

Rapid consecutive three-component coupling-Fiesselmann synthesis of luminescent 2,4-disubstituted thiophenes and oligothiophenes

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Supporting Information

Table of Contents

1	GENERAL CONSIDERATIONS	1
2	PREPARATION OF STARTING MATERIALS	2
2.1	Preparation of Alkynes 4	2
3	SONOGASHIRA-COUPPLING-MICHAEL-ADDITION-ALDOL-CONDENSATION SEQUENCE	3
3.1	General procedure for the use of monofunctionalized starting materials	3
3.2	General procedure for the use of bifunctionalized starting materials	6
3.3	Analytical Data.....	8
3.3.1	Ethyl 3-(4-methoxyphenyl)-5-phenylthiophene-2-carboxylate (1a).....	8
3.3.2	Ethyl 5-(4-(<i>tert</i> -butyl)phenyl)-3-(4-methoxyphenyl)thiophene-2-carboxylate (1b).....	9
3.3.3	Ethyl 5-(4-(<i>tert</i> -butyl)phenyl)-3-(4-cyanophenyl)thiophene-2-carboxylate (1c) .	9
3.3.4	Ethyl 5-(4-cyanophenyl)-3-(<i>p</i> -tolyl)thiophene-2-carboxylate (1d)	10
3.3.5	Ethyl 5-(4-methoxyphenyl)-3-(<i>p</i> -tolyl)thiophene-2-carboxylate (1e)	11
3.3.6	Ethyl 5-(4-(methoxycarbonyl)phenyl)-3-(<i>p</i> -tolyl)thiophene-2-carboxylate (1f)	12
3.3.7	Ethyl 5-(4-fluorophenyl)-3-(<i>p</i> -tolyl)thiophene-2-carboxylate (1g).....	13
3.3.8	Ethyl 5-(pyridin-2-yl)-3-(<i>p</i> -tolyl)thiophene-2-carboxylate (1h).....	14
3.3.9	Ethyl 5-butyl-3-(<i>p</i> -tolyl)thiophene-2-carboxylate (1i)	14
3.3.10	Ethyl 3-(<i>p</i> -tolyl)-5-(trimethylsilyl)thiophene-2-carboxylate (1j)	15
3.3.11	Ethyl 5-ferrocenyl-3-(<i>p</i> -tolyl)thiophene-2-carboxylate (1k)	16
3.3.12	Ethyl 5'-phenyl-[2,3'-bithiophene]-2'-carboxylate (1l).....	17
3.3.13	Ethyl 5'-(4-(<i>tert</i> -butyl)phenyl)-[2,3'-bithiophene]-2'-carboxylate (1m)	17
3.3.14	Ethyl 4-(<i>p</i> -tolyl)-[2,2'-bithiophene]-5-carboxylate (1n)	18
3.3.15	Ethyl [2,2':4',2''-terthiophene]-5'-carboxylate (1o).....	19
3.3.16	Diethyl 5,5''-bis(4-chlorophenyl)-[3,2':5',3''-terthiophene]-2,2''-dicarboxylate (7a)	20
3.3.17	Diethyl 5,5''-bis(4-methoxyphenyl)-[3,2':5',3''-terthiophene]-2,2''-dicarboxylate (7b).....	20

3.3.18	Diethyl [2,2':4',2'':5'',3''':5''',2''''-quinguethiophene]-2''',5'-dicarboxylate (7c) ...	21
4	UV SPECTRA OF OLIGOTHIOPHENES	23
5	¹H AND ¹³C NMR SPECTRA	24
6	PHOTOGRAPHS	51

1 GENERAL CONSIDERATIONS

All cross coupling reactions were carried out in oven-dried *Schlenk* glassware using septa and syringes under nitrogen or argon atmosphere. THF was dried using MBraun system MB-SPS-800, and triethylamine was refluxed under argon over ketyl sodium, distilled and stored in a *Schlenk* flask over potassium hydroxide pellets under argon atmosphere.

Commercial grade reagents were used as supplied without further purification and were purchased from Sigma-Aldrich Chemie GmbH, Fluka AG, ABCR GmbH & Co. KG, Alfa Aesar GmbH & Co. KG and Riedel-de Haën. Some of the alkynes **4** were prepared according to the procedures in chapter 2 (Preparation of starting materials). The catalysts were prepared according to literature.

The purification of products was performed on silica gel 60 (0.04-0.063 mm) from Machery-Nagel GmbH & Co. KG using flash technique and under pressure of 2 bar or using the automatic chromatography system Biotage SP4.

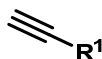
The crude mixtures were adsorbed on Celite® 545 (0.02-0.10 mm) from Merck KGaA Darmstadt or silica gel 60 (0.2-0.5 mm) from Merck Darmstadt prior to chromatographic purification.

The reaction progress was monitored qualitatively using TLC Silica gel 60 F254 5 x 7.5 cm aluminium sheets obtained by Merck KGaA Darmstadt. The spots were detected with UV light at 254 nm and using aqueous potassium permanganate solution.

¹H, ¹³C, and 135-DEPT NMR spectra were recorded on Bruker DRX 500 spectrometer. CDCl₃ and DMSO-d₆ were used as deuterated solvents. TMS was used as reference (δ = 0.0) or the resonances of the solvents were locked as internal standards (CDCl₃: ¹H δ 7.24, ¹³C δ 77.2). The multiplicities of signals were abbreviated as follows: s: singlet; d: doublet; t: triplet; dd: doublet of doublets, m: multiplet and br: broad signal. The type of carbon nuclei was determined on the basis of 135-DEPT NMR spectra. EI mass spectra were measured on Finnigan MAT 8200 spectrometer. IR spectra were obtained on Bruker Vector 22 FT-IR. The solids were measured as KBr pellets and oils as films on KBr plates. The intensity of signals is abbreviated as follows: s (strong), m (medium) and w (weak). The melting points (uncorrected) were measured on Reichert-Jung Thermovar. Combustion analyses were carried out on Perkin Elmer Series II Analyser 2400 in the microanalytical laboratory of Institut für Pharmazeutische und Medizinische Chemie at the Heinrich-Heine-Universität Düsseldorf.

2 PREPARATION OF STARTING MATERIALS

2.1 Preparation of Alkynes 4



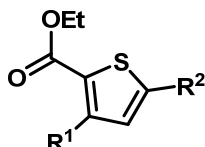
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A *Schlenk* flask of appropriate size was charged with Pd(PPh₃)₂Cl₂ (0.02 equiv) and CuI (0.04 equiv) at RT. Subsequently, THF (4 mL) and PPh₃ (0.04 equiv per mmol of aryl iodide) were added. The resulting solution was stirred for 10 min to give an orange solution. Then, the (hetero)aryl iodide (1.00 equiv) and TMSA (1.50 equiv) were added. Finally, triethylamine (1.50 equiv) was added and the reaction mixture was stirred for 12 h at RT to give a dark brown solution with a light precipitate. For workup the crude product was filtered through a short plug of silica gel and was washed several times with THF and methanol. Then, the volatile components were removed under reduced pressure and the crude product (brown oil) was, as in the case of 2-thienyl acetylene (**4k**), purified by fractionized distillation under reduced pressure (5 · 10⁻² mbar, bath temperature 82 °C, bp 53 °C; the product flask was cooled in a dry ice/acetone bath at -70 °C). In all other cases, the crude product was purified by column chromatography (*n*-hexane/ethyl acetate) on fine silica gel.

For deprotection the intermediate was dissolved in methanol (1.5 mL per 1.00 mmol). Then, an aqueous 1.0 M KOH solution (1.1 mL per 1.00 mmol) was added at 0 °C. This solution was finally stirred for 12 hours at RT under exclusion of oxygen and light. Subsequently, as in the case of 2-thienyl acetylene (**4k**) the reaction solution was extracted five times (dichloromethane/water) and the solvent of the combined organic phases was removed under reduced pressure. The resulting residue purified by fractionized distillation under reduced pressure (2.0 mbar, bath temperature 45 °C, bp 30 °C; the product flask was cooled in a dry ice/acetone bath at -70 °C). In all other cases, the volatile components were removed under reduced pressure and the crude product was purified by column chromatography (*n*-hexane/ethyl acetate) on fine silica gel. In the case of 2-thienyl acetylene (**4k**) the desired product could be obtained with an overall yield of 81 %.

3 SONOGASHIRA-COUPPLING-MICHAEL-ADDITION-ALDOL-CONDENSATION SEQUENCE

3.1 General procedure for the use of monofunctionalized starting materials

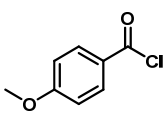
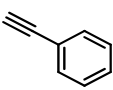
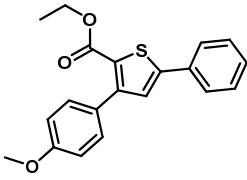
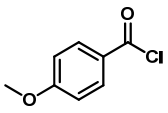
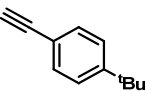
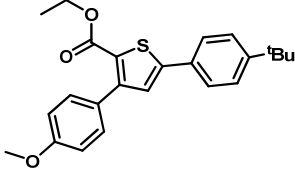
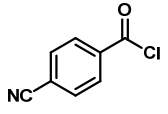
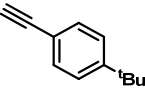
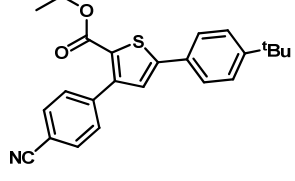
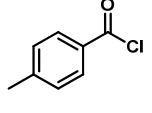
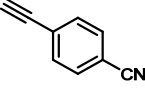
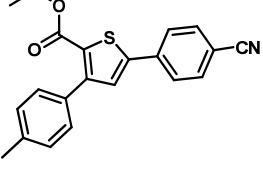
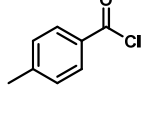
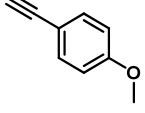
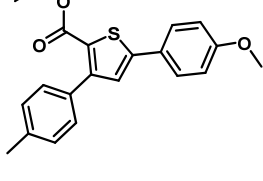
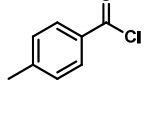
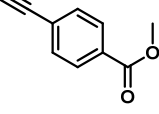
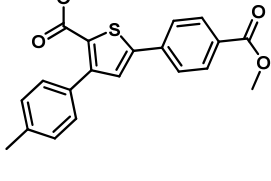


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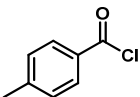
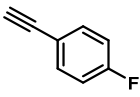
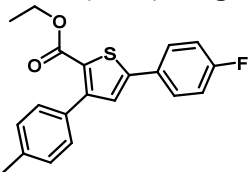
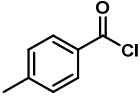
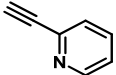
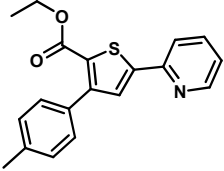
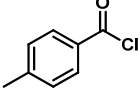
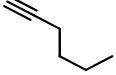
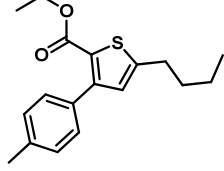
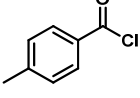
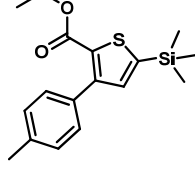
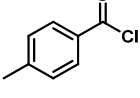
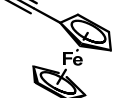
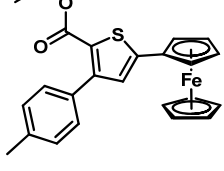
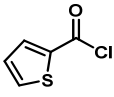
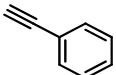
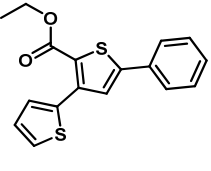
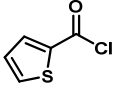
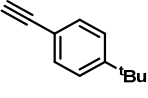
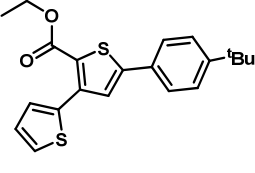
A 25 mL *Schlenk* tube was charged with $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.02 mmol, 15 mg) and CuI (0.04 mmol, 8 mg) at RT. Then THF (10 mL) was added and the resulting solution was stirred for 10 min (yellow solution). After that alkyne **4** (1.10 mmol) and acid chloride **3** (1.00 mmol) was subsequently added (for experimental details see Table 1). Thereafter triethylamine (1.05 mmol, 107 mg, 150 μL) was added and the resulting solution was stirred for 2 h at RT (dark brown solution, light precipitation). To the resulting reaction mixture, ethyl 2-mercaptoacetate (**5**) (1.20 mmol, 144 mg, 153 μL) and ethanol (1 mL) were added. Immediately DBU (1.50 mmol, 228 mg, 217 μL) was added. Finally, the solution was stirred for 12-24 h at RT (dark brown solution). For workup, the volatile components were removed under reduced pressure. The crude product was absorbed on silica gel and purified by column chromatography (n-hexane/ethyl acetate) on fine silica gel.

SONOGASHIRA-COUPPLING-MICHAEL-ADDITION-ALDOL-CONDENSATION SEQUENCE - 3

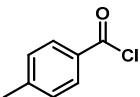
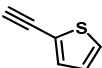
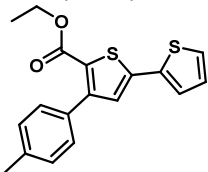
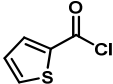
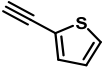
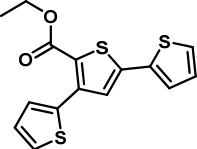
Table 1: Overview of the synthesized thiophenes **1** from monofunctionalized starting materials.

Entry	(Hetero)Aroyl chloride 3 [mg] (mmol)	Alkyne 4 [mg] (mmol)	Thiophene 1 [mg] (yield)
1	171 (1.00) of 3a 	112 (1.10) of 4a 	327 (97 %) of 1a 
2	171 (1.00) of 3a 	174 (1.10) of 4b 	359 (91%) of 1b 
3	166 (1.00) of 3b 	174 (1.10) of 4b 	343 (88 %) of 1c 
4	155 (1.00) of 3c 	140 (1.10) of 4c 	235 (68 %) of 1d 
5	155 (1.00) of 3c 	145 (1.10) of 4d 	293 (83 %) of 1e 
6	155 (1.00) of 3c 	176 (1.10) of 4e 	339 (89 %) of 1f 

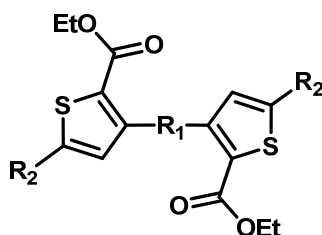
SONOGASHIRA-COUPPLING-MICHAEL-ADDITION-ALDOL-CONDENSATION SEQUENCE - 3

7	155 (1.00) of 3c 	132 (1.10) of 4f 	317 (93 %) of 1g 
8	155 (1.00) of 3c 	113 (1.10) of 4g 	104 (32%) of 1h 
9	155 (1.00) of 3c 	90 (1.10) of 4h 	151 (50 %) of 1i 
10	155 (1.00) of 3c 	108 (1.10) of 4i 	143 (45 %) of 1j 
11	155 (1.00) of 3c 	231 (1.10) of 4j 	392 (91 %) of 1k 
12	147 (1.00) of 3d 	112 (1.10) of 2a 	283 (90 %) of 1l 
13	147 (1.00) of 3d 	174 (1.10) of 2b 	345 (93 %) of 1m 

SONOGASHIRA-COUPPLING-MICHAEL-ADDITION-ALDOL-CONDENSATION SEQUENCE - 3

14	155 (1.00) of 3c	162 (1.50) of 4k	262 (80 %) of 1n
			
15	147 (1.00) of 3d	162 (1.50) of 4k	301 (94 %) of 1o
			

3.2 General procedure for the use of bifunctionalized starting materials

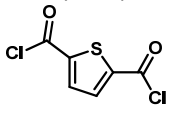
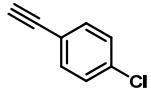
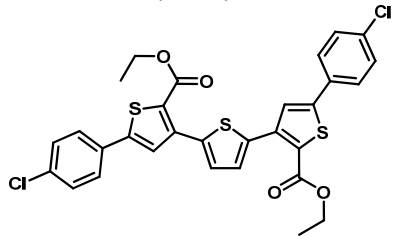
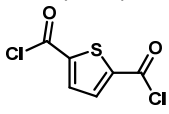
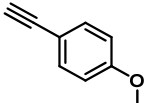
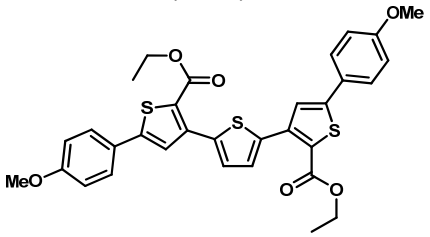
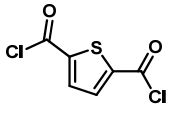
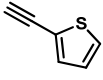
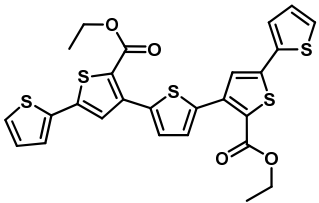


7

A 25 mL *Schlenk* vessel was charged with $Pd(PPh_3)_4$ (84.0 mg, 0.08 mmol) and CuI (30 mg, 0.16 mmol). Then THF (15 mL) was added and the resulting solution was stirred for 10 min to give a yellow solution. Subsequently 2,5-thiophene dicarbonyldichloride **6** (209 mg, 1.00 mmol), the respective alkyne **4** (3.00 mmol), and triethylamine (223 mg, 2.20 mmol) were added and the solution was stirred for 4 h at RT to give a dark brown solution with light precipitation (for experimental details see Table 2). Then ethanol (2 mL), ethyl 2-mercaptoacetate (**5**) (300 mg, 2.50 mmol) and DBU (533 mg, 3.50 mmol) were added at 0 °C and the resulting solution was stirred for 12-24 h and allowed to come to RT. For workup, the volatile components were removed under reduced pressure. The crude product was extracted three times with a mixture of CH_2Cl_2 and aqueous 1M HCl. The combined organic layers were dried with anhydrous $MgSO_4$, absorbed on coarse silica gel, and purified by automated column chromatography on fine silica gel (*n*-hexane/THF, gradient: 10% to 30% in 10 column volume, 100 g). A further purification can easily be achieved by recrystallization from ethanol.

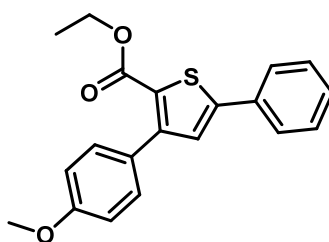
SONOGASHIRA-COUPPLING-MICHAEL-ADDITION-ALDOL-CONDENSATION SEQUENCE - 3

Table 2: Overview of synthesized oligothiophenes **7** from bifunctionalized starting materials.

Entry	Diacidchloride 6 [mg] (mmol)	Alkyne 4 [mg] (mmol)	Oligothiophene 7 [mg] (yield)
1	210 (1.00) of 6 	410 (3.00) of 4l 	399 (84 %) of 7a 
2	210 (1.00) of 6 	396 (3.00) of 4d 	327 (74 %) of 7b 
3	210 (1.00) of 6 	324 (3.00) of 4k 	312 (76 %) of 7c 

3.3 Analytical Data

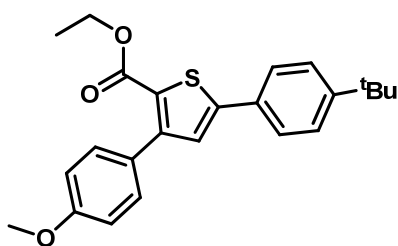
3.3.1 Ethyl 3-(4-methoxyphenyl)-5-phenylthiophene-2-carboxylate (1a)



1a
C₂₀H₁₈O₃S
[338.42]

Yellow solid, mp 109 °C. **¹H NMR (500 MHz, CDCl₃):** δ 1.30 (t, ³J = 7.1 Hz, 3 H), 3.86 (s, 3 H), 4.27 (q, ³J = 7.1 Hz, 2 H), 6.96 (d, ³J = 8.8 Hz, 2 H), 7.28 (s, 1 H), 7.35-7.38 (m, 1 H), 7.40-7.38 (m, 2 H), 7.47 (d, ³J = 8.8 Hz, 2 H), 7.65-7.68 (m, 2 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.2 (CH₃), 55.3 (CH₃), 60.9 (CH₂), 113.2 (2 CH), 125.3 (C_{quat}), 126.1 (2 CH), 127.4 (CH), 128.1 (C_{quat}), 128.8 (CH), 129.0 (2 CH), 130.5 (2 CH), 133.2 (C_{quat}), 148.1 (C_{quat}), 149.1 (C_{quat}), 159.4 (C_{quat}), 162.1 (C_{quat}). **EI MS(70 eV) m/z (%):** 340 (14), 339 (27), 338 ([M]⁺, 100), 337 (13), 310 (17), 294 (16), 293 (48), 267 (13), 266 (36), 251 (14), 250 (14), 222 (16), 221 (34), 189 (12), 178 (18), 135 (35), 121 (21), 108 (24), 105 (17), 89 (11), 77 (47), 69 (36). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 3057 (w), 2988 (w), 2959 (w), 2837 (w), 1686 (s), 1609 (m), 1543 (m), 1512 (m), 1492 (m), 1474 (w), 1460 (w), 1432 (m), 1377 (s), 1287 (s), 1248 (s), 1177 (m), 1096 (s), 1031 (m), 1014 (w), 963 (w), 867 (w), 831 (m), 785 (w), 766 (m), 714 (w), 691 (m), 598 (w), 561 (w), 510 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 270 nm (16100), 316 (21100). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 406 nm (7000 cm⁻¹). **Emission (solid):** λ_{max} (Stokes shift) 411 nm (7300 cm⁻¹). **Anal. calcd.** for C₂₀H₁₈O₃S (338.4): C 70.98, H 5.36; Found: C 71.27, H 5.27.

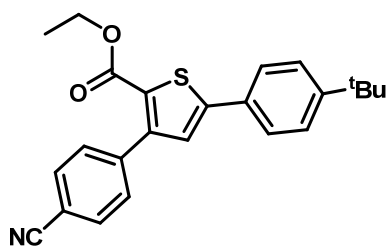
3.3.2 Ethyl 5-(4-(*tert*-butyl)phenyl)-3-(4-methoxyphenyl)thiophene-2-carboxylate (1b)



1b
C₂₄H₂₆O₃S
[394.53]

Pale yellow solid, mp 94 °C. **¹H NMR (500 MHz, CDCl₃):** δ 1.29 (t, ³J = 7.1 Hz, 3 H), 1.35 (s, 9 H), 3.86 (s, 3 H), 4.25 (q, ³J = 7.1 Hz, 2 H), 6.96 (d, ³J = 8.8 Hz, 2 H), 7.25 (s, 1 H), 7.44 (d, ³J = 8.5 Hz, 2 H), 7.47 (d, ³J = 8.8 Hz, 2 H), 7.60 (d, ³J = 8.5 Hz, 2 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.2 (CH₃), 31.2 (3 CH₃), 34.7 (C_{quat}), 55.3 (CH₃), 60.8 (CH₂), 113.2 (2 CH), 124.8 (C_{quat}), 125.8 (2 CH), 126.0 (2 CH), 127.0 (CH), 128.2 (C_{quat}), 130.49 (C_{quat}), 130.52 (2 CH), 148.3 (C_{quat}), 149.1 (C_{quat}), 152.1 (C_{quat}), 159.4 (C_{quat}), 162.2 (C_{quat}). **EI MS (70 eV) m/z (%):** 396 (8), 395 (27), 394 ([M]⁺, 100), 381 (7), 380 (23), 379 (90), 351 (12), 349 (8), 323 (9), 322 (7), 307 (7), 306 (5), 291 (6), 190 (27), 176 (12), 162 (35), 153 (7), 146 (12), 117 (7), 57 (7). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 2962 (m), 1682 (s), 1610 (w), 1501 (m), 1440 (m), 1377 (m), 1295 (s), 1246 (s), 1179 (w), 1095 (m), 1034 (w), 837 (m), 582 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 270 nm (15400), 320 (21900). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 403 nm (6400 cm⁻¹). **Anal. calcd.** for C₂₄H₂₆O₃S (394.5): C 73.06, H 6.64; Found: C 72.95, H 6.43.

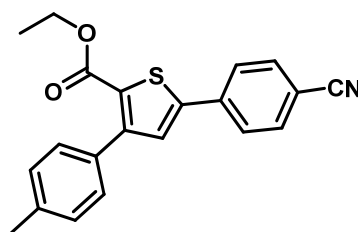
3.3.3 Ethyl 5-(4-(*tert*-butyl)phenyl)-3-(4-cyanophenyl)thiophene-2-carboxylate (1c)



1c
C₂₄H₂₃NO₂S
[389.51]

Yellow solid, mp 172 °C. **¹H NMR (500 MHz, CDCl₃):** δ 1.27 (t, ³J = 7.1 Hz, 3 H), 1.35 (s, 9 H), 4.25 (q, ³J = 7.1 Hz, 2 H), 7.22 (s, 1 H), 7.45 (d, ³J = 8.5 Hz, 2 H), 7.59 (d, ³J = 6.3 Hz, 2 H), 7.61 (d, ³J = 6.3 Hz, 2 H), 7.71 (d, ³J = 8.5 Hz, 2 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.1 (CH₃), 31.2 (3 CH₃), 34.8 (C_{quat}), 61.2 (CH₂), 111.6 (C_{quat}), 118.9 (C_{quat}), 125.9 (2 CH), 126.1 (2 CH), 126.2 (CH), 126.5 (C_{quat}), 129.9 (C_{quat}), 130.0 (2 CH), 131.6 (2 CH), 140.7 (C_{quat}), 146.9 (C_{quat}), 149.4 (C_{quat}), 152.6 (C_{quat}), 161.7 (C_{quat}). **EI MS (70 eV) m/z (%):** 390 (15), 389 ([M]⁺, 51), 376 (9), 375 (26), 374 (100), 376 (12), 318 (11), 288 (6), 240 (5), 173 (8), 159 (18), 151 (18), 115 (7). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 2962 (m), 2229 (m), 1692 (s), 1609 (w), 1497 (w), 1439 (m), 1408 (m), 1379 (m), 1292 (s), 1102 (m), 839 (m), 765 (w), 584 (w), 560 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 277 nm (28400), 325 (18400). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 400 nm (5800 cm⁻¹). **Anal. calcd.** for C₂₄H₂₃NO₂S (389.5): C 74.00, H 5.95, N 3.60; Found: C 73.70, H 5.90, N 3.34.

3.3.4 Ethyl 5-(4-cyanophenyl)-3-(p-tolyl)thiophene-2-carboxylate (1d)



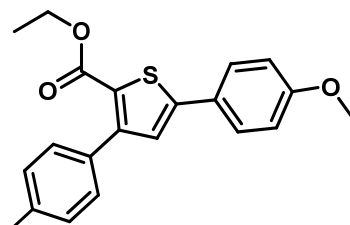
1d
C₂₁H₁₇NO₂S
[347.43]

Colorless solid, mp 160 °C. **¹H NMR (500 MHz, CDCl₃):** δ 1.31 (t, ³J = 7.1 Hz, 3 H), 2.44 (s, 3 H), 4.30 (q, ³J = 7.1 Hz, 2 H), 7.28 (d, ³J = 7.9 Hz, 2 H), 7.39 (s, 1 H), 7.42 (d, ³J = 7.9 Hz, 2 H), 7.73 (d, ³J = 8.2 Hz, 2 H), 7.78 (d, ³J = 8.2 Hz, 2 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.1 (CH₃), 21.3 (CH₃), 61.2 (CH₂), 112.0 (C_{quat}), 118.5 (C_{quat}), 126.4 (2 CH), 127.8 (C_{quat}), 128.6 (2 CH), 129.0 (2 CH), 129.1 (CH), 132.3 (C_{quat}), 132.9 (2 CH), 137.5 (C_{quat}), 138.2 (C_{quat}), 145.2 (C_{quat}), 149.5 (C_{quat}), 161.7 (C_{quat}). **EI MS (70 eV) m/z (%):** 349 (8), 348 (25), 347 ([M]⁺,

SONOGASHIRA-COUPPLING-MICHAEL-ADDITION-ALDOL-CONDENSATION SEQUENCE - 3

100), 319 (20), 318 (14), 303 (13), 302 (54), 288 (8), 276 (13), 275 (68), 274 (10), 273 (6), 272 (9), 260 (7), 259 (29), 241 (9), 240 (15), 230 (6), 227 (9), 214 (5), 146 (13), 115 (10), 103 (7), 102 (6), 101 (5), 77 (8). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 3075 (w), 2981 (w), 2224 (m), 1716 (s), 1605 (m), 1547 (w), 1500 (m), 1476 (w), 1445 (m), 1413 (w), 1369 (m), 1260 (s), 1240 (m), 1219 (w), 1205 (w), 1185 (w), 1129 (m), 1082 (m), 1024 (w), 831 (m), 805 (m), 762 (w), 670 (w), 573 (w), 536 (w), 480 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 280 nm (21400), 318 (32900). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 392 nm (5900 cm⁻¹). **Anal. calcd.** for C₂₁H₁₇NO₂S (347.4): C 72.60, H 4.93, N 4.03; Found: C 72.49, H 4.74, N 3.88.

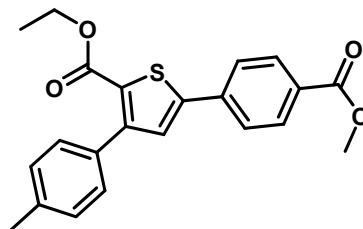
3.3.5 Ethyl 5-(4-methoxyphenyl)-3-(p-tolyl)thiophene-2-carboxylate (1e)



1e
C₂₁H₂₀O₃S
[352.45]

Pale yellow solid, mp 75 °C. **¹H NMR (500 MHz, CDCl₃):** δ 1.28 (t, ³J = 7.1 Hz, 3 H), 2.41 (s, 3 H), 3.85 (s, 3 H), 4.25 (q, ³J = 7.1 Hz, 2 H), 6.94 (d, ³J = 8.8 Hz, 2 H), 7.18 (s, 1 H), 7.23 (d, ³J = 7.9 Hz, 2 H), 7.41 (d, ³J = 7.9 Hz, 2 H), 7.59 (d, ³J = 8.8 Hz, 2 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.2 (CH₃), 21.3 (CH₃), 55.3 (CH₃), 60.8 (CH₂), 114.4 (2 CH), 124.6 (C_{quat}), 126.0 (C_{quat}), 126.4 (CH), 127.4 (2 CH), 128.5 (2 CH), 129.0 (2 CH), 133.0 (C_{quat}), 137.7 (C_{quat}), 148.2 (C_{quat}), 149.5 (C_{quat}), 160.2 (C_{quat}), 162.1 (C_{quat}). **EI MS (70 eV) m/z (%):** 354 (8), 353 (23), 352 ([M]⁺, 100), 324 (16), 309 (12), 308 (7), 307 (27), 281 (13), 280 (50), 265 (11), 235 (8), 221 (9), 139 (5), 117 (7). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 2992 (m), 1677 (s), 1606 (m), 1573 (w), 1522 (w), 1500 (m), 1475 (w), 1435 (s), 1421 (s), 1373 (s), 1299 (s), 1282 (s), 1257 (s), 1181 (s), 1136 (w), 1116 (w), 1080 (m), 1028 (m), 886 (w), 833 (m), 805 (w), 764 (w), 706 (w), 678 (w), 632 (w), 615 (w), 581 (w), 550 (m), 507 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 265 nm (17100), 325 (20300). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 405 nm (6100 cm⁻¹). **Anal. calcd.** for C₂₁H₂₀O₃S (352.5): C 71.56, H 5.72; Found: C 71.55, H 5.59.

