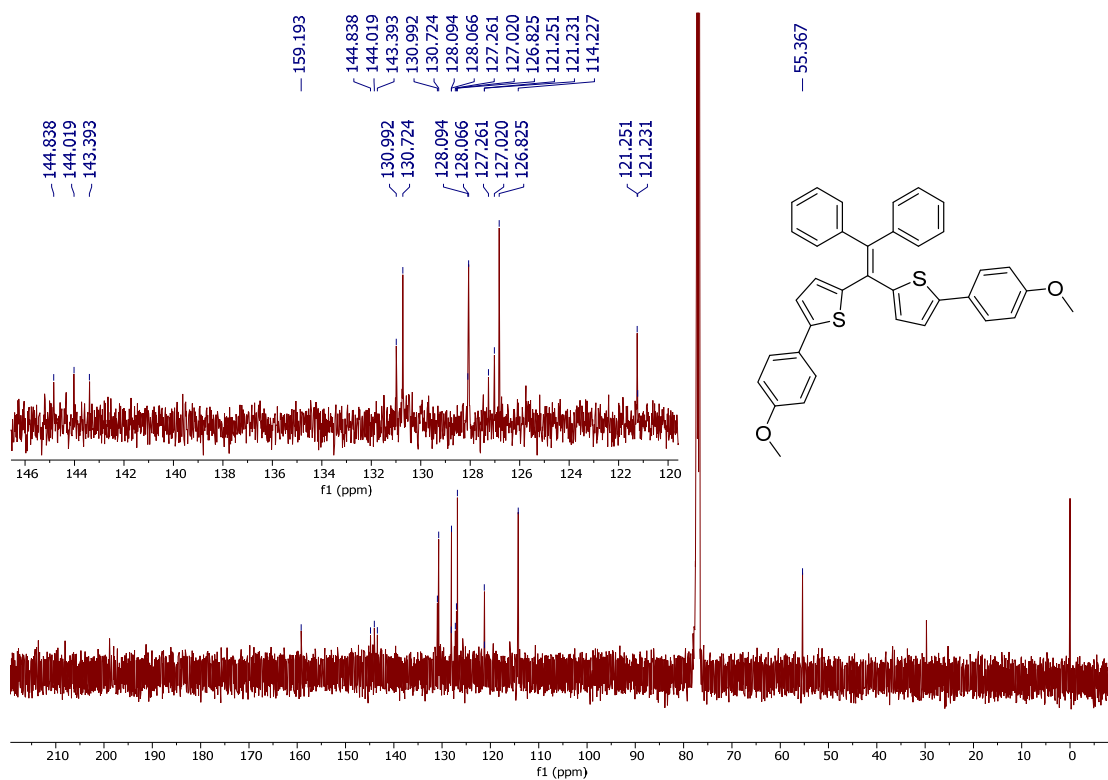
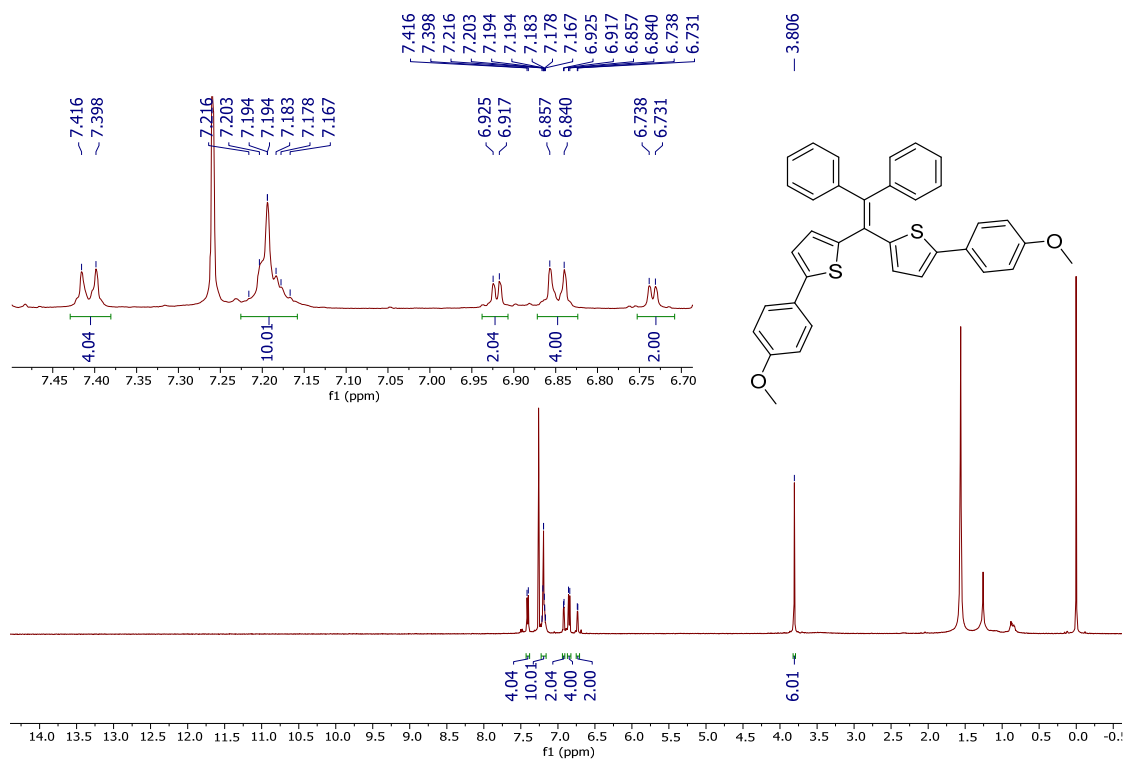




