

Supporting Information

Formal [1+2+3] Annulations: Domino Access to Carbazoles and Indolocarbazole Alkaloids

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1. General Information

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. All reactions were carried out without any particular precautions to extrude moisture or oxygen, unless otherwise indicated. All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). The products were purified by flash column chromatography on silica gel (300–400 mesh). NMR spectra were obtained on a Varian Inova 400, 500 or a Bruker 400 spectrometer, with CDCl₃ or DMSO-*d*₆ as solvents. All chemical shifts are given in ppm. High-resolution mass spectra (HRMS) were recorded on a Bruker micro TOF IV focus spectrometer.

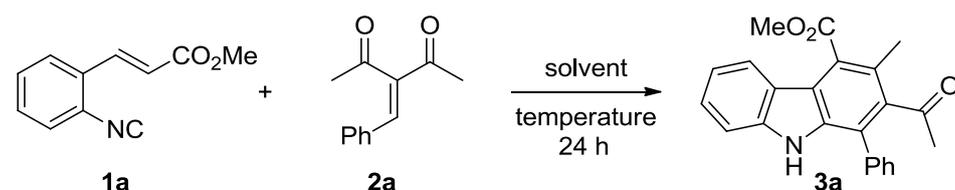
2. Experimental Procedures

2.1 Synthesis of starting materials.

Isocyanides **1** were synthesized according to known literature procedure.^{1,2,3} Ketones **2** were synthesized according to known literature procedure.^{4,5,6,7,8,9}

2.2 Optimization of reaction conditions

Table S1. Optimization of Reaction Conditions^a



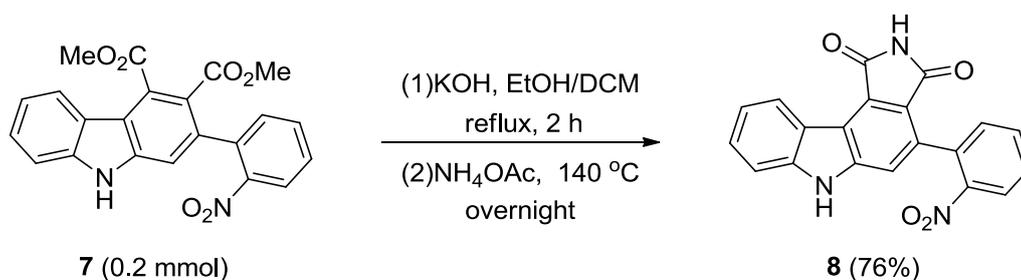
entry	Solvent	Temp. (°C)	Yield of 3a (%)
1	EtOH	60	10 ^b
2	EtOH	80	85 ^b
3	EtOH	100	89 ^b
4	EtOH	120	57 ^b
5	MeOH	100	49 ^c
6	CF ₃ CH ₂ OH	100	80 ^c
7	<i>i</i> -PrOH	100	73 ^c
8	<i>t</i> -BuOH	100	64 ^c
9	DMF	100	56 ^c
10	toluene	100	20 ^c
11	CH ₃ CN	100	33 ^c
12	THF	100	10 ^c

^aReaction conditions: **1a** (0.45 mmol), **2a** (0.3 mmol), solvent (1 mL).

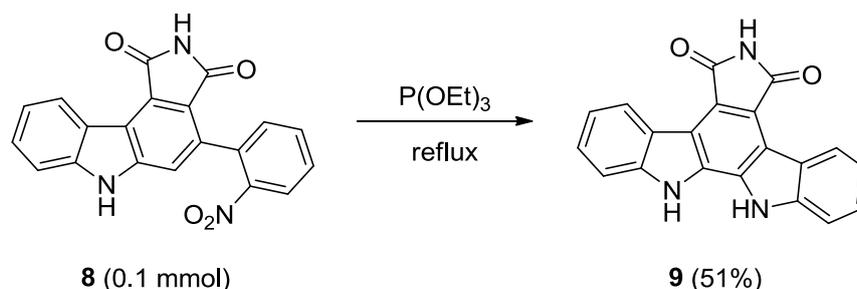
^bIsolated yields. ^cDetermined by ¹H NMR spectroscopy using 1,2-dibromoethane as an internal standard.

2.3 Synthesis of products **3**, **9** and **12**

General synthetic procedures of **3** (taking **3a** for example)

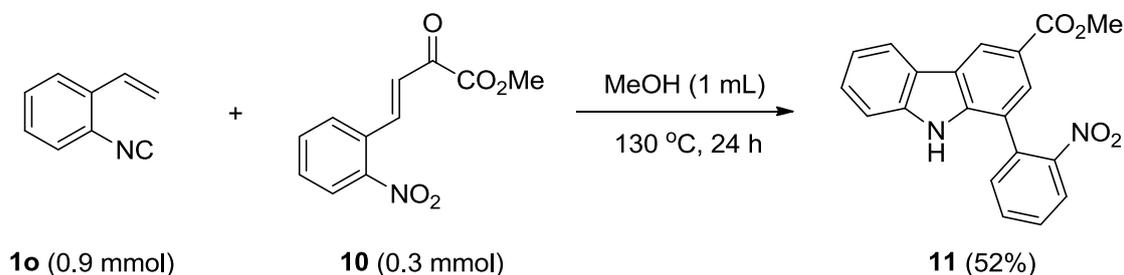


To a stirred solution of **7** (80.8 mg, 0.2 mmol) in EtOH (1 mL) and DCM (0.5 mL) was added potassium hydroxide (112 mg, 2.0 mmol). The mixture was refluxed until TLC indicated complete consumption of the compound **7**. The mixture was cooled to room temperature and then quenched with 1N HCl. The mixture was extracted with ethyl acetate (3 x 5 mL), dried over MgSO₄, and concentrated in vacuo to afford the crude anhydride, which was used in the next step without further purification. The crude anhydride with ammonium acetate (5 g) was heated to 140 °C overnight. The mixture was cooled to room temperature, dissolved in DCM, washed with brine, and extracted with DCM (3 x 5 mL). The organic layer was combined and dried over MgSO₄. The solvent was removed in vacuo and the residue was purified by flash column chromatography (silica gel; petroleum: ethyl acetate = 10:1 to 1:1) to give carbazole **8** (54.2 mg, 76% yield) as a bright yellow solid.

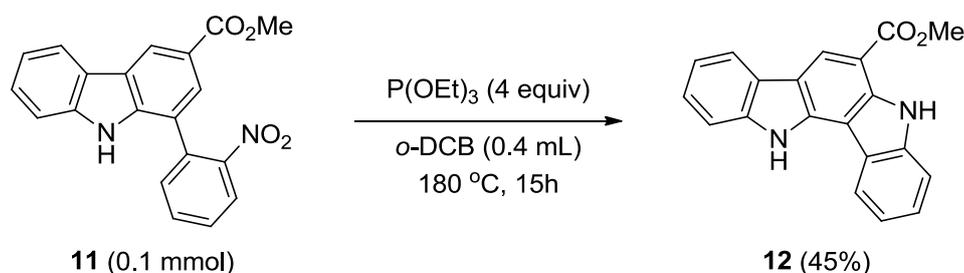


Carbazole **8** (35.7 mg, 0.1 mmol) was dissolved in P(OEt)₃ (0.5 mL) and refluxed for 4h as TLC indicated complete consumption of the compound **8**. The mixture was cooled to room temperature, evaporated under reduced pressure and purified by flash column chromatography (silica gel; petroleum: ethyl acetate = 15:1 to 5:1) to give Arcyriaflavin A **9** (16.6 mg, 51% yield) as an orange solid.

Synthetic procedure of **Racemosin B**



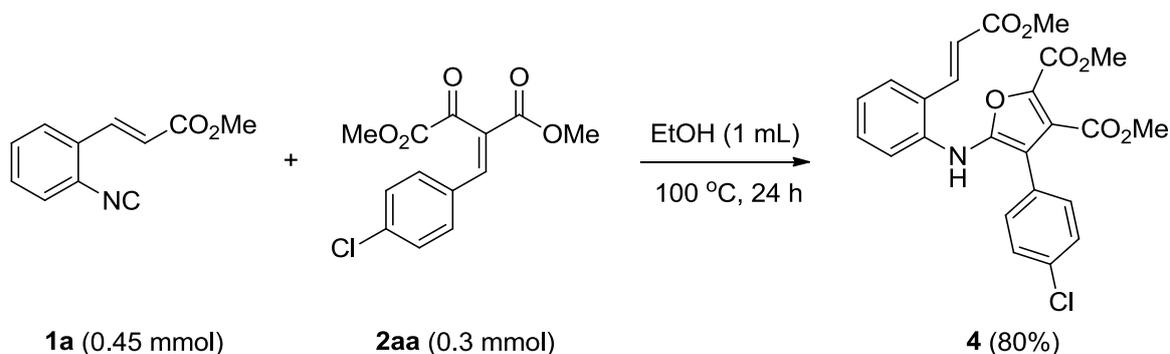
Isocyanide **10** (116 mg, 128 μL, 0.9 mmol), ketoester **10** (70.5 mg, 0.3 mmol) and MeOH (1 mL) were added into a sealed tube, and the reaction mixture was stirred in a pre-heated (130 °C) metal block until ketoester **10** was completely consumed as indicated by TLC. Cooled to room temperature, the reaction mixture was concentrated in vacuo and purified by flash column chromatography (silica gel; petroleum: dichloromethane = 1:3) to give carbazole **11** (54.1 mg, 52% yield) as a yellow solid.



Carbazole **11** (34.6 mg, 0.1 mmol), triethyl phosphite (66.4 mg, 69 μL , 0.4 mmol) and 1,2-dichlorobenzene (0.4 mL) were added into a sealed tube. Then the reaction mixture was set in a pre-heated (180 $^\circ\text{C}$) metal block and kept stirring until carbazole **11** was completely consumed as indicated by TLC. The reaction mixture was concentrated in vacuo and purified by flash column chromatography (silica gel; petroleum: ethyl acetate = 25:1-15:1) to give Racemosin B **12** (14.1 mg, 45% yield) as a white solid.

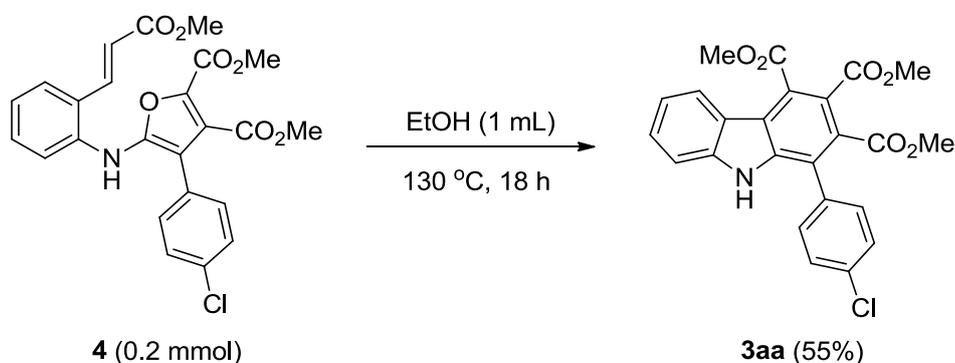
2.4 Control Experiments.

From **1a** and **2aa** to **4**



Isocyanide **1a** (84.2 mg, 0.45 mmol) and ketone **2aa** (84.8 mg, 0.3 mmol) were dissolved in EtOH (1 mL) in a sealed tube, the reaction mixture was set in a pre-heated (100 $^\circ\text{C}$) metal block and kept stirring until ketone **2aa** was completely consumed as indicated by TLC. Cooled to room temperature, the reaction mixture was concentrated in vacuo and purified by flash column chromatography (silica gel; petroleum: ethyl acetate = 25:1-15:1) to give furan **4** (113.2 mg, 80% yield) as a deep yellow solid.

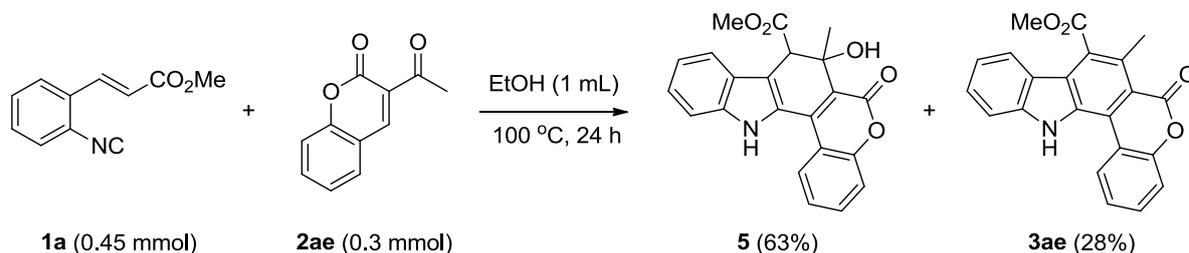
From **4** to **3aa**



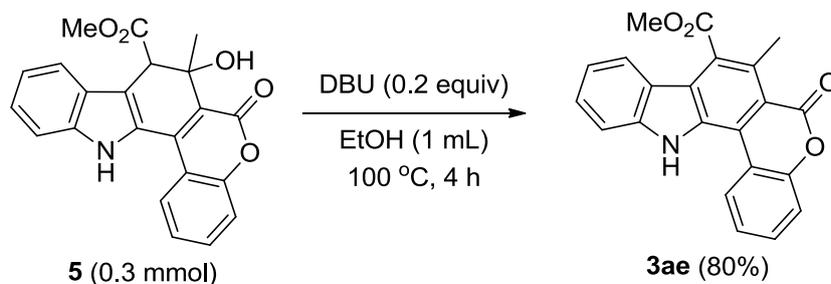
Furan **4** (93.9 mg, 0.2 mmol) was dissolved in EtOH (1 mL) in a sealed tube and the reaction was carried out in a pre-heated (130 $^\circ\text{C}$) metal block. The reaction mixture was kept stirring for 18 h and then cooled to room temperature. The solvent was removed in vacuo and the residue was purified by flash column

chromatography (silica gel; petroleum: ethyl acetate = 25:1-15:1) to give carbazole **3aa** (49.7 mg, 55% yield) as a yellow solid and recover **4** (34.7 mg, 37%).

From **1a** and **2ae** to **3ae** and **5**



Isocyanide **1a** (84.2 mg, 0.45 mmol), ketone **2ae** (56.4 mg, 0.3 mmol) and EtOH (1 mL) were added into a sealed tube. After the reaction mixture was stirred in a pre-heated (100 °C) metal block for 24 h, ketone **2ae** was completely consumed as indicated by TLC. The reaction mixture was cooled to room temperature and the solvent was removed in vacuo. The crude product was purified by flash column chromatography (silica gel; petroleum: ethyl acetate = 15:1-1:1) to afford hydroxyl carbazole **5** (70.5 mg, 63% yield) as a yellow solid and carbazole **3ae** (15.8 mg, 28% yield) as a yellow solid.

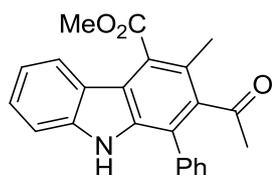


Hydroxyl carbazole **5** (56.4 mg, 0.3 mmol), DBU (9.1 mg, 9 μ L, 0.06 mmol) and EtOH (1 mL) were added into a sealed tube. After the reaction mixture was set in a pre-heated (100 °C) metal block for 4 h, hydroxyl carbazole **5** was completely consumed as indicated by TLC in. Cooled to room temperature, the reaction mixture was concentrated and purified by flash column chromatography (silica gel; petroleum: ethyl acetate = 15:1-5:1) to give carbazole **3ae** (85.6 mg, 80% yield).