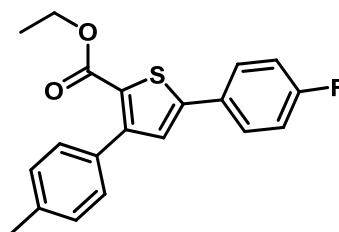
3.3.6 Ethyl 5-(4-(methoxycarbonyl)phenyl)-3-(*p*-tolyl)thiophene-2-carboxylate (1f)



1f
C₂₂H₂₀O₄S
[380.46]

Pale yellow solid, mp 155 °C. **¹H NMR (500 MHz, CDCl₃):** δ 1.28 (t, ³*J* = 7.1 Hz, 3 H), 2.41 (s, 3 H), 3.94 (s, 3 H), 4.26 (q, ³*J* = 7.1 Hz, 2 H), 7.23 (d, ³*J* = 7.9 Hz, 2 H), 7.37 (s, 1 H), 7.40 (d, ³*J* = 7.9 Hz, 2 H), 7.72 (d, ³*J* = 8.6 Hz, 2 H), 8.08 (d, ³*J* = 8.6 Hz, 2 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.1 (CH₃), 21.3 (CH₃), 52.2 (CH₃), 61.0 (CH₂), 125.8 (2 CH), 127.0 (C_{quat}), 128.6 (3 CH), 129.0 (2 CH), 130.0 (C_{quat}), 130.4 (2 CH), 132.5 (C_{quat}), 137.4 (C_{quat}), 138.0 (C_{quat}), 146.4 (C_{quat}), 149.5 (C_{quat}), 161.8 (C_{quat}), 166.5 (C_{quat}). **EI MS (70 eV) *m/z* (%):** 382 (8), 381 (23), 380 ([M]⁺, 100), 352 (14), 351 (8), 349 (5), 336 (10), 335 (41), 321 (11), 309 (13), 308 (55), 277 (8), 249 (6), 248 (18), 247 (14), 245 (5), 234 (6), 215 (10), 203 (5), 202 (7), 189 (6), 160 (7), 153 (7), 145 (6), 138 (13), 123 (10), 111 (5), 103 (5), 101 (10), 59 (6). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 2985 (w), 1702 (s), 1606 (m), 1500 (w), 1479 (w), 1433 (m), 1412 (m), 1374 (m), 1286 (s), 1237 (m), 1189 (m), 1112 (s), 1097 (m), 1017 (m), 852 (w), 821 (m), 767 (m), 692 (m), 601 (w), 505 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 278 nm (21500), 321 (33500). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 387 nm (5300 cm⁻¹). **Anal. calcd.** for C₂₂H₂₀O₄S (380.5): C 69.45, H 5.30; Found: C 69.31, H 5.21.

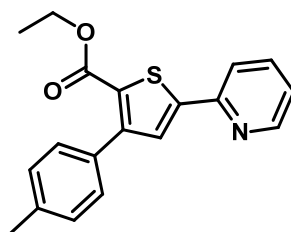
3.3.7 Ethyl 5-(4-fluorophenyl)-3-(*p*-tolyl)thiophene-2-carboxylate (1g)



1g
C₂₀H₁₇FO₂S
[340.41]

Yellow solid, mp 110 °C. **¹H NMR (500 MHz, CDCl₃):** δ 1.28 (t, ³J = 7.1 Hz, 3 H), 2.41 (s, 3 H), 4.26 (q, ³J = 7.1 Hz, 2 H), 7.09-7.13 (m, 2 H), 7.21 (s, 1 H), 7.23 (d, ³J = 7.9 Hz, 2 H), 7.40 (d, ³J = 7.9 Hz, 2 H), 7.61-7.64 (m, 2 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.2 (CH₃), 21.3 (CH₃), 60.9 (CH₂), 116.1 (d, ³J_{CF} = 22.0 Hz, 2 CH), 125.7 (C_{quat}), 127.4 (CH), 127.9 (d, ²J_{CF} = 8.2 Hz, 2 CH), 128.5 (2 CH), 129.0 (2 CH), 129.6 (d, ¹J_{CF} = 3.4 Hz, C_{quat}), 132.7 (C_{quat}), 137.9 (C_{quat}), 146.9 (C_{quat}), 149.5 (C_{quat}), 161.9 (C_{quat}), 163.0 (d, ⁴J_{CF} = 249.0 Hz, C_{quat}). **EI MS (70 eV) *m/z* (%):** 342 (7), 341 (22), 340 ([M]⁺, 100), 312 (17), 311 (12), 296 (11), 295 (53), 269 (14), 268 (74), 267 (6), 265 (8), 253 (6), 252 (29), 234 (9), 233 (13), 223 (7), 220 (9), 207 (5), 139 (11), 115 (6), 107 (5), 103 (6), 77 (5). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 2988 (w), 1685 (s), 1599 (w), 1546 (w), 1519 (w), 1499 (m), 1474 (w), 1437 (m), 1414 (m), 1374 (m), 1292 (s), 1232 (m), 1163 (m), 1135 (w), 1097 (s), 1010 (m), 966 (w), 835 (s), 806 (s), 764 (m), 702 (w), 682 (w), 613 (w), 578 (w), 544 (m). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 259 nm (19200), 312 (23300). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 380 nm (5700 cm⁻¹). **Anal. calcd.** for C₂₀H₁₇FO₂S (340.4): C 70.57, H 5.03; Found: C 70.32, H 4.98.

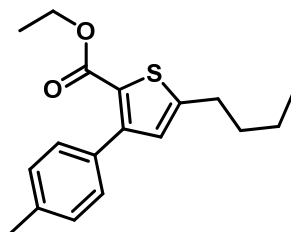
3.3.8 Ethyl 5-(pyridin-2-yl)-3-(p-tolyl)thiophene-2-carboxylate (1h)



1h
C₁₉H₁₇NO₂S
[323.41]

Pale yellow solid, mp 134 °C. **¹H NMR (500 MHz, CDCl₃):** δ 1.28 (t, $^3J = 7.1$ Hz, 3 H), 2.40 (s, 3 H), 4.26 (q, $^3J = 7.1$ Hz, 2 H), 7.21-7.25 (m, 3 H), 7.41 (d, $^3J = 7.8$ Hz, 2 H), 7.53 (s, 1 H), 7.69-7.74 (m, 2 H), 8.61-8.62 (m, 1 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.1 (CH₃), 21.3 (CH₃), 60.9 (CH₂), 119.2 (CH), 123.0 (CH), 127.9 (C_{quat}), 128.2 (CH), 128.5 (2 CH), 129.0 (2 CH), 132.8 (C_{quat}), 136.8 (CH), 137.8 (C_{quat}), 147.9 (C_{quat}), 149.2 (C_{quat}), 149.8 (CH), 151.5 (C_{quat}), 162.0 (C_{quat}). **EI MS (70 eV) *m/z* (%)**: 325 (7), 324 (22), 323 ([M]⁺, 100), 295 (13), 294 (13), 279 (13), 278 (72), 253 (5), 252 (14), 251 (68), 250 (15), 249 (7), 248 (7), 246 (6), 235 (9), 234 (5), 218 (13), 217 (20), 204 (7), 191 (6), 171 (5), 124 (9), 103 (6), 102 (6), 78 (14), 51 (6). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 2986 (w), 1687 (s), 1585 (m), 1561 (w), 1546 (w), 1510 (w), 1472 (m), 1439 (m), 1426 (s), 1398 (w), 1377 (s), 1285 (s), 1264 (m), 1134 (w), 1098 (s), 1009 (w), 995 (m), 876 (w), 832 (w), 814 (m), 779 (s), 738 (m), 716 (w), 682 (w), 597 (w), 558 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 262 nm (29800), 317 (41400). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 385 nm (5600 cm⁻¹). **Anal. calcd.** for C₁₉H₁₇NO₂S (323.4): C 70.56, H 5.30, N 4.33; Found: C 70.33, H 5.20, N 4.30.

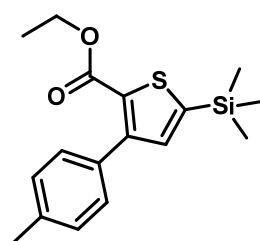
3.3.9 Ethyl 5-butyl-3-(p-tolyl)thiophene-2-carboxylate (1i)



1i
C₁₈H₂₂O₂S
[302.43]

Orange oil. **¹H NMR (500 MHz, CDCl₃):** δ 0.95 (t, ³J = 7.4 Hz, 3 H), 1.25 (t, ³J = 7.1 Hz, 3 H), 1.42 (m, 2 H), 1.70 (m, 2 H), 2.38 (s, 3 H), 2.82 (t, ³J = 7.6 Hz, 2 H), 4.22 (q, ³J = 7.1 Hz, 2 H), 6.78 (s, 1 H), 7.19 (d, ³J = 7.9 Hz, 2 H), 7.35 (d, ³J = 7.9 Hz, 2 H). **¹³C NMR (125 MHz, CDCl₃):** δ 13.7 (CH₃), 14.2 (CH₃), 21.3 (CH₃), 22.1 (CH₂), 29.9 (CH₂), 33.3 (CH₂), 60.6 (CH₂), 124.1 (C_{quat}), 128.4 (2 CH), 129.1 (2 CH), 129.2 (CH), 133.1 (C_{quat}), 137.5 (C_{quat}), 148.7 (C_{quat}), 151.0 (C_{quat}), 162.1 (C_{quat}). **EI MS (70 eV) m/z (%):** 304 (7), 303 (20), 302 ([M]⁺, 100), 261 (8), 260 (34), 259 (74), 258 (8), 257 (39), 232 (9), 231 (41), 230 (26), 201 (7), 188 (11), 187 (46), 186 (5), 185 (20), 184 (8), 173 (6), 172 (10), 171 (16), 152 (5), 142 (9), 141 (9), 129 (5), 128 (10), 115 (12). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 2980 (m), 2930 (m), 1712 (s), 1680 (m), 1511 (m), 1458 (m), 1375 (m), 1275 (m), 1226 (m), 1108 (m), 1075 (m), 815 (m), 763 (w), 721 (w), 542 (w). **Anal. calcd.** for C₁₈H₂₂O₂S (302.4): C 71.48, H 7.33; Found: C 71.54, H 7.18.

3.3.10 Ethyl 3-(p-tolyl)-5-(trimethylsilyl)thiophene-2-carboxylate (1j)

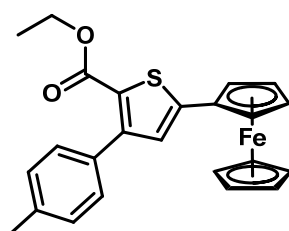


1j
C₁₇H₂₂O₂SSi
[318.51]

Yellow oil. **¹H NMR (500 MHz, CDCl₃):** δ 0.35 (s, 9 H), 1.27 (t, ³J = 7.1 Hz, 3 H), 2.39 (s, 3 H), 4.24 (q, ³J = 7.1 Hz, 2 H), 7.16 (s, 1 H), 7.21 (d, ³J = 7.8 Hz, 2 H), 7.36 (d, ³J = 7.8 Hz, 2 H). **¹³C NMR (125 MHz, CDCl₃):** δ -0.4 (3 CH₃), 14.2 (CH₃), 21.3 (CH₃), 60.8 (CH₂), 128.5 (2 CH), 129.1 (2 CH), 131.6 (C_{quat}), 132.9 (C_{quat}), 137.5 (C_{quat}), 138.0 (CH), 146.4 (C_{quat}), 149.2 (C_{quat}), 162.0 (C_{quat}). **EI MS (70 eV) m/z (%):** 320 (6), 319 (15), 318 ([M]⁺, 62), 305 (11), 304 (23), 303 (100), 275 (21), 273 (11), 137 (5), 130 (7), 129 (5), 115 (9), 83 (13), 75

(19), 73 (24). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 2957 (m), 1718 (s), 1680 (m), 1542 (w), 1502 (m), 1421 (m), 1366 (w), 1341 (m), 1252 (s), 1203 (m), 1119 (m), 1075 (m), 1004 (s), 842 (s), 816 (m), 764 (m), 721 (w), 697 (w), 627 (w), 542 (w), 521 (w). **Anal. calcd.** for C₁₇H₂₂O₂SSi (318.5): C 64.11, H 6.96; Found: C 64.10, H 6.69.

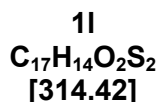
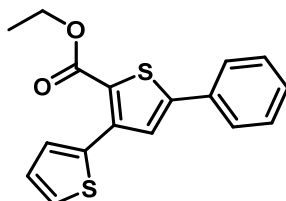
3.3.11 Ethyl 5-ferrocenyl-3-(*p*-tolyl)thiophene-2-carboxylate (1k)



1k
C₂₄H₂₂FeO₂S
[430.34]

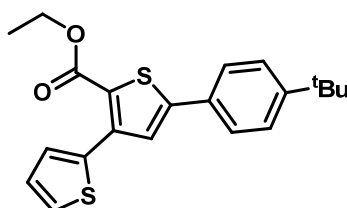
Red brown solid, mp 108 °C. **¹H NMR (500 MHz, CDCl₃):** δ 1.28 (t, ³*J* = 7.1 Hz, 3 H), 2.40 (s, 3 H), 4.13 (s, 5 H), 4.25 (q, ³*J* = 7.1 Hz, 2 H), 4.36 (s, 2 H), 4.64 (s, 2 H), 6.97 (s, 1 H), 7.22 (d, ³*J* = 7.8 Hz, 2 H), 7.40 (d, ³*J* = 7.8 Hz, 2 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.2 (CH₃), 21.3 (CH₃), 60.7 (CH₂), 67.3 (2 CH), 69.5 (2 CH), 70.3 (5 CH), 78.1 (C_{quat}), 123.4 (C_{quat}), 126.5 (CH), 128.4 (2 CH), 129.1 (2 CH), 133.0 (C_{quat}), 137.7 (C_{quat}), 148.8 (C_{quat}), 149.1 (C_{quat}), 162.1 (C_{quat}). **EI MS (70 eV) *m/z* (%):** 432 (10), 431 (27), 430 ([M]⁺, 100), 428 (7), 403 (10), 402 (37), 264 (20), 236 (9), 235 (21), 234 (7), 221 (17), 215 (7), 203 (18), 202 (9), 201 (8), 193 (6), 192 (7), 189 (5), 178 (8), 121 (14), 56 (7). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 3107 (w), 2982 (w), 1681 (s), 1518 (w), 1478 (m), 1414 (m), 1397 (s), 1379 (m), 1330 (m), 1286 (s), 1127 (w), 1090 (s), 999 (w), 843 (m), 813 (m), 763 (w), 685 (w), 598 (w), 544 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 284 nm (14700), 317 (14400). **Anal. calcd.** for C₂₄H₂₂FeO₂S (430.3): C 66.98, H 5.15; Found: C 66.93, H 5.13.

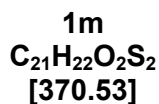
3.3.12 Ethyl 5'-phenyl-[2,3'-bithiophene]-2'-carboxylate (1l)



Pale yellow solid, mp 83 °C. **¹H NMR (500 MHz, CDCl₃):** δ 1.36 (t, ³J = 7.1 Hz, 3 H), 4.34 (q, ³J = 7.1 Hz, 2 H), 7.11 (dd, ³J = 5.1 Hz, ³J = 3.7 Hz, 1 H), 7.36-7.46 (m, 4 H), 7.44 (s, 1 H), 7.62 (dd, ³J = 3.7 Hz, ⁴J = 1.1 Hz, 1 H), 7.65-7.68 (m, 2 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.2 (CH₃), 61.1 (CH₂), 125.2 (C_{quat}), 126.1 (2 CH), 126.4 (CH), 127.1 (CH), 127.2 (CH), 128.9 (CH), 129.0 (CH), 129.1 (2 CH), 132.9 (C_{quat}), 136.4 (C_{quat}), 140.7 (C_{quat}), 148.1 (C_{quat}), 161.9 (C_{quat}). **EI MS (70 eV) m/z (%):** 316 (11), 315 (20), 314 ([M]⁺, 100), 286 (21), 271 (7), 270 (12), 269 (64), 253 (10), 244 (8), 243 (14), 242 (79), 241 (8), 240 (20), 208 (12), 197 (22), 165 (6), 152 (7), 139 (8), 121 (8), 120 (6), 98 (6), 95 (13), 89 (5), 69 (6). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 3105 (w), 2980 (w), 1706 (s), 1546 (m), 1491 (m), 1472 (m), 1454 (m), 1439 (m), 1423 (m), 1366 (w), 1341 (w), 1254 (s), 1217 (s), 1104 (m), 1076 (m), 1043 (m), 1017 (m), 957 (w), 904 (w), 840 (m), 827 (m), 793 (w), 762 (s), 712 (s), 685 (s), 617 (w), 565 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 281 nm (17800), 320 (18200). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 399 nm (6200 cm⁻¹). **Anal. calcd.** for C₁₇H₁₄O₂S₂ (314.4): C 64.94, H 4.49; Found: C 65.04, H 4.43.

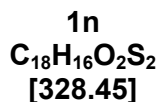
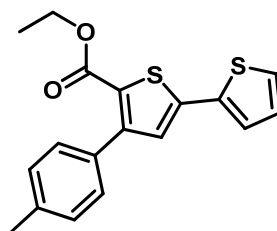
3.3.13 Ethyl 5'-(4-(tert-butyl)phenyl)-[2,3'-bithiophene]-2'-carboxylate (1m)





Yellow oil. **¹H NMR (500 MHz, CDCl₃):** δ 1.36 (t, ³J = 7.1 Hz, 3 H), 1.36 (s, 9 H), 4.34 (q, ³J = 7.1 Hz, 2 H), 7.11 (dd, ³J = 5.1 Hz, ³J = 3.7 Hz, 1 H), 7.39 (dd, ³J = 5.1 Hz, ⁴J = 1.0 Hz, 1 H), 7.41 (s, 1 H), 7.45 (d, ³J = 8.4 Hz, 2 H), 7.60 (d, ³J = 8.4 Hz, 2 H), 7.62 (dd, ³J = 3.7 Hz, ⁴J = 1.0 Hz, 1 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.3 (CH₃), 31.2 (3 CH₃), 34.7 (C_{quat}), 61.1 (CH₂), 124.7 (C_{quat}), 125.9 (2 CH), 126.0 (2 CH), 126.4 (CH), 126.8 (CH), 127.1 (CH), 128.9 (CH), 130.1 (C_{quat}), 136.5 (C_{quat}), 140.7 (C_{quat}), 148.2 (C_{quat}), 152.3 (C_{quat}), 162.0 (C_{quat}). **EI MS (70 eV) m/z (%):** 372 (10), 371 (19), 370 ([M]⁺, 82), 357 (12), 356 (23), 355 (100), 327 (15), 325 (7), 299 (10), 298 (5), 283 (7), 282 (6), 269 (6), 267 (5), 178 (15), 164 (10), 150 (32), 141 (13), 133 (6), 127 (9), 121 (6), 115 (8), 105 (8). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 3074 (w), 2963 (s), 2904 (m), 2868 (m), 1714 (s), 1549 (m), 1505 (m), 1453 (s), 1423 (m), 1366 (m), 1241 (s), 1105 (m), 1079 (m), 1019 (w), 826 (m), 762 (w), 699 (m), 580 (w), 538 (w), 505.5 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 282 nm (18600), 325 (20800). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 395 nm (5500 cm⁻¹). **Anal. calcd.** for C₂₁H₂₂O₂S₂ (370.5): C 68.07, H 5.98; Found: C 68.14, H 5.96.

3.3.14 Ethyl 4-(*p*-tolyl)-[2,2'-bithiophene]-5-carboxylate (1n)

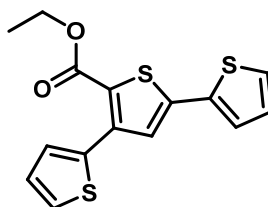


Pale yellow solid, mp 57 °C. **¹H NMR (500 MHz, CDCl₃):** δ 1.28 (t, ³J = 7.1 Hz, 3 H), 2.41 (s, 3 H), 4.25 (q, ³J = 7.1 Hz, 2 H), 7.06 (dd, ³J = 4.8 Hz, ³J = 4.0 Hz, 1 H), 7.14 (s, 1 H), 7.23 (d, ³J = 7.9 Hz, 2 H), 7.30-7.31 (m, 2 H), 7.39 (d, ³J = 7.9 Hz, 2 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.2 (CH₃), 21.3 (CH₃), 60.9 (CH₂), 124.8 (C_{quat}), 125.2 (CH), 126.0 (CH), 127.6 (CH), 128.1 (CH), 128.5 (2 CH), 129.0 (2 CH), 132.5 (C_{quat}), 136.2 (C_{quat}), 137.9 (C_{quat}), 141.2 (C_{quat}),

SONOGASHIRA-COUPPLING-MICHAEL-ADDITION-ALDOL-CONDENSATION SEQUENCE - 3

149.3 (C_{quat}), 161.8 (C_{quat}). **EI MS (70 eV)** *m/z* (%): 330 (11), 329 (20), 328 ([M]⁺, 100), 301 (5), 300 (22), 299 (11), 284 (8), 283 (45), 258 (9), 257 (15), 256 (81), 255 (5), 254 (5), 253 (6), 240 (21), 222 (9), 221 (16), 211 (11), 208 (6), 127 (11), 120 (5), 115 (6), 105 (5), 103 (5), 77 (5), 69 (6). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 2983 (w), 1717 (s), 1677 (s), 1527 (w), 1500 (m), 1475 (w), 1449 (s), 1420 (m), 1373 (s), 1331 (w), 1282 (s), 1256 (s), 1225 (m), 1110 (m), 1076 (s), 911 (w), 841 (m), 814 (s), 762 (m), 717 (m), 549 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 272 nm (13300), 344 (17400). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 404 nm (4300 cm⁻¹). **Anal. calcd.** for C₁₈H₁₆O₂S₂ (328.5): C 65.84, H 4.91; Found: C 65.68, H 4.63.

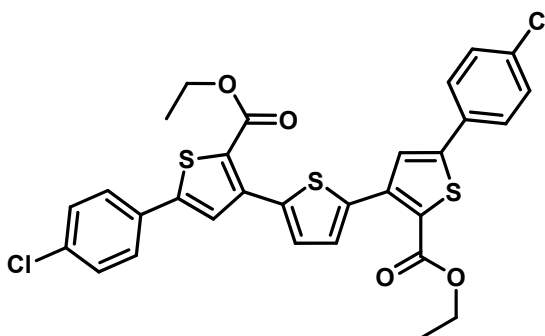
3.3.15 Ethyl [2,2':4',2''-terthiophene]-5'-carboxylate (1o)



1o
C₁₅H₁₂O₂S₃
[320.45]

Pale yellow solid, mp 64 °C. **¹H NMR (500 MHz, CDCl₃):** δ 1.35 (t, ³*J* = 7.1 Hz, 3 H), 4.33 (q, ³*J* = 7.1 Hz, 2 H), 7.06 (dd, ³*J* = 5.1 Hz, ³*J* = 3.7 Hz, 1 H), 7.10 (dd, ³*J* = 5.1 Hz, ³*J* = 3.7 Hz, 1 H), 7.29 (s, 1 H), 7.31-7.33 (m, 2 H), 7.39 (dd, ³*J* = 5.1 Hz, ⁴*J* = 1.1 Hz, 1 H), 7.60 (dd, ³*J* = 3.7 Hz, ⁴*J* = 1.1 Hz, 1 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.2 (CH₃), 61.2 (CH₂), 124.2 (C_{quat}), 125.4 (CH), 126.3 (CH), 126.6 (CH), 127.1 (CH), 127.3 (CH), 128.1 (CH), 129.0 (CH), 135.8 (C_{quat}), 136.0 (C_{quat}), 140.6 (C_{quat}), 141.2 (C_{quat}), 161.7 (C_{quat}). **EI MS (70 eV)** *m/z* (%): 322 (15), 321 (18), 320 ([M]⁺, 100), 292 (27), 277 (7), 276 (9), 275 (51), 259 (9), 250 (12), 249 (13), 248 (85), 247 (8), 246 (20), 214 (7), 203 (30), 171 (7), 139 (9), 127 (9), 123 (6), 108 (6), 101 (9), 95 (19), 69 (13). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 3105 (w), 2977 (w), 1705 (s), 1655 (w), 1638 (w), 1560 (w), 1509 (w), 1476 (w), 1451 (m), 1422 (m), 1366 (w), 1342 (w); 1258 (s), 1235 (m), 1219 (m), 1103 (m), 1080 (m), 1020 (w), 1010 (w), 830 (w), 821 (m), 758 (w), 706 (m), 659 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 296 nm (12600), 338 (15600). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 411 nm (5300 cm⁻¹). **Anal. calcd.** for C₁₅H₁₂O₂S₃ (320.5): C 56.22, H 3.77; Found: C 56.28, H 3.71.

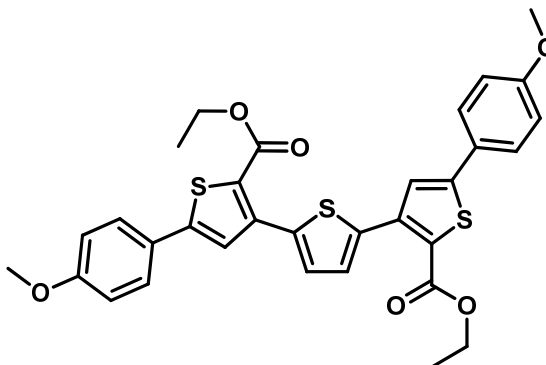
3.3.16 Diethyl 5,5''-bis(4-chlorophenyl)-[3,2':5',3''-terthiophene]-2,2''-dicarboxylate (7a)

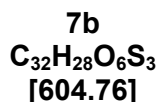


7a
C₃₀H₂₂Cl₂O₄S₃
[613.59]

Yellow solid, decomposition 130 °C. **¹H NMR (300 MHz, CDCl₃):** δ 1.38 (t, J = 7.1 Hz, 6 H), 4.35 (q, J = 7.1 Hz, 4 H), 7.40 (d, J = 8.6 Hz, 4 H), 7.46 (s, 2 H), 7.59 (d, J = 8.6 Hz, 4 H), 7.63 (s, 2 H). **¹³C NMR (75 MHz, CDCl₃):** δ 14.3 (CH₃), 61.3 (CH₂), 125.4 (C_{quat}), 127.2 (CH), 127.3 (CH), 129.3 (CH), 129.3 (CH), 131.4 (C_{quat}), 135.0 (C_{quat}), 137.3 (C_{quat}), 140.3 (C_{quat}), 146.7 (C_{quat}), 161.7 (C_{quat}). **MALDI MS m/z (%):** 614 ([M]⁺, 100), 569 ([M] – C₂H₅O, 90). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 2982 (w), 1715 (s), 1682 (m), 1555 (w), 1489 (m), 1468 (w), 1429 (m), 1269 (m), 1240 (s), 1182 (m), 1094 (s), 1076 (s), 1013 (m), 893 (w), 816 (s), 797 (m), 756 (m), 692 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 318 nm (40900). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 442 nm (8800 cm⁻¹). **Anal. calcd.** for C₃₀H₂₂Cl₂O₄S₃ (613.6): C 58.72, H 3.61; Found: C 58.53, H 3.55.

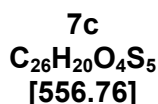
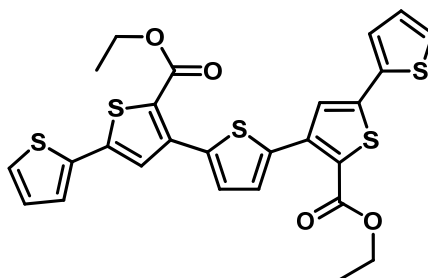
3.3.17 Diethyl 5,5''-bis(4-methoxyphenyl)-[3,2':5',3''-terthiophene]-2,2''-dicarboxylate (7b)





Orange solid, mp 145 °C. **¹H NMR (300 MHz, CDCl₃):** δ 1.37 (t, J = 7.1 Hz, 6 H), 3.85 (s, 6 H), 4.35 (q, J = 7.1 Hz, 4 H), 6.95 (d, J = 8.9 Hz, 4 H), 7.39 (s, 2 H), 7.60 (d, J = 8.8 Hz, 4 H), 7.62 (s, 2 H). **¹³C NMR (75 MHz, CDCl₃):** δ 14.3 (CH₃), 55.3 (CH₃), 61.1 (CH₂), 114.5 (CH), 124.0 (CH), 125.7 (C_{quat}), 126.0 (CH), 127.5 (C_{quat}), 129.2 (C_{quat}), 137.5 (C_{quat}), 140.5 (C_{quat}), 148.2 (C_{quat}), 160.4 (C_{quat}), 162.0 (C_{quat}). **MALDI MS m/z (%)**: 604 ([M]⁺, 85), 559 ([M] – C₂H₅O, 100). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 2959 (w), 2930 (w), 2862 (w), 1699 (s), 1605 (m), 1541 (w), 1504 (m), 1464 (m), 1427 (m), 1416 (m), 1292 (w), 1236 (s), 1177 (s), 1101 (s), 1074 (s), 1032 (s), 866 (w), 808 (s), 758 (m), 704 (w), 658 (w). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 340 nm (54800). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 443 nm (6800 cm⁻¹). **Quantum Yield (CH₂Cl₂):** Φ_f = 0.08. **Anal. calcd.** for C₃₂H₂₈O₆S₃ (604.8): C 63.55, H 4.67; Found: C 63.36, H 4.82.