1,1-Di(2-(4-methoxyphenyl)thien-5-yl)-2,2-diphenyl ethene (3i)



3i (34 mg, 31 %), yellow solid. ¹H-NMR δ_H (500 MHz, CDCl₃, δ ppm): δ 7.41 (4H, *d*, *J* = 9.0 Hz), δ 6.85 (4H, *d*, *J* = 8.5 Hz), δ 6.92 (2H, *d*, *J* = 4.0 Hz), δ 7.23-7.16 (10H, *m*), δ 6.73 (2H, *d*, *J* = 3.5 Hz), δ 3.81 (6H, *s*); ¹³C-NMR δ_C (125 MHz, CDCl₃, δ ppm): δ 159.2, 144.8, 144.0, 143.4, 131.0, 130.7, 128.2, 128.1, 127.5, 127.3, 127.0, 126.8, 125.8, 121.3, 114.2, 55.4. HR-MS calcd for C₃₆H₂₈O₂S₂ ([M]⁺): 556.1531, found: 556.1507.



4. Photophysical properties

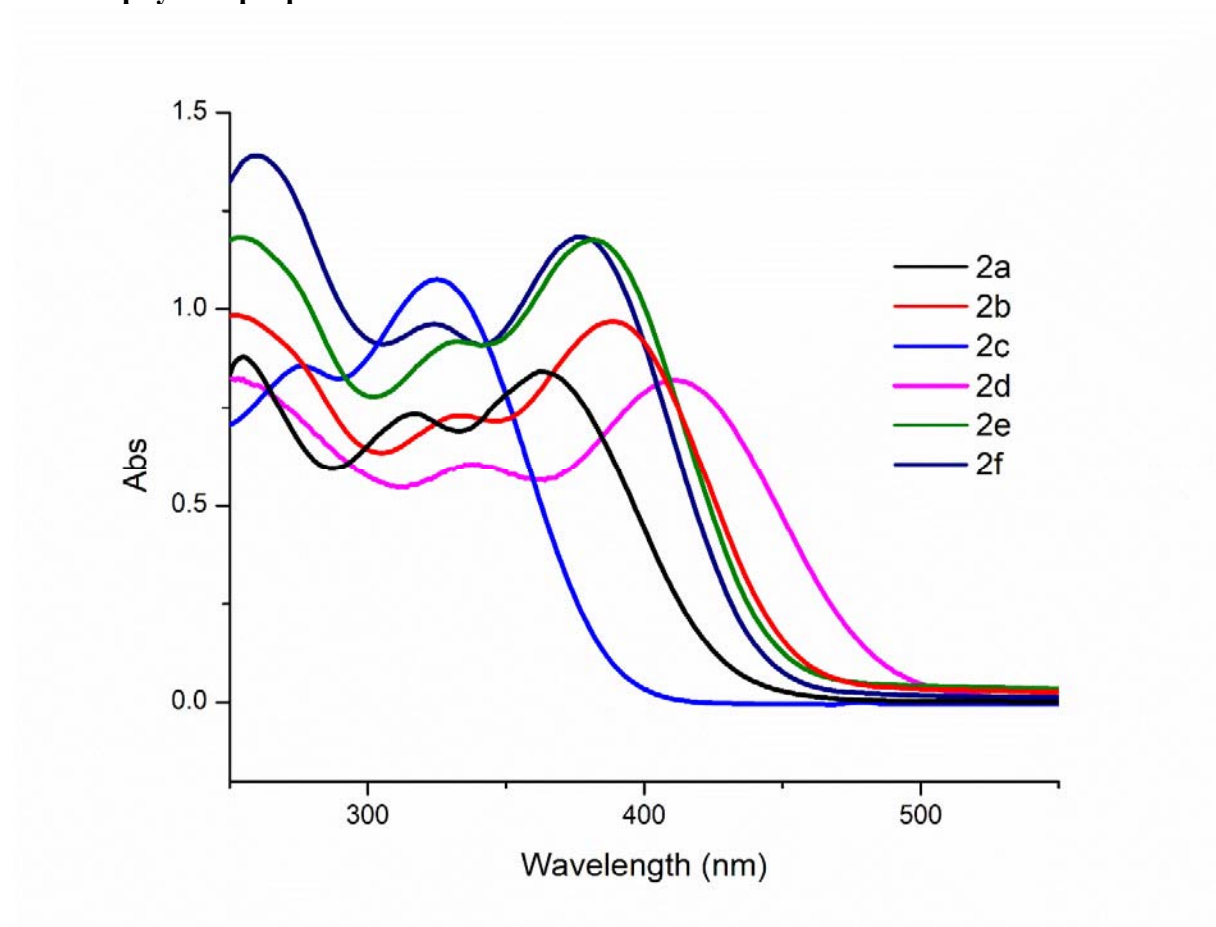


Fig. 1 Absorption spectra of the monoarylated DPDTEs (**2a-f**) at 298K in CHCl_3 solution ($C = 10^{-5} \text{ M}$).