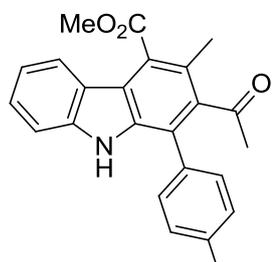
2.5 References:

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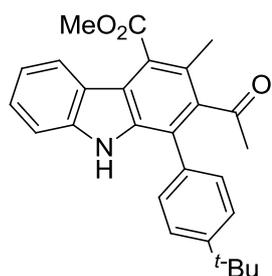
3. Analytical data of compounds 3-5, 7-9, 11, 12.



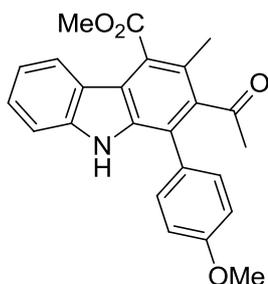
3a, Methyl 2-acetyl-3-methyl-1-phenyl-9H-carbazole-4-carboxylate. White solid in 89% yield, 95.3 mg, m.p. 161-163 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 2.03 (s, 3H), 2.41 (s, 3H), 4.14 (s, 3H), 7.22 (t, $J = 7.5$ Hz, 1H), 7.35 (d, $J = 8.0$ Hz, 1H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.48 (m, 3H), 7.53 (m, 2H), 7.89 (d, $J = 8.0$ Hz, 1H), 8.10 (s, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 16.5, 32.6, 52.5, 110.9, 119.9, 120.1, 121.2, 121.6, 121.7, 122.4, 126.7, 126.8, 128.7, 129.4, 129.7, 135.5, 136.1, 139.6, 140.3, 170.0, 206.9. **HRMS (ESI-TOF)** m/z calculated for $\text{C}_{23}\text{H}_{19}\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 380.1257, found 380.1244.



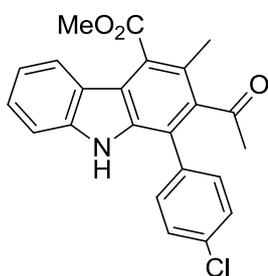
3b, Methyl 2-acetyl-3-methyl-1-(p-tolyl)-9H-carbazole-4-carboxylate. Yellow solid in 86% yield, 95.7 mg, m.p. 214-215 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.04 (s, 3H), 2.40 (s, 3H), 2.45 (s, 3H), 4.14 (s, 3H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.32-7.37 (m, 5H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 8.11 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.5, 21.3, 32.7, 52.5, 110.9, 119.7, 120.0, 121.2, 121.6, 121.7, 122.5, 126.4, 126.7, 129.5, 130.1, 132.4, 136.1, 138.6, 139.5, 140.2, 170.0, 207.1. **HRMS (ESI-TOF)** m/z calculated for $\text{C}_{24}\text{H}_{21}\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 394.1414, found 394.1422.



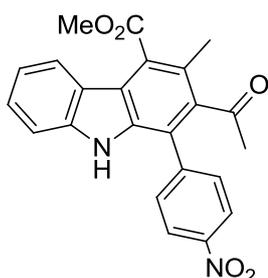
3c, Methyl 2-acetyl-1-(4-tert-butylphenyl)-3-methyl-9H-carbazole-4-carboxylate. Yellow solid in 70% yield, 86.7 mg, m.p. 282-284 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.40 (s, 9H), 2.03 (s, 3H), 2.40 (s, 3H), 4.14 (s, 3H), 7.22 (t, $J = 8.0$ Hz, 1H), 7.36-7.44 (m, 4H), 7.55 (d, $J = 8.4$ Hz, 2H), 7.88 (d, $J = 8.0$ Hz, 1H), 8.09 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.5, 31.3, 32.6, 52.5, 110.9, 119.7, 120.0, 121.2, 121.6, 121.7, 122.5, 126.4 (2C), 126.8, 129.3, 132.4, 136.2, 139.6, 140.3, 151.8, 170.0, 207.2. **HRMS (ESI-TOF)** m/z calculated for $\text{C}_{27}\text{H}_{27}\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 436.1883, found 436.1893.



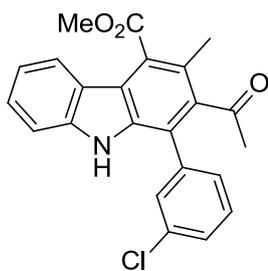
3d, Methyl 2-acetyl-1-(4-methoxyphenyl)-3-methyl-9H-carbazole-4-carboxylate. Yellow solid in 73% yield, 87.8 mg, m.p. 258-260 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.04 (s, 3H), 2.39 (s, 3H), 3.88 (s, 3H), 4.13 (s, 3H), 7.05 (d, $J = 8.4$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.34-7.44 (m, 4H), 7.88 (d, $J = 8.0$ Hz, 1H), 8.12 (s, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 16.5, 32.6, 52.5, 55.4, 110.9, 114.8, 119.7, 120.0, 121.2, 121.6, 121.7, 122.2, 126.3, 126.7, 127.4, 130.9, 136.3, 139.6, 140.3, 159.8, 170.0, 207.2. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{24}\text{H}_{21}\text{NNaO}_4^+$ ($[\text{M}+\text{Na}]^+$) 410.1363, found 410.1359.



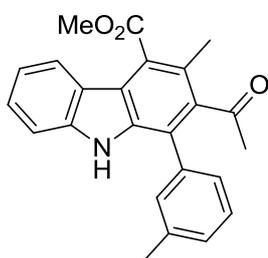
3e, Methyl 2-acetyl-1-(4-chlorophenyl)-3-methyl-9H-carbazole-4-carboxylate. Colorless crystal in 89% yield, 104.5 mg, m.p. 212-213 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 2.07 (s, 3H), 2.39 (s, 3H), 4.14 (s, 3H), 7.23 (t, $J = 7.5$ Hz, 1H), 7.35 (d, $J = 8.0$ Hz, 1H), 7.40-7.44 (m, 3H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.87 (d, $J = 8.0$ Hz, 1H), 8.06 (s, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 16.5, 32.8, 52.6, 110.9, 120.0, 120.2, 121.1, 121.6, 121.7, 127.0, 129.7, 131.1, 133.8, 134.9, 135.9, 139.6, 140.3, 169.8, 206.7. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{23}\text{H}_{18}\text{ClNNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 414.0867, found 414.0877.



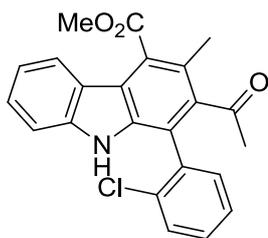
3f, Methyl 2-acetyl-3-methyl-1-(4-nitrophenyl)-9H-carbazole-4-carboxylate. Deep yellow solid in 93% yield, 112.2 mg, m.p. 253-254 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.10 (s, 3H), 2.40 (s, 3H), 4.15 (s, 3H), 7.25 (t, $J = 7.2$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 1H), 7.46 (t, $J = 7.4$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 8.08 (s, 1H), 8.38 (d, $J = 8.4$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.5, 32.9, 52.7, 111.0, 119.7, 120.4, 120.5, 120.9, 121.6, 121.8, 124.5, 127.3, 127.8, 130.9, 135.6, 139.6, 140.4, 142.5, 147.8, 169.6, 206.2. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{NaO}_5^+$ ($[\text{M}+\text{Na}]^+$) 425.1108, found 425.1090.



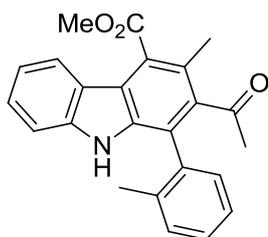
3g, Methyl 2-acetyl-1-(3-chlorophenyl)-3-methyl-9H-carbazole-4-carboxylate. White solid in 90% yield, 105.7 mg, m.p. 156 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.09 (s, 3H), 2.39 (s, 3H), 4.14 (s, 3H), 7.23 (t, $J = 7.2$ Hz, 1H), 7.30-7.40 (m, 2H), 7.41 (d, $J = 7.2$ Hz, 1H), 7.43-7.48 (m, 2H), 7.50 (s, 1H), 7.87 (d, $J = 7.6$ Hz, 1H), 8.12 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.5, 32.7, 52.6, 111.0, 120.1, 120.2, 120.7, 121.1, 121.6, 121.7, 127.0, 127.1, 128.2, 128.9, 129.5, 130.7, 135.3, 135.9, 137.3, 139.6, 140.3, 169.8, 206.5. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{23}\text{H}_{18}\text{ClNNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 414.0867, found 414.0867.



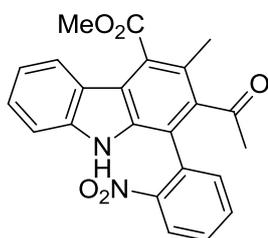
3h, Methyl 2-acetyl-3-methyl-1-(*m*-tolyl)-9H-carbazole-4-carboxylate. Colorless crystal in 95% yield, 105.7 mg, m.p. 160-161 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.04 (s, 3H), 2.40 (s, 3H), 2.43 (s, 3H), 4.13 (s, 3H), 7.21 (t, $J = 7.8$ Hz), 7.25-7.30 (m, 3H), 7.35 (d, $J = 8.0$ Hz, 1H), 7.41 (t, $J = 7.2$ Hz, 2H), 7.88 (d, $J = 7.6$ Hz, 1H), 8.10 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.5, 21.5, 32.6, 52.5, 110.9, 119.8, 120.0, 121.2, 121.6, 121.7, 122.7, 126.5, 126.7, 126.8, 129.3, 129.5, 130.2, 135.4, 136.1, 139.2, 139.5, 140.3, 170.0, 206.9. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{24}\text{H}_{21}\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 394.1414, found 394.1416.



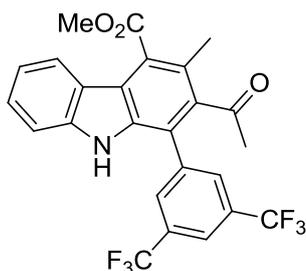
3i, Methyl 2-acetyl-1-(2-chlorophenyl)-3-methyl-9H-carbazole-4-carboxylate. Colorless crystal in 60% yield, 70.5 mg, m.p. 185-187 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.13 (s, 3H), 2.42 (s, 3H), 4.15 (s, 3H), 7.23 (t, $J = 7.8$ Hz, 1H), 7.33 (dd, $J_1 = 7.6$ Hz, $J_2 = 2.0$ Hz, 1H), 7.35-7.49 (m, 4H), 7.59 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H), 7.84 (s, 1H), 7.89 (d, $J = 8.0$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.6, 32.0, 52.5, 111.0, 119.6, 119.8, 120.1, 121.2, 121.4, 121.7, 126.9, 127.3, 127.6, 130.1, 130.4, 133.2, 133.7, 134.0, 136.0, 139.9, 140.5, 169.9, 206.2. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{23}\text{H}_{18}\text{ClNNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 414.0867, found 414.0868.



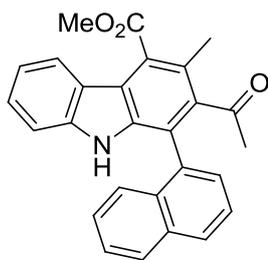
3j, Methyl 2-acetyl-3-methyl-1-(*o*-tolyl)-9*H*-carbazole-4-carboxylate. White solid in 77% yield, 85.7 mg, m.p. 181-183 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.08 (s, 3H), 2.10 (s, 3H), 2.41 (s, 3H), 4.15 (s, 3H), 7.20-7.27 (m, 2H), 7.27-7.35 (m, 2H), 7.35-7.42 (m, 3H), 7.76 (s, 1H), 7.89 (d, $J = 8.0$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.6, 19.8, 32.2, 52.5, 110.9, 119.6, 120.1, 121.3, 121.6, 121.7, 121.9, 126.4, 126.6, 126.8, 129.1, 130.6, 130.9, 134.4, 136.1, 137.3, 139.9, 140.3, 170.1, 206.3. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{24}\text{H}_{21}\text{NO}_3\text{Na}^+$ ($[\text{M}+\text{Na}]^+$) 394.1414, found 394.1414.



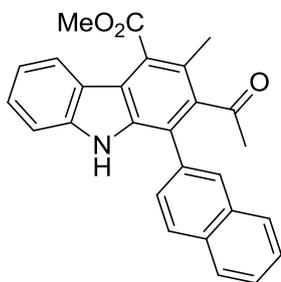
3k, Methyl 2-acetyl-3-methyl-1-(2-nitrophenyl)-9*H*-carbazole-4-carboxylate. Yellow solid in 82% yield, 98.9 mg, m.p. 220-221 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.20 (s, 3H), 2.42 (s, 3H), 4.15 (s, 3H), 7.22 (t, $J = 7.2$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.39-7.45 (m, 2H), 7.63 (td, $J_1 = 7.8$ Hz, $J_2 = 1.6$ Hz, 1H), 7.70 (td, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 7.79 (s, 1H), 7.87 (d, $J = 8.0$ Hz), 8.11 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.7, 32.2, 52.6, 111.1, 118.0, 120.2, 120.4, 121.1, 121.5, 121.8, 124.9, 127.1, 127.5, 129.7, 130.1, 133.5, 133.8, 135.9, 139.2, 140.5, 149.3, 169.7, 206.0. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{NaO}_5^+$ ($[\text{M}+\text{Na}]^+$) 425.1108, found 425.1112.



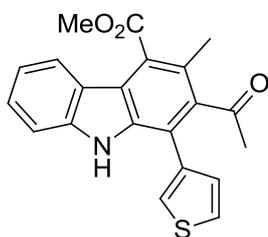
3l, Methyl 2-acetyl-1-(3,5-bis(trifluoromethyl)phenyl)-3-methyl-9*H*-carbazole-4-carboxylate. Colorless crystal in 70% yield, 103.5 mg, m.p. 243-244 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.14 (s, 3H), 2.41 (s, 3H), 4.15 (s, 3H), 7.26 (t, $J = 7.2$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 1H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.88 (d, $J = 8.4$ Hz, 1H), 7.91 (s, 1H), 7.95 (s, 2H), 8.03 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.5, 32.9, 52.7, 111.1, 118.8, 120.6 (2C), 121.0, 121.6, 121.8, 122.9 (q, $J = 271.6$ Hz), 122.5-122.7 (m), 127.4, 128.0, 130.0-130.2 (m), 132.8 (q, $J = 33.5$ Hz), 135.8, 137.8, 140.0, 140.4, 169.5, 205.7. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{25}\text{H}_{17}\text{F}_6\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 516.1005, found 516.1026.



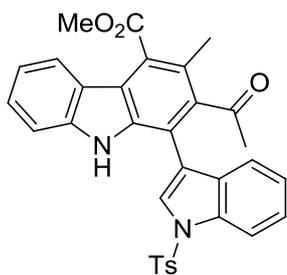
3m, Methyl 2-acetyl-3-methyl-1-(naphthalen-1-yl)-9H-carbazole-4-carboxylate. White solid in 71% yield, 86.7 mg, m.p. 208-209 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.89 (s, 3H), 2.46 (s, 3H), 4.18 (s, 3H), 7.22 (t, $J = 8.0$ Hz, 1H), 7.35-7.42 (m, 2H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.50 (d, $J = 8.4$ Hz, 1H), 7.55 (t, $J = 8.0$ Hz, 1H), 7.59 (t, $J = 7.8$ Hz, 1H), 7.64 (s, 1H), 7.92 (d, $J = 7.6$ Hz, 1H), 7.99 (t, $J = 7.2$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.6, 32.2, 52.6, 110.9, 119.6, 120.1, 120.6, 121.1, 121.7, 121.8, 125.7, 125.9, 126.6, 126.8, 127.0, 127.1, 128.7, 129.4, 129.5, 131.2, 132.4, 133.8, 136.7, 140.3, 140.7, 170.1, 206.4. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{27}\text{H}_{21}\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 430.1414, found 430.1410.