3.3.18 Diethyl [2,2':4',2'':5'',3''':5''',2''''-quinquethiophene]-2''',5'-dicarboxylate (7c)

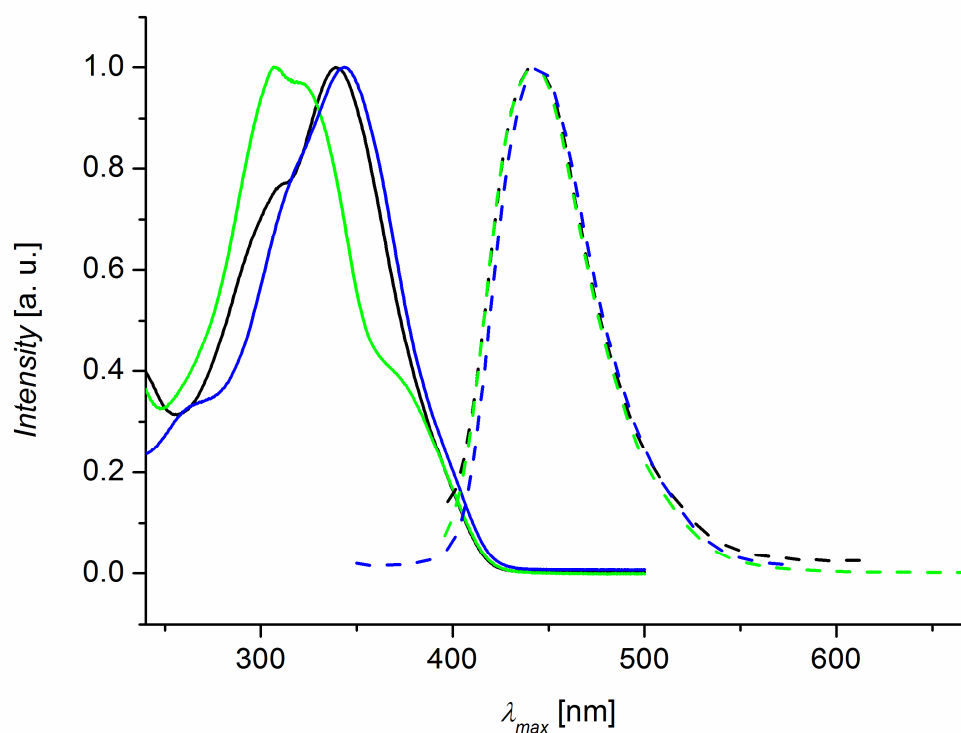


Yellow solid, mp 141 °C. **¹H NMR (500 MHz, CDCl₃):** δ 1.37 (t, 3J = 7.1 Hz, 6 H), 4.35 (q, 3J = 7.1 Hz, 4 H), 7.07 (dd, 3J = 5.0 Hz, 3J = 3.7 Hz, 2 H), 7.33 (m, 4 H), 7.35 (s, 2 H), 7.61 (s, 2 H). **¹³C NMR (125 MHz, CDCl₃):** δ 14.3 (2 CH₃), 61.2 (2 CH₂), 124.2 (2 C_{quat}), 125.5 (2 CH), 126.4 (2 CH), 127.1 (2 CH), 128.2 (2 CH), 129.3 (2 CH), 135.8 (2 C_{quat}), 137.2 (2 C_{quat}), 140.2 (2 C_{quat}), 141.3 (2 C_{quat}), 161.7 (2 C_{quat}). **MALDI MS m/z (%)**: 556 ([M]⁺, 88), 511 ([M] – C₂H₅O, 100). **IR (KBr):** $\tilde{\nu}$ [cm⁻¹] 2977 (w), 1710 (s), 1701 (s), 1655 (w), 1638 (w), 1551 (w), 1509 (w), 1474 (w), 1434 (m), 1387 (w), 1232 (s), 1104 (m), 1076 (m), 1019 (w), 805 (m),

SONOGASHIRA-COUPPLING-MICHAEL-ADDITION-ALDOL-CONDENSATION SEQUENCE - 3

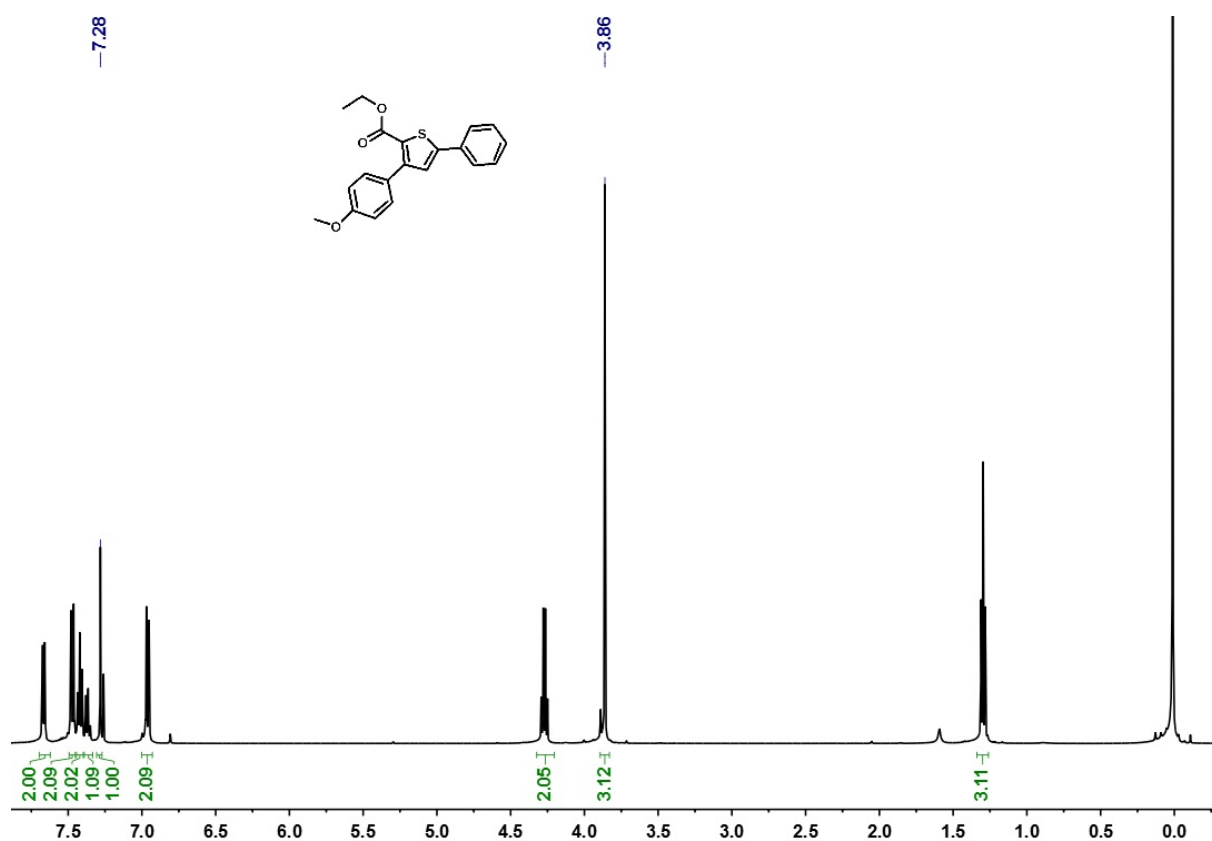
758 (m), 733 (m), 690 (m). **UV/Vis (CH₂Cl₂):** λ_{max} (ϵ) 344 nm (63800). **Emission (CH₂Cl₂):** λ_{max} (Stokes shift) 445 nm (6600 cm⁻¹). **Emission (film):** λ_{max} (Stokes shift) 481 nm (8300 cm⁻¹). **Emission (solid):** λ_{max} (Stokes shift) 512 nm (9500 cm⁻¹). **Quantum Yield (CH₂Cl₂):** Φ_f = 0.11. **Anal. calcd.** for C₂₆H₂₀O₄S₅ (556.8): C 56.09, H 3.62; Found: C 56.17, H 3.76.

4 UV SPECTRA OF OLIGOTHIOPHENES 7

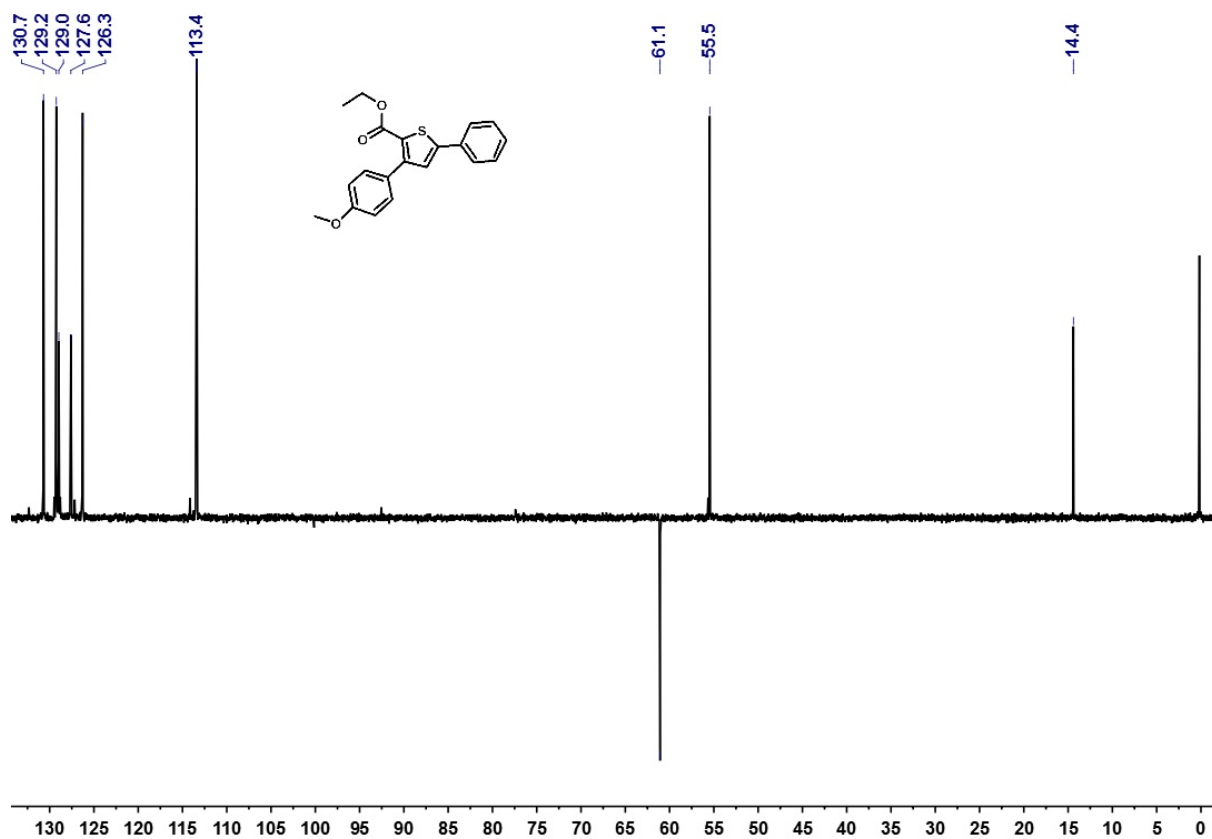


Normalized absorption (solid lines) and emission (dashed lines) spectra of compounds **7a** (green), **7b** (black), and **7c** (blue) (recorded at $T = 293$ K in dichloromethane).

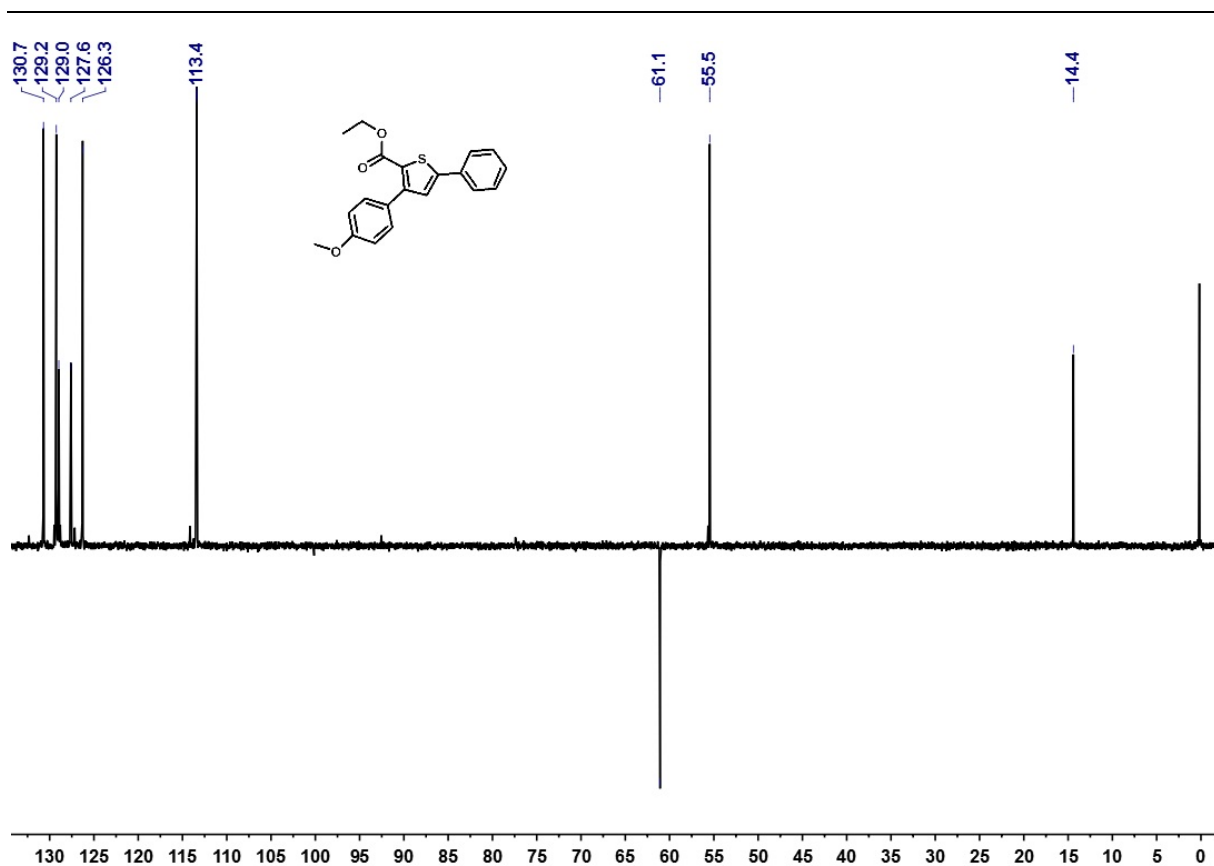
5 ^1H AND ^{13}C NMR SPECTRA



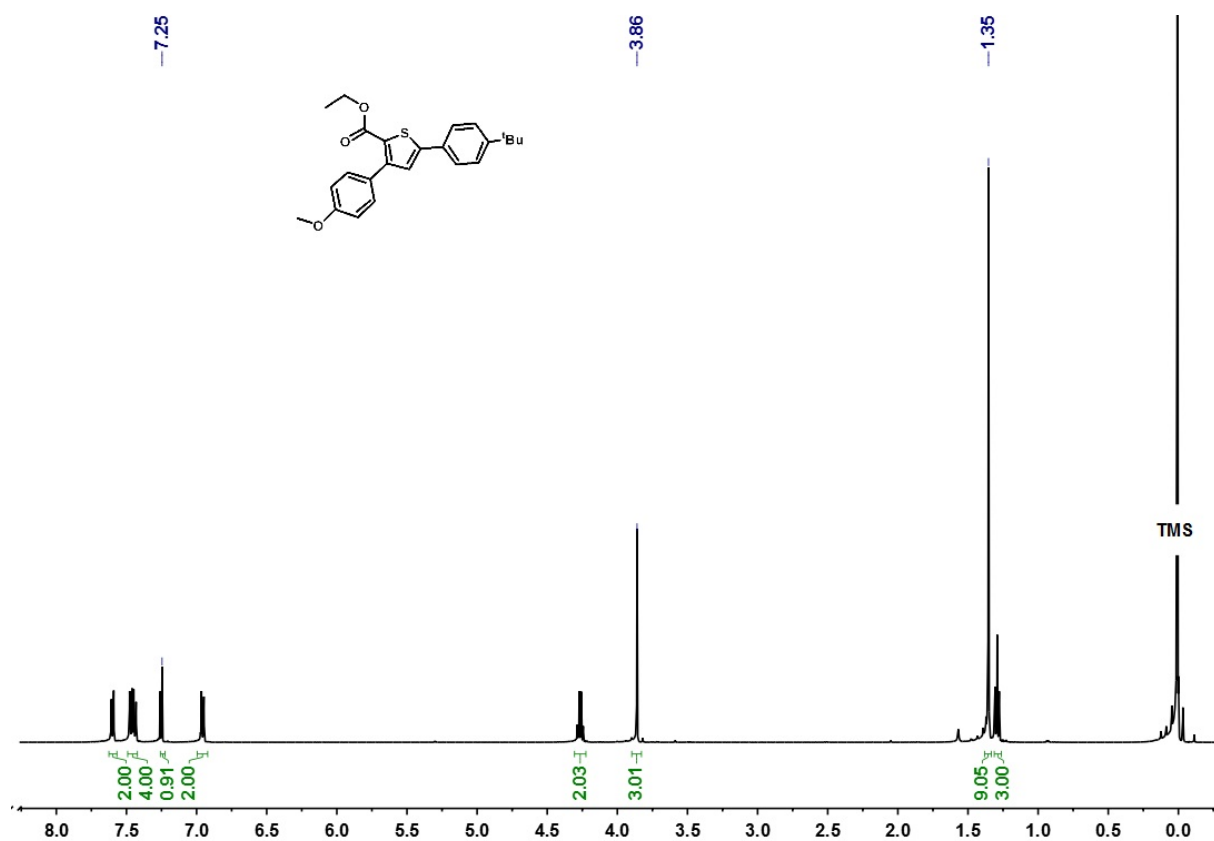
^1H -NMR of 1a (CDCl_3 , 500 MHz, 296 K)



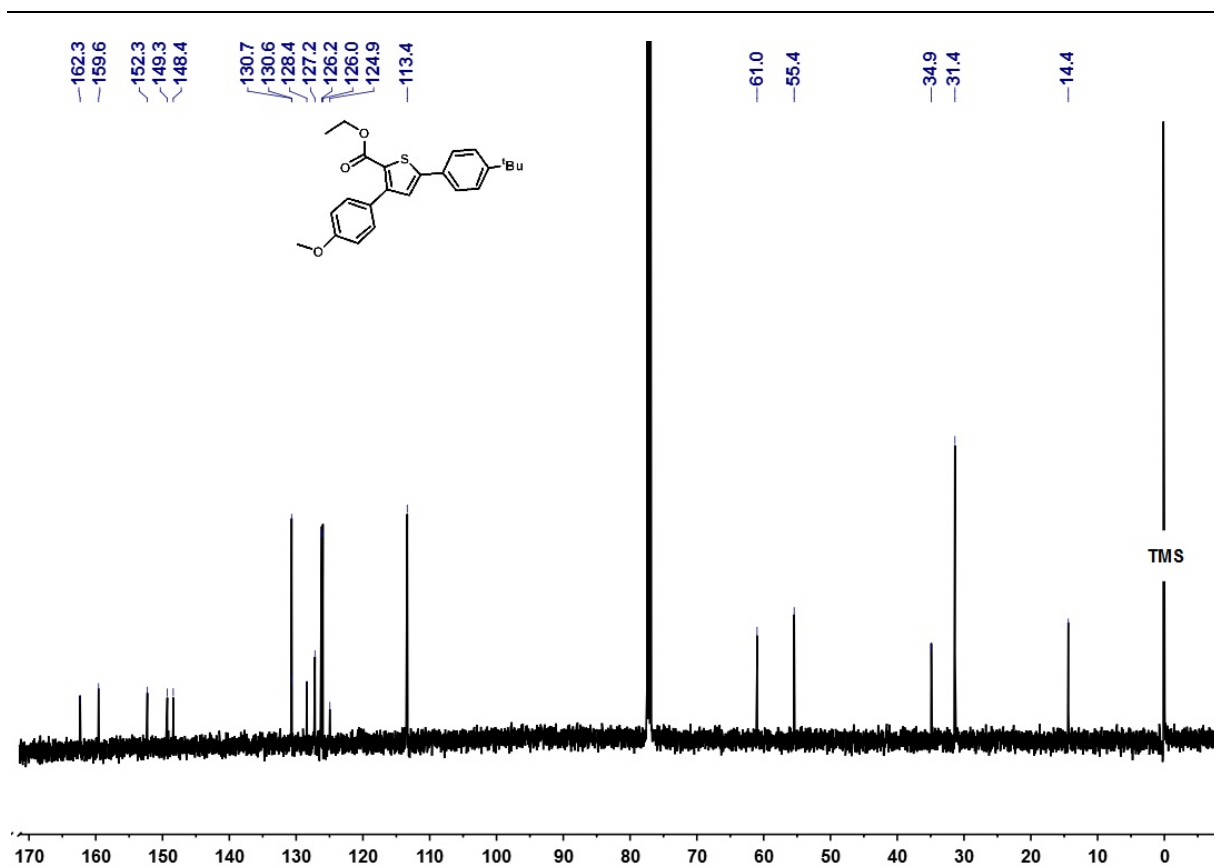
^{13}C -NMR of 1a (CDCl_3 , 125 MHz, 296 K)



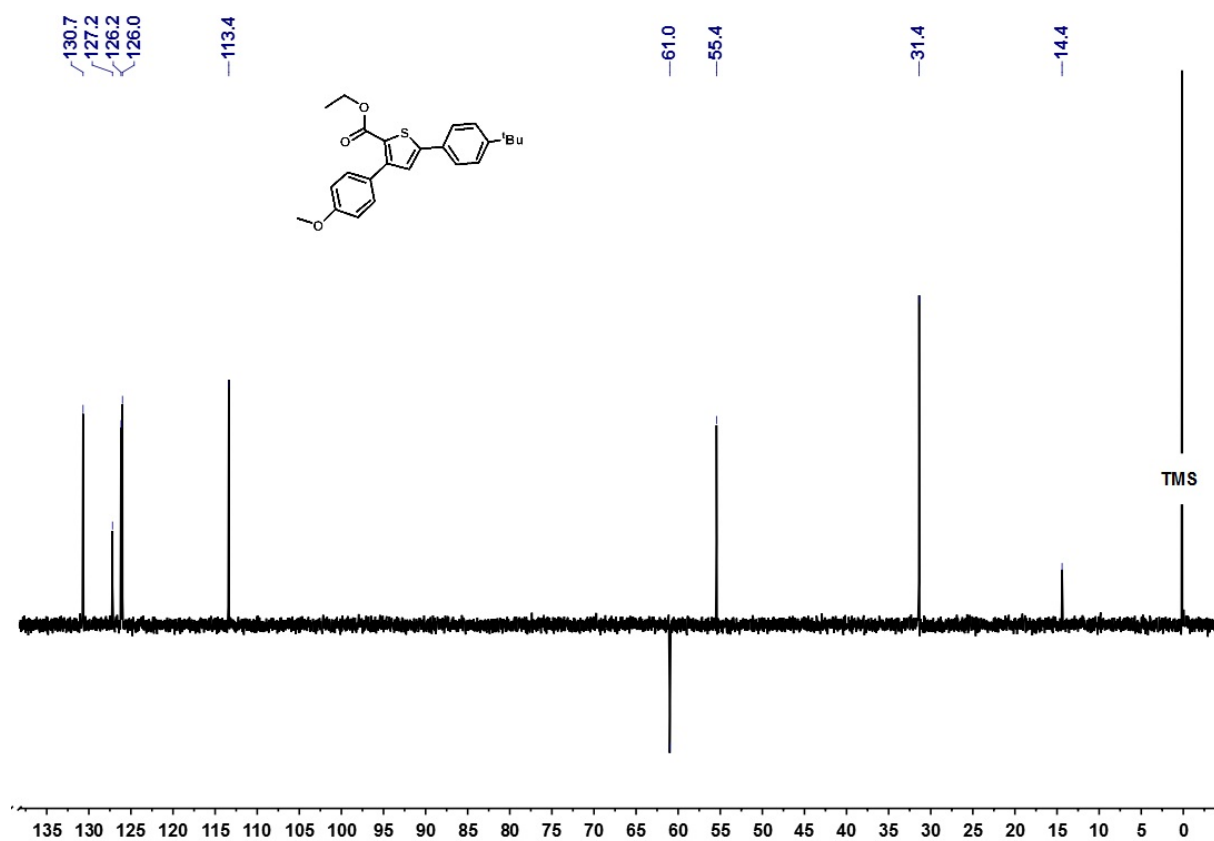
135-DEPT of 1a (CDCl_3 , 125 MHz, 296 K)



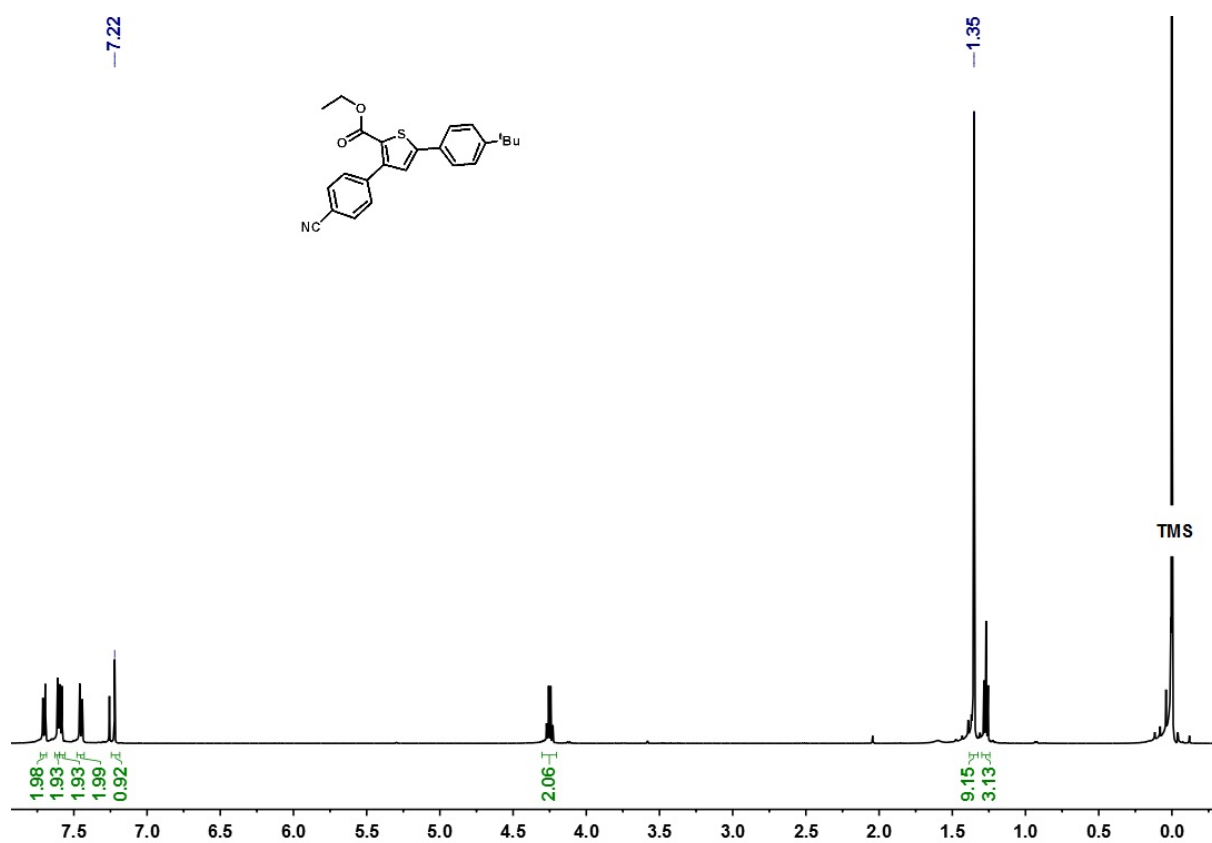
^1H -NMR of 1b (CDCl_3 , 500 MHz, 296 K)



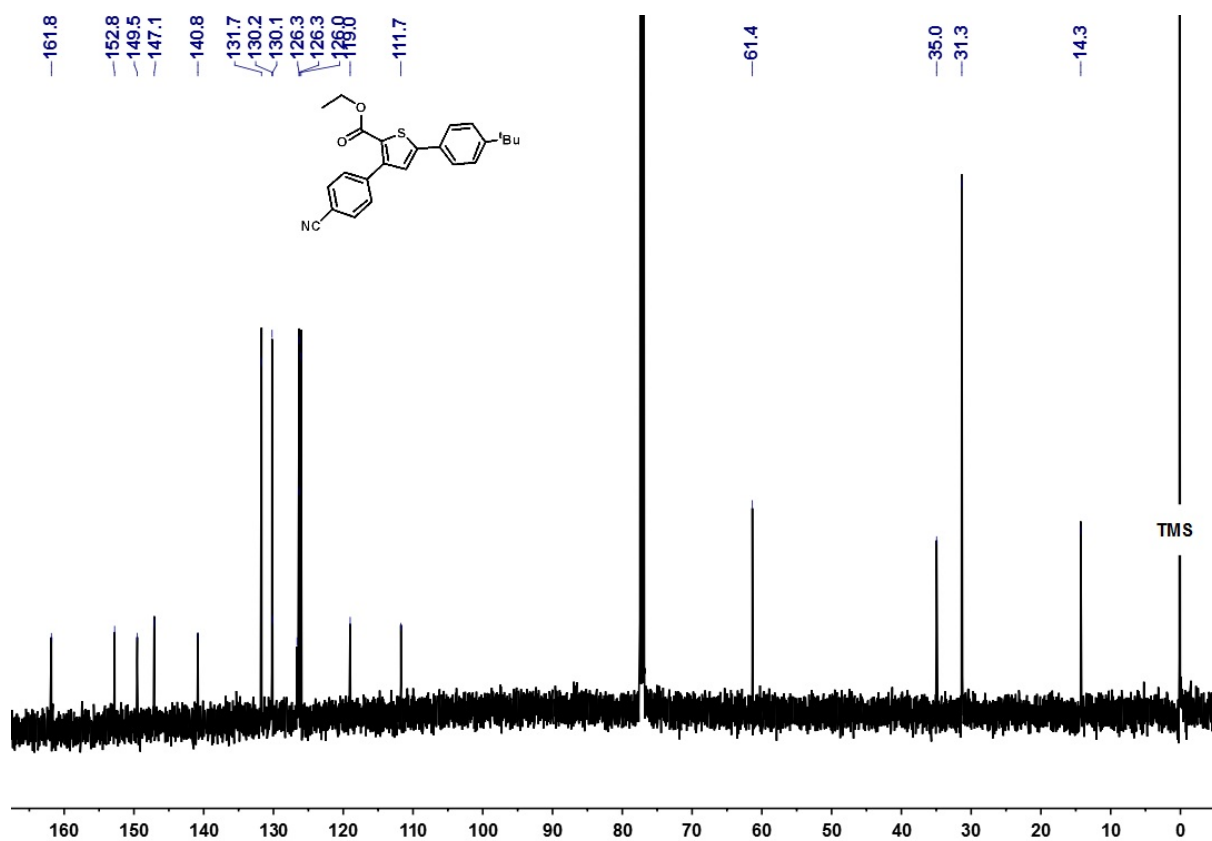
^{13}C -NMR of 1b (CDCl_3 , 125 MHz, 296 K)