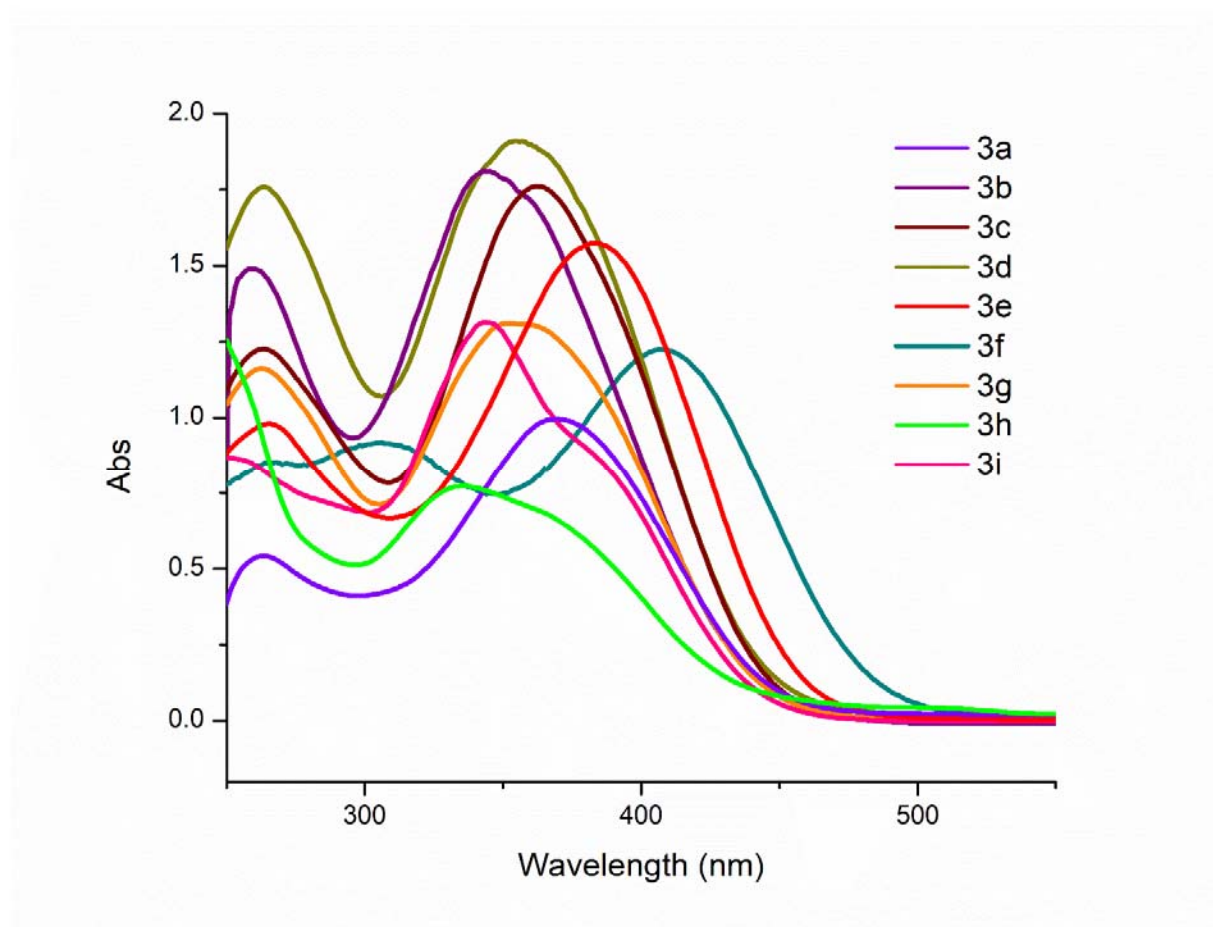


Fig. 2 Absorption spectra of the diarylated DPDTEs (**3a-i**) at 298K in CHCl_3 solution ($C = 10^{-5} \text{ M}$).