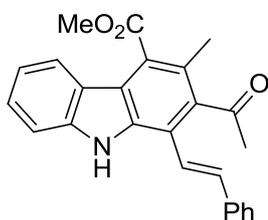
3n, Methyl 2-acetyl-3-methyl-1-(naphthalen-2-yl)-9H-carbazole-4-carboxylate. Light yellow crystal in 70% yield, 85.5 mg, m.p. 215 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.01 (s, 3H), 2.43 (s, 3H), 4.15 (s, 3H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.33 (d, $J = 8.4$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.56-7.59 (m, 3H), 7.88-7.95 (m, 4H), 8.01 (d, $J = 8.4$ Hz, 1H), 8.15 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.5, 32.7, 52.6, 110.9, 119.9, 120.1, 121.2, 121.8, 122.4, 126.8, 126.9 (2C), 126.99, 127.02, 127.9, 128.3, 129.1, 129.3, 132.9, 133.0, 133.5, 136.3, 139.8, 140.3, 170.0, 206.9. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{27}\text{H}_{21}\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 430.1414, found 430.1432.



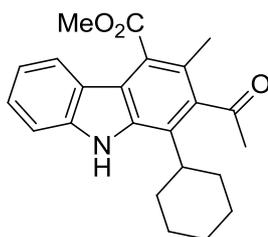
3p, Methyl 2-acetyl-3-methyl-1-(thiophen-3-yl)-9H-carbazole-4-carboxylate. White solid in 77% yield, 83.9 mg, m.p. 158-160 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.08 (s, 3H), 2.39 (s, 3H), 4.13 (s, 3H), 7.22 (t, $J = 8.0$ Hz, 1H), 7.28 (dd, $J_1 = 5.2$ Hz, $J_2 = 1.2$ Hz, 1H), 7.38 (d, $J = 7.6$ Hz, 1H), 7.40-7.45 (m, 2H), 7.54-7.57 (m, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 8.21 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.4, 32.3, 52.5, 110.9, 117.4, 119.9, 120.1, 121.2, 121.5, 121.7, 125.6, 126.7, 126.9, 127.5, 128.3, 135.3, 136.2, 139.7, 140.2, 169.9, 207.3. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{21}\text{H}_{17}\text{NNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 386.0821, found 386.0821.



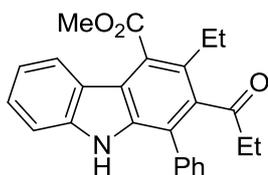
3q, Methyl 2-acetyl-3-methyl-1-(1-tosyl-1H-indol-3-yl)-9H-carbazole-4-carboxylate. Colorless crystal in 84% yield, 138.6 mg, m.p. 219-221 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.79 (s, 3H), 2.37 (s, 3H), 2.40 (s, 3H), 4.15 (s, 3H), 7.22 (t, $J = 7.0$ Hz, 1H), 7.24-7.31 (m, 5H), 7.37-7.46 (m, 2H), 7.63 (s, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 8.07 (s, 1H), 8.14 (d, $J = 8.4$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.4, 21.5, 32.1, 52.6, 111.0, 112.5, 114.2, 116.6, 119.9, 120.1, 120.5, 120.9, 121.2, 121.6, 124.1, 125.7, 126.9, 127.0, 127.2, 129.0, 130.0, 134.8, 135.0, 136.6, 140.2, 140.6, 145.4, 169.9, 206.5. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{32}\text{H}_{26}\text{N}_2\text{NaO}_5\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 573.1455, found 573.1473.



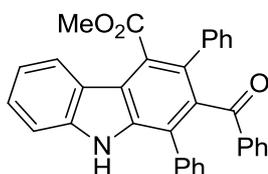
3r, (E)-Methyl 2-acetyl-3-methyl-1-styryl-9H-carbazole-4-carboxylate. Colorless crystal in 87% yield, 100.0 mg, m.p. 210-212 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.38 (s, 3H), 2.51 (s, 3H), 4.12 (s, 3H), 7.13 (d, $J = 16.8$ Hz, 1H), 7.21-7.25 (m, 1H), 7.27 (d, $J = 16.4$ Hz, 1H), 7.33-7.38 (m, 1H), 7.40-7.47 (m, 4H), 7.55 (d, $J = 7.2$ Hz, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 8.44 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.3, 33.0, 52.5, 111.0, 118.3, 120.2, 120.3, 121.2, 121.3, 121.7, 122.0, 126.5, 126.7, 126.9, 128.7, 128.9, 135.7, 135.8, 136.3, 139.3, 140.2, 169.9, 207.7. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{25}\text{H}_{21}\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 406.1414, found 406.1400.



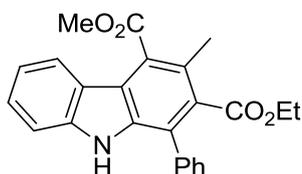
3s, Methyl 2-acetyl-1-cyclohexyl-3-methyl-9H-carbazole-4-carboxylate. White solid in 94% yield, 102.4 mg, m.p. 202-203 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.34-1.52 (m, 3H), 1.77-2.08 (m, 7H), 2.32 (s, 3H), 2.54 (s, 3H), 2.65-2.75 (m, 1H), 4.10 (s, 3H), 7.19 (t, $J = 7.2$ Hz, 1H), 7.41 (t, $J = 7.4$ Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 8.31 (d, $J = 18.8$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.2, 26.0, 26.7, 31.4, 42.0, 52.4, 110.8, 119.8, 120.3, 120.4, 120.7, 121.3, 125.3, 125.5, 126.5, 135.7, 139.7, 139.9, 170.1, 208.5. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{23}\text{H}_{25}\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 386.1727, found 386.1724.



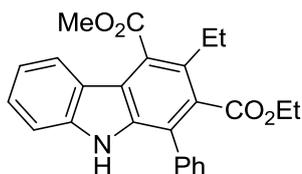
3t, Methyl 3-ethyl-1-phenyl-2-propionyl-9H-carbazole-4-carboxylate. Colorless crystal in 74% yield, 85.5 mg, m.p. 153-154 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 0.81 (t, $J = 7.2$ Hz, 3H), 1.28 (t, $J = 7.4$ Hz, 3H), 2.26 (q, $J = 7.2$ Hz, 2H), 2.70 (q, $J = 7.6$ Hz, 2H), 4.15 (s, 3H), 7.22 (t, $J = 7.8$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.41 (d, $J = 7.2$ Hz, 1H), 7.43-7.56 (m, 5H), 7.85 (d, $J = 8.4$ Hz, 1H), 8.09 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 7.7, 17.1, 24.5, 38.7, 52.5, 110.9, 119.9, 120.0, 121.3, 121.6, 122.5, 126.3, 126.8, 128.6, 129.4, 129.8, 135.7, 136.0, 139.5, 140.3, 170.1, 209.6. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{25}\text{H}_{23}\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 408.1570, found 408.1564.



3u, Methyl 2-benzoyl-1,3-diphenyl-9H-carbazole-4-carboxylate. Colorless crystal in 66% yield, 95.2 mg, m.p. 214-215 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.68 (s, 3H), 7.11-7.15 (m, 5H), 7.44-7.50 (m, 13H), 8.05 (d, $J = 8.0$ Hz, 1H), 8.21 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 52.2, 111.0, 119.9, 120.1, 121.2, 122.0, 124.3, 126.4, 127.0, 127.1, 127.4, 127.7, 128.1, 128.7, 129.2, 129.8, 132.5, 135.0, 136.5, 137.2, 137.8, 138.3, 140.5, 169.5, 197.8. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{33}\text{H}_{23}\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 504.1570, found 504.1569.

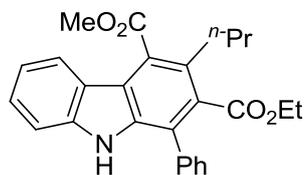


3v, 2-Ethyl 4-methyl 3-methyl-1-phenyl-9H-carbazole-2,4-dicarboxylate. Light orange crystal in 77% yield, 89.4 mg, m.p. 187-188 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 0.96 (t, $J = 7.0$ Hz, 3H), 2.51 (s, 3H), 4.06 (q, $J = 6.8$ Hz, 2H), 4.14 (s, 3H), 7.22 (t, $J = 7.2$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.45-7.55 (m, 5H), 7.90 (d, $J = 8.0$ Hz, 1H), 8.08 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 13.7, 16.8, 52.5, 61.0, 110.9, 120.0, 120.3, 121.2, 121.9, 123.4, 124.4, 126.3, 126.9, 128.3, 129.0, 131.6, 136.1, 140.4, 169.1, 169.9. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{24}\text{H}_{21}\text{NNaO}_4^+$ ($[\text{M}+\text{Na}]^+$) 410.1363, found 410.1363.

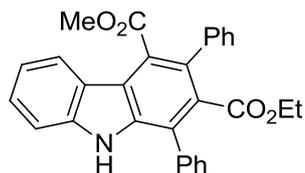


3w, 2-Ethyl 4-methyl 3-ethyl-1-phenyl-9H-carbazole-2,4-dicarboxylate. Colorless crystal in 80% yield, 96.5 mg, m.p. 157-159 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 0.95 (t, $J = 7.2$ Hz, 3H), 1.31 (t, $J = 7.6$ Hz, 3H), 2.87 (q, $J = 7.6$ Hz, 2H), 4.04 (q, $J = 7.2$ Hz, 2H), 4.14 (s, 3H), 7.22 (t, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.42 (t, $J = 7.8$ Hz, 1H), 7.45-7.55 (m, 5H), 7.87 (d, $J = 8.0$ Hz, 1H), 8.05 (s, 1H). $^{13}\text{C NMR}$

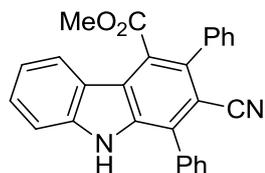
(100 MHz, CDCl₃) δ 13.6, 16.7, 24.8, 52.4, 61.0, 110.9, 120.0, 120.3, 121.3, 121.7, 124.6, 126.0, 126.9, 128.3, 129.0, 129.2, 129.9, 131.3, 136.2, 140.4, 169.2, 169.9. **HRMS** (ESI-TOF) m/z calculated for C₂₅H₂₃NNaO₄⁺ ([M+Na]⁺) 424.1519, found 424.1516.



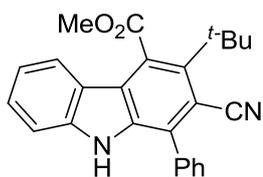
3x, 2-Ethyl 4-methyl 1-phenyl-3-propyl-9H-carbazole-2,4-dicarboxylate. Colorless crystal in 66% yield, 82.4 mg, m.p. 132-134 °C. **¹H NMR** (400 MHz, CDCl₃) δ 0.95 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 6.8 Hz, 3H), 1.68-1.74 (m, 2H), 2.79-2.85 (m, 2H), 4.03 (q, J = 7.2 Hz, 2H), 4.14 (s, 3H), 7.22 (t, J = 7.8 Hz, 1H), 7.39-7.42 (m, 5H), 7.87 (d, J = 8.0 Hz, 1H), 8.02 (s, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 13.6, 14.5, 25.6, 33.5, 52.4, 61.0, 110.9, 120.0, 120.3, 121.3, 121.8, 124.6, 126.1, 126.9, 128.3, 128.7, 129.0, 129.2, 131.5, 136.1, 136.2, 140.4, 169.2, 170.0. **HRMS** (ESI-TOF) m/z calculated for C₂₆H₂₅NNaO₄⁺ ([M+Na]⁺) 438.1676, found 438.1674.



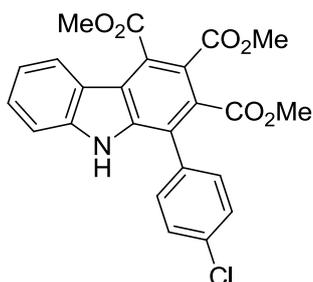
3y, 2-Ethyl 4-methyl 1,3-diphenyl-9H-carbazole-2,4-dicarboxylate. Colorless crystal in 77% yield, 103.9 mg, m.p. 168-170 °C. **¹H NMR** (400 MHz, CDCl₃) δ 0.74 (t, J = 7.2 Hz, 3H), 3.69 (s, 3H), 3.76 (q, J = 7.2 Hz, 2H), 7.24 (t, J = 8.4 Hz, 1H), 7.33-7.40 (m, 4H), 7.41-7.50 (m, 4H), 7.50-7.58 (m, 4H), 8.00 (d, J = 8.0 Hz, 1H), 8.14 (s, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 13.4, 52.2, 60.9, 110.9, 120.0, 120.2, 121.4, 122.3, 124.2, 126.4, 127.2, 127.4, 127.7, 128.5, 129.0, 129.3, 129.7, 129.9, 131.5, 135.7, 137.0, 138.6, 140.5, 168.3, 169.3. **HRMS** (ESI-TOF) m/z calculated for C₂₉H₂₃NNaO₄⁺ ([M+Na]⁺) 472.1519, found 472.1522.



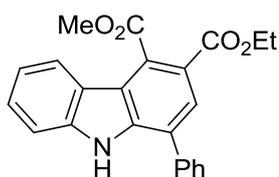
3z, Methyl 2-cyano-1,3-diphenyl-9H-carbazole-4-carboxylate. Yellow solid in 80% yield, 96.5 mg, m.p. 236-237 °C. **¹H NMR** (400 MHz, CDCl₃) δ 3.72 (s, 3H), 7.28 (t, J = 7.8 Hz, 1H), 7.41-7.58 (m, 8H), 7.62 (t, J = 7.4 Hz, 2H), 7.67 (m, 2H), 8.01 (d, J = 8.4 Hz, 1H), 8.36 (s, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 52.5, 108.6, 111.3, 117.7, 120.8 (2C), 122.5, 122.6, 126.7, 128.3, 128.4, 129.4, 129.5, 129.7, 130.7, 134.2, 135.3, 136.6, 137.3, 141.2, 168.6. **HRMS** (ESI-TOF) m/z calculated for C₂₇H₁₈N₂NaO₂⁺ ([M+Na]⁺) 425.1260, found 425.1266.



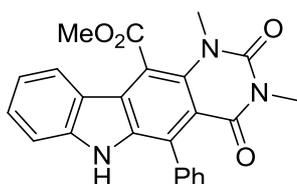
3aa, Methyl 3-(*tert*-butyl)-2-cyano-1-phenyl-9*H*-carbazole-4-carboxylate. Colorless crystal in 72% yield, 82.5 mg, m.p. 260-262 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.76(s, 9H), 4.13 (s, 3H), 7.24 (t, $J = 7.2$ Hz, 1H), 7.36 (d, $J = 8.4$ Hz, 1H), 7.43-7.48 (m, 1H), 7.53-7.63 (m, 5H), 7.81 (d, $J = 8.0$ Hz, 1H), 8.11 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 31.4, 37.8, 52.8, 108.4, 111.3, 120.0, 120.6, 121.0, 121.5, 122.2, 125.6, 127.9, 129.3 (2C), 129.5, 133.5, 134.9, 135.4, 140.0, 140.9, 171.1. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{NaO}_2^+$ ($[\text{M}+\text{Na}]^+$) 405.1573, found 405.1583.