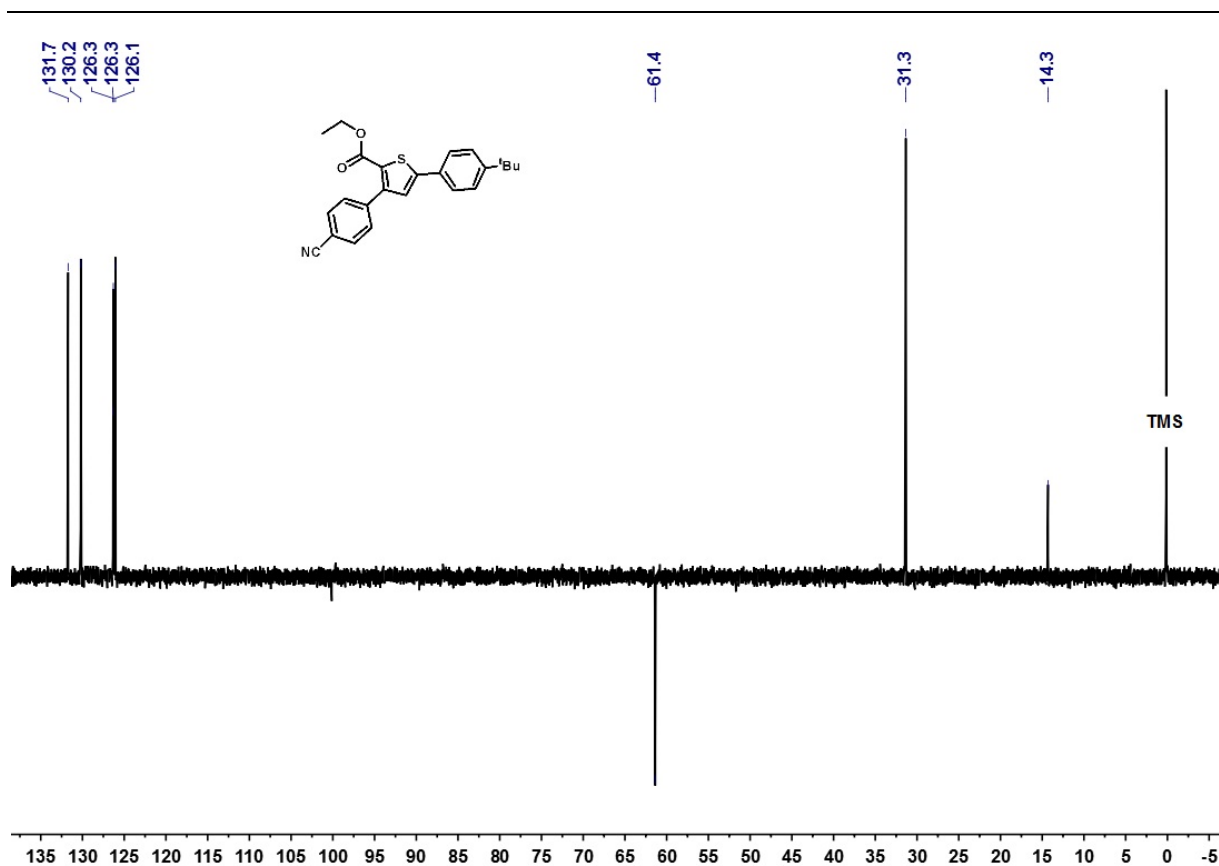
$^{135}\text{-DEPT}$ of 1b (CDCl_3 , 125 MHz, 296 K)



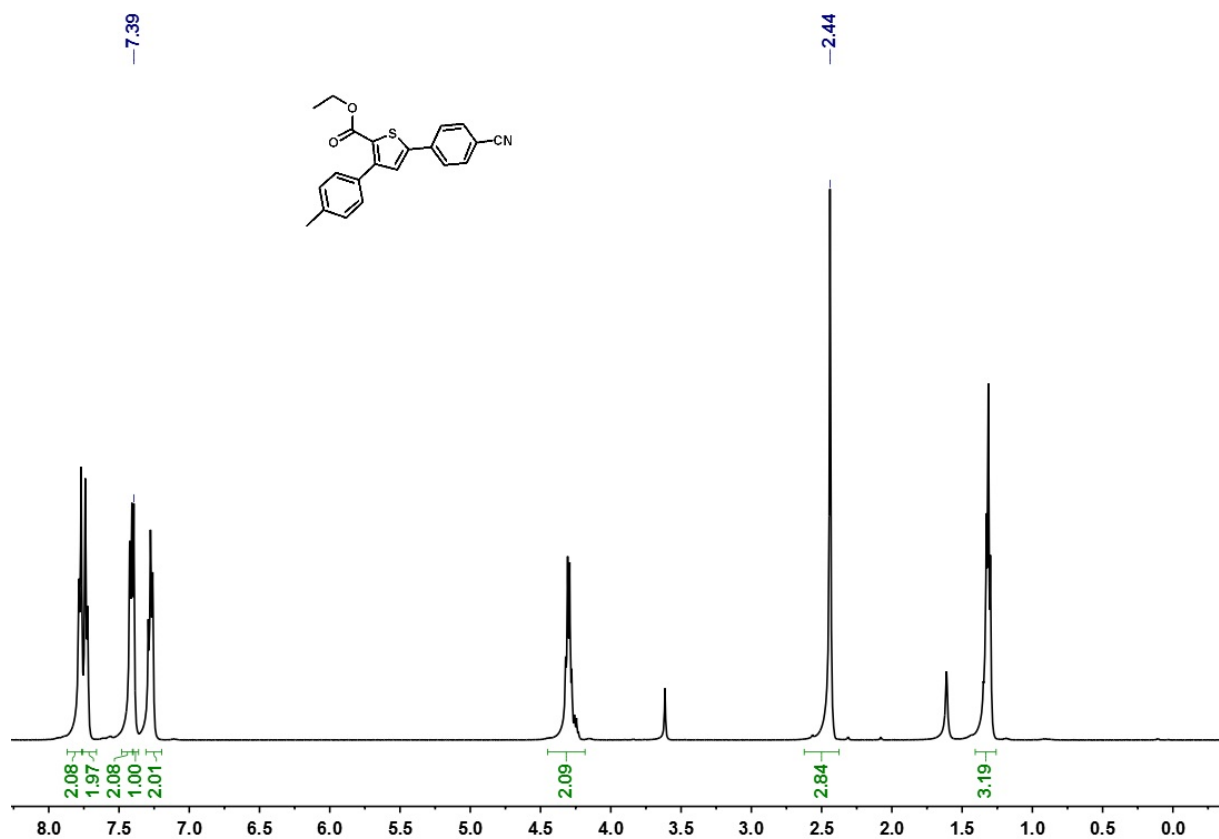
^1H -NMR of **1c** (CDCl_3 , 500 MHz, 296 K)



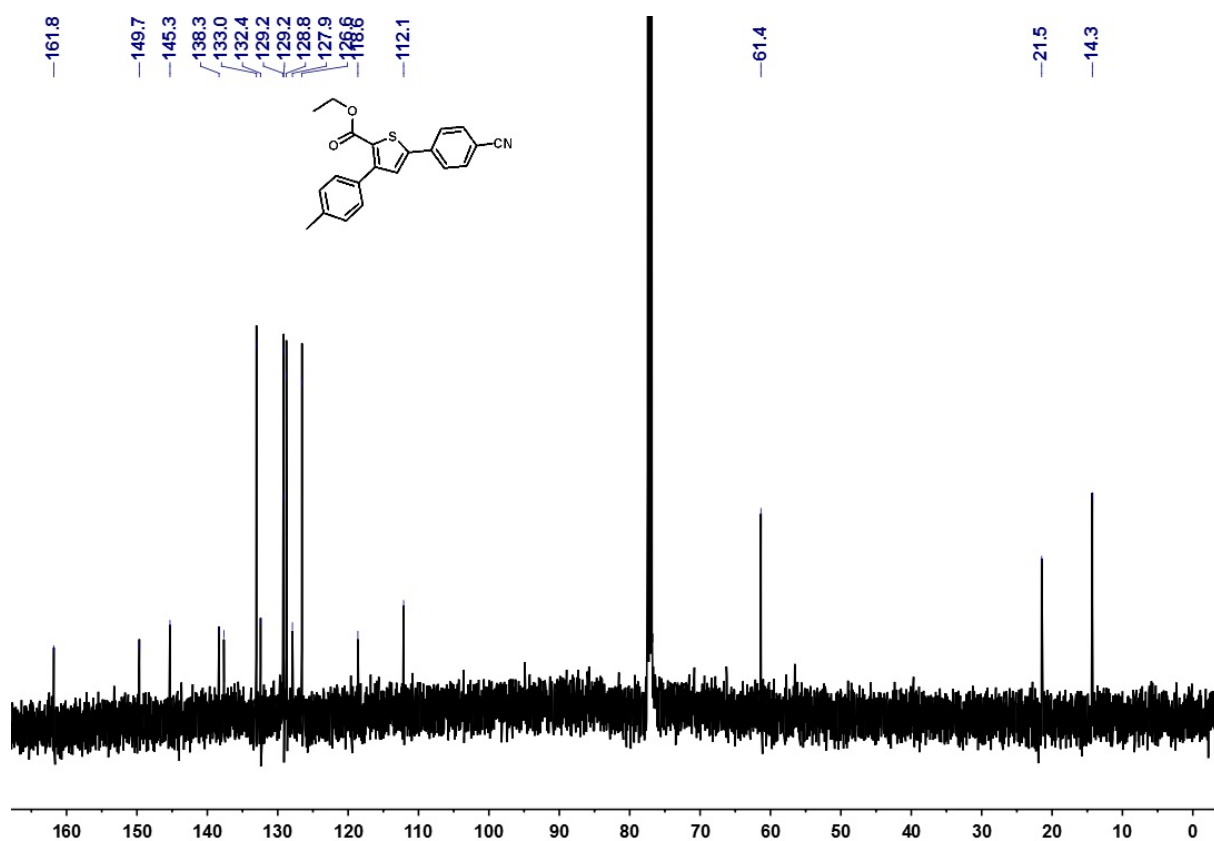
^{13}C -NMR of **1c** (CDCl_3 , 125 MHz, 296 K)



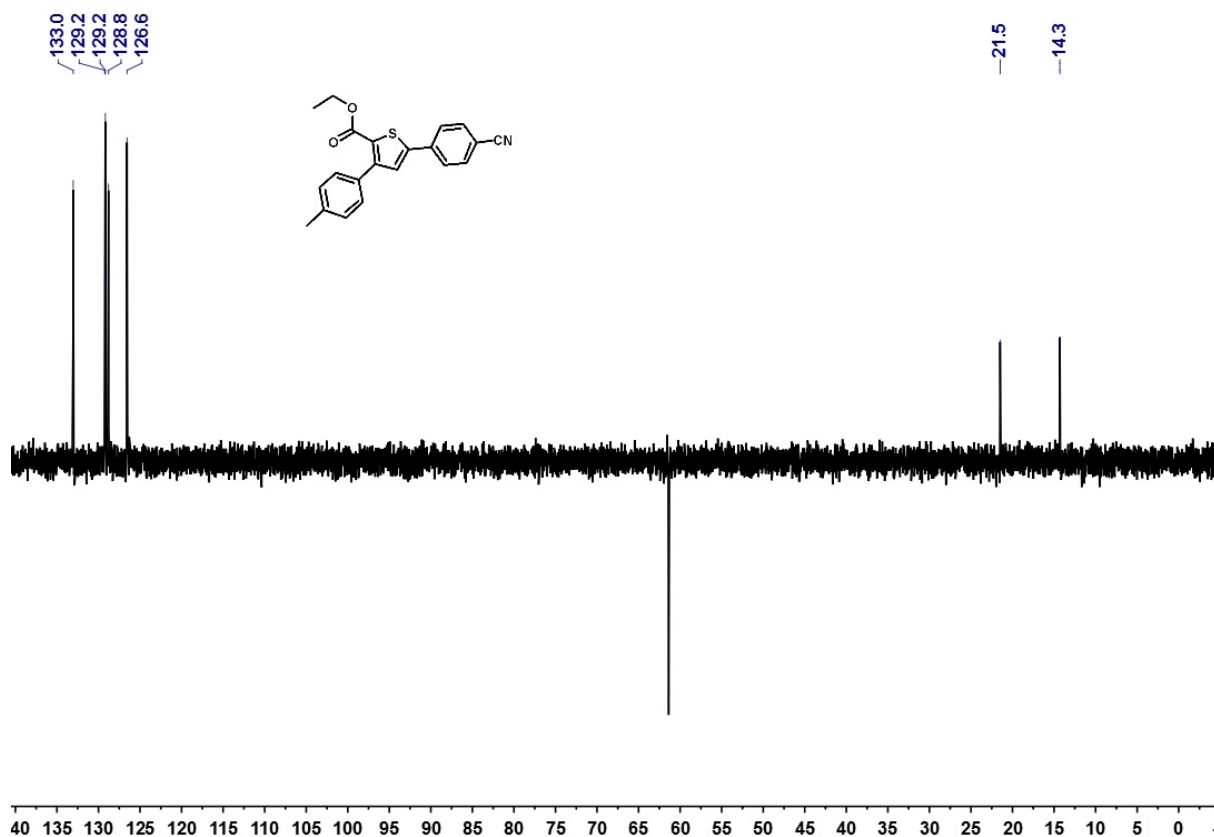
135-DEPT of 1c (CDCl_3 , 125 MHz, 296 K)



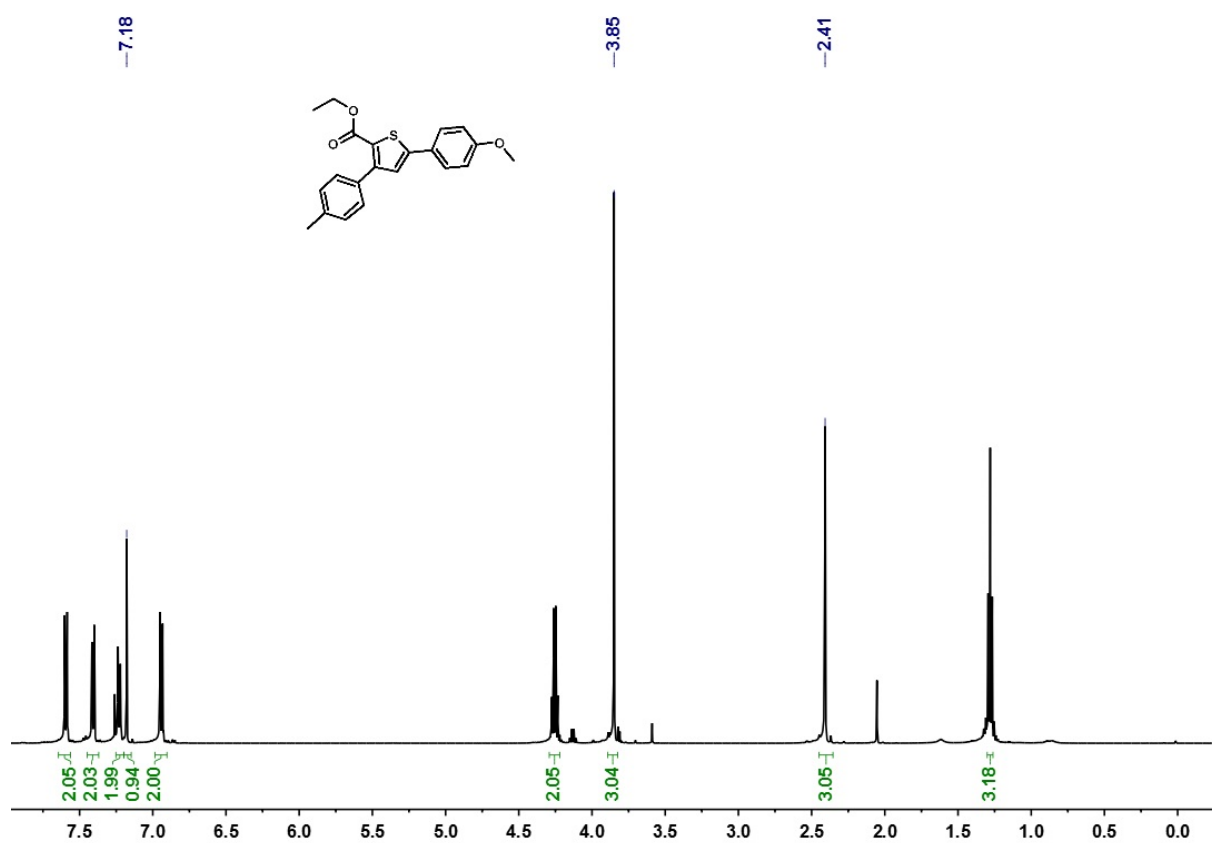
^1H -NMR of 1d (CDCl_3 , 500 MHz, 296 K)



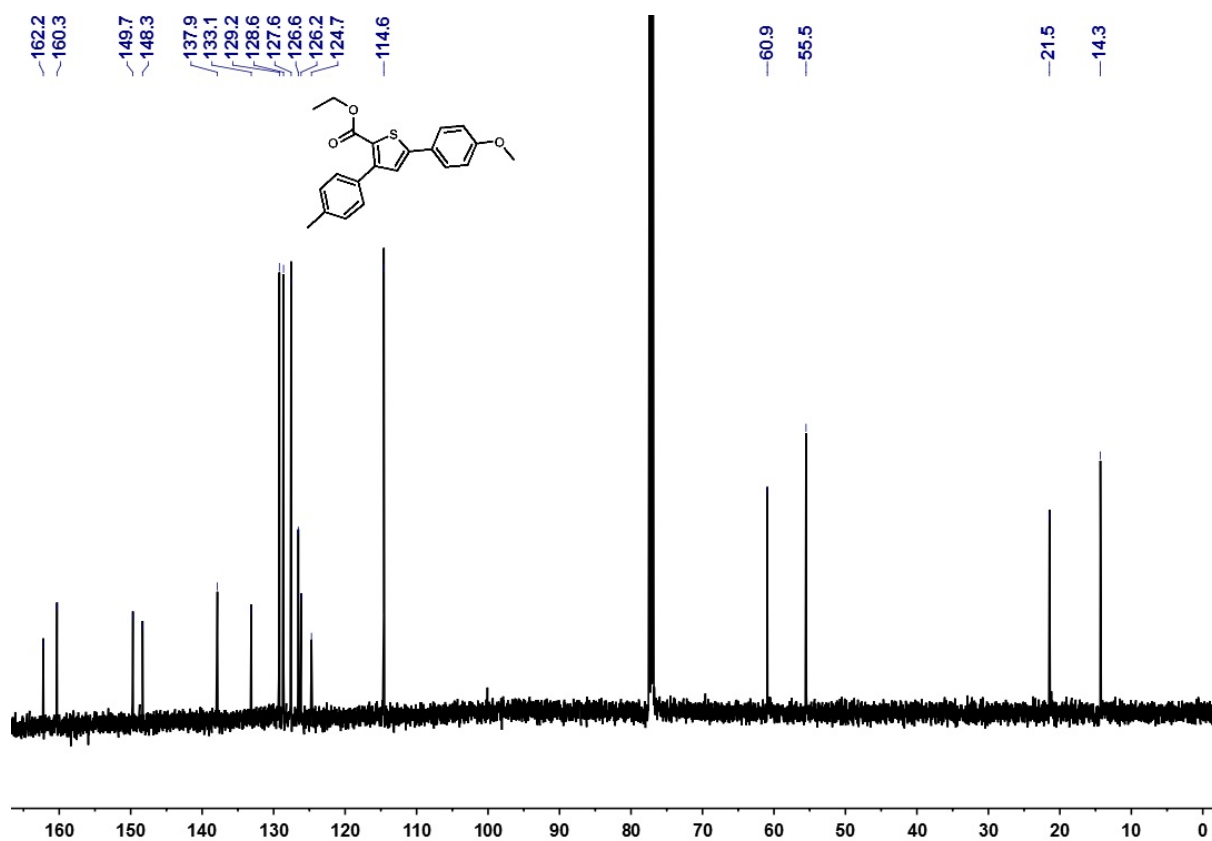
^{13}C -NMR of 1d (CDCl_3 , 125 MHz, 296 K)



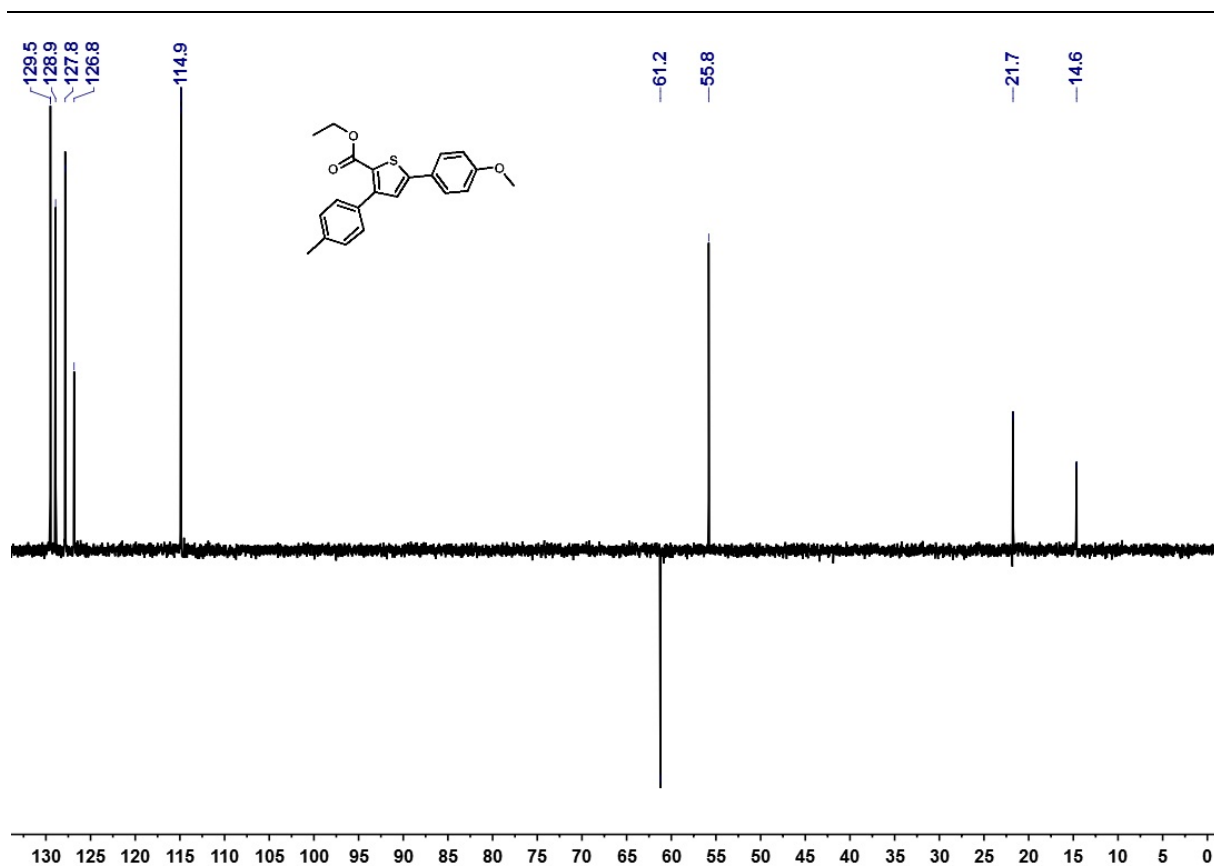
$^{135}\text{-DEPT}$ of 1d (CDCl_3 , 125 MHz, 296 K)



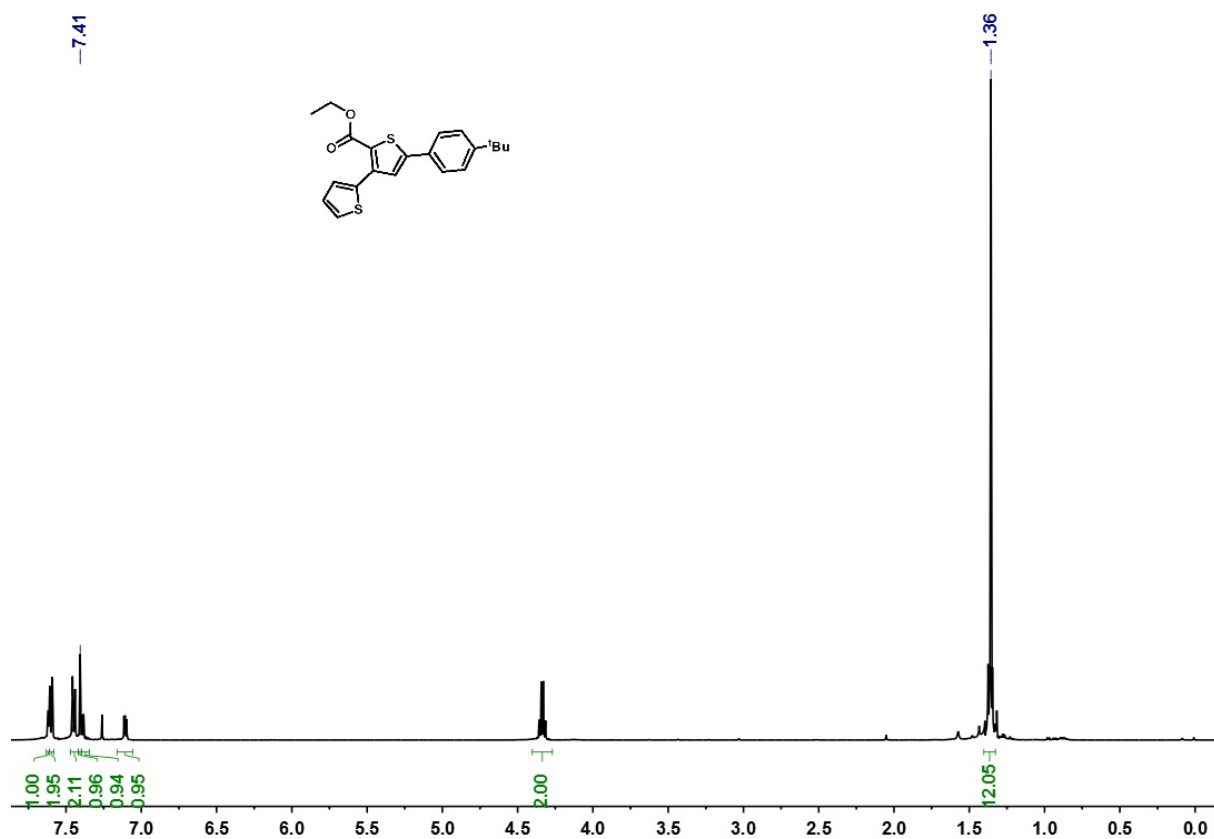
^1H -NMR of 1e (CDCl_3 , 500 MHz, 296 K)



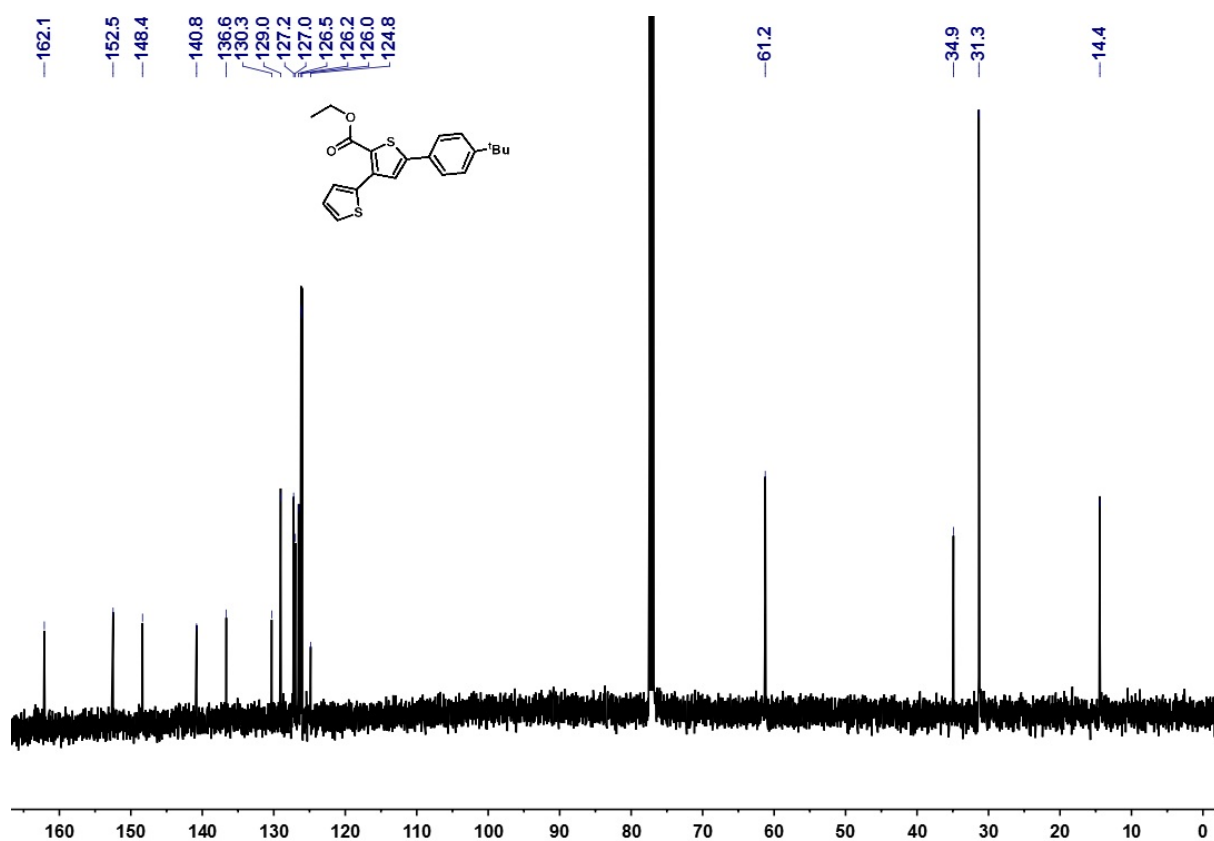
^{13}C -NMR of 1e (CDCl_3 , 125 MHz, 296 K)



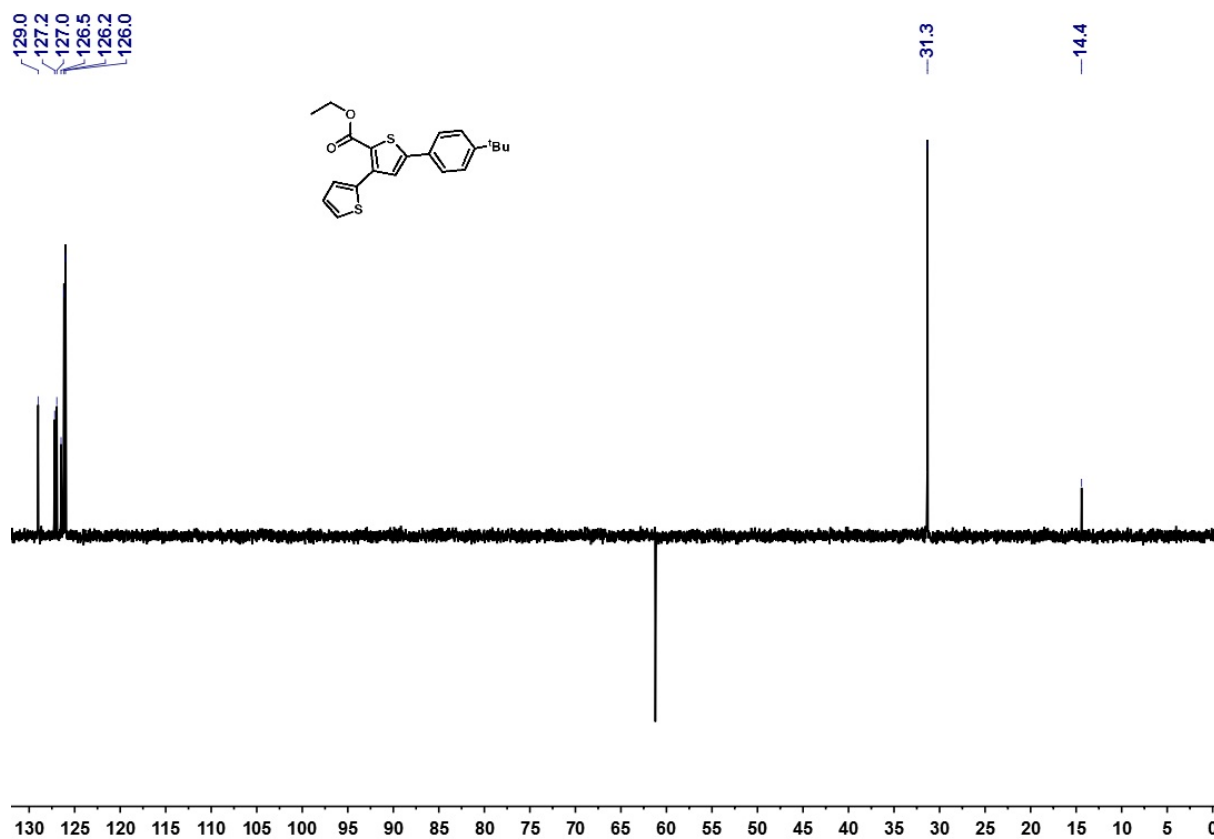
135-DEPT of 1e (CDCl_3 , 125 MHz, 296 K)