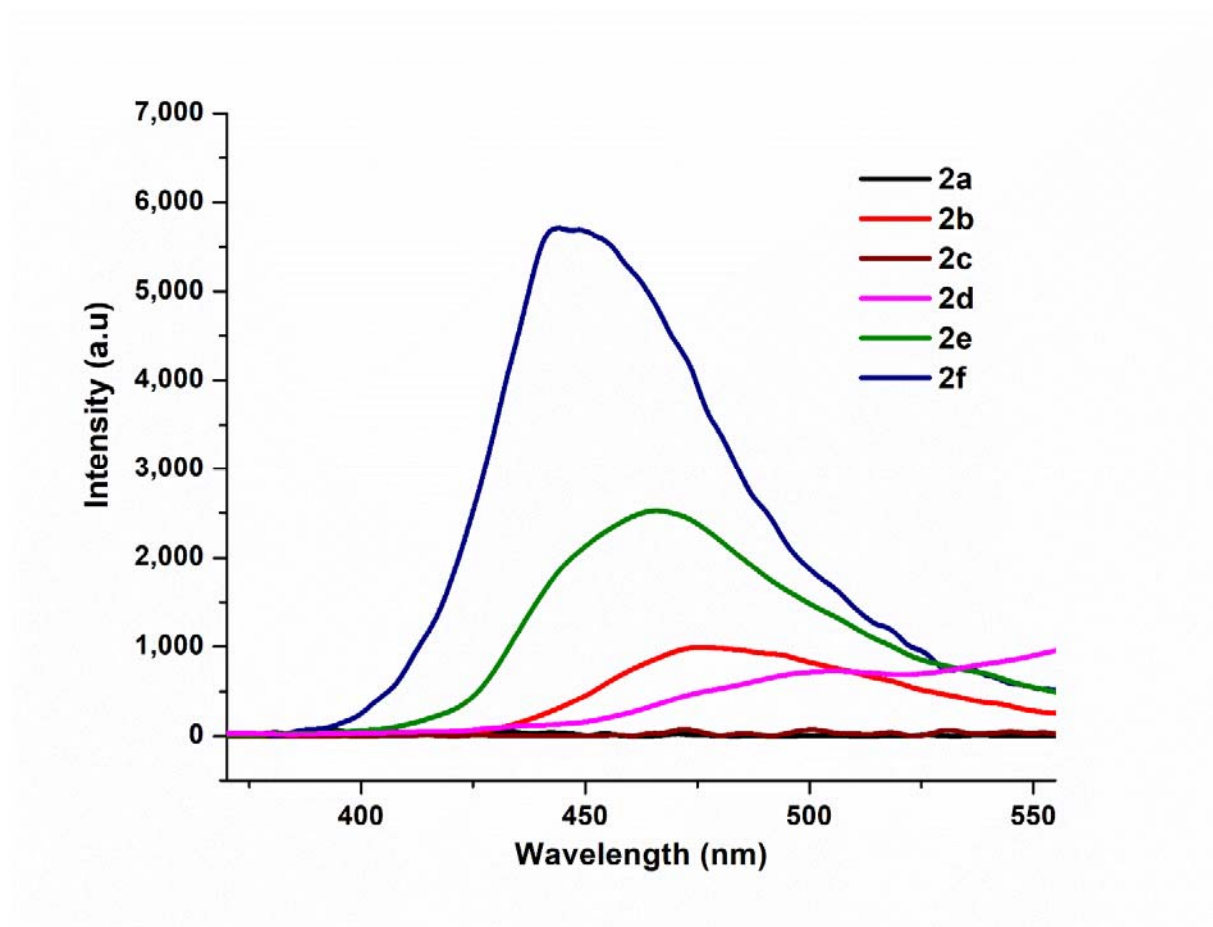


Fig. 3 Emission spectra of the monoarylated DPDTEs (**2a-f**) in CHCl_3 at 298K ($C = 10^{-5}\text{M}$) with $\lambda_{\text{ex}} = 360 \text{ nm}$.