3ab, Trimethyl 1-(4-chlorophenyl)-9*H*-carbazole-2,3,4-tricarboxylate. Yellow solid in 73% yield, 98.7 mg, m.p. 211-213 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.61 (s, 3H), 3.72 (s, 3H), 4.02 (s, 3H), 7.23-7.28 (m, 1H), 7.28-7.32 (m, 2H), 7.34-7.38 (m, 2H), 7.48-7.57 (m, 2H), 7.88 (d, $J = 8.0$ Hz, 1H), 10.11 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 51.3, 51.5, 51.9, 108.0, 110.4, 119.1, 119.9, 120.5, 120.9, 126.4, 126.96, 127.04, 130.4, 130.5, 132.3, 133.1, 134.3, 138.1, 139.7, 165.0, 167.2, 167.6. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{24}\text{H}_{18}\text{ClNNaO}_6^+$ ($[\text{M}+\text{Na}]^+$) 474.0715, found 474.0713.

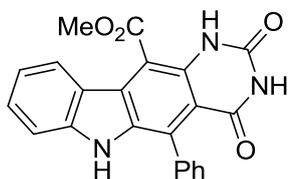


3ac, 3-Ethyl 4-methyl 1-phenyl-9*H*-carbazole-3,4-dicarboxylate. White crystal in 47% yield, 52.8 mg, m.p. 155-157 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.41 (t, $J = 7.2$ Hz, 3H), 4.17 (s, 3H), 4.40 (q, $J = 7.2$ Hz, 2H), 7.24-7.29 (m, 1H), 7.41-7.49 (m, 3H), 7.57 (t, $J = 7.6$ Hz, 2H), 7.66 (d, $J = 7.2$ Hz, 2H), 7.93 (d, $J = 8.0$ Hz, 1H), 8.12 (s, 1H), 8.68 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 14.3, 52.9, 61.3, 111.1, 119.0, 120.1, 120.8, 121.5, 121.6, 125.4, 127.1, 127.2, 128.3, 128.4, 128.7, 129.4, 137.3, 139.9, 140.0, 166.2, 170.0. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{23}\text{H}_{19}\text{NNaO}_4^+$ ($[\text{M}+\text{Na}]^+$) 396.1206, found 396.1210.

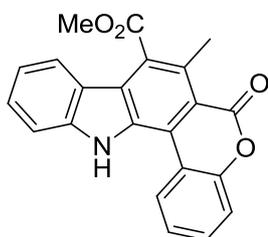


3ad, Methyl 1,3-dimethyl-2,4-dioxo-5-phenyl-2,3,4,6-tetrahydro-1*H*-pyrimido[5,4-*b*]carbazole-11-carboxylate. Yellow solid in 64% yield, 81.8 mg, m.p. 291-293 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.35 (s, 3H), 3.72 (s, 3H), 4.18 (s, 3H), 7.21-7.27 (m, 1H), 7.33-7.37 (m, 3H), 7.46-7.60 (m, 4H), 7.93 (s, 1H),

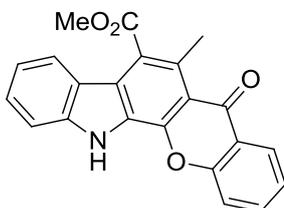
8.05 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 28.6, 35.5, 53.1, 111.3, 112.4, 113.4, 120.3, 120.6, 122.9, 124.4, 127.9, 128.1, 128.4, 128.7, 128.8, 133.1, 135.5, 137.2, 141.8, 151.6, 161.3, 169.2. HRMS (ESI-TOF) m/z calculated for $\text{C}_{24}\text{H}_{19}\text{N}_3\text{NaO}_4^+$ ($[\text{M}+\text{Na}]^+$) 436.1268, found 436.1268.



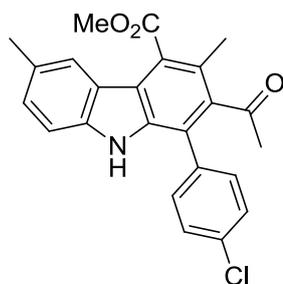
3ae, Methyl 2,4-dioxo-5-phenyl-2,3,4,6-tetrahydro-1H-pyrimido[5,4-*b*]carbazole-11-carboxylate. Yellow solid in 93% yield, 107.4 mg, m.p. 274-276 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 4.13 (s, 3H), 7.17 (t, $J = 7.2$ Hz, 1H), 7.33 (d, $J = 6.0$ Hz, 2H), 7.43-7.57 (m, 5H), 8.03 (d, $J = 8.0$ Hz, 1H), 10.48 (s, 1H), 10.69 (s, 1H), 11.13 (s, 1H). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 53.5, 110.0, 110.7, 112.8, 119.8, 120.1, 123.8, 124.3, 127.8, 128.6, 128.8, 129.2, 130.1, 132.8, 135.7, 137.3, 143.5, 150.2, 162.2, 167.5. HRMS (ESI-TOF) m/z calculated for $\text{C}_{22}\text{H}_{15}\text{N}_3\text{NaO}_4^+$ ($[\text{M}+\text{Na}]^+$) 408.0955, found 408.0958.



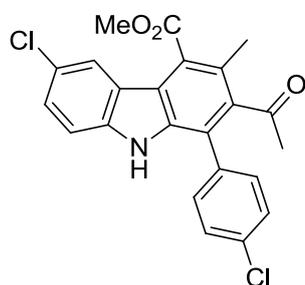
3af, Methyl 7-methyl-6-oxo-6,13-dihydrochromeno[4,3-*a*]carbazole-8-carboxylate. Yellow solid in 83% yield, 88.9 mg, m.p. 273-276 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 2.76 (s, 3H), 4.12 (s, 3H), 7.32 (t, $J = 8.0$ Hz, 1H), 7.49 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.52-7.57 (m, 1H), 7.58-7.67 (m, 2H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 8.71 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 12.06 (s, 1H). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 20.3, 53.5, 113.5, 117.2, 117.3, 117.5, 119.5, 121.2, 121.4, 122.8, 124.0, 125.1, 126.7, 128.6, 128.7, 129.4, 130.9, 132.9, 143.0, 151.0, 160.1, 169.8. HRMS (ESI-TOF) m/z calculated for $\text{C}_{22}\text{H}_{15}\text{NNaO}_4^+$ ($[\text{M}+\text{Na}]^+$) 380.0893, found 380.0900.



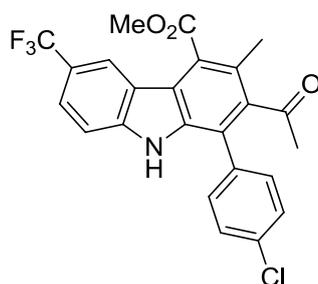
3ag, Methyl 6-methyl-7-oxo-7,13-dihydrochromeno[2,3-*a*]carbazole-5-carboxylate. Light yellow solid in 63% yield, 67.5 mg, m.p. 246-248 °C. ^1H NMR (400 MHz, CDCl_3) δ 2.92 (s, 3H), 4.15 (s, 3H), 7.05 (t, $J = 7.2$ Hz, 1H), 7.35 (t, $J = 7.4$ Hz, 1H), 7.40 (t, $J = 7.2$ Hz, 1H), 7.42-7.45 (m, 2H), 7.65-7.71 (m, 2H), 8.28 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 8.81 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 19.2, 52.6, 111.5, 116.4, 117.0, 120.5, 120.9, 121.5, 123.3, 123.5, 124.2, 126.1, 126.9, 127.6, 128.4, 134.1, 140.5, 145.0, 154.4, 170.2, 177.9. HRMS (ESI-TOF) m/z calculated for $\text{C}_{22}\text{H}_{15}\text{NNaO}_4^+$ ($[\text{M}+\text{Na}]^+$) 380.0893, found 380.0894.



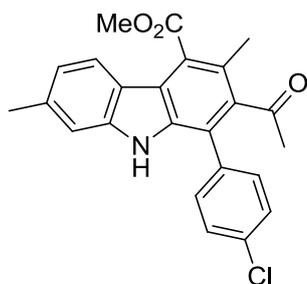
3be, Methyl 2-acetyl-1-(4-chlorophenyl)-3,6-dimethyl-9H-carbazole-4-carboxylate. Light yellow solid in 95% yield, 115.6 mg, m.p. 186-188 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.06 (s, 3H), 2.37 (s, 3H), 2.49 (s, 3H), 4.14 (s, 3H), 7.24 (s, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.47-7.51 (m, 2H), 7.63 (s, 1H), 8.00 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.4, 21.6, 32.7, 52.5, 110.6, 119.8, 120.9, 121.2, 121.3, 121.5, 126.9, 128.4, 129.4, 129.6, 131.1, 133.9, 134.8, 136.2, 138.6, 139.4, 169.9, 206.8. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{24}\text{H}_{20}\text{ClNNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 428.1024, found 428.1028.



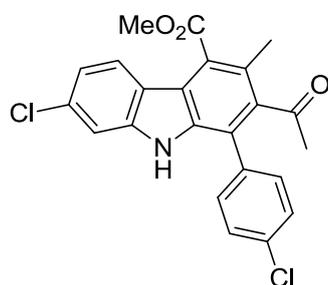
3ce, Methyl 2-acetyl-6-chloro-1-(4-chlorophenyl)-3-methyl-9H-carbazole-4-carboxylate. White solid in 75% yield, 95.8 mg, m.p. 220-221 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.06 (s, 3H), 2.36 (s, 3H), 4.13 (s, 3H), 7.24 (d, $J = 2.8$ Hz, 1H), 7.35 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 1H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.81 (d, $J = 1.6$ Hz, 2H), 8.08 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.5, 32.7, 52.7, 111.9, 119.2, 121.3, 121.6, 122.2, 122.3, 125.6, 127.0, 127.2, 129.7, 131.1, 133.5, 135.1, 136.5, 138.6, 140.3, 169.4, 206.4. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{23}\text{H}_{17}\text{Cl}_2\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 448.0478, found 448.0486.



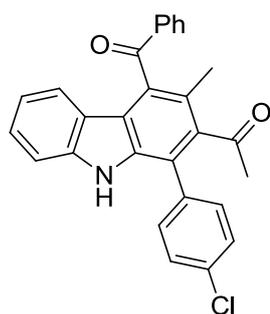
3de, Methyl 2-acetyl-1-(4-chlorophenyl)-3-methyl-6-(trifluoromethyl)-9H-carbazole-4-carboxylate. Yellow solid in 34%, 46.9 mg, m.p. 212-213 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.08 (s, 3H), 2.40 (s, 3H), 4.15 (s, 3H), 7.41 (t, $J = 8.0$ Hz, 3H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 8.4$ Hz, 1H), 8.16 (s, 1H), 8.31 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.6, 32.7, 52.6, 111.2, 119.5 (q, $J = 4.2$ Hz), 119.7, 120.8, 121.5, 122.5 (q, $J = 32.0$ Hz), 123.0, 123.7 (q, $J = 3.2$ Hz), 124.9 (q, $J = 269.3$ Hz), 127.1, 129.8, 131.0, 133.3, 135.3, 136.5, 140.7, 141.7, 169.3, 206.3. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{24}\text{H}_{17}\text{ClF}_3\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 482.0741, found 482.0760.



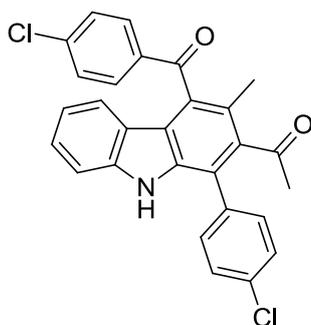
3ee, Methyl 2-acetyl-1-(4-chlorophenyl)-3,7-dimethyl-9H-carbazole-4-carboxylate. White solid in 82% yield, 99.7 mg, m.p. 222-224 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.06 (s, 3H), 2.38 (s, 3H), 2.47 (s, 3H), 4.12 (s, 3H), 7.04 (d, $J = 8.0$ Hz, 1H), 7.13 (s, 1H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.98 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.6, 22.1, 32.9, 52.6, 111.1, 118.9, 120.3, 121.0, 121.5, 121.6, 122.0, 126.6, 129.7, 131.2, 134.1, 134.9, 136.0, 137.5, 139.2, 141.0, 170.0, 207.0. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{24}\text{H}_{20}\text{ClNNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 428.1024, found 428.1029.



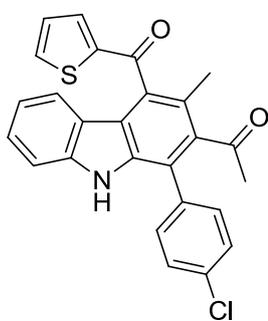
3fe, Methyl 2-acetyl-7-chloro-1-(4-chlorophenyl)-3-methyl-9H-carbazole-4-carboxylate. White solid in 64% yield, 81.8 mg, m.p. 246-247 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.06 (s, 3H), 2.37 (s, 3H), 4.12 (s, 3H), 7.18 (dd, $J_1 = 8.6$ Hz, $J_2 = 1.8$ Hz, 1H), 7.33 (d, $J = 1.6$ Hz, 1H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 7.78 (d, $J = 8.4$ Hz, 1H), 8.09 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.5, 32.7, 52.6, 111.0, 119.5, 119.8, 120.9, 121.2, 122.3, 122.7, 126.8, 129.8, 131.0, 132.8, 133.5, 135.1, 136.2, 140.0, 140.8, 169.6, 206.5. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{23}\text{H}_{17}\text{Cl}_2\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$) 448.0478, found 448.0485.



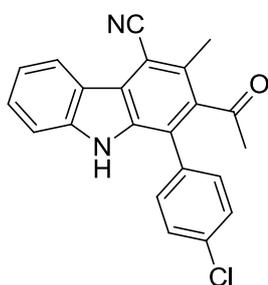
3ge, 1-(4-Benzoyl-1-(4-chlorophenyl)-3-methyl-9H-carbazol-2-yl)ethanone. Colorless crystal in 85% yield, 111.5 mg, m.p. 173-174 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.09 (s, 3H), 2.21 (s, 3H), 6.96-7.10 (m, 1H), 7.28-7.34 (m, 2H), 7.45-7.52 (m, 5H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.62 (t, $J = 7.4$ Hz, 1H), 7.99 (d, $J = 7.2$ Hz, 2H), 8.18 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.3, 32.8, 110.8, 120.1, 120.2, 120.4, 120.7, 121.3, 122.3, 126.7, 129.1, 129.7, 129.9, 133.7, 134.1, 134.3, 134.9, 135.9, 136.6, 139.7, 140.2, 199.3, 207.2. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{28}\text{H}_{20}\text{ClNNaO}_2^+$ ($[\text{M}+\text{Na}]^+$) 460.1075, found 460.1074.