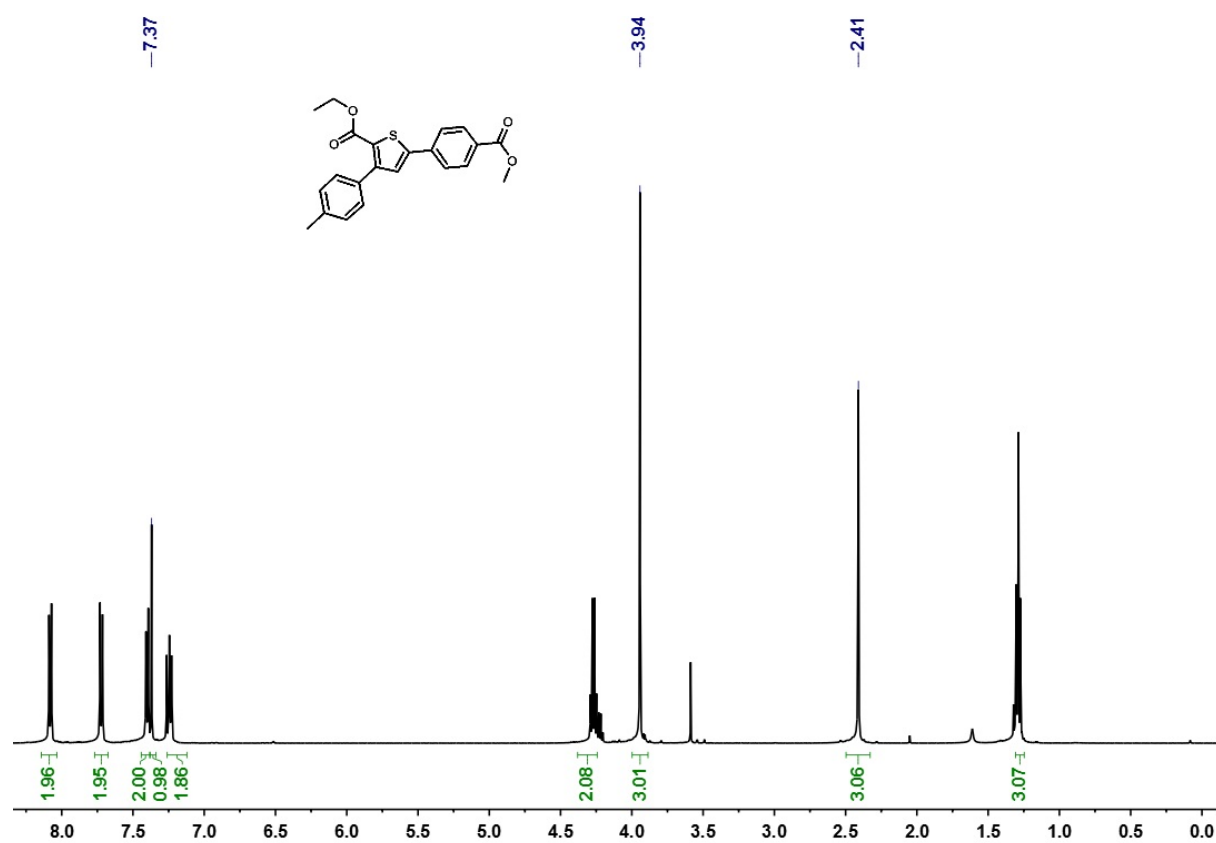
^1H -NMR of 1f (CDCl_3 , 500 MHz, 296 K)



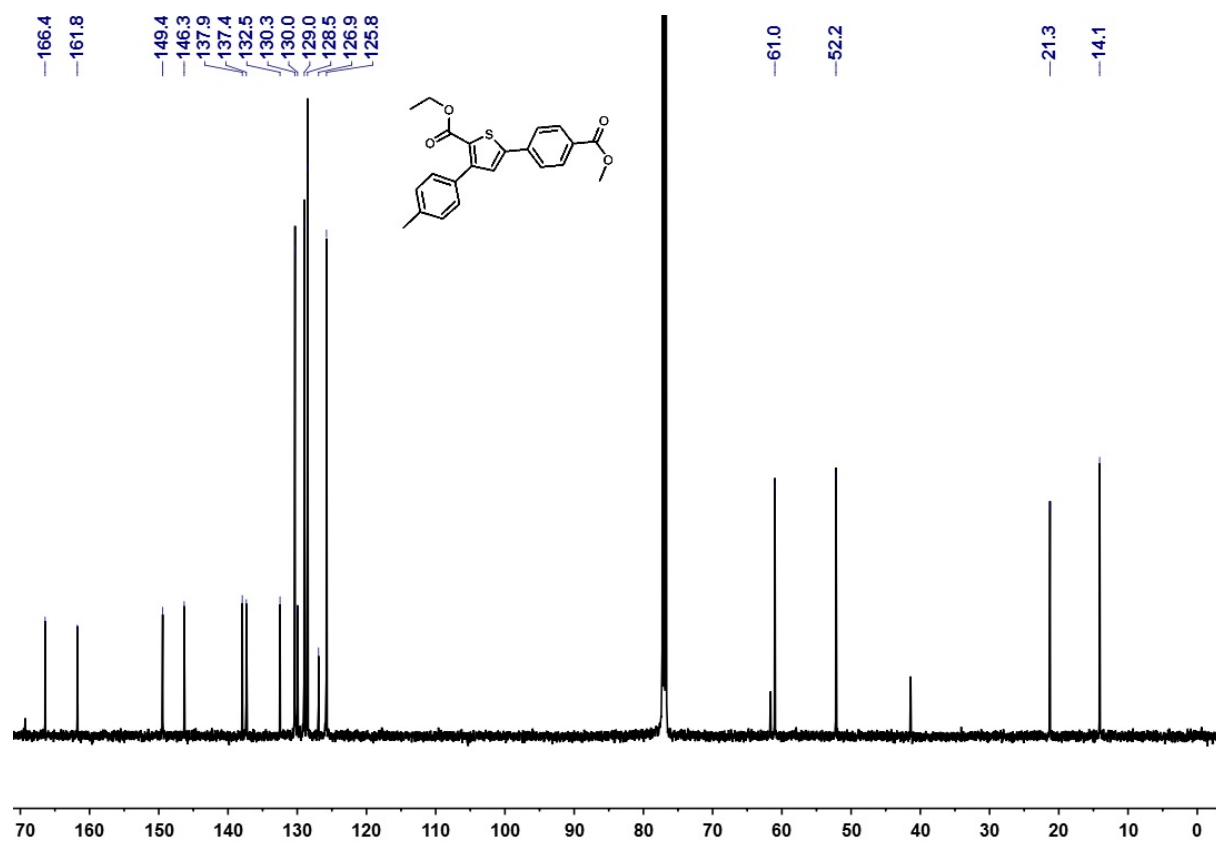
^{13}C -NMR of 1f (CDCl_3 , 125 MHz, 296 K)



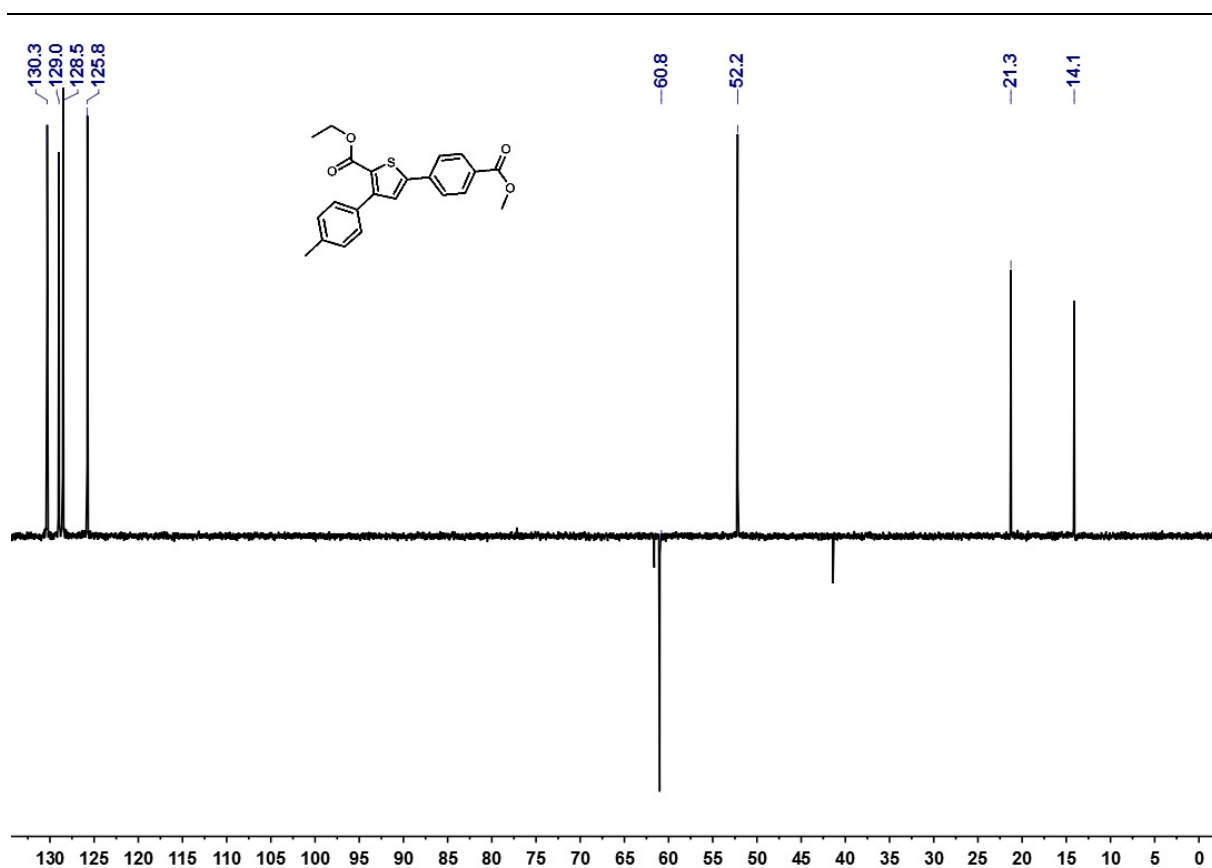
$^{135}\text{-DEPT}$ of 1f (CDCl_3 , 125 MHz, 296 K)



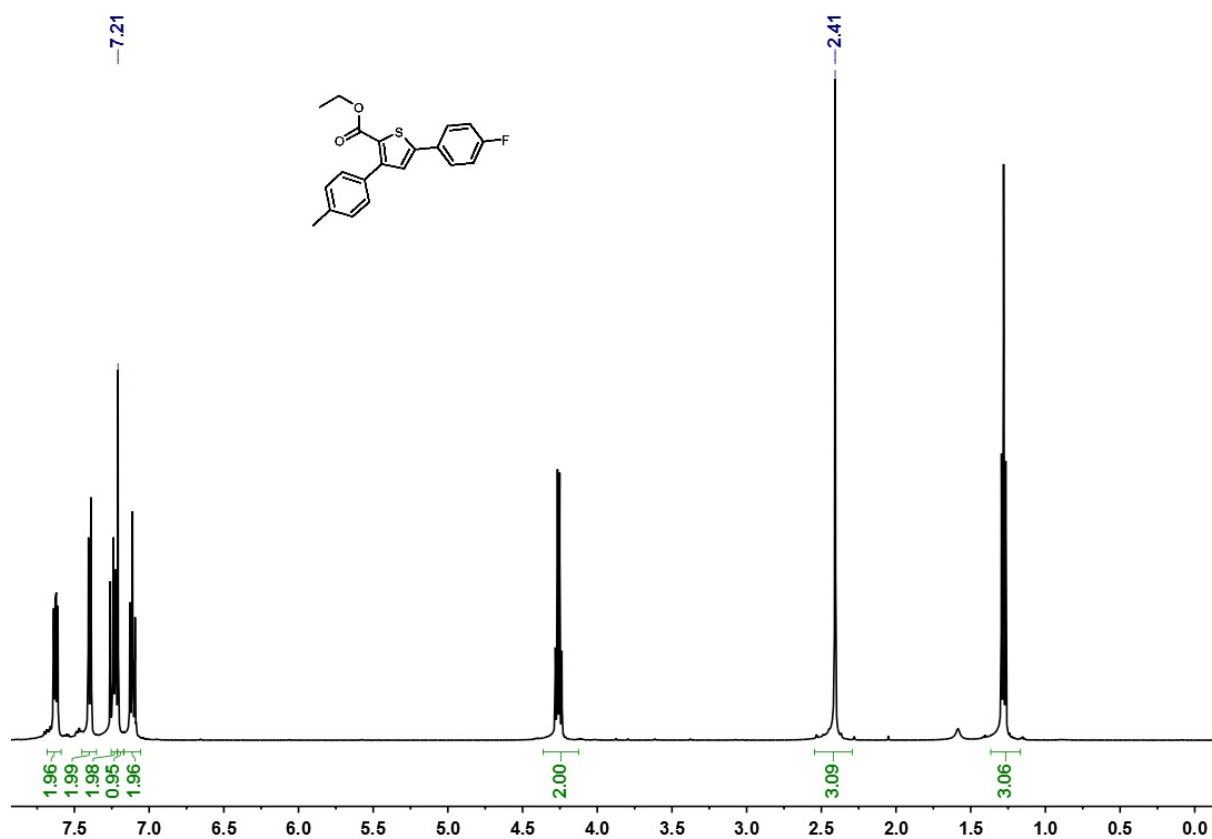
^1H -NMR of 1g (CDCl_3 , 500 MHz, 296 K)



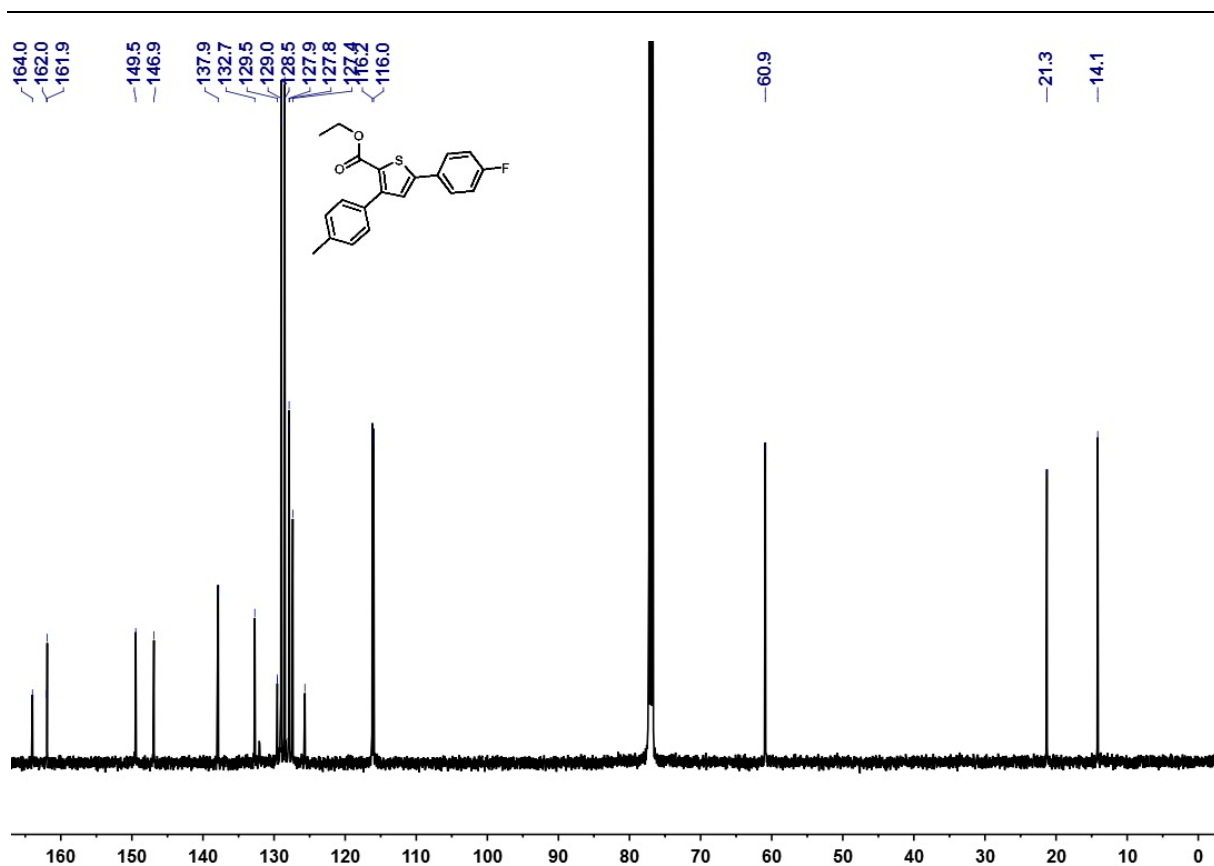
^{13}C -NMR of 1g (CDCl_3 , 125 MHz, 296 K)



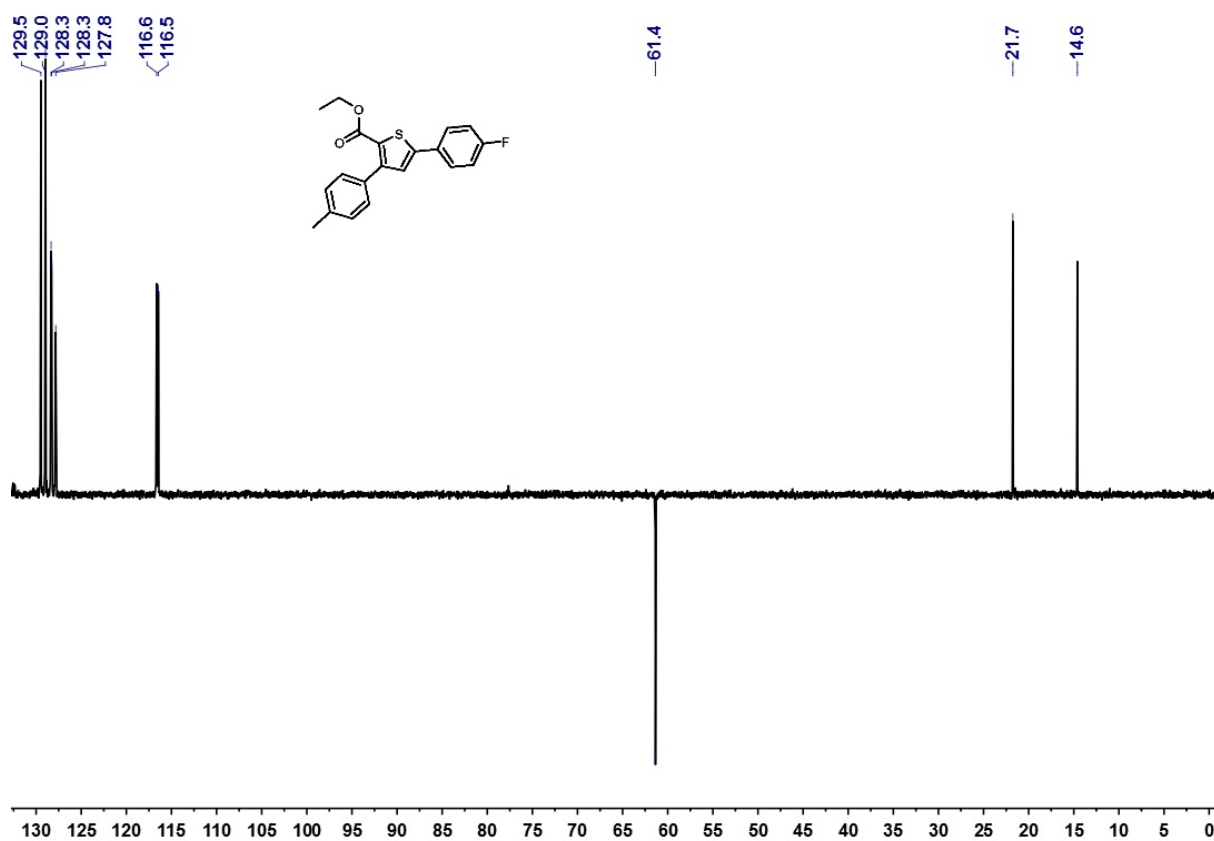
135-DEPT of 1g (CDCl_3 , 125 MHz, 296 K)



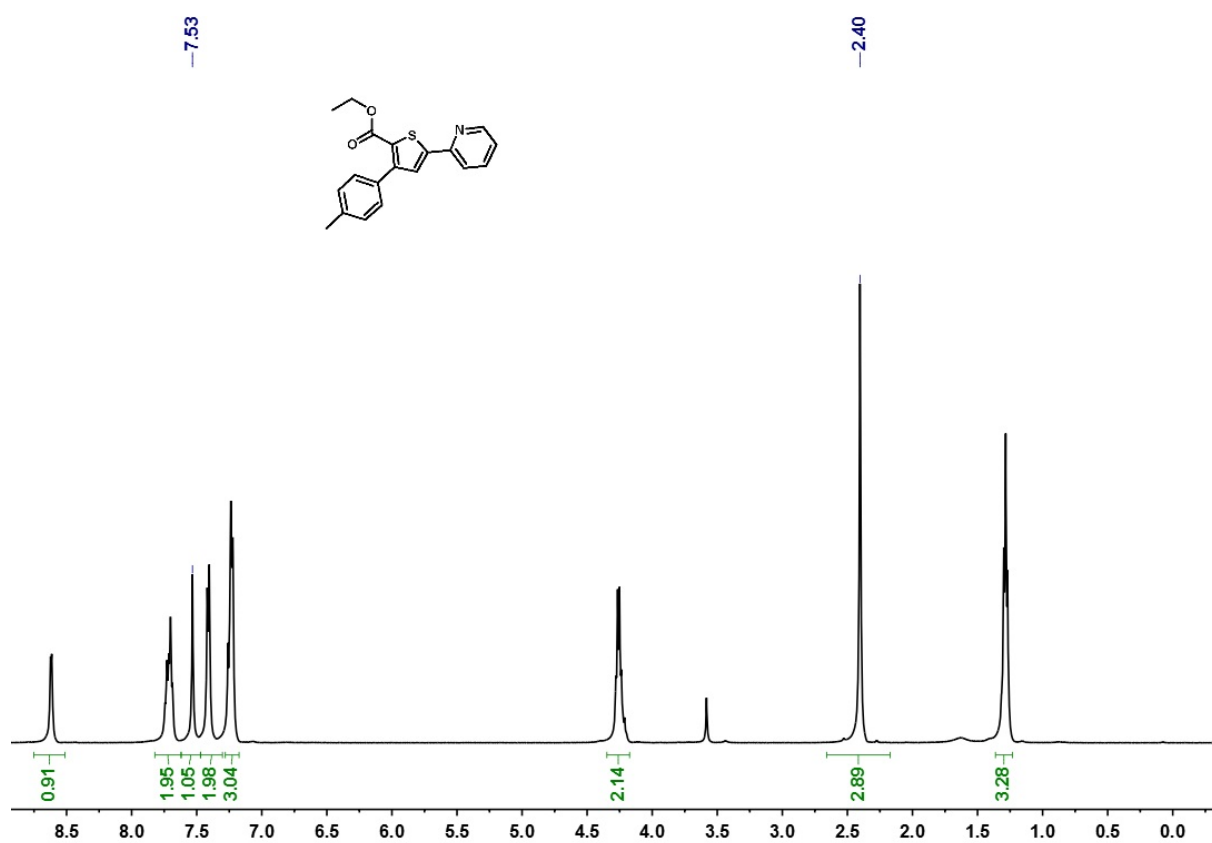
^1H -NMR of 1h (CDCl_3 , 500 MHz, 296 K)



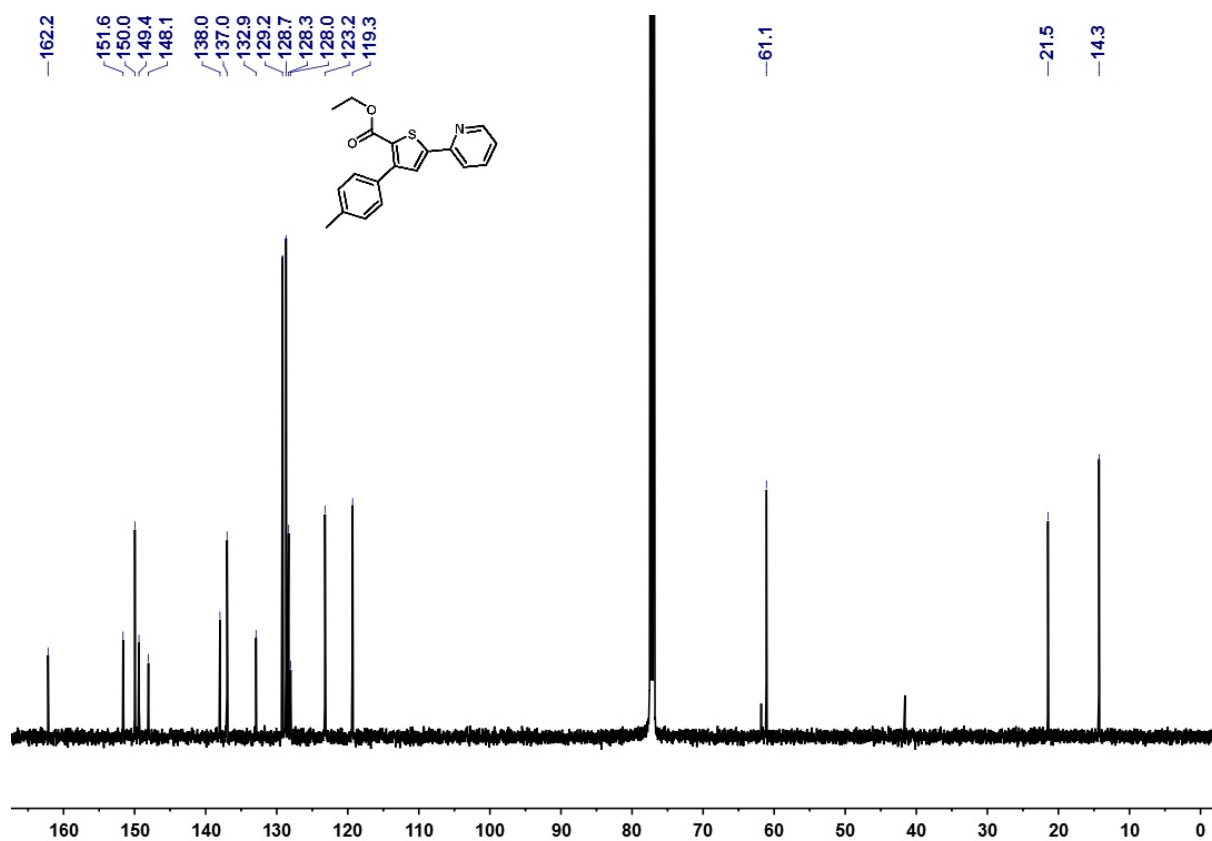
^{13}C -NMR of 1h (CDCl_3 , 125 MHz, 296 K)



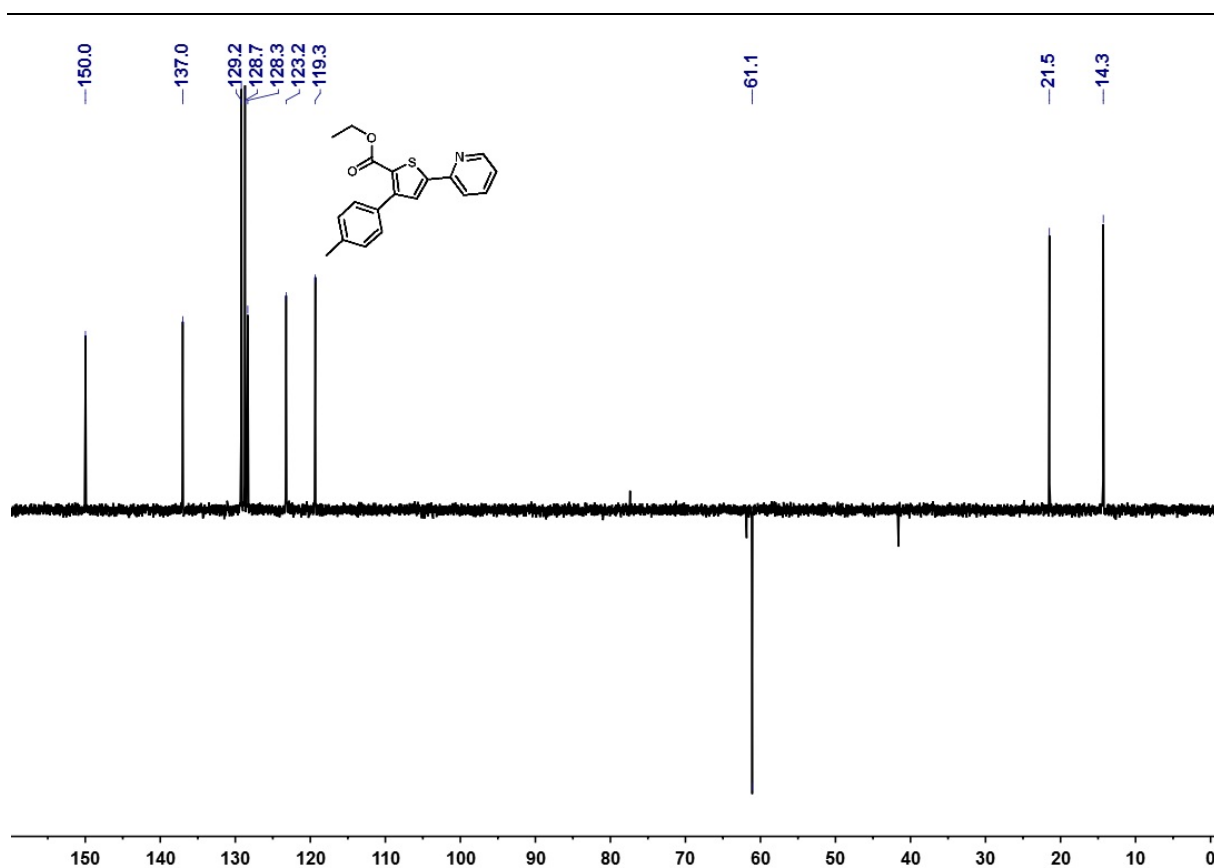
$^{135}\text{-DEPT}$ of 1h (CDCl_3 , 125 MHz, 296 K)