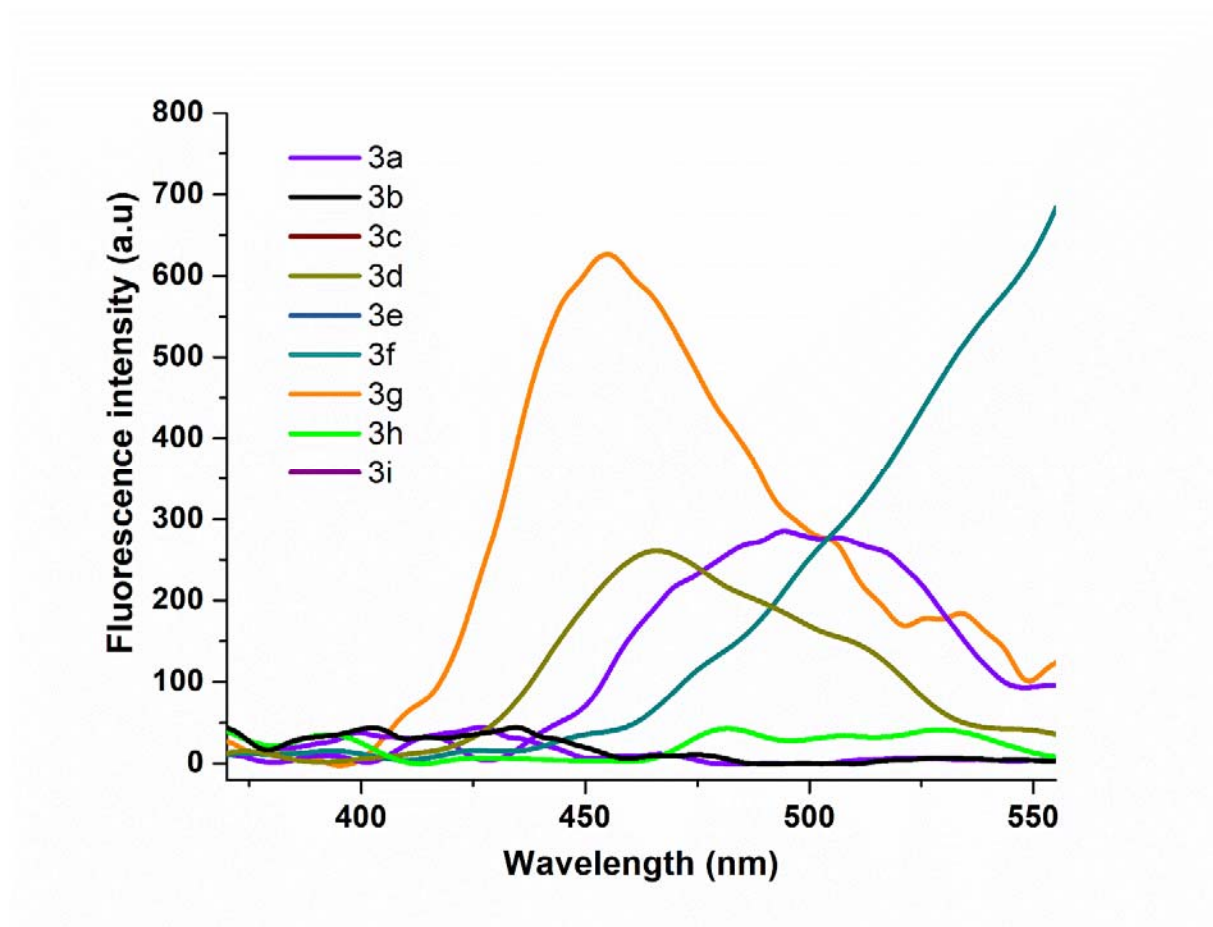


Fig. 4 Emission spectra of the diarylated DPDTEs (**3a-i**) in CHCl_3 at 298K ($C = 10^{-5}\text{M}$) with $\lambda_{\text{ex}} = 360\text{ nm}$.