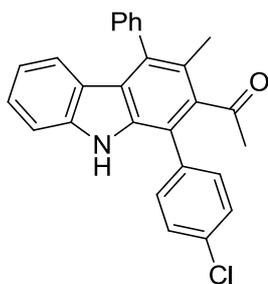
3he, 1-(4-(4-Chlorobenzoyl)-1-(4-chlorophenyl)-3-methyl-9H-carbazol-2-yl)ethanone. Light yellow crystal in 80% yield, 120.3 mg, m.p. 246-248 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.10 (s, 3H), 2.20 (s, 3H), 6.99-7.03 (m, 1H), 7.31-7.36 (m, 2H), 7.42-7.50 (m, 5H), 7.55 (d, $J = 8.8$ Hz, 2H), 7.93 (d, $J = 8.0$ Hz, 2H), 8.13 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.3, 32.8, 110.9, 120.1, 120.3, 120.6, 120.7, 121.1, 122.1, 126.8, 129.5, 129.8, 131.2, 133.1, 133.9, 135.0, 135.9, 139.8, 140.2, 140.9, 198.0, 207.0. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{28}\text{H}_{19}\text{Cl}_2\text{NNaO}_2^+$ ($[\text{M}+\text{Na}]^+$) 494.0685, found 494.0698.



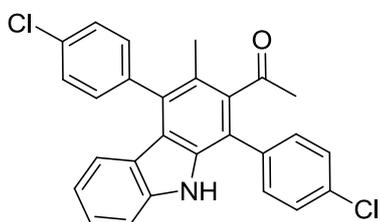
3ie, 1-(1-(4-Chlorophenyl)-3-methyl-4-(thiophene-2-carbonyl)-9H-carbazol-2-yl)ethanone. Light yellow crystal in 92% yield, 122.4 mg, m.p. 148-150 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.09 (s, 3H), 2.30 (s, 3H), 7.01-7.07 (m, 2H), 7.30-7.36 (m, 2H), 7.43-7.48 (m, 3H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.79 (dd, $J_1 = 5.0$ Hz, $J_2 = 1.0$ Hz, 1H), 8.18 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.2, 32.7, 110.8, 120.1, 120.2, 120.6, 120.8, 121.2, 122.3, 126.7, 128.7, 129.7, 133.4, 134.0, 134.9, 135.9, 136.1 (2C), 139.7, 140.2, 144.2, 191.1, 207.1. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{26}\text{H}_{18}\text{ClNNaO}_2\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 466.0639, found 466.0654.



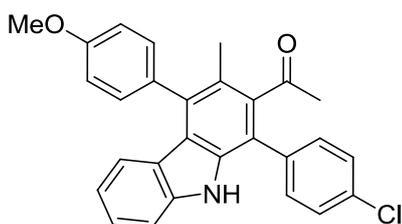
3je, 2-Acetyl-1-(4-chlorophenyl)-3-methyl-9H-carbazole-4-carbonitrile. White solid in 85% yield, 91.4 mg, m.p. 306 °C. $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 2.08 (s, 3H), 2.53 (s, 3H), 7.31 (t, $J = 6.8$ Hz, 1H), 7.46 (d, $J = 7.6$ Hz, 2H), 7.50-7.57 (m, 2H), 7.66 (d, $J = 7.6$ Hz, 2H), 8.42 (d, $J = 8.0$ Hz, 1H), 11.39 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO}-d_6$) δ 17.8, 32.9, 103.3, 112.7, 117.9, 120.0, 120.4, 120.9, 122.9, 125.0, 128.3, 128.7, 129.7, 132.1, 133.8, 134.3, 136.4, 139.5, 142.0, 205.6. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{22}\text{H}_{15}\text{ClN}_2\text{NaO}^+$ ($[\text{M}+\text{Na}]^+$) 381.0765, found 381.0774.



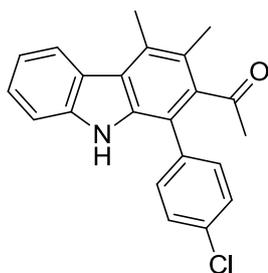
3ke, 1-(1-(4-Chlorophenyl)-3-methyl-4-phenyl-9H-carbazol-2-yl)ethanone. Colorless crystal in 47% yield, 57.7 mg, m.p. 236-238 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.15 (s, 3H), 2.16 (s, 3H), 6.69 (d, $J = 8.0$ Hz, 1H), 6.87-6.91 (m, 1H), 7.27-7.33 (m, 2H), 7.39-7.43 (m, 2H), 7.49-7.61 (m, 7H), 7.98 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.5, 32.9, 110.4, 118.5, 119.5, 122.1, 122.3, 122.5, 123.1, 126.0, 127.7, 129.0, 129.2, 129.6, 131.3, 134.5, 134.6, 135.6, 136.9, 139.7, 140.2, 208.1. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{27}\text{H}_{20}\text{ClNNaO}^+$ ($[\text{M}+\text{Na}]^+$) 432.1126, found 432.1121.



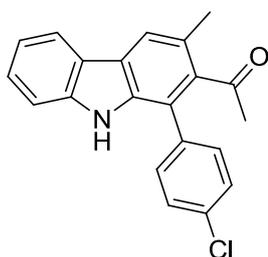
3le, 1-(1,4-Bis(4-chlorophenyl)-3-methyl-9H-carbazol-2-yl)ethanone. Colorless crystal in 59% yield, 78.6 mg, m.p. 241-242 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.14 (s, 3H), 2.14 (s, 3H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.92-6.95 (m, 1H), 7.32 (d, $J = 3.6$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 2H), 8.02 (s, 1H), 9.03 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.5, 32.9, 110.6, 118.9, 119.6, 122.1, 122.2, 122.3, 122.8, 126.2, 129.3, 129.6, 130.7, 131.2, 133.7, 134.4, 134.6, 135.4, 135.7, 138.1, 139.7, 140.2, 207.9. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{27}\text{H}_{19}\text{Cl}_2\text{NNaO}^+$ ($[\text{M}+\text{Na}]^+$) 466.0736, found 466.0749.



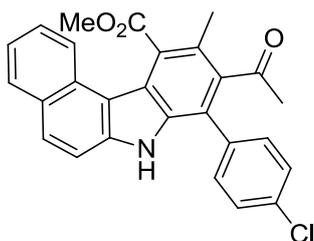
3me, 1-(1-(4-Chlorophenyl)-4-(4-methoxyphenyl)-3-methyl-9H-carbazol-2-yl)ethanone. White solid in 43% yield, 56.7 mg, m.p. 266-268 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.14 (s, 3H), 2.16 (s, 3H), 3.95 (s, 3H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.89-6.94 (m, 1H), 7.11 (d, $J = 8.4$ Hz, 1H), 7.29-7.35 (m, 4H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.96 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.6, 32.9, 55.3, 110.4, 114.4, 118.4, 119.5, 122.5, 122.6, 122.7, 123.2, 126.0, 129.6, 130.3, 131.2, 134.5, 134.6, 135.6, 136.6, 139.7, 140.1, 159.0, 208.2. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{28}\text{H}_{22}\text{ClNNaO}_2^+$ ($[\text{M}+\text{Na}]^+$) 462.1231, found 462.1239.



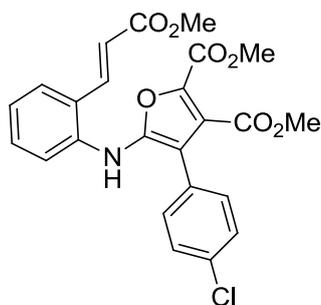
3ne, 1-(1-(4-Chlorophenyl)-3,4-dimethyl-9H-carbazol-2-yl)ethanone. White solid in 55% yield, 57.3 mg, m.p. 249-251 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.11 (s, 3H), 2.38 (s, 3H), 2.88 (s, 3H), 7.27 (t, $J = 7.0$ Hz, 1H), 7.37 (d, $J = 7.6$ Hz, 1H), 7.40-7.46 (m, 3H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.92 (s, 1H), 8.28 (d, $J = 8.0$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.0, 16.6, 33.1, 110.6, 116.7, 119.7, 122.0, 122.4, 123.1, 123.7, 125.7, 129.5, 131.4, 132.3, 134.3, 134.7, 135.7, 139.9, 140.1, 208.5. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{22}\text{H}_{18}\text{ClNNaO}^+$ ($[\text{M}+\text{Na}]^+$) 370.0969, found 370.0977.



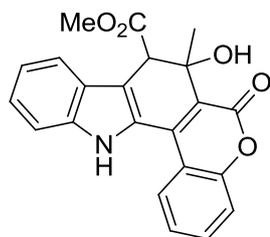
3pe, 1-(1-(4-Chlorophenyl)-3-methyl-9H-carbazol-2-yl)ethanone. White solid in 92% yield, 92.0 mg, m.p. 244-246 °C. $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 2.03 (s, 3H), 2.39 (s, 3H), 7.14-7.19 (m, 1H), 7.38 (td, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 7.43-7.47 (m, 3H), 7.60-7.65 (m, 2H), 8.03 (s, 1H), 8.12 (d, $J = 8.0$ Hz, 1H), 10.84 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO}-d_6$) δ 19.8, 33.0, 112.0, 119.4, 120.2, 120.9, 121.6, 122.3, 123.4, 123.5, 126.5, 129.5, 132.2, 133.4, 135.5, 136.4, 139.5, 141.5, 207.2. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{21}\text{H}_{16}\text{ClNNaO}^+$ ($[\text{M}+\text{Na}]^+$) 356.0813, found 356.0815.



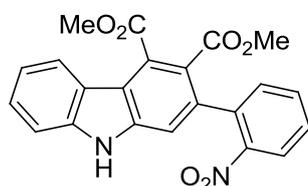
3qe, Methyl 9-acetyl-8-(4-chlorophenyl)-10-methyl-7H-benzo[c]carbazole-11-carboxylate. White solid in 83% yield, 109.8 mg, m.p. 233-235 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.10 (s, 3H), 2.48 (s, 3H), 4.02 (s, 3H), 7.40-7.42 (m, 2H), 7.44-7.48 (m, 2H), 7.49-7.52 (m, 2H), 7.60-7.65 (m, 1H), 7.81 (d, $J = 8.8$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 8.21 (d, $J = 8.4$ Hz, 1H), 8.49 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.9, 32.8, 52.2, 112.4, 114.7, 120.7, 121.4, 122.6, 123.2, 124.0, 126.6, 127.3, 129.3, 129.6, 131.2, 133.6, 135.0, 135.0, 138.3, 138.8, 171.3, 206.7. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{27}\text{H}_{21}\text{ClNO}_3^+$ ($[\text{M}+\text{H}]^+$) 442.1204, found 442.1206.



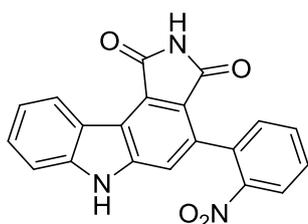
4, (E)-Dimethyl 4-(4-chlorophenyl)-5-((2-(3-methoxy-3-oxoprop-1-en-1-yl) phenyl)amino)furan-2,3-dicarboxylate. Deep yellow solid in 80% yield, 113.2 mg, m.p. 153-155 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.81 (s, 3H), 3.88 (s, 3H), 3.93 (s, 3H), 6.48 (d, $J = 15.6$ Hz, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.33 (d, $J = 8.8$ Hz, 2H), 7.44 (d, $J = 7.8$ Hz, 1H), 7.48 (d, $J = 8.8$ Hz, 2H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.64 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 15.6$ Hz, 1H), 8.81 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 29.7, 51.80, 51.85, 52.8, 92.0, 113.7, 121.0, 124.8, 126.2, 127.1, 128.1, 129.0, 131.1, 134.1, 136.2, 138.9, 141.7, 157.2, 164.4, 165.1, 166.8. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{24}\text{H}_{20}\text{ClNNaO}_7^+$ ($[\text{M}+\text{Na}]^+$) 492.0821, found 492.0822.



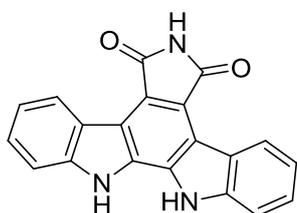
5, Methyl 7-hydroxy-7-methyl-6-oxo-6,7,8,13-tetrahydrochromeno[4,3-a]carbazole-8-carboxylate. Yellow solid in 63% yield, 70.5 mg, m.p. 188-190 °C. $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 1.98 (s, 3H), 3.64 (s, 3H), 4.39 (s, 2H), 7.04 (s, 1H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.36 (d, $J = 7.6$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.76 (t, $J = 7.8$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 8.22 (d, $J = 8.0$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO}-d_6$) δ 24.2 31.8, 52.7, 88.1, 107.6, 111.3, 115.2, 117.9, 120.7, 121.6, 125.2, 125.4, 127.3, 130.6, 133.2, 133.4, 133.5, 133.6, 143.4, 155.1, 156.5, 171.8. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{22}\text{H}_{18}\text{NO}_5^+$ ($[\text{M}+\text{H}]^+$) 376.1179, found 376.1161.



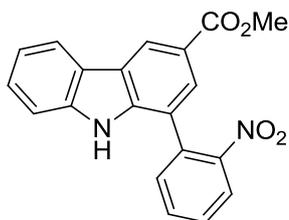
7, Methyl 3-methyl-2-(2-nitrophenyl)-9H-carbazole-4-carboxylate. Light yellow solid in 67% yield, 81.2 mg, m.p. 167-168 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.58 (s, 3H), 4.07 (s, 3H), 7.20 (s, 1H), 7.20-7.25 (m, 2H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.41-7.45 (m, 1H), 7.49 (td, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 7.55 (td, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 8.01 (d, $J = 8.0$ Hz, 1H), 8.05 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 8.56 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 52.3, 52.9, 111.1, 112.9, 119.7, 120.0, 120.7, 121.0, 122.3, 124.0, 127.4, 128.4, 128.6, 131.9, 132.4, 136.3, 136.6, 140.5, 140.6, 148.3, 167.3, 169.2. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{NaO}_6^+$ ($[\text{M}+\text{Na}]^+$) 427.0901, found 427.0916.



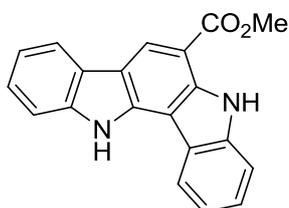
8, 4-(2-Nitrophenyl)pyrrolo[3,4-c]carbazole-1,3(2H,6H)-dione. Bright yellow solid in 76% yield, 54.2 mg, m.p. > 300 °C. $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 7.36 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.64-7.68 (m, 2H), 7.71 (s, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.86 (t, J = 7.4 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 8.88 (d, J = 7.6 Hz, 1H), 11.14 (s, 1H), 12.18 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, DMSO- d_6) δ 112.2, 116.4, 118.4, 120.3, 120.4, 120.9, 124.6, 125.3, 127.3, 129.9, 132.6, 133.3, 134.1, 142.3, 144.4, 148.8, 170.2, 170.3. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{20}\text{H}_{11}\text{N}_3\text{NaO}_4^+$ ($[\text{M}+\text{Na}]^+$) requires m/z 380.0642, found 380.0656.



9, 12,13-Dihydro-5H-indolo[2,3-a]pyrrolo[3,4-c]carbazole-5,7(6H)-dione. Orange solid in 44% yield, 14.3 mg, m.p. > 300 °C. $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 7.27 (t, J = 7.4 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 8.96 (d, J = 8.0 Hz, 2H), 10.91 (s, 1H), 12.63 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, DMSO- d_6) δ 112.3, 115.9, 120.2, 120.4, 122.0, 124.7, 126.9, 129.8, 141.0, 171.9. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{20}\text{H}_{11}\text{N}_3\text{NaO}_2^+$ ($[\text{M}+\text{Na}]^+$) 348.0743, found 348.0746.