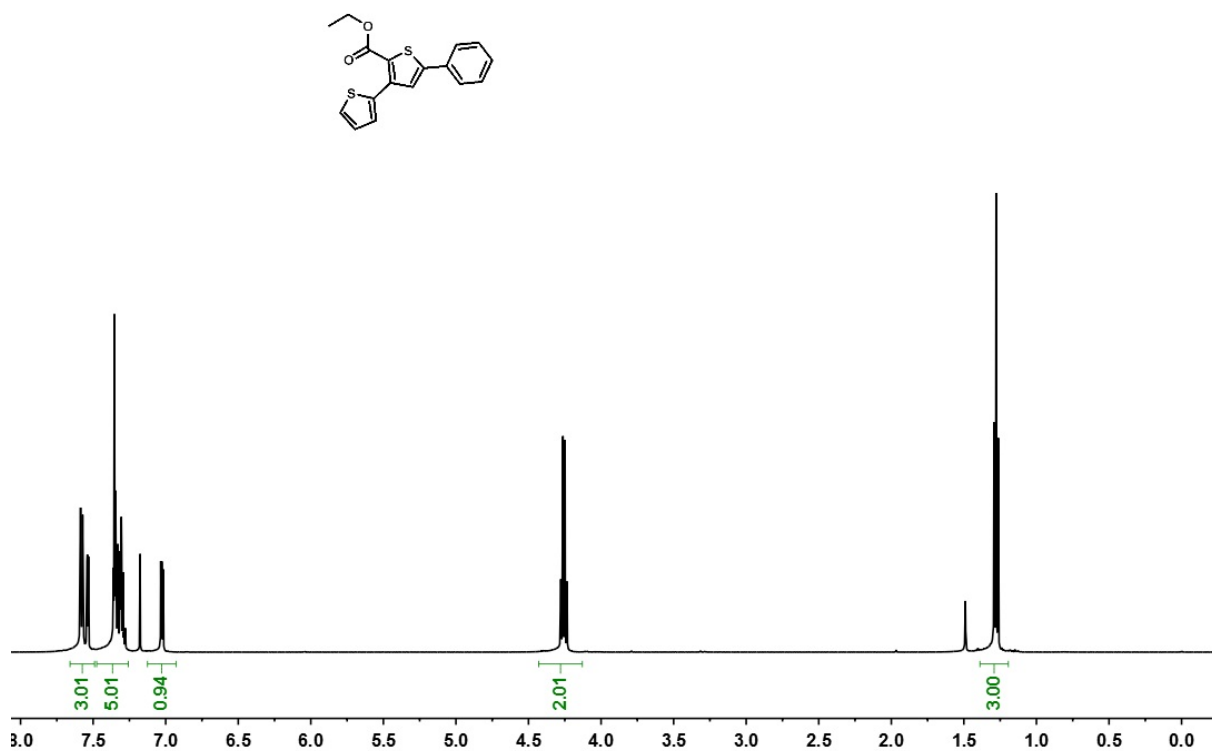
^1H -NMR of 1i (CDCl₃, 500 MHz, 296 K)



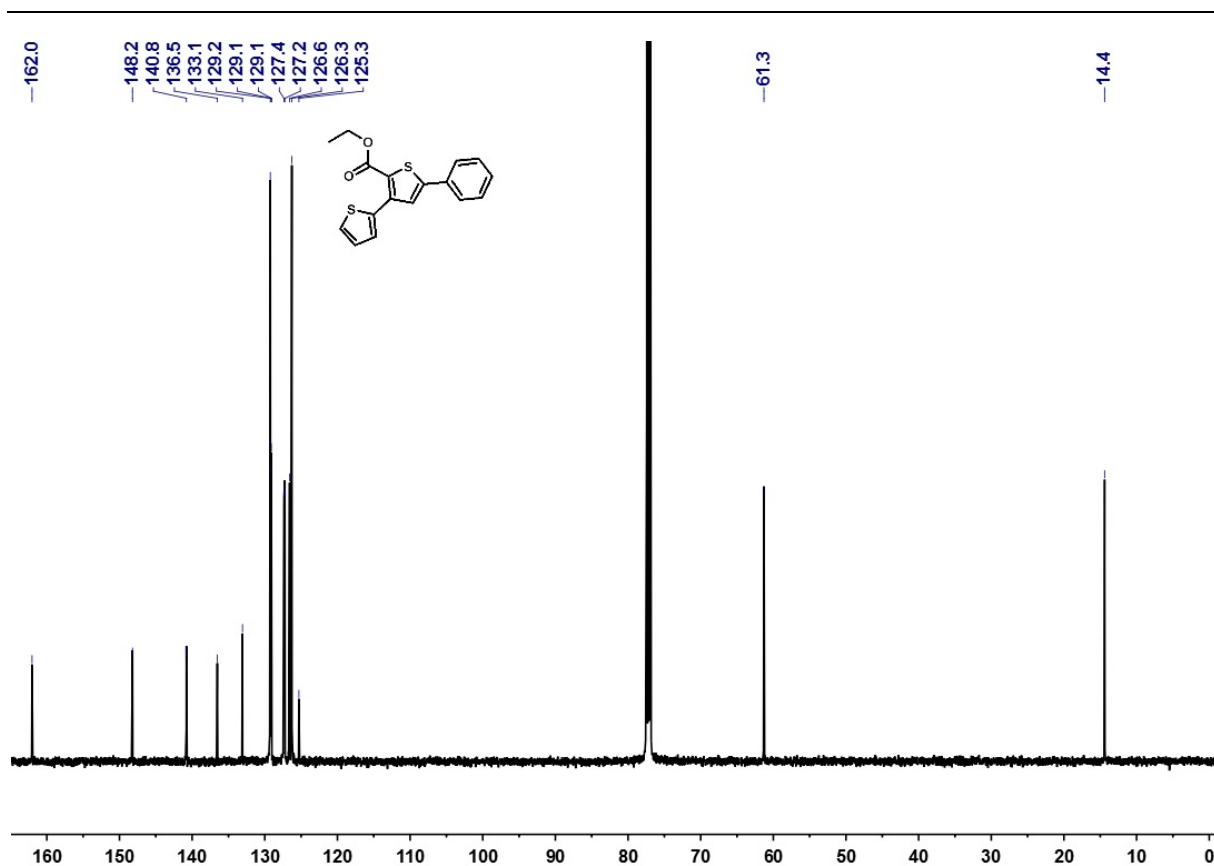
^{13}C -NMR of 1i (CDCl₃, 125 MHz, 296 K)



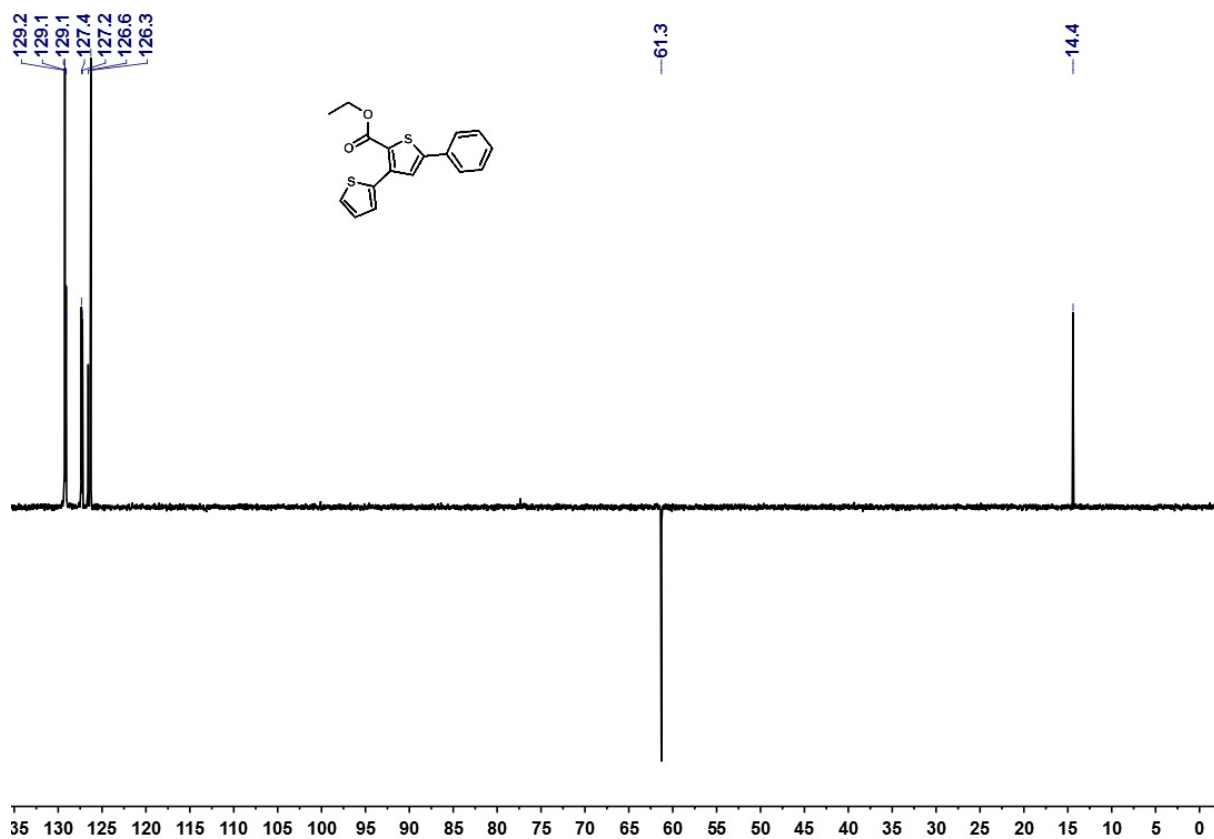
135-DEPT of 1i (CDCl_3 , 125 MHz, 296 K)



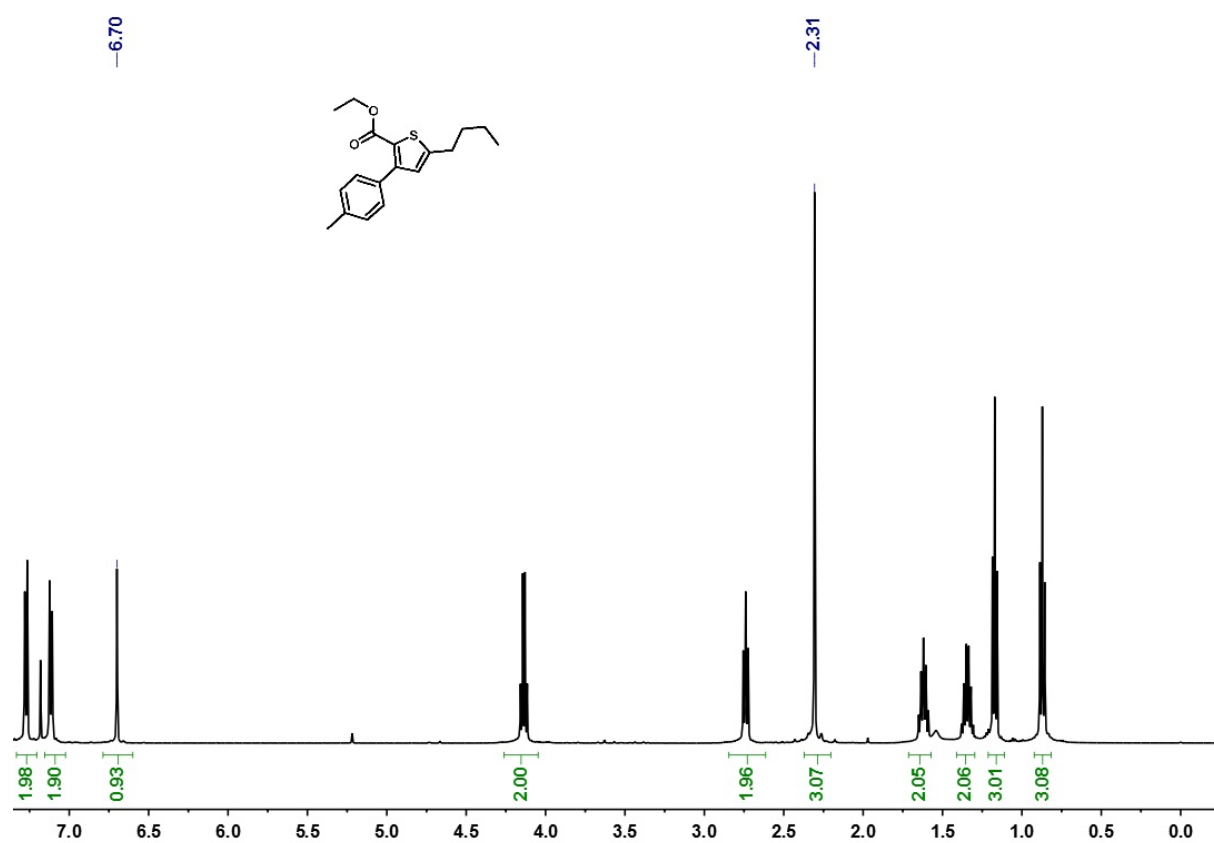
^1H -NMR of 1j (CDCl_3 , 500 MHz, 296 K)



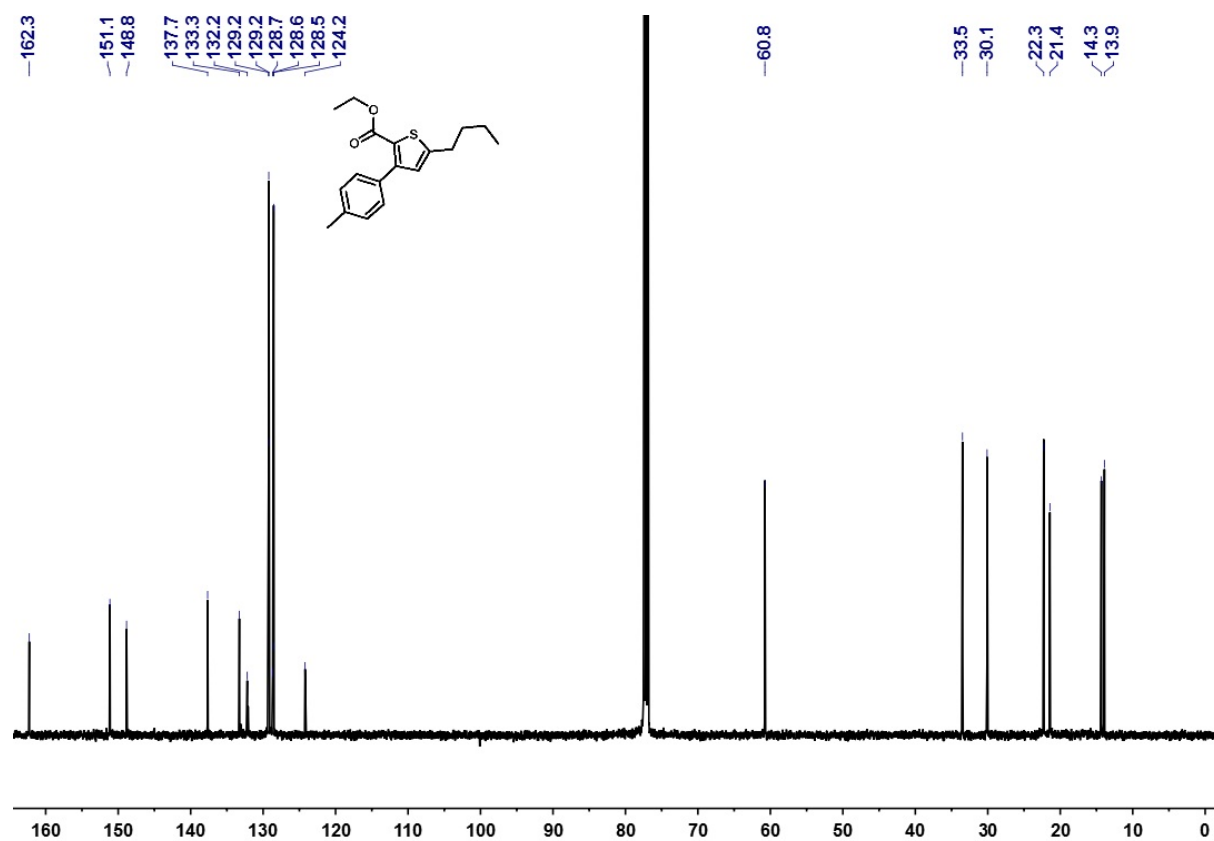
^{13}C -NMR of 1j (CDCl_3 , 125 MHz, 296 K)



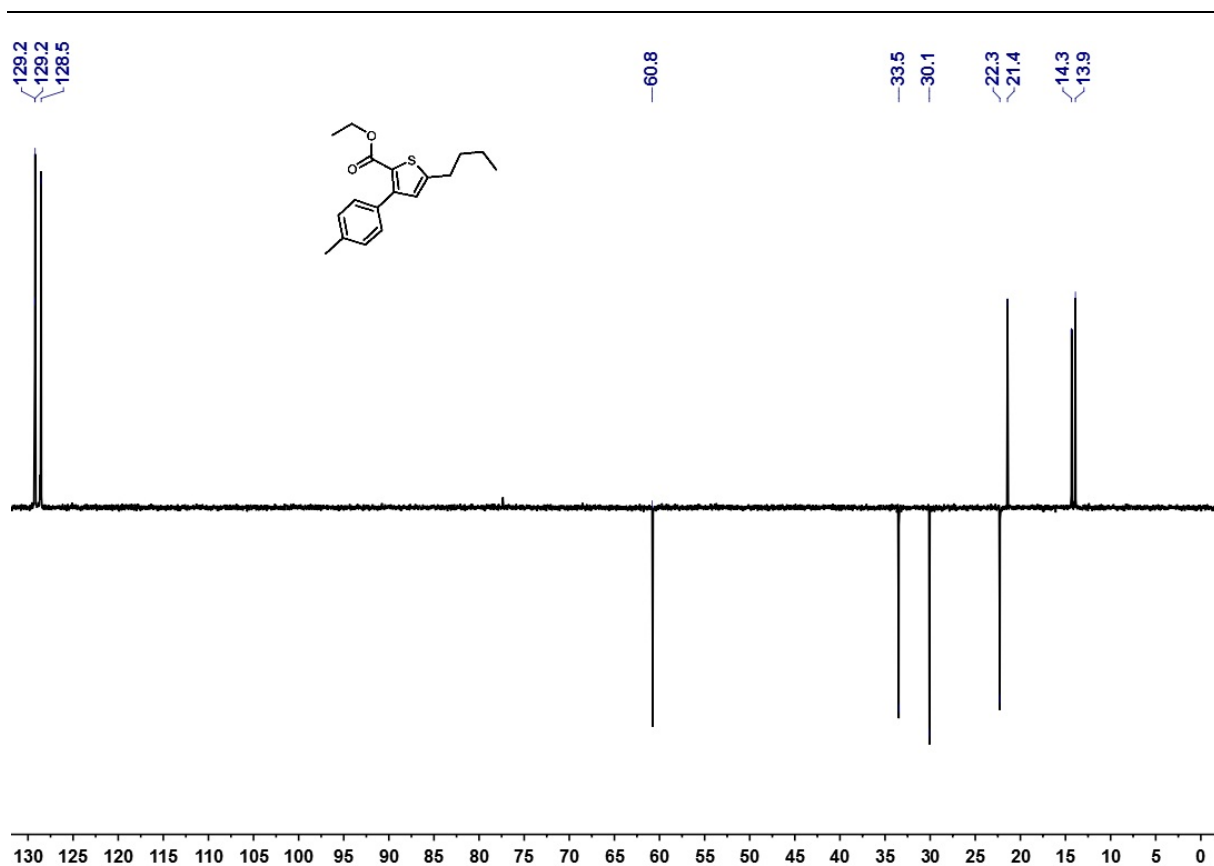
$^{135}\text{-DEPT}$ of 1j (CDCl_3 , 125 MHz, 296 K)



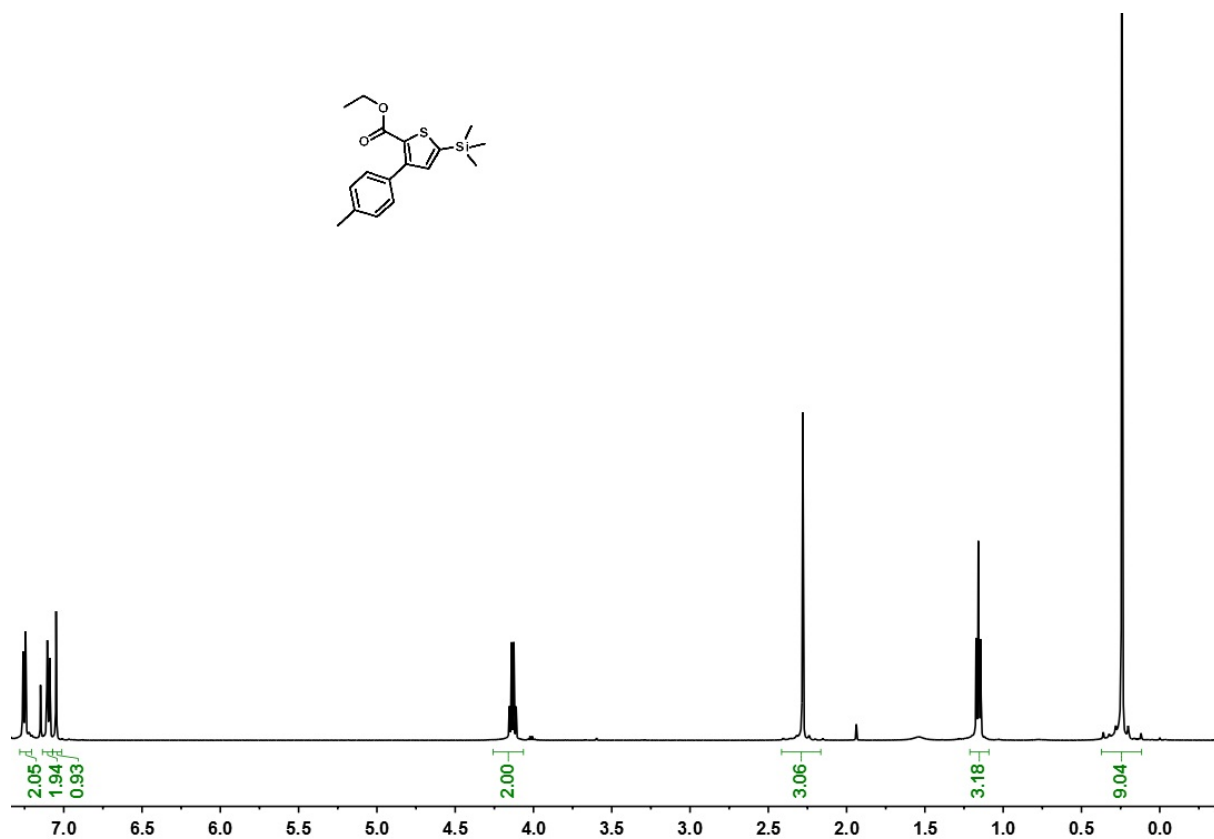
^1H -NMR of 1k (CDCl₃, 500 MHz, 296 K)



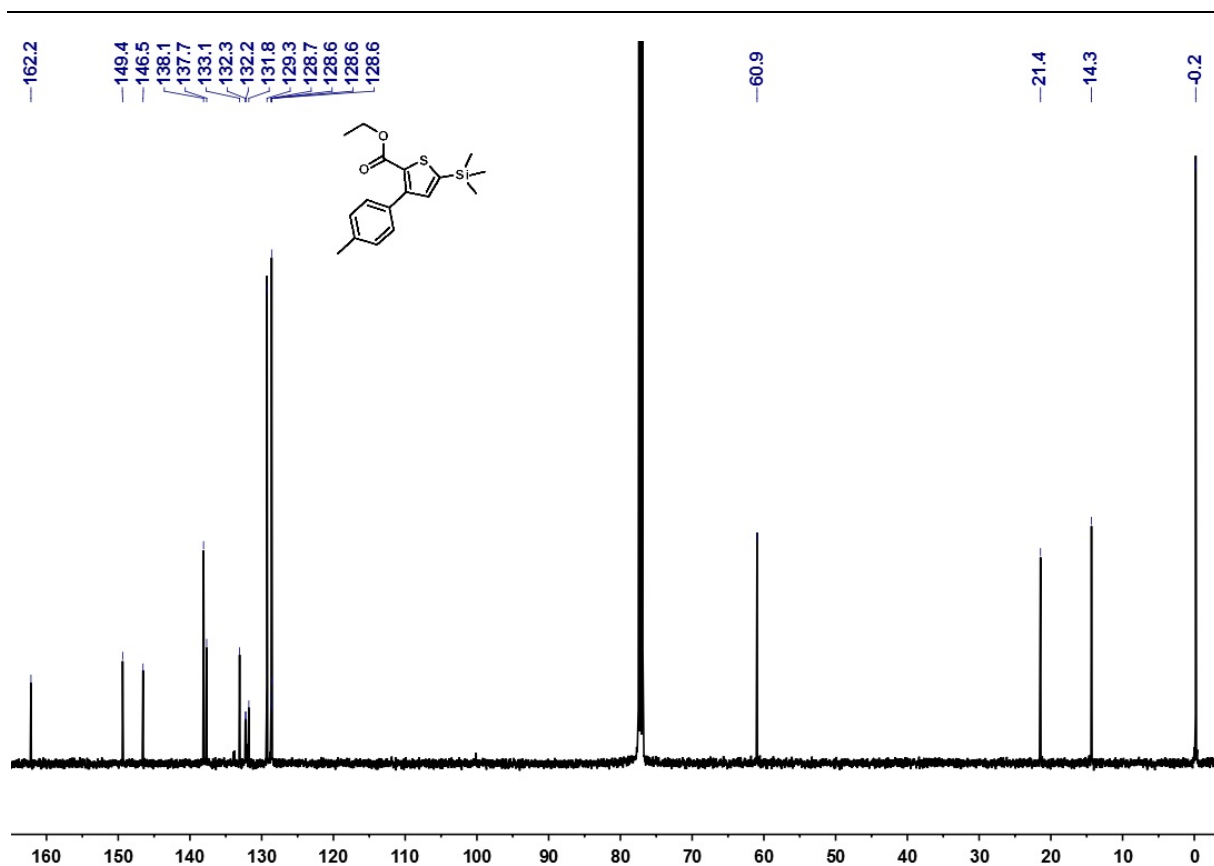
^{13}C -NMR of 1k (CDCl₃, 125 MHz, 296 K)



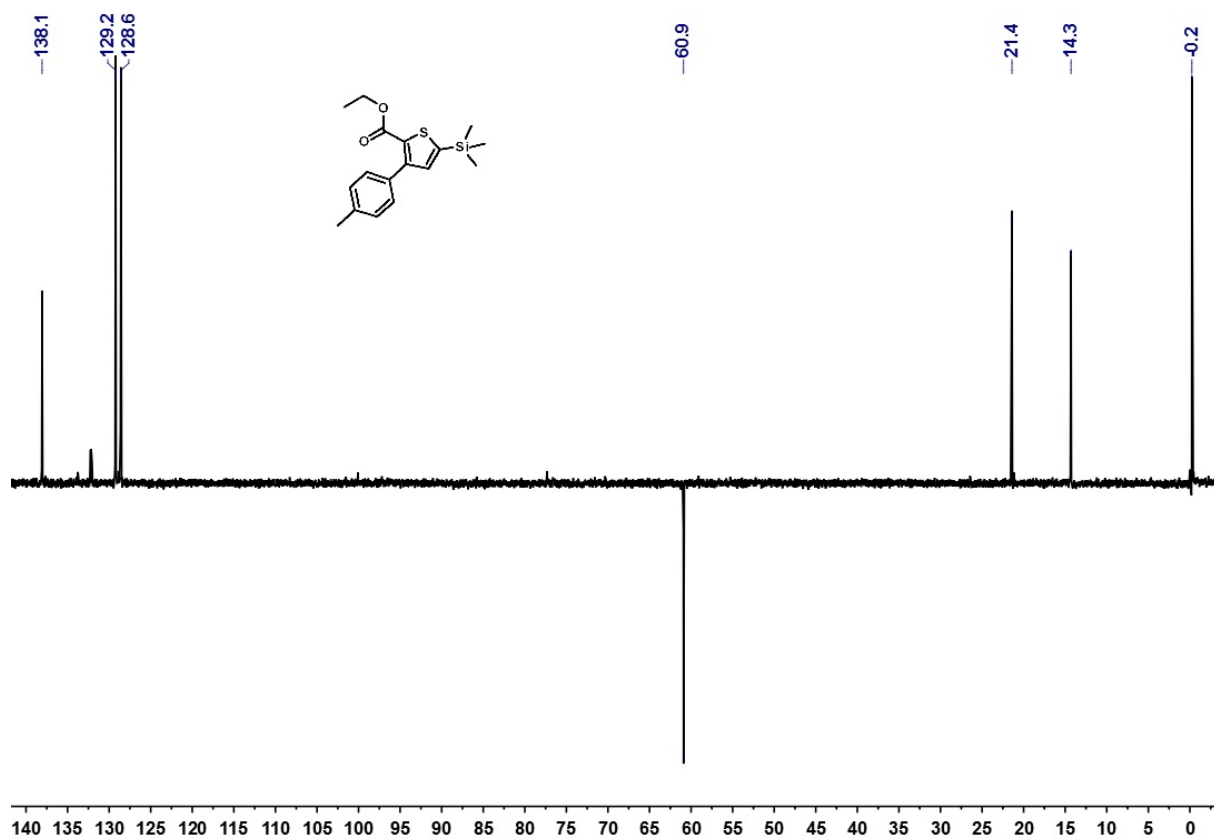
135-DEPT of 1k (CDCl_3 , 125 MHz, 296 K)