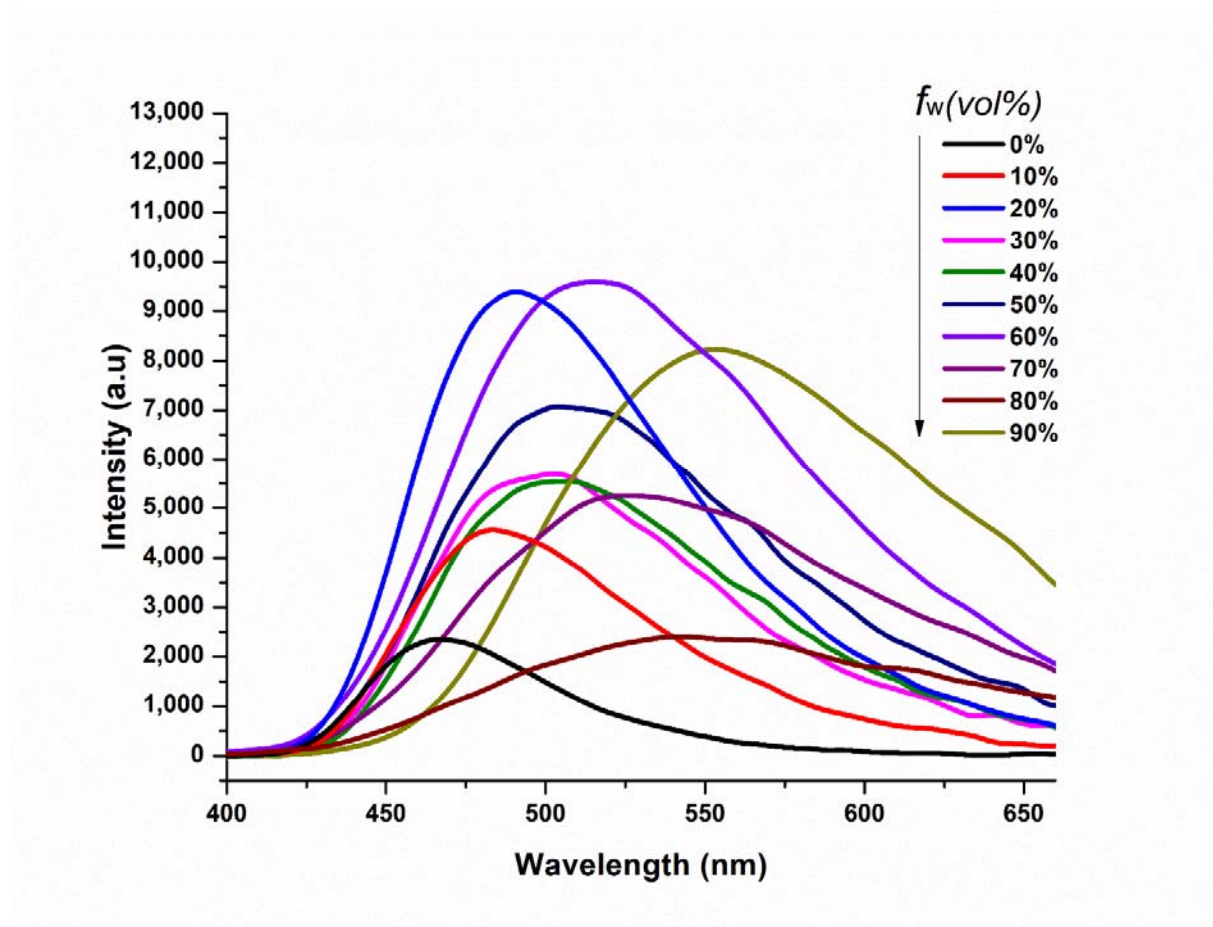


Fig.5a The AIE spectra of **2b** in THF/H₂O mixture, with $\lambda_{\text{ex}} = 360$ nm

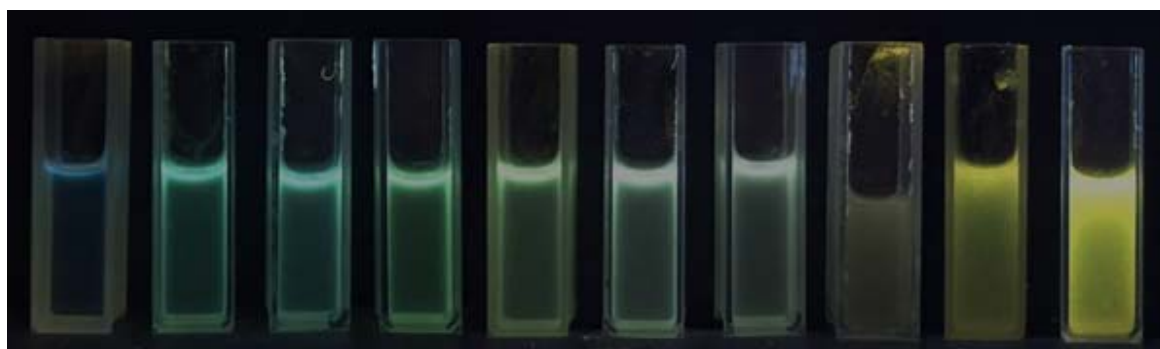


Fig. 5b Photograph of **2b** in THF/H₂O mixture, under UV lamp ($\lambda_{\text{ex}} = 365$ nm)