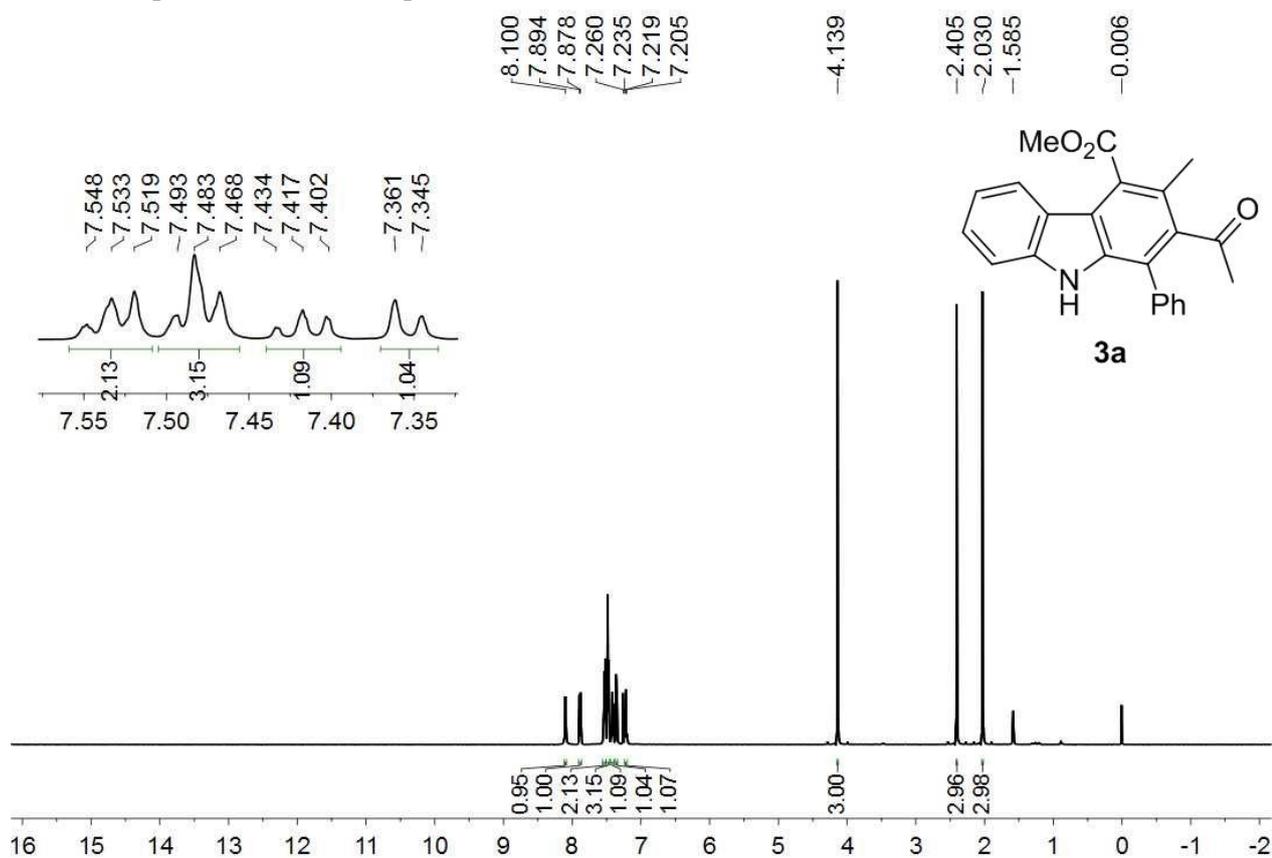
11, Methyl 1-(2-nitrophenyl)-9H-carbazole-3-carboxylate. Yellow solid in 52% yield, 54.1 mg, m.p. 233-235 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.97 (s, 3H), 7.32 (t, J = 7.8 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.43-7.48 (m, 1H), 7.60 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.65 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.76 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.99 (d, J = 1.2 Hz, 1H), 8.06 (s, 1H), 8.09 (dd, J_1 = 8.2 Hz, J_2 = 1.0 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.85 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 52.1, 111.1, 120.2, 120.76, 120.84, 121.8, 122.9, 123.45, 123.55, 124.8, 126.9, 127.0, 129.4, 132.1, 132.7, 133.2, 139.9, 140.3, 149.5, 167.4. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{NaO}_4^+$ ($[\text{M}+\text{Na}]^+$) 369.0846, found 369.0852.



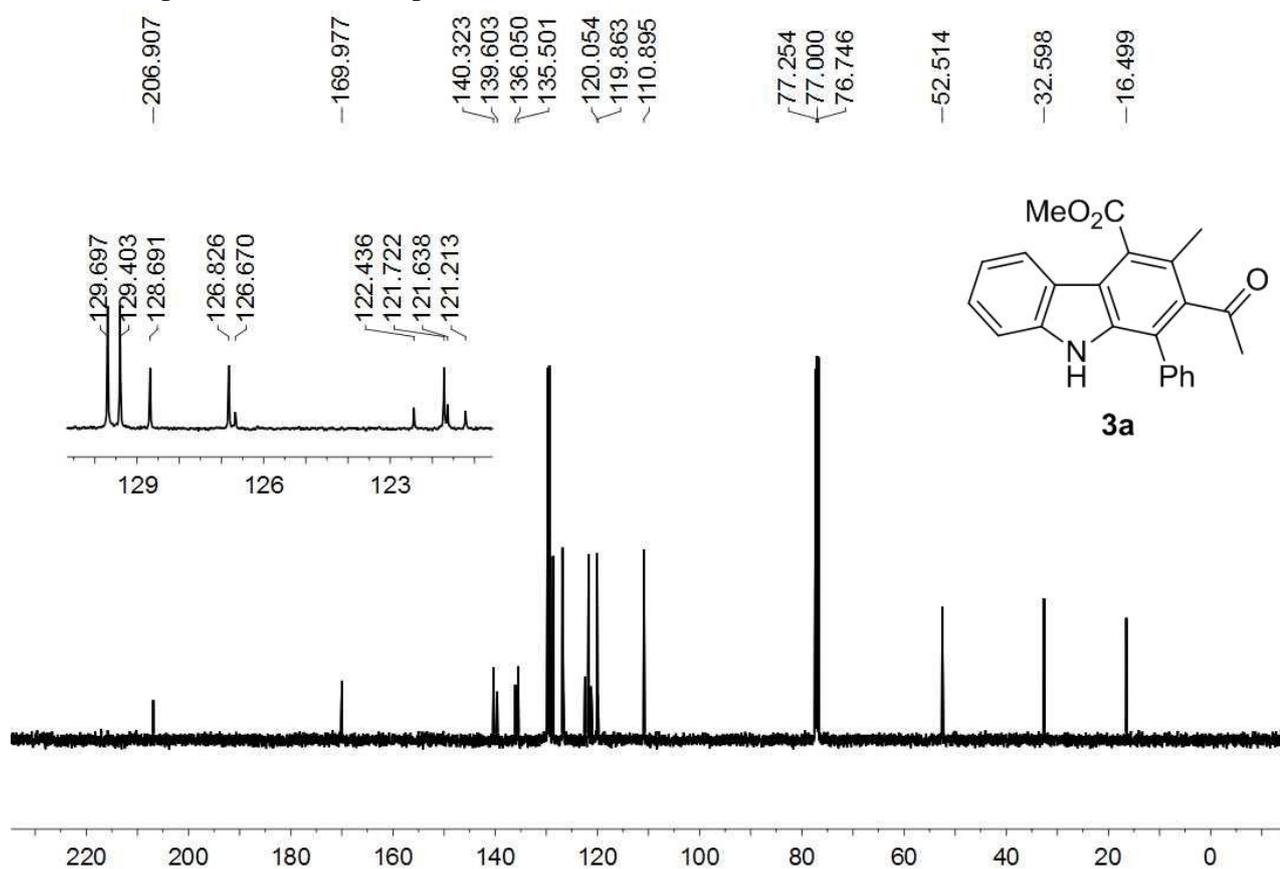
12, Methyl 5,12-dihydroindolo[3,2-*a*]carbazole-6-carboxylate (Racemosin B). White solid in 45% yield, 14.1 mg, m.p. 265-267 °C. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 4.03 (s, 3H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.38-7.51 (m, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 7.2 Hz, 1H), 8.69 (d, *J* = 7.6 Hz, 1H), 8.85 (s, 1H), 11.61 (s, 1H), 12.11 (s, 1H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 52.2, 105.0, 107.2, 111.9, 112.6, 115.5, 120.0, 120.1, 120.5, 121.1, 121.5, 121.7, 124.0, 125.26, 125.31, 137.7, 138.8, 139.5, 140.7, 167.5. **HRMS** (ESI-TOF) *m/z* calculated for C₂₀H₁₄N₂NaO₂⁺ ([M+Na]⁺) 337.3266, found 337.3254.

4. Copies of ^1H NMR and ^{13}C NMR spectra of compounds 3-5, 7-9, 11, 12.

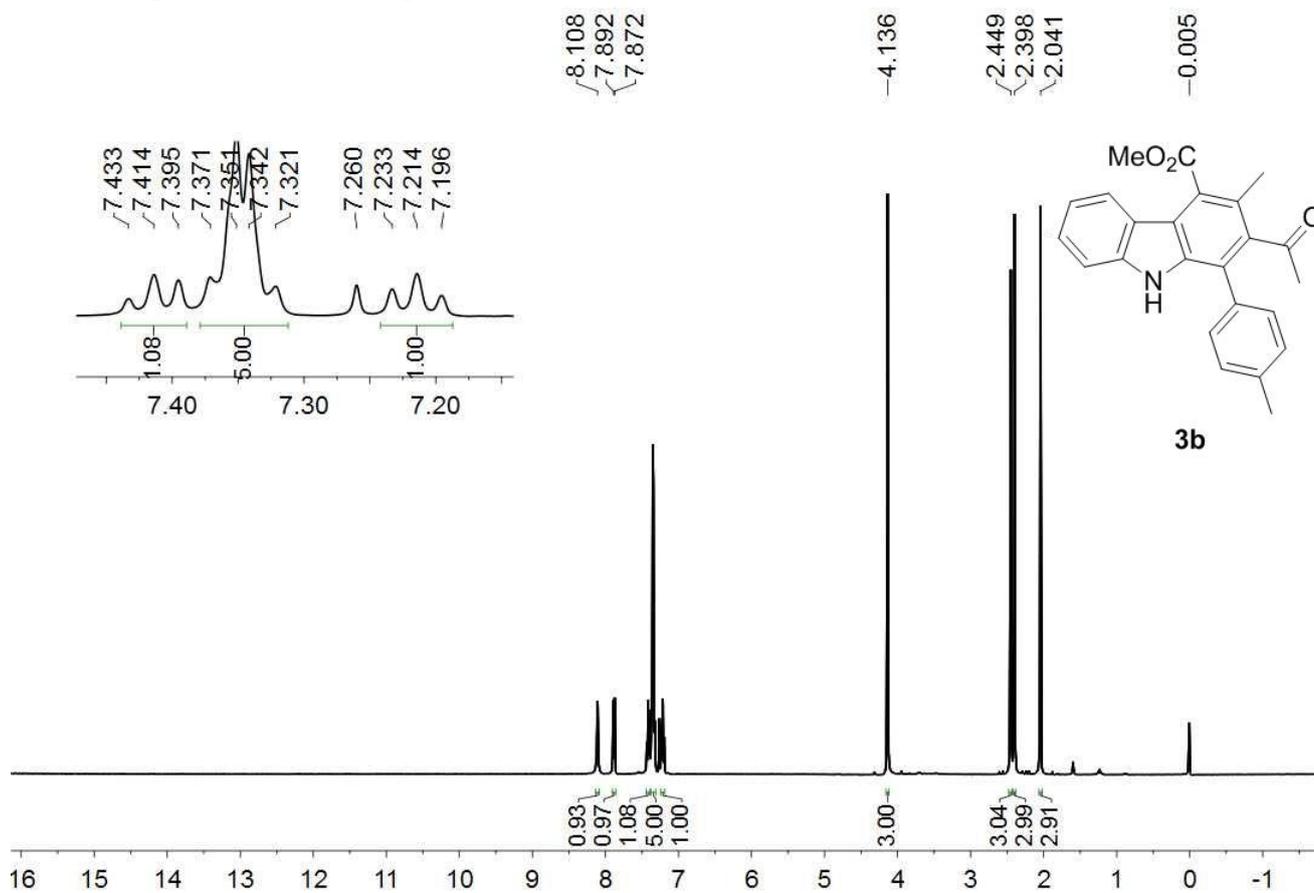
^1H NMR spectrum of the compound **3a** (500 MHz, CDCl_3)



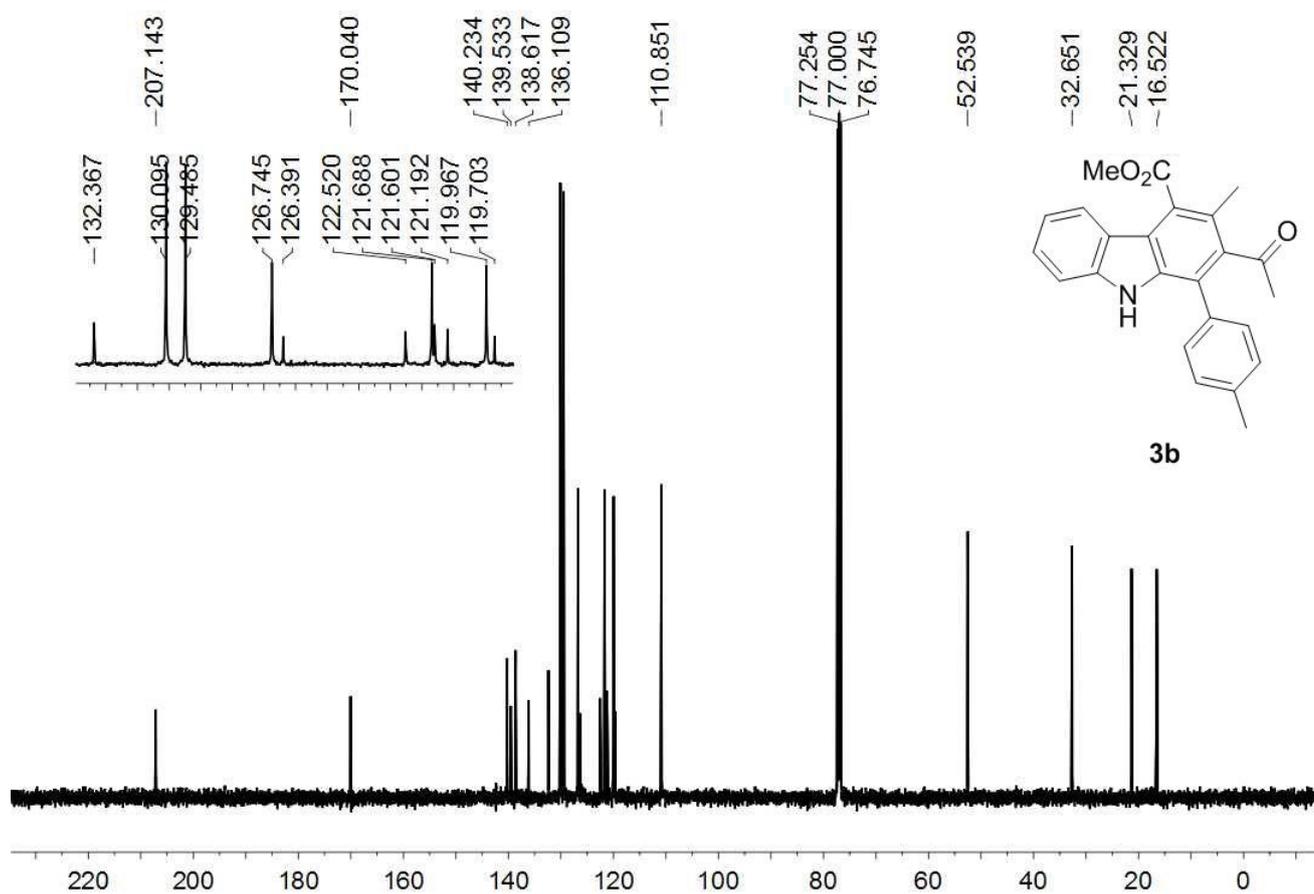
^{13}C NMR spectrum of the compound **3a** (125 MHz, CDCl_3)