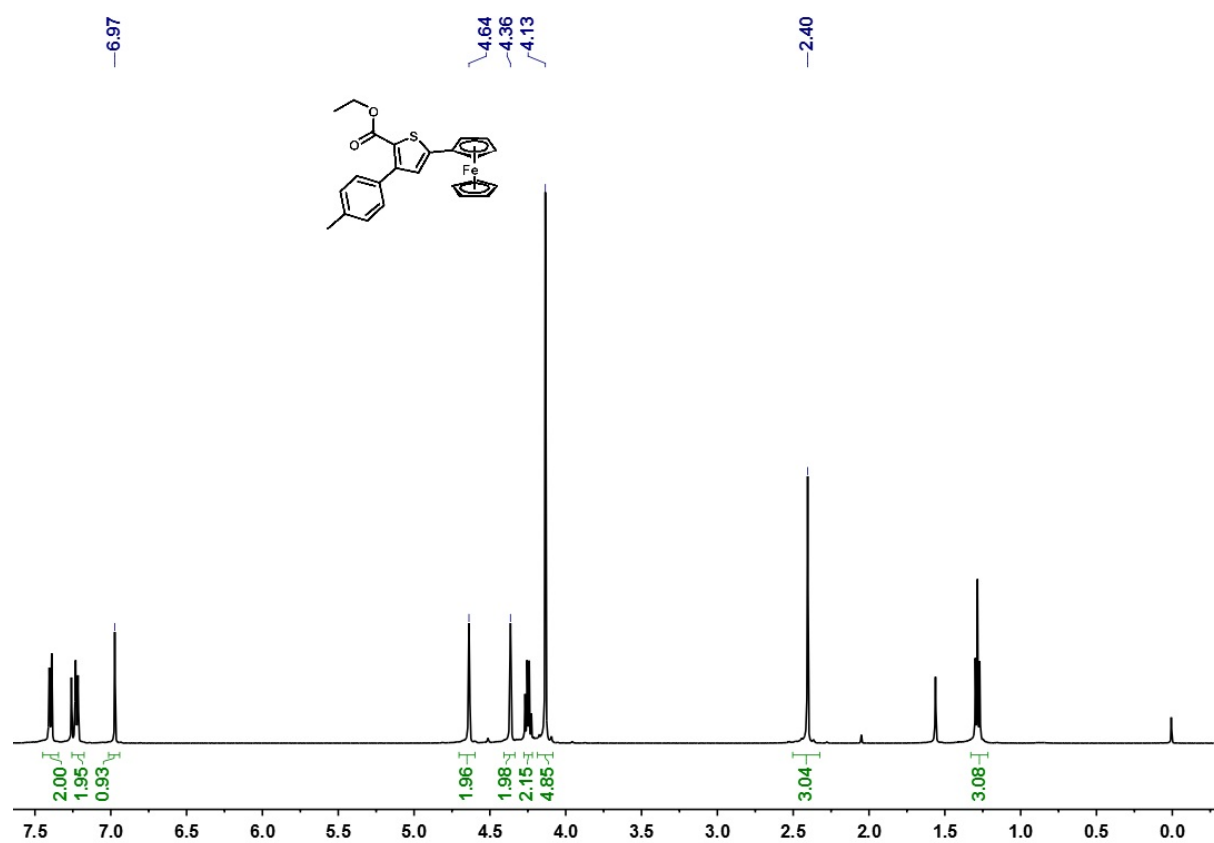
^1H -NMR of 1l (CDCl_3 , 500 MHz, 296 K)



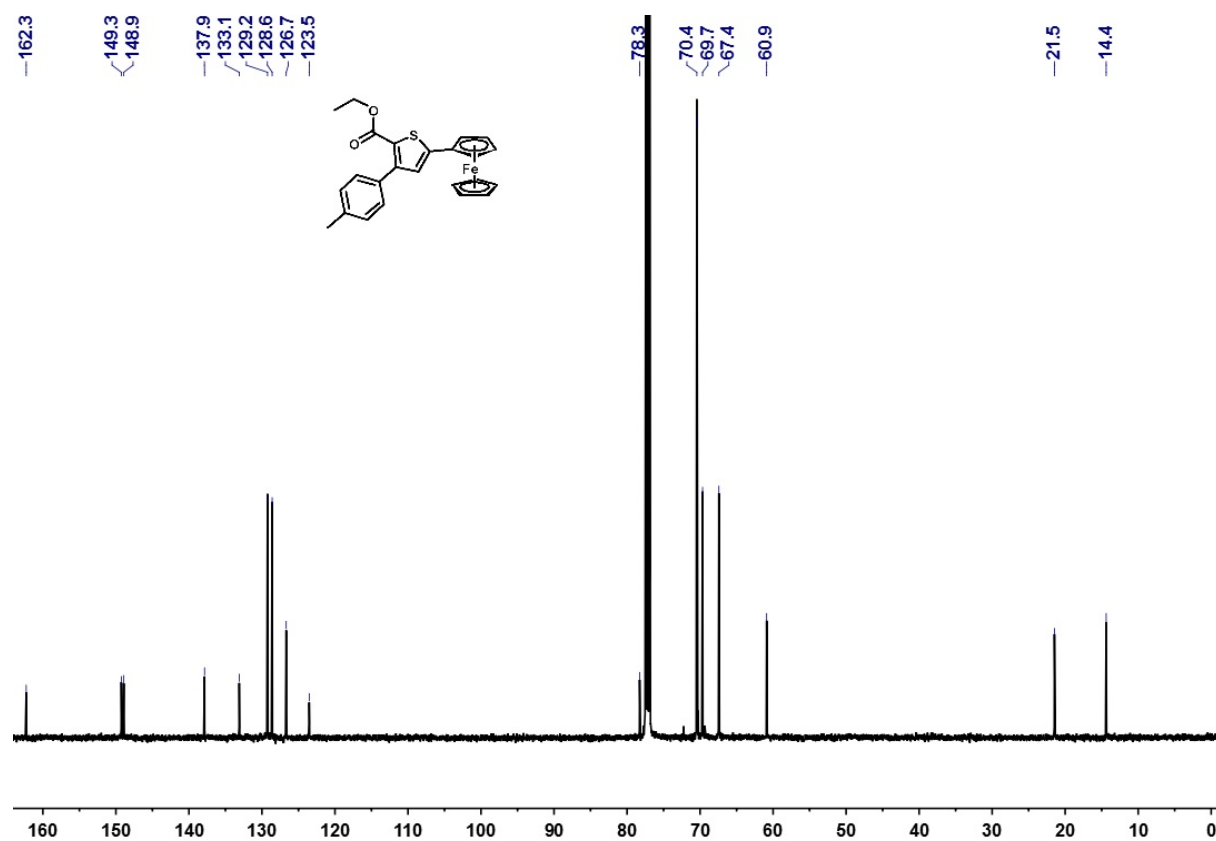
^{13}C -NMR of 1I (CDCl_3 , 125 MHz, 296 K)



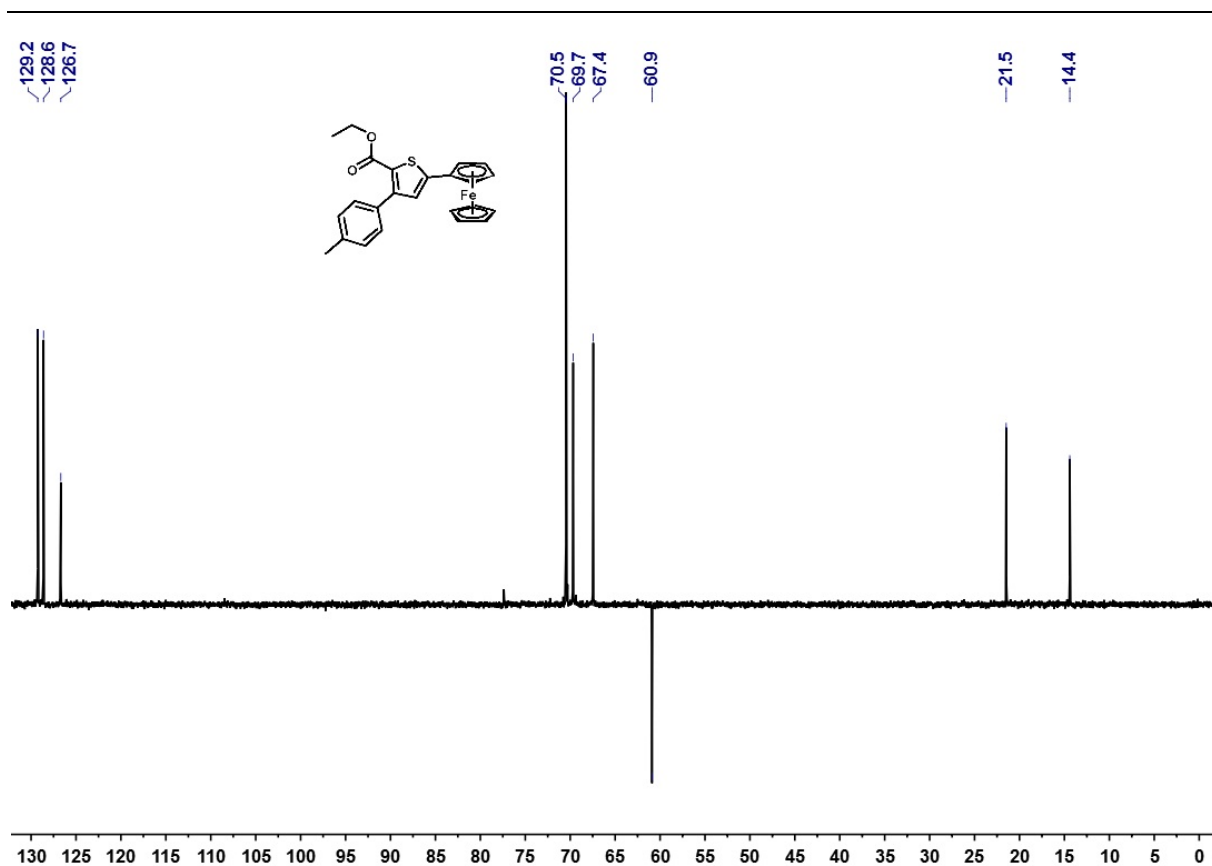
$^{135}\text{-DEPT}$ of 1I (CDCl_3 , 125 MHz, 296 K)



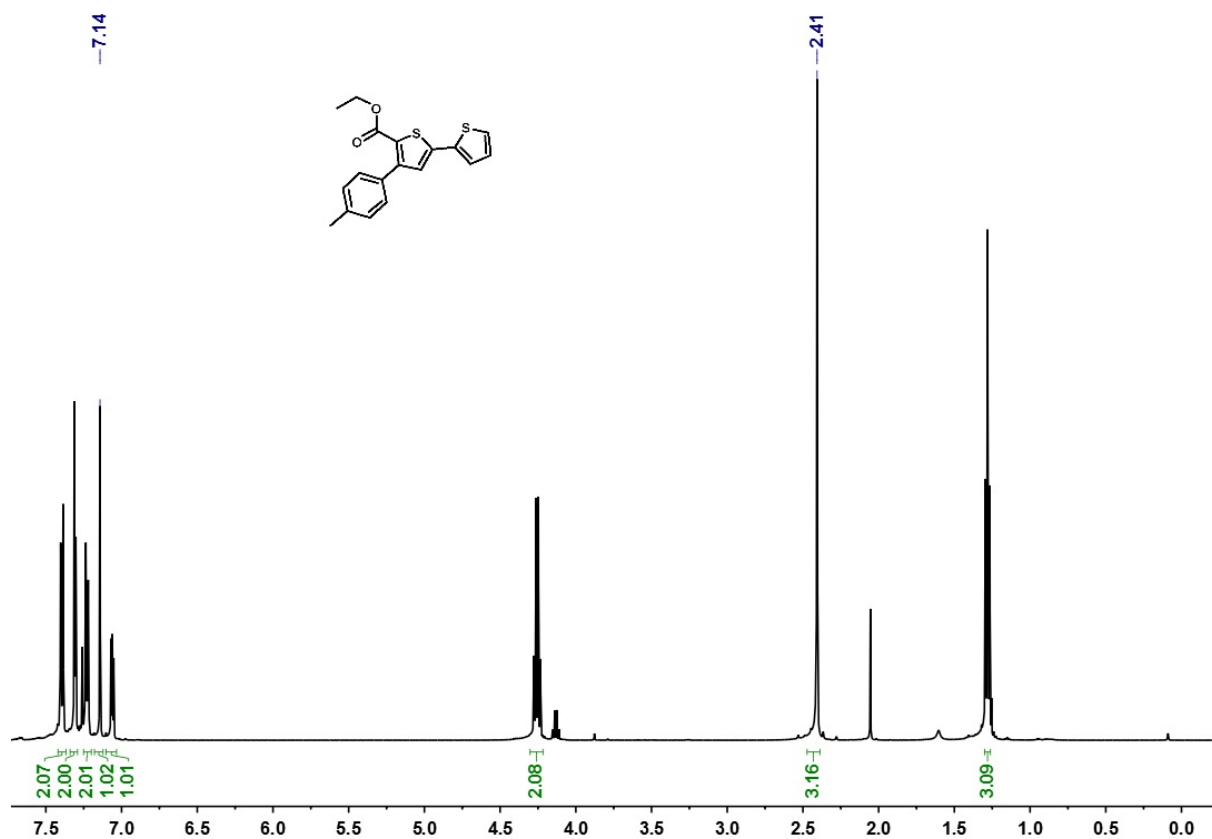
^1H -NMR of 1m (CDCl_3 , 500 MHz, 296 K)



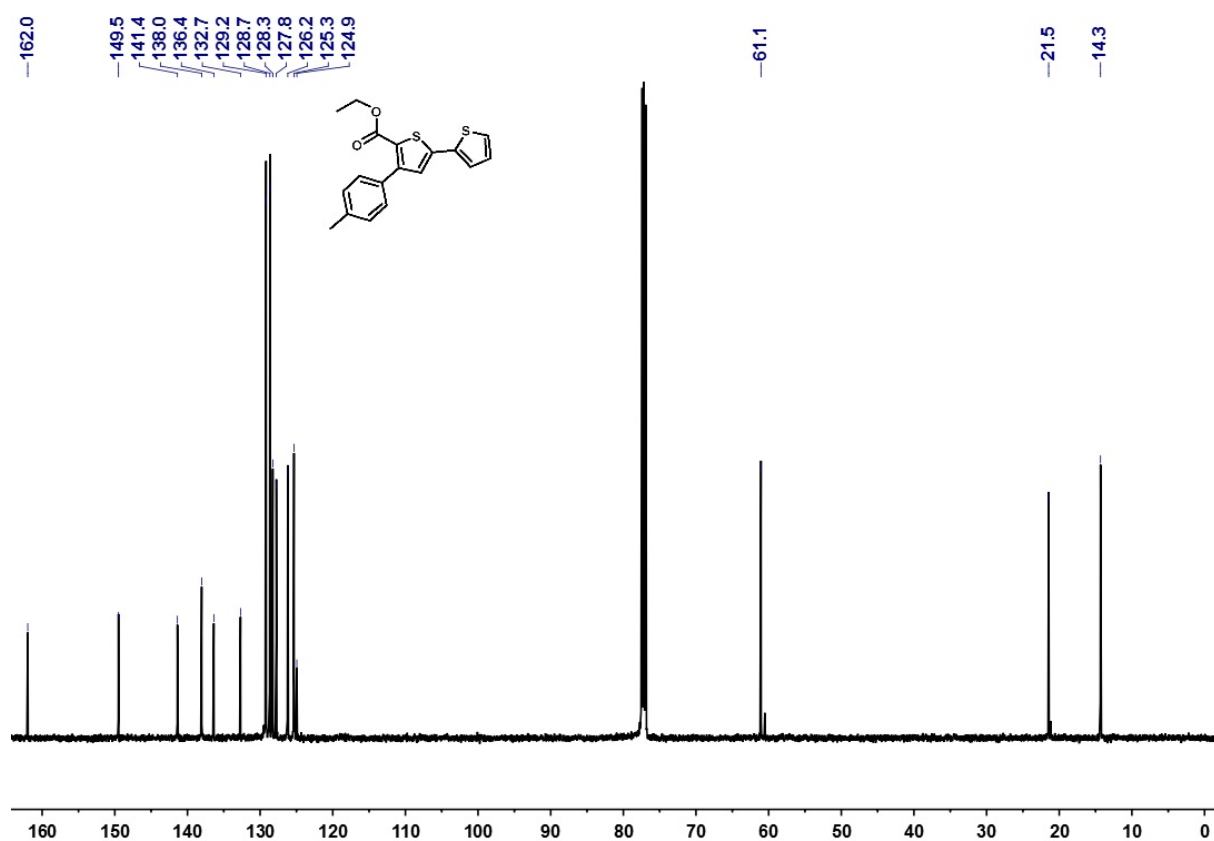
^{13}C -NMR of 1m (CDCl_3 , 125 MHz, 296 K)



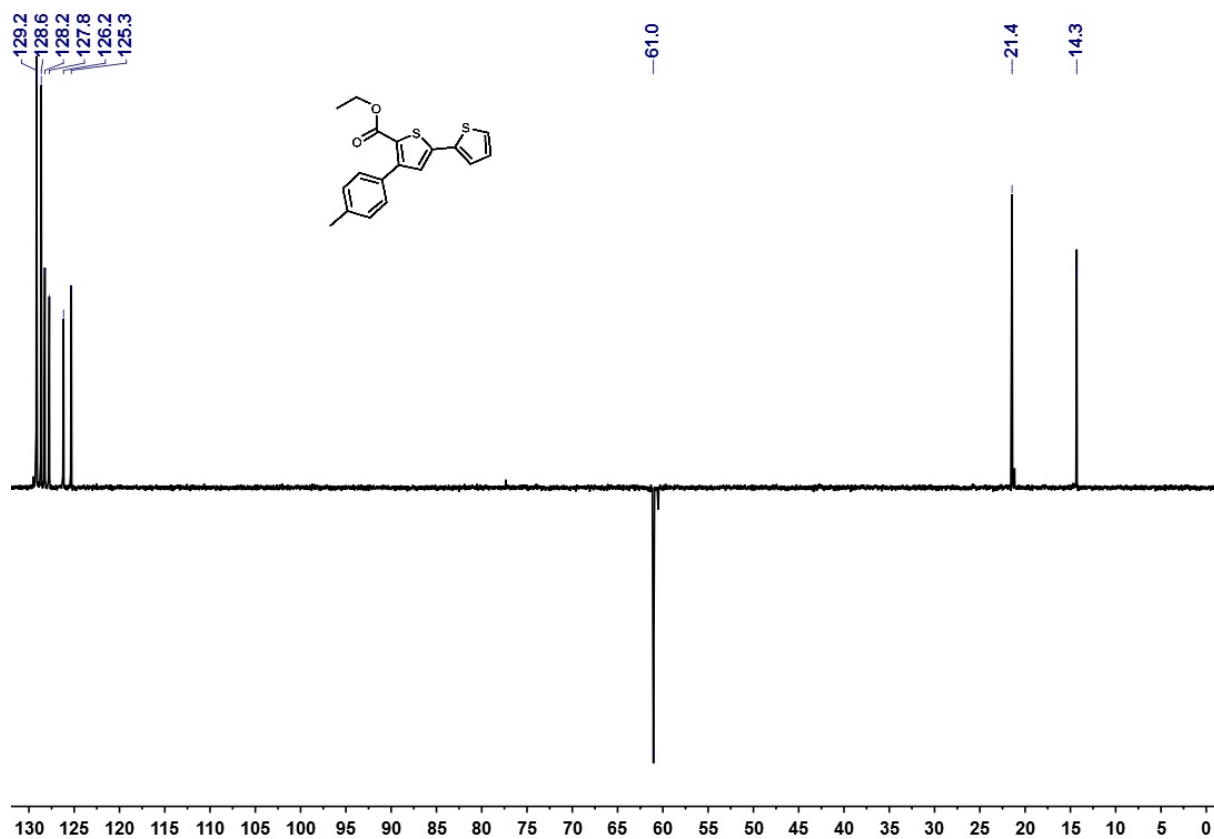
135-DEPT of 1m (CDCl_3 , 125 MHz, 296 K)



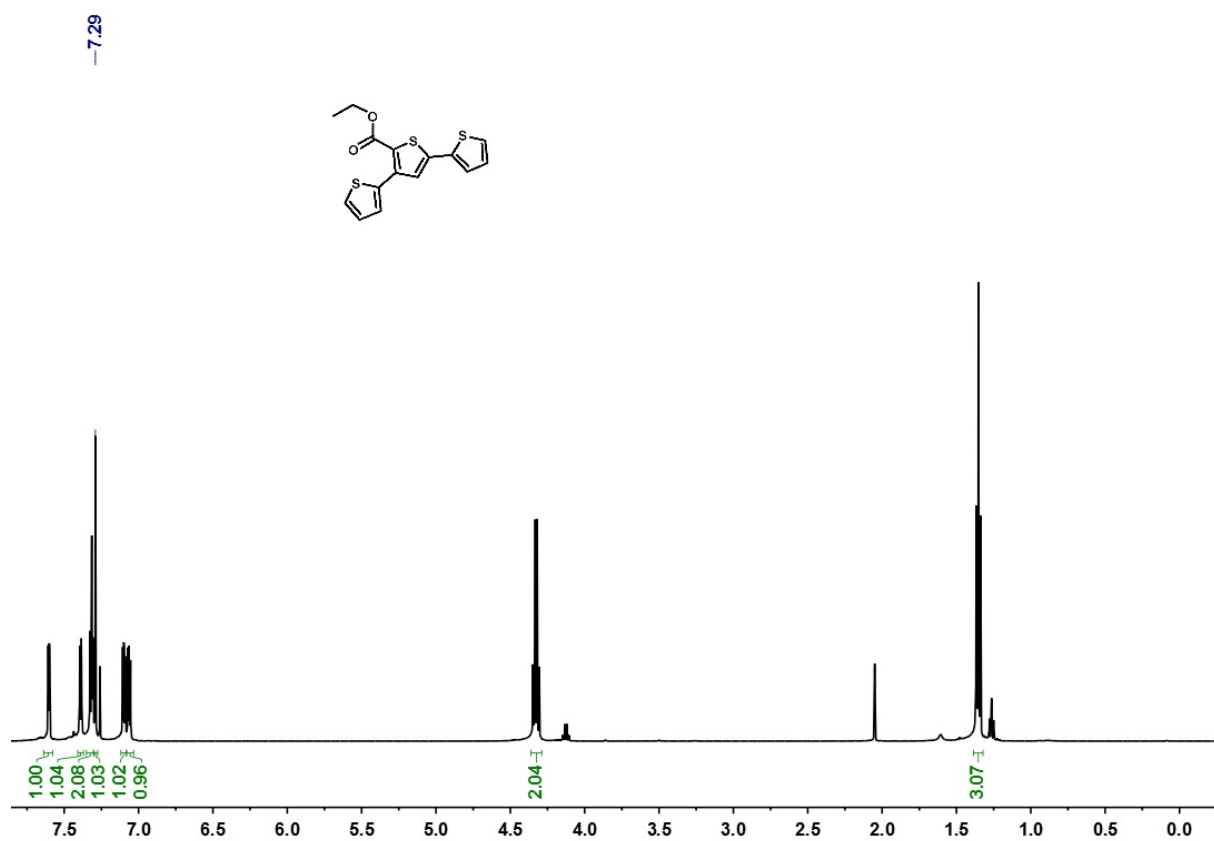
^1H -NMR of 1n (CDCl_3 , 500 MHz, 296 K)



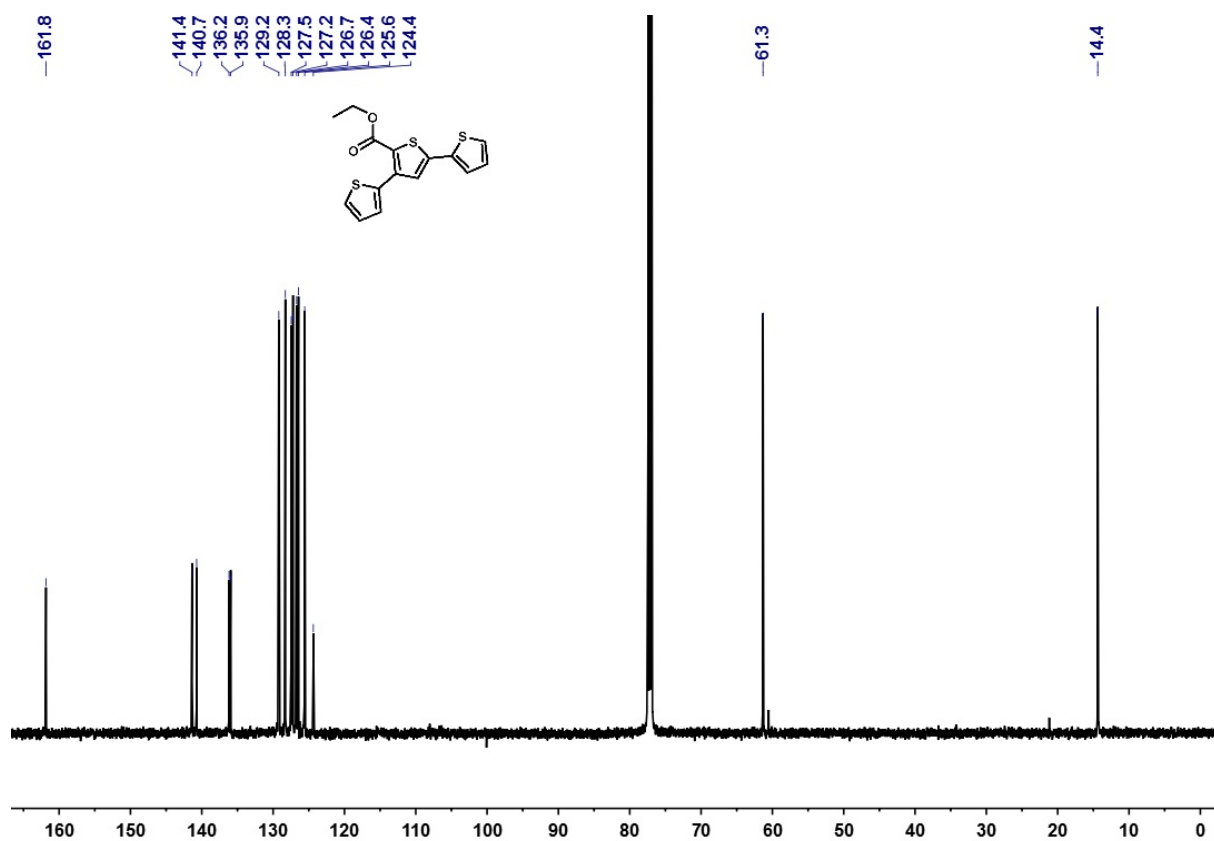
^{13}C - NMR of 1n (CDCl₃, 125 MHz, 296 K)



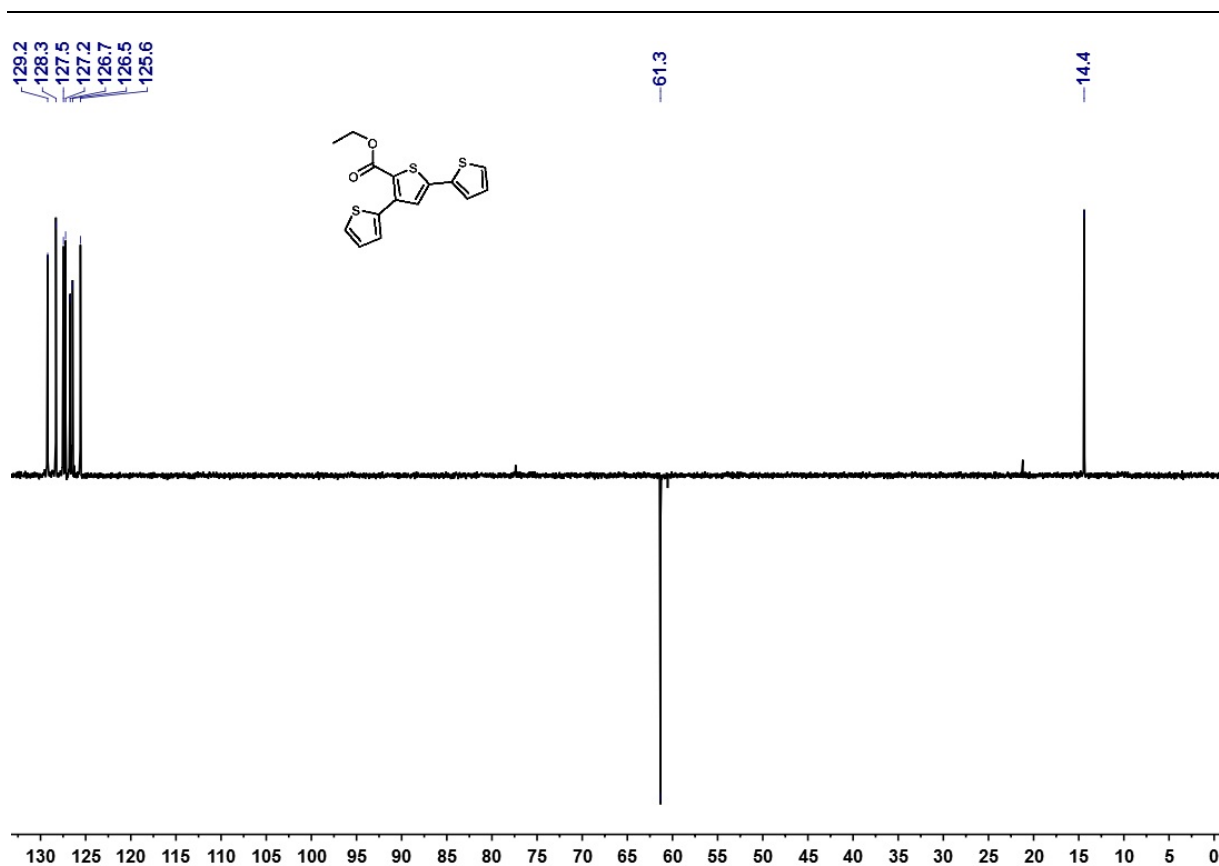
$^{135}\text{-DEPT}$ of 1n (CDCl₃, 125 MHz, 296 K)



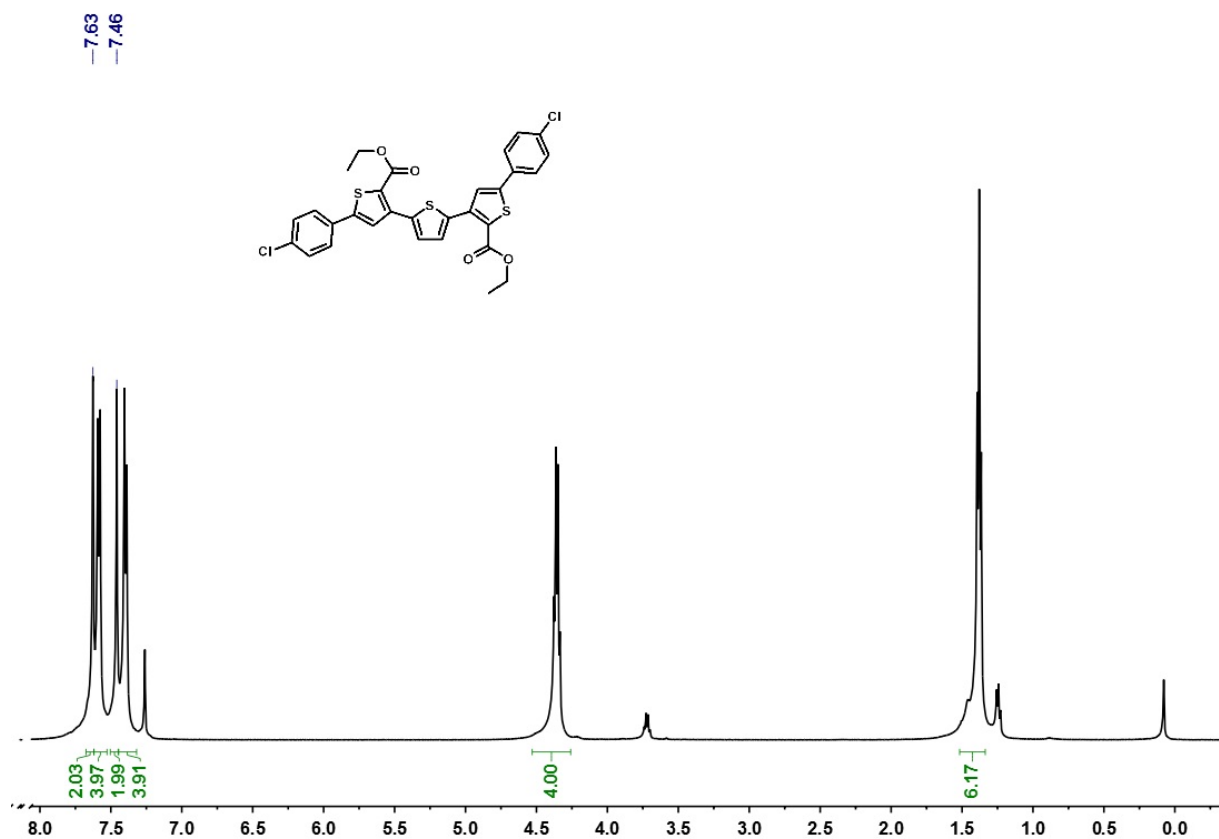
^1H -NMR of 1o (CDCl₃, 500 MHz, 296 K)