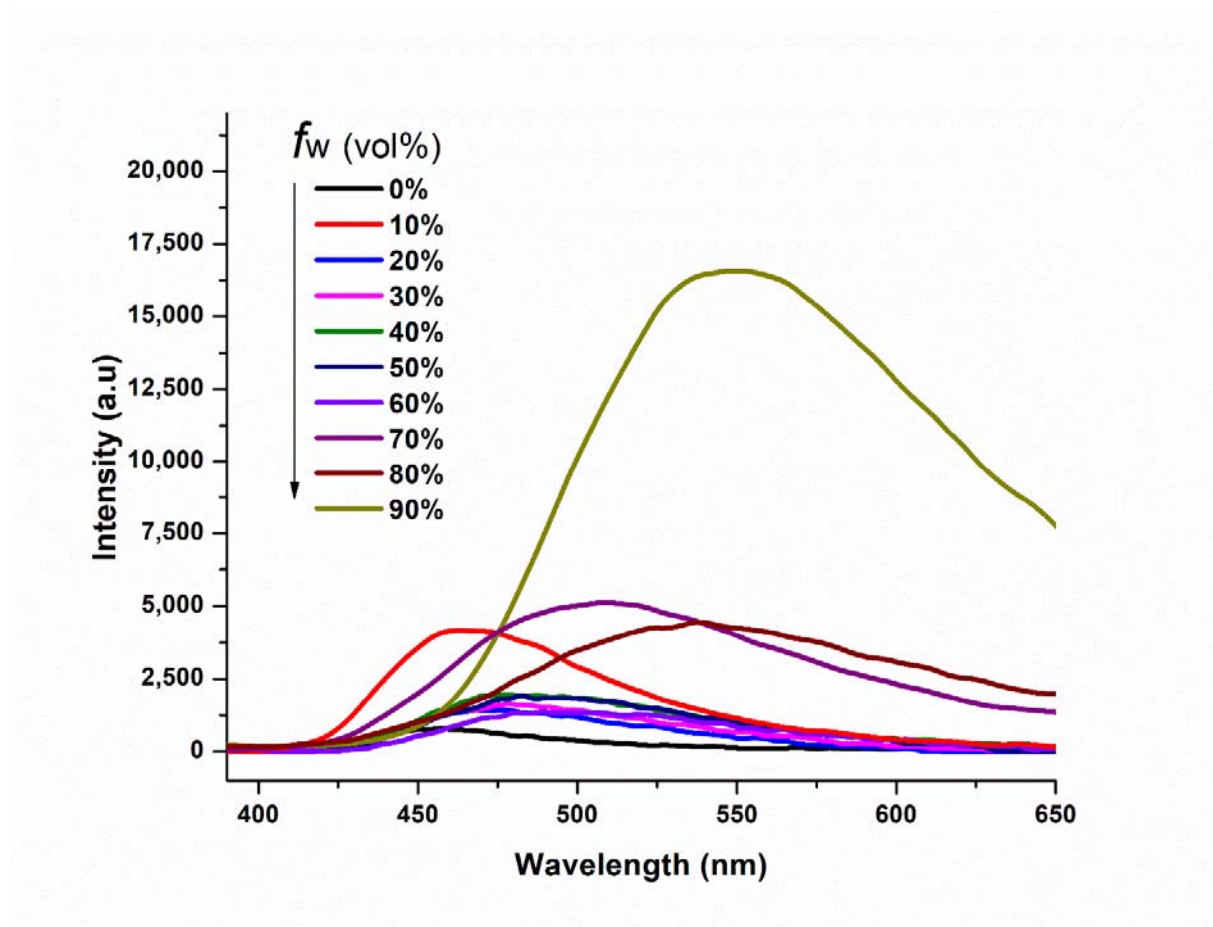


Fig. 6a The AIE spectra of **2e** in THF/H₂O mixture, with $\lambda_{\text{ex}} = 360$ nm

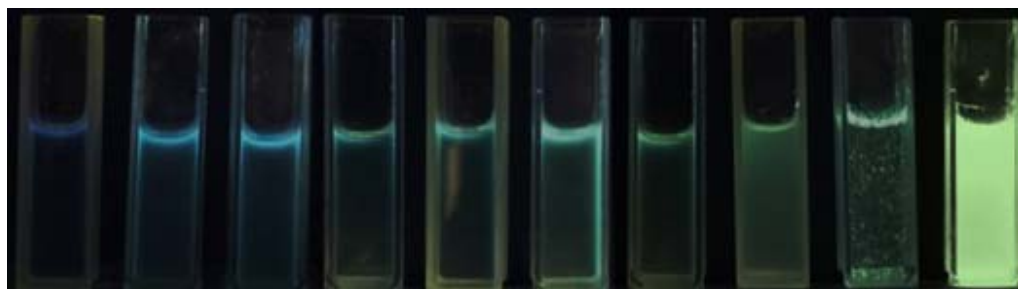


Fig. 6b Photograph of **2e** in THF/H₂O mixture, under UV lamp ($\lambda_{\text{ex}} = 365$ nm)

Table 2: Photophysical data of the arylated DPDTE (**2a-f**, **3a-i**)

	Absorption	Emission at 298 K ^a	
	λ_{abs}^a / nm (ϵ 10 ³ /M ⁻¹ cm ⁻¹)	λ_{em}^a / nm	Intensity (a.u)
2a	256(73.5), 316(60.8), 363(70.4)	475	982.0
2b	334(18.1), 389(24.0)	476	1026.9
2c	277(21.4), 327(26.9)		<100
2d	337(25.0), 413(33.3)		<100
2e	253(25.0), 332(19.4), 385(24.4)	467	2536.7
2f	261(23.3), 323(16.2), 376(19.9)	446	5733.3
3a	263(21.8), 370(40.0)	495	284.8
3b	260(59.2), 344(72.5)		<100
3c	263(44.2), 362(62.9)		<100
3d	264(29.3), 357(31.9)		<100
3e	268(32.3), 384(52.7)		<100
3f	269(34.0), 306(36.6), 409(49.2)		<100
3g	263(29.0), 355(33.0)	452	621.7
3h	336(48.5)		<100
3i	253(36.2), 344(54.6), 385(36.5)		<100

^a Measured in CHCl₃ solution at 298K (C= 10⁻⁵M), with 360 nm excitation