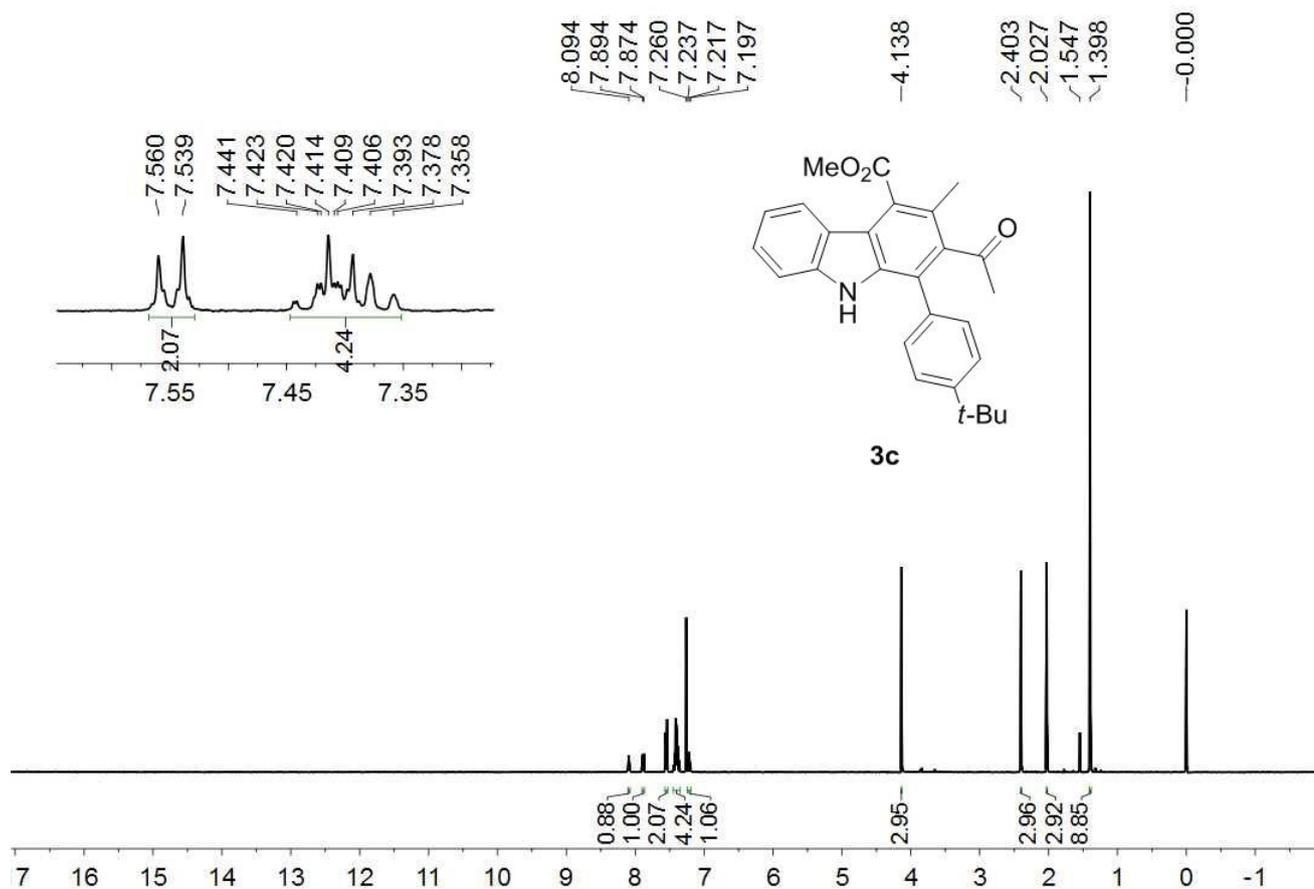
^1H NMR spectrum of the compound **3b** (400 MHz, CDCl_3)



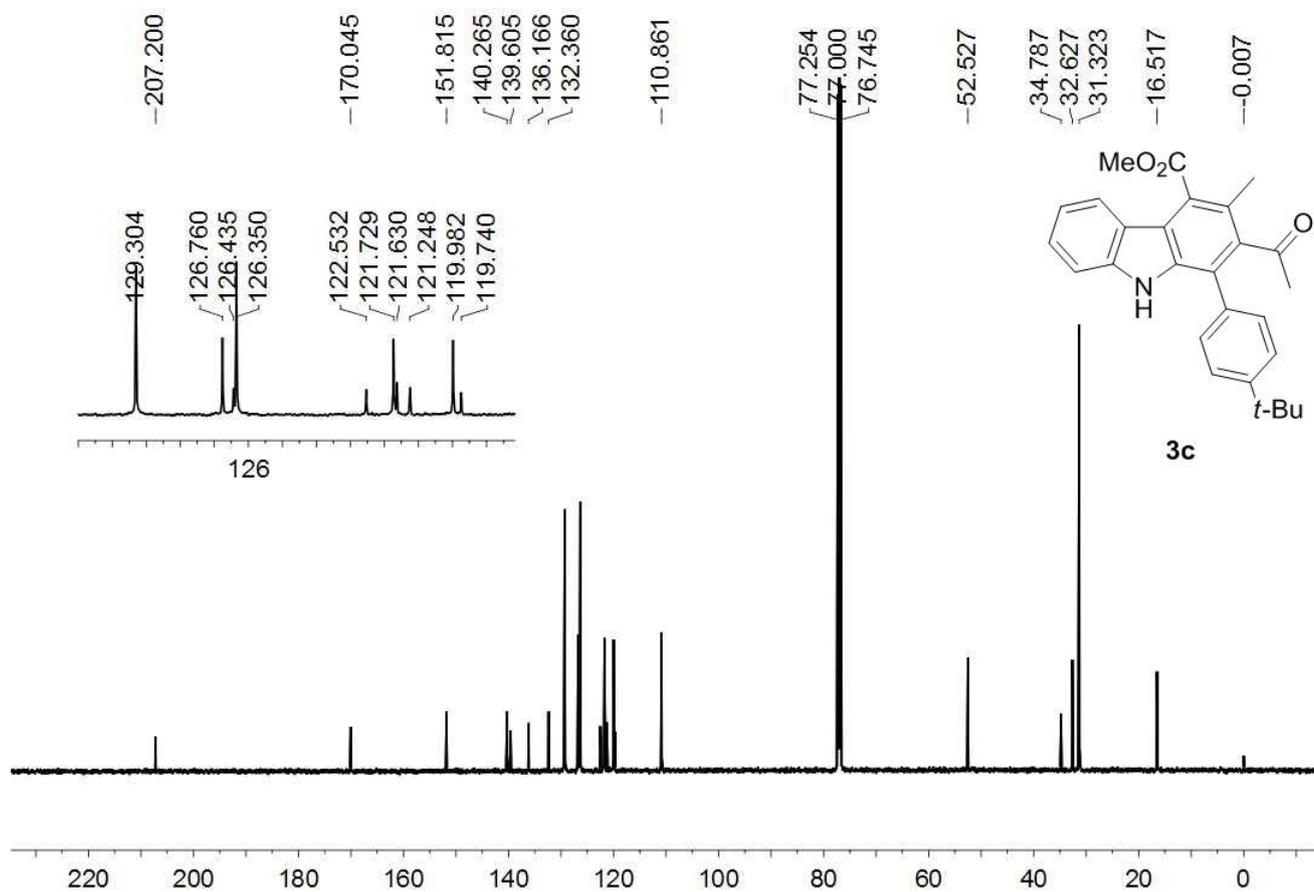
^{13}C NMR spectrum of the compound **3b** (100 MHz, CDCl_3)



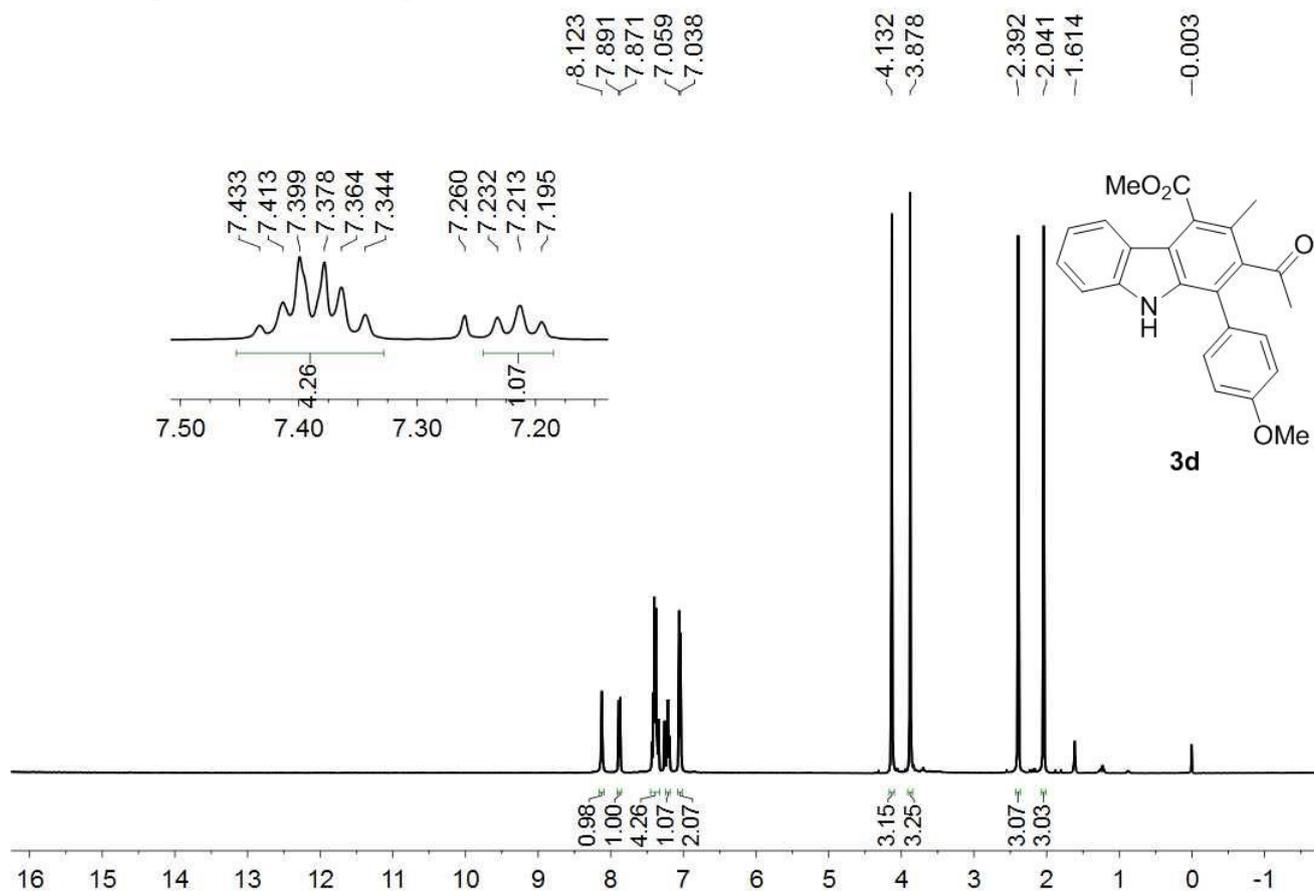
^1H NMR spectrum of the compound **3c** (400 MHz, CDCl_3)



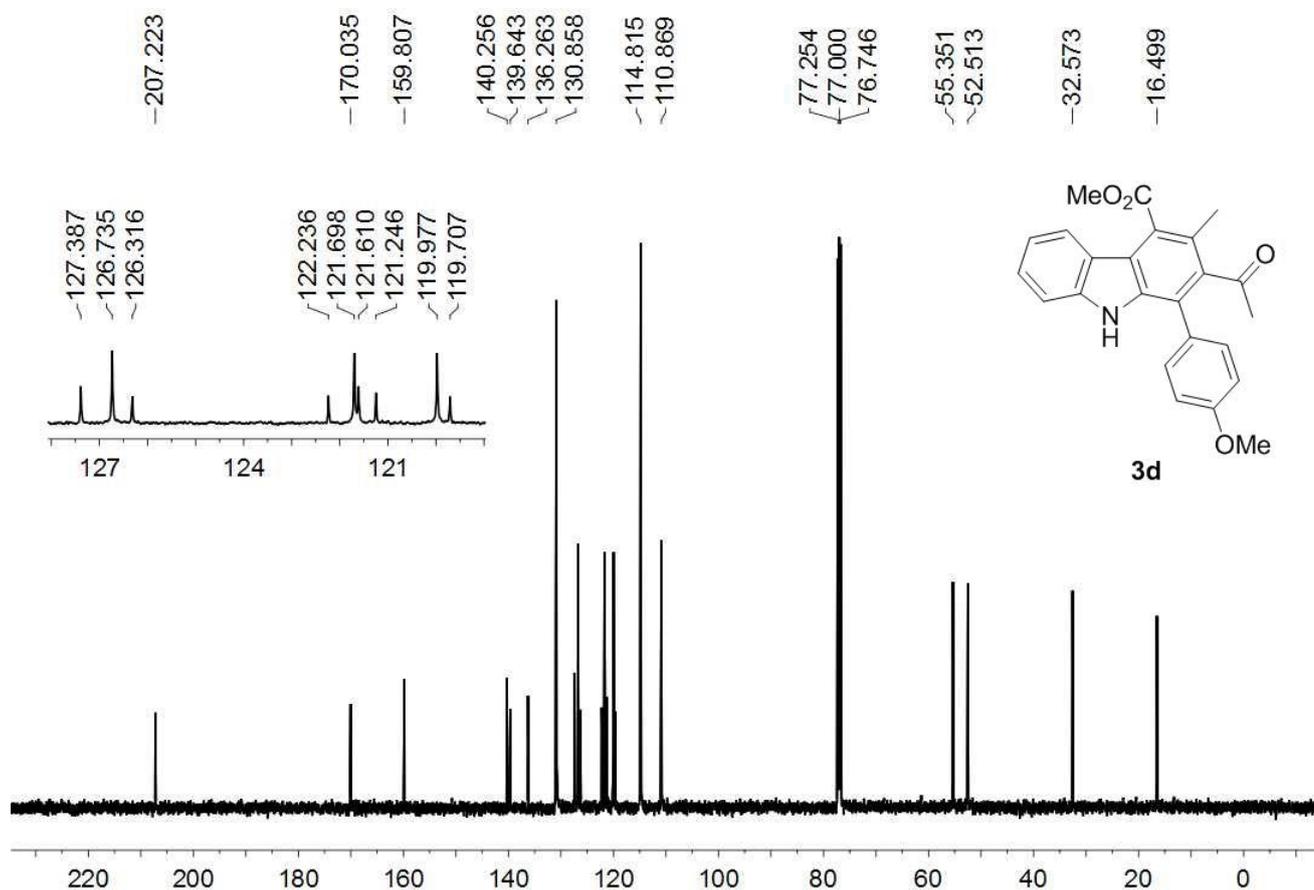
^{13}C NMR spectrum of the compound **3c** (100 MHz, CDCl_3)