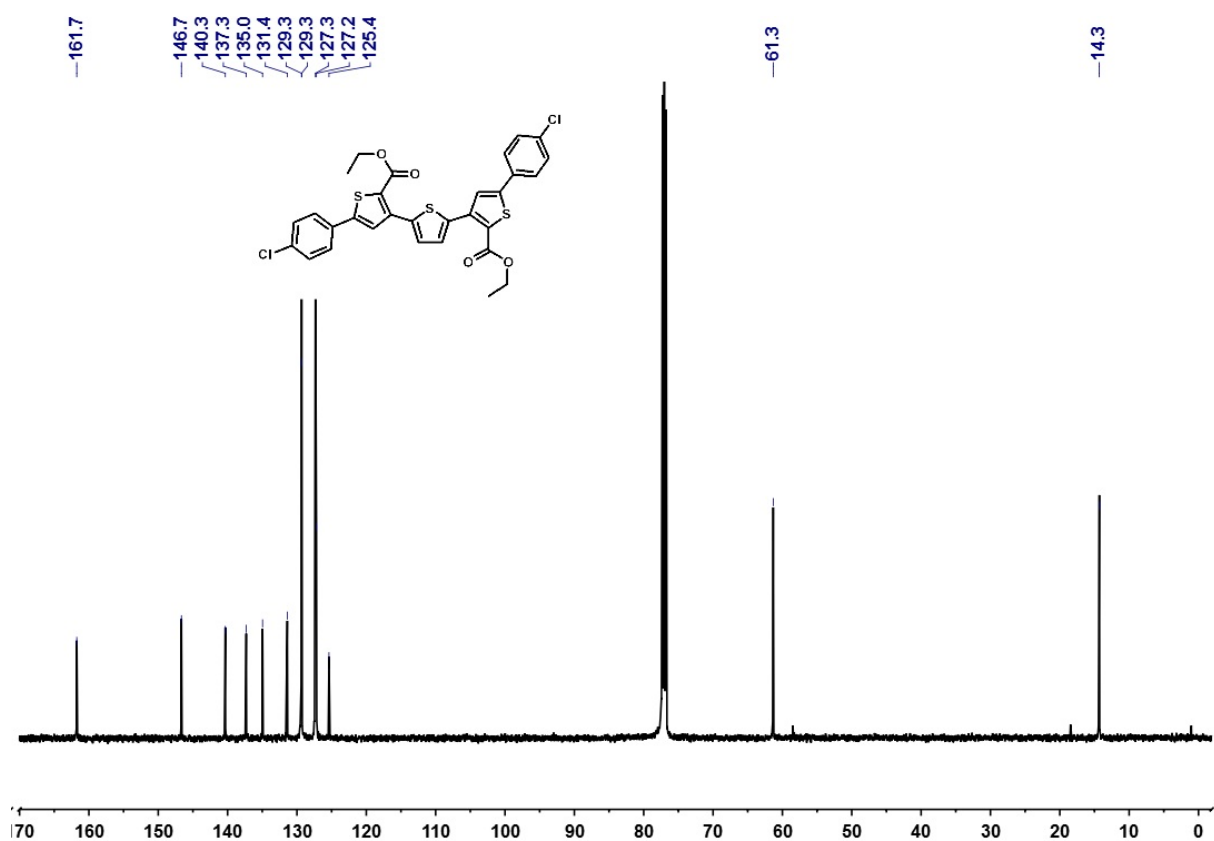
^{13}C -NMR of 1o (CDCl₃, 125 MHz, 296 K)



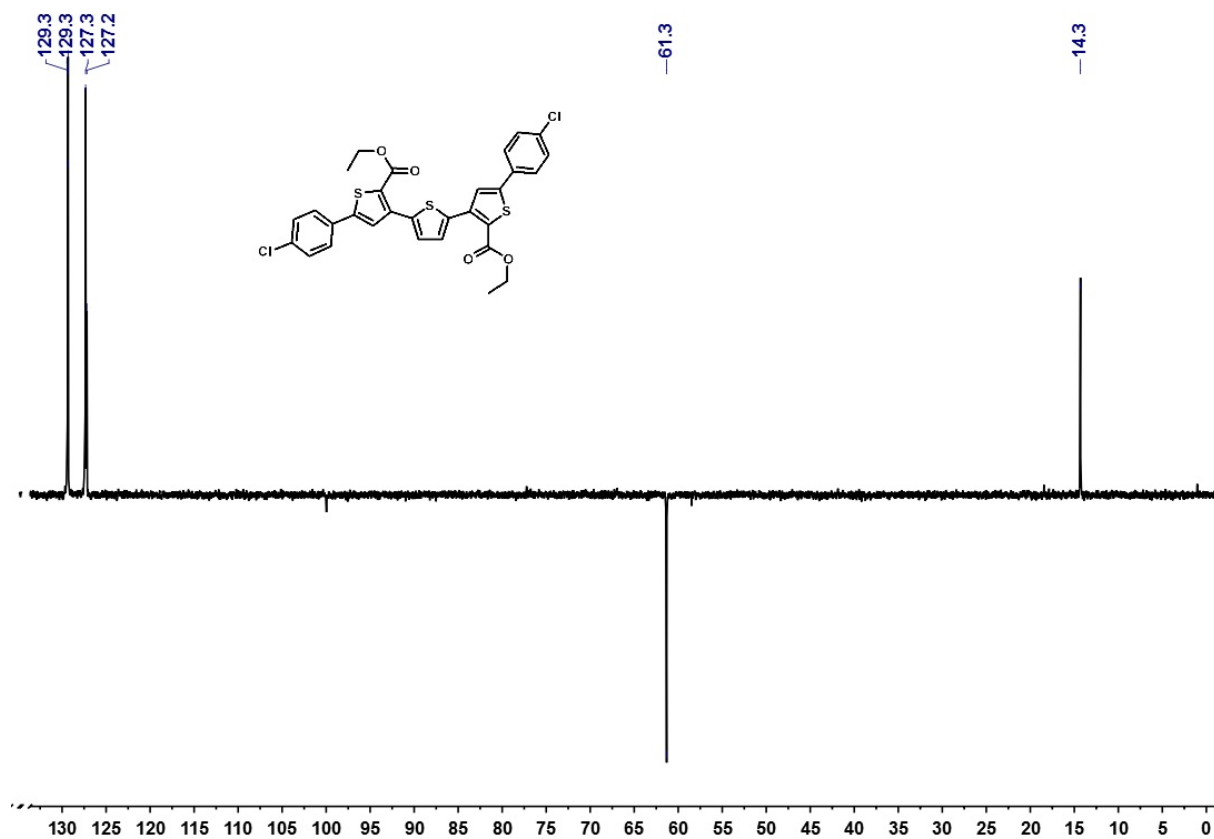
135-DEPT of 1o (CDCl_3 , 125 MHz, 296 K)



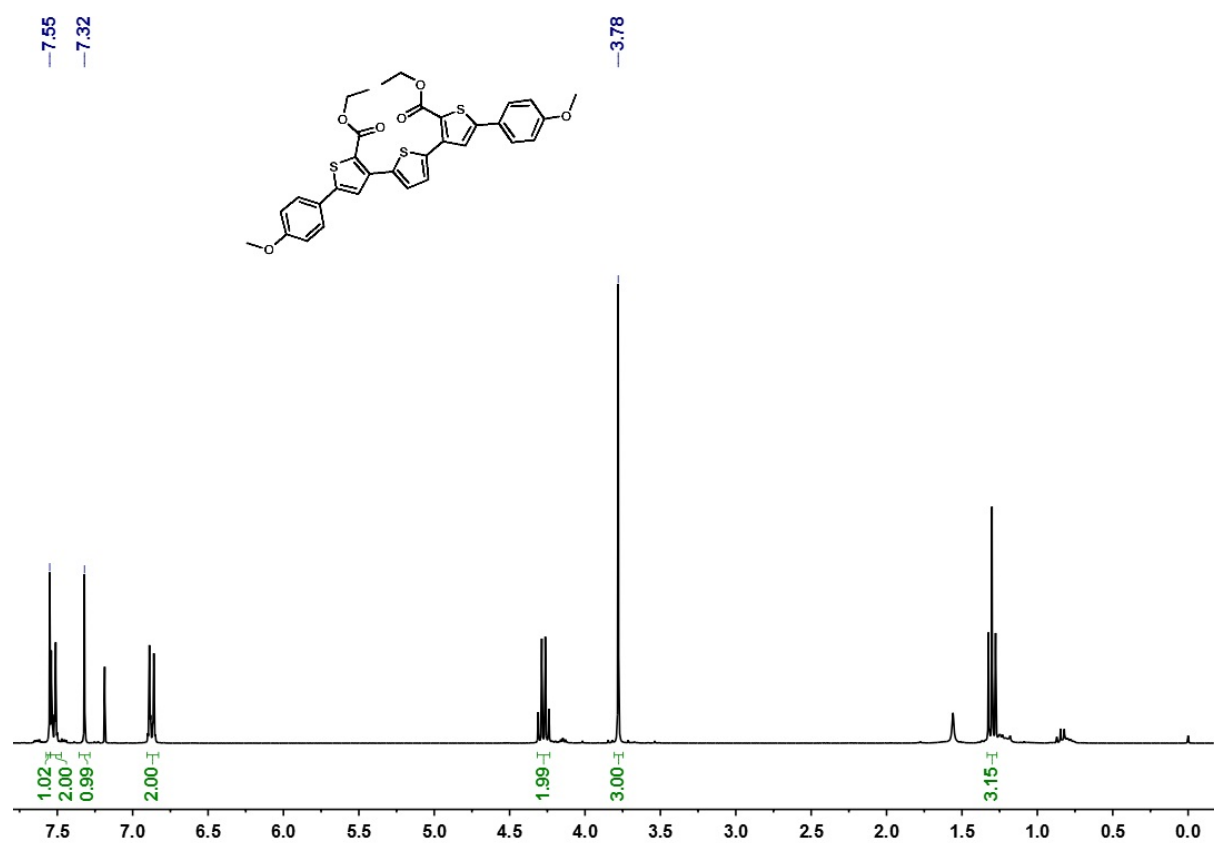
^1H -NMR of 7a (CDCl_3 , 500 MHz, 296 K)



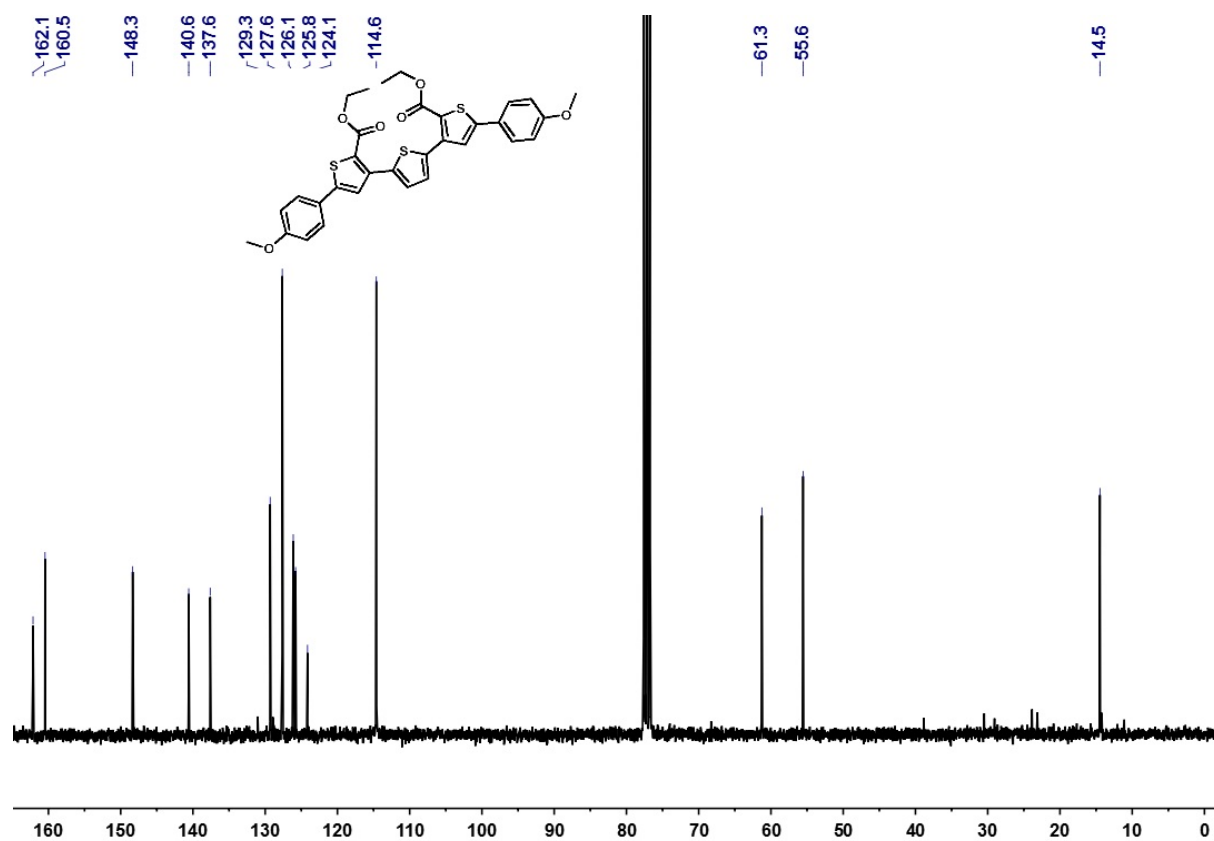
^{13}C -NMR of 7a (CDCl₃, 125 MHz, 296 K)



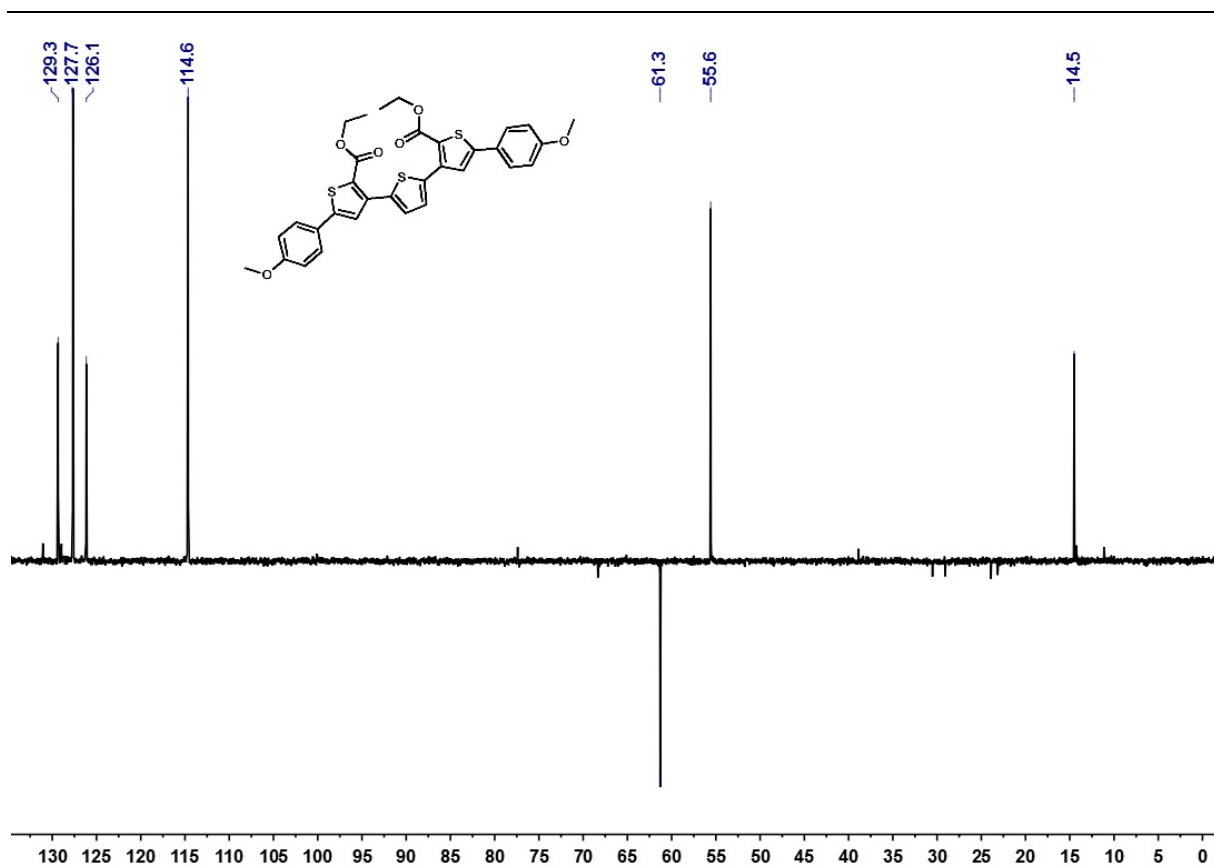
$^{135}\text{-DEPT}$ of 7a (CDCl₃, 125 MHz, 296 K)



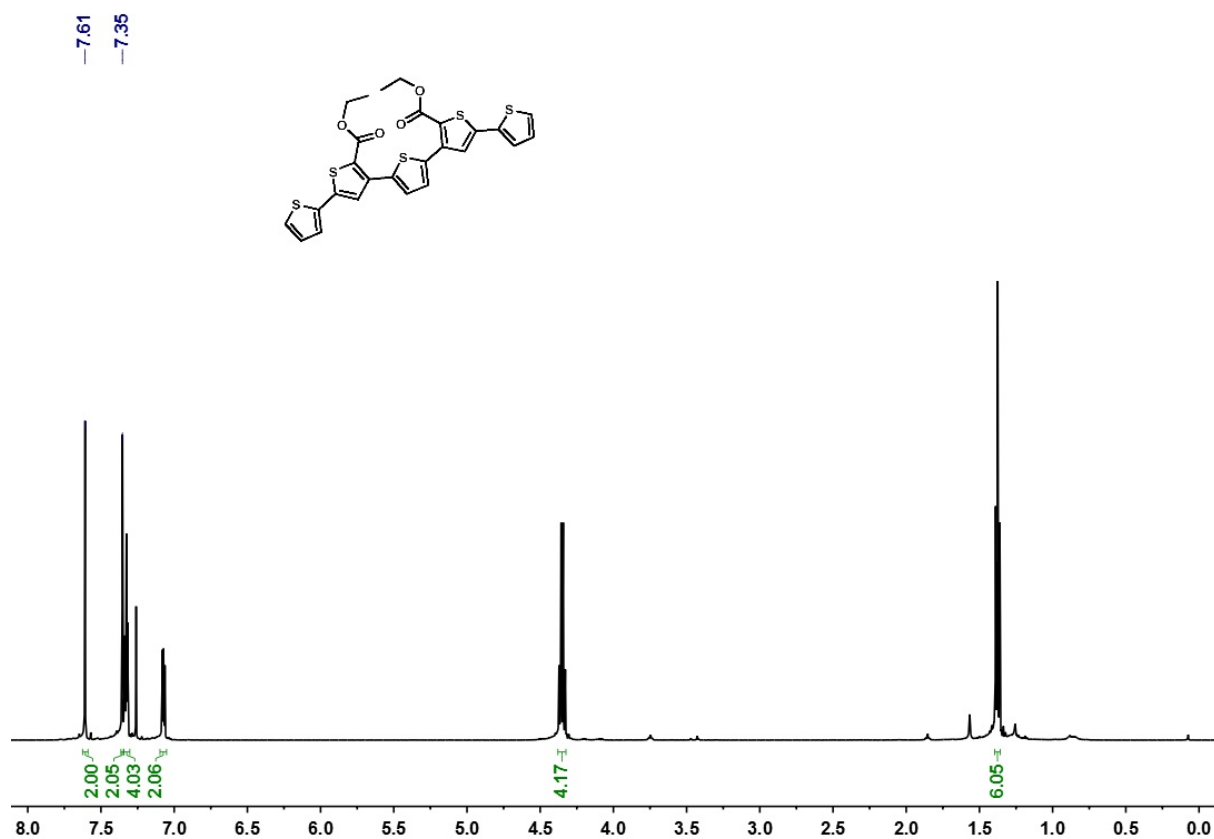
^1H -NMR of 7b (CDCl_3 , 500 MHz, 296 K)



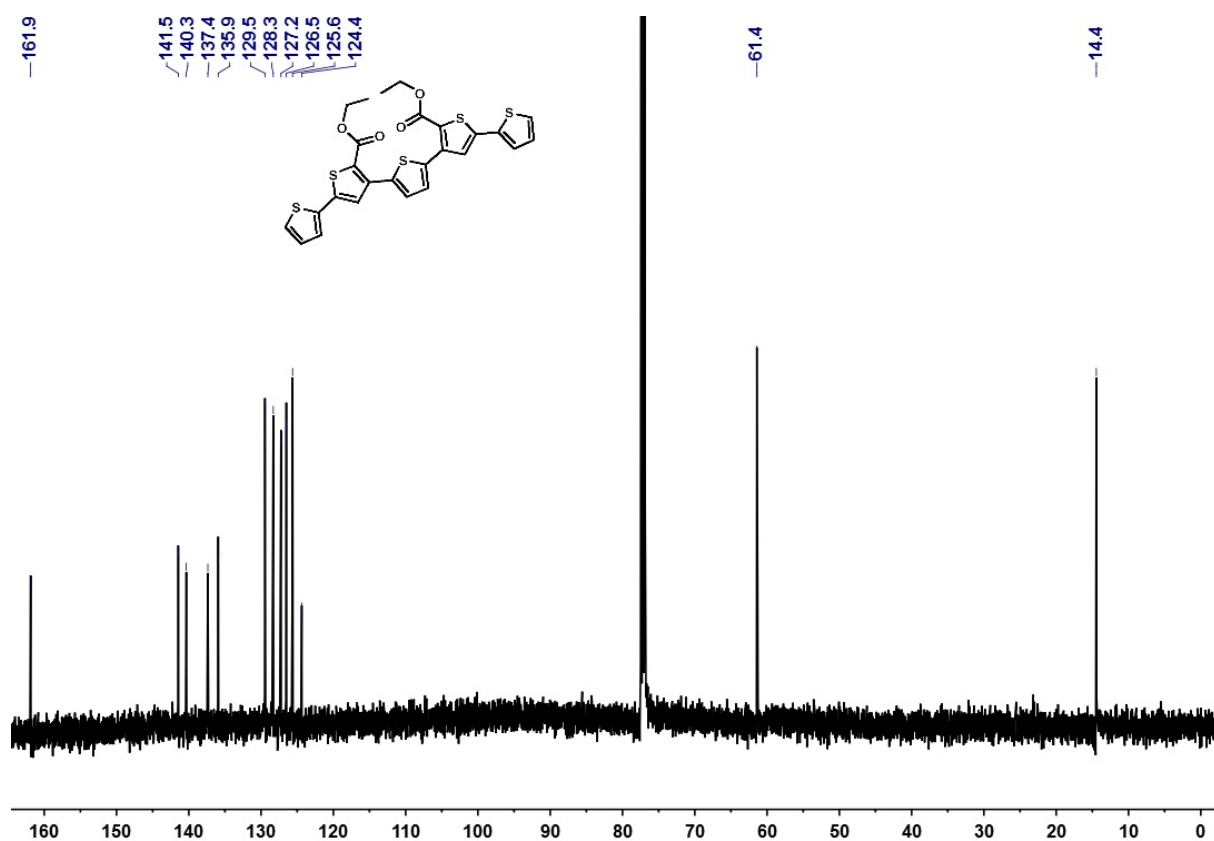
^{13}C -NMR of 7b (CDCl_3 , 125 MHz, 296 K)



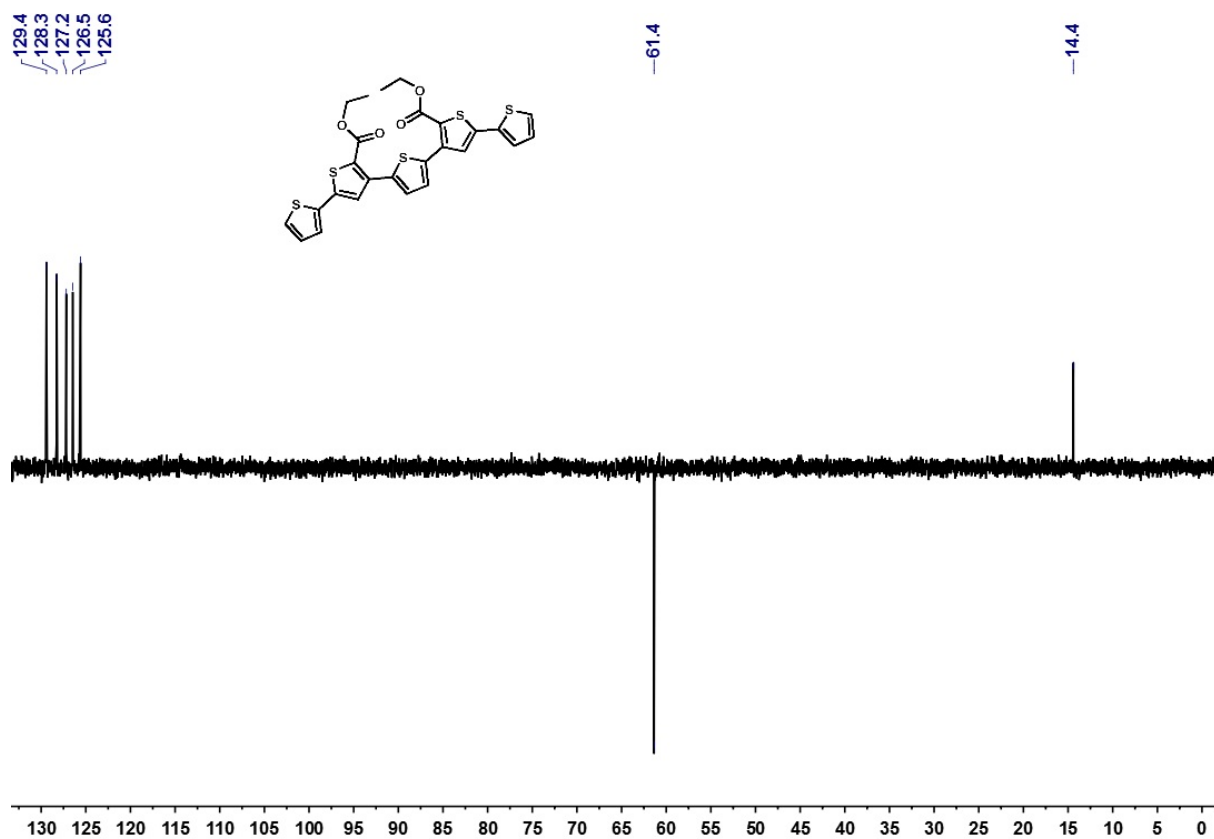
135-DEPT of 7b (CDCl_3 , 125 MHz, 296 K)



^1H -NMR of 7c (CDCl_3 , 500 MHz, 296 K)



^{13}C -NMR of 7c (CDCl_3 , 125 MHz, 296 K)

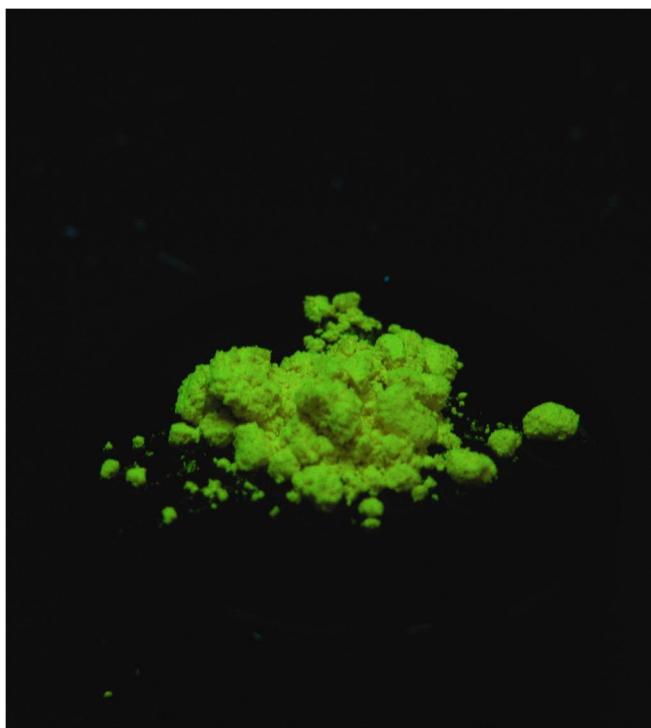


$^{135}\text{-DEPT}$ of 7c (CDCl_3 , 125 MHz, 296 K)

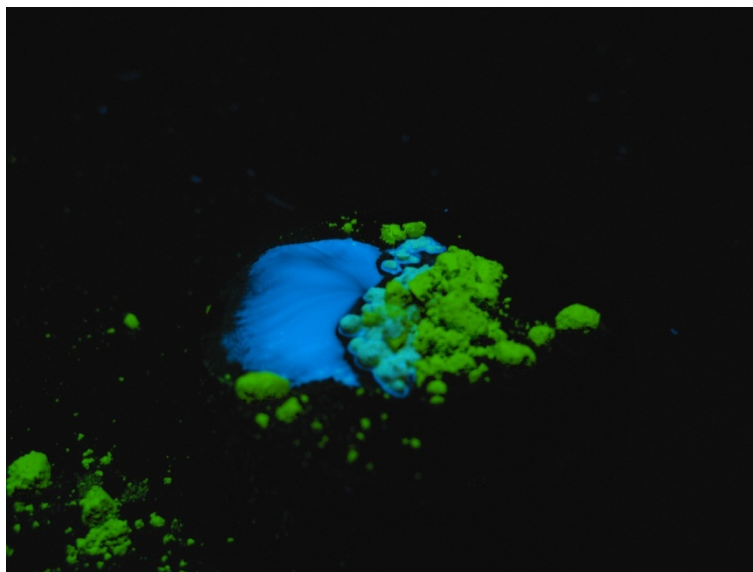
6 PHOTOGRAPHS



Solution fluorescence of compound **7c** (in dichloromethane, upon irradiation at $\lambda_{exc} = 366$ nm).



Solid state fluorescence of compound **7c** (upon irradiation at $\lambda_{exc} = 366$ nm).



Fluorescence color change upon partial solution of compound **7c** (upon addition of a drop of dichloromethane, upon irradiation at $\lambda_{exc} = 366$ nm)