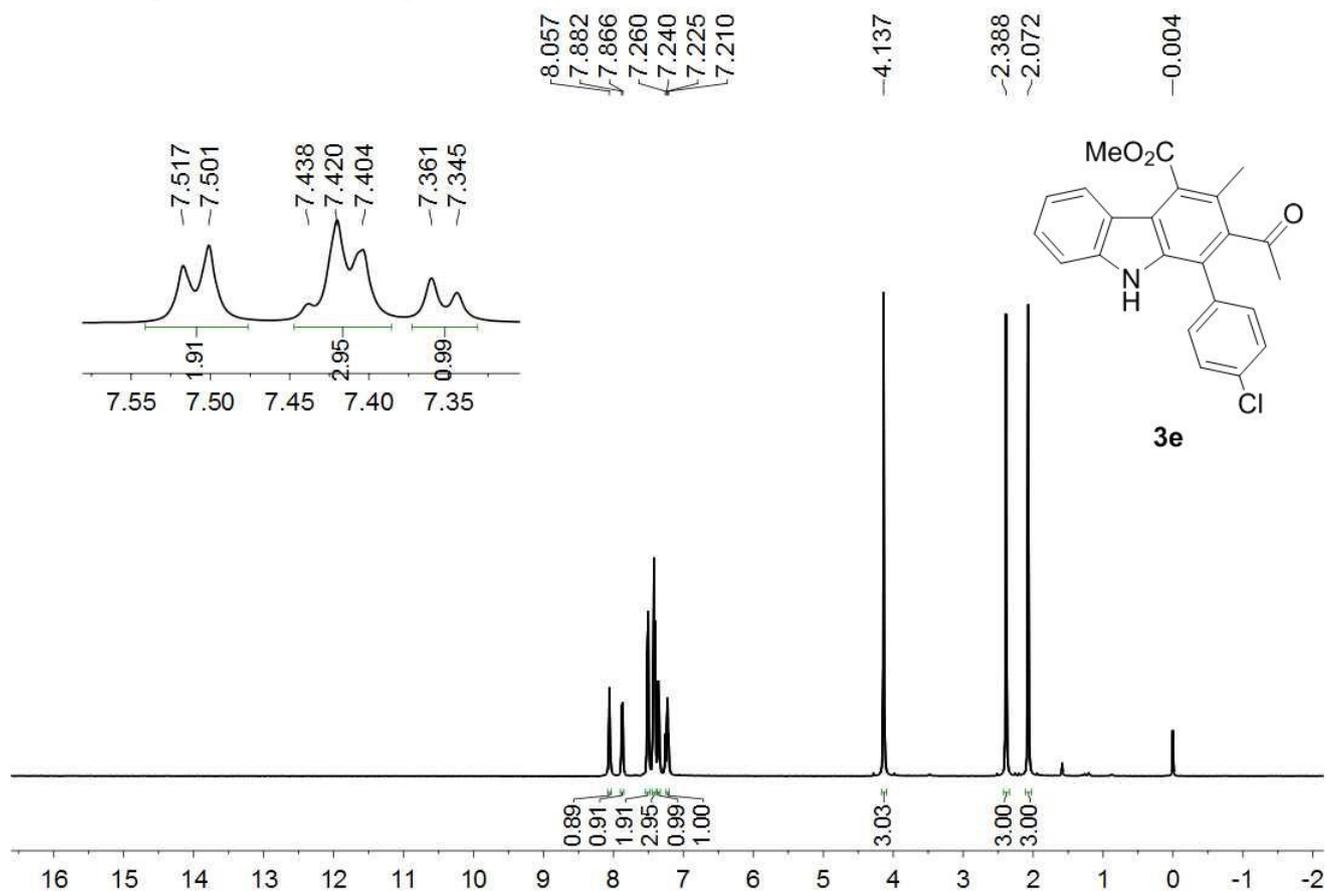
^1H NMR spectrum of the compound **3d** (400 MHz, CDCl_3)



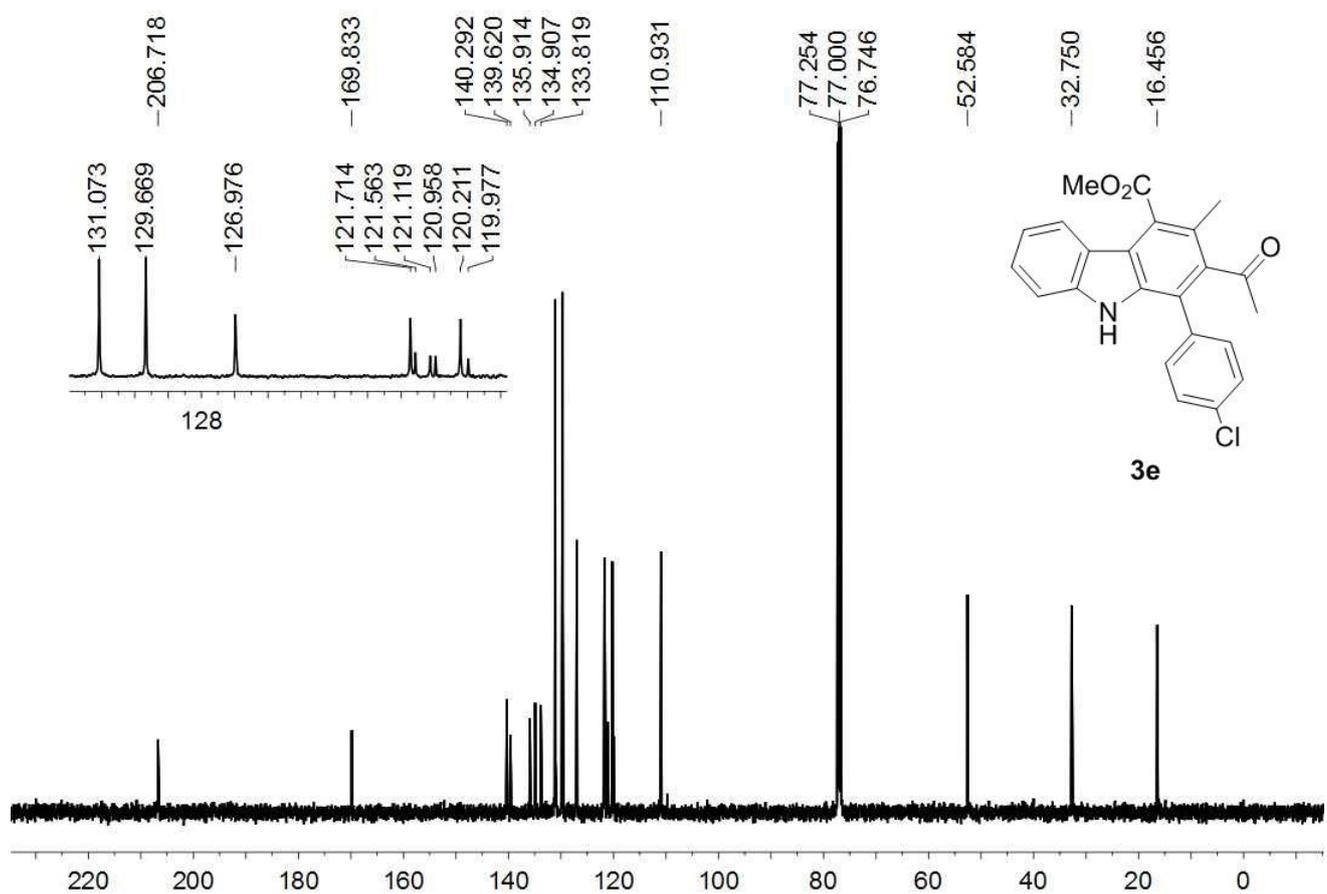
^{13}C NMR spectrum of the compound **3d** (125 MHz, CDCl_3)



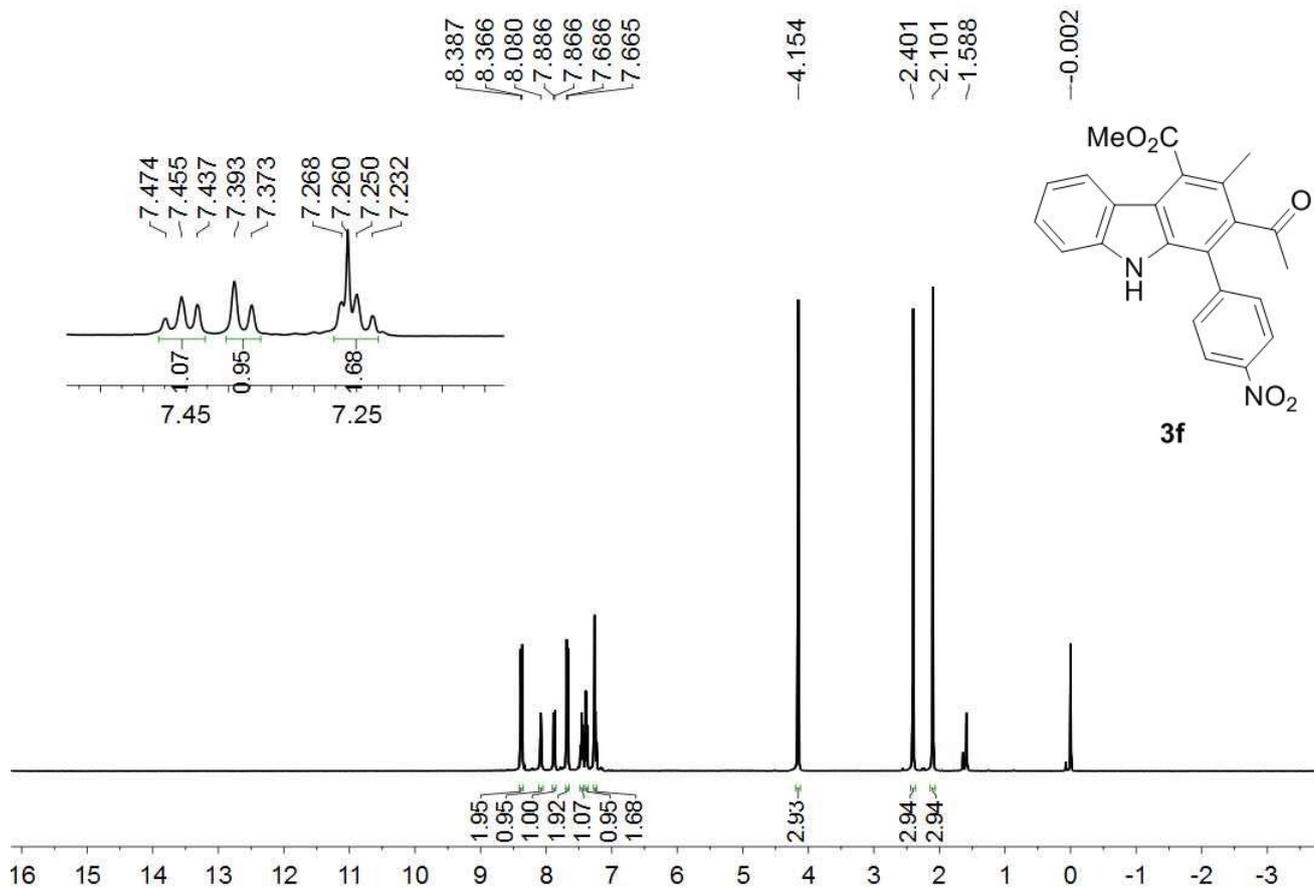
^1H NMR spectrum of the compound **3e** (500 MHz, CDCl_3)



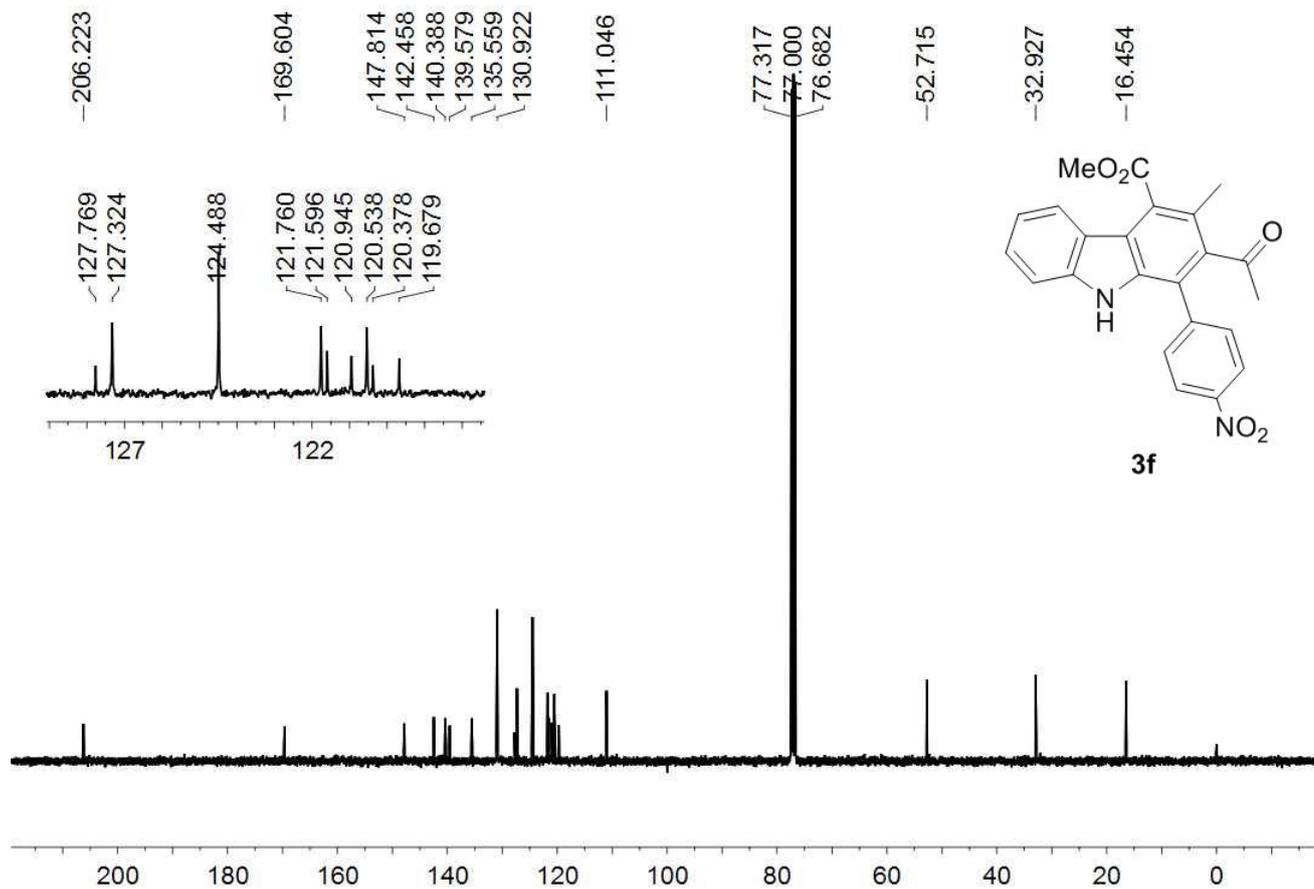
^{13}C NMR spectrum of the compound **3e** (125 MHz, CDCl_3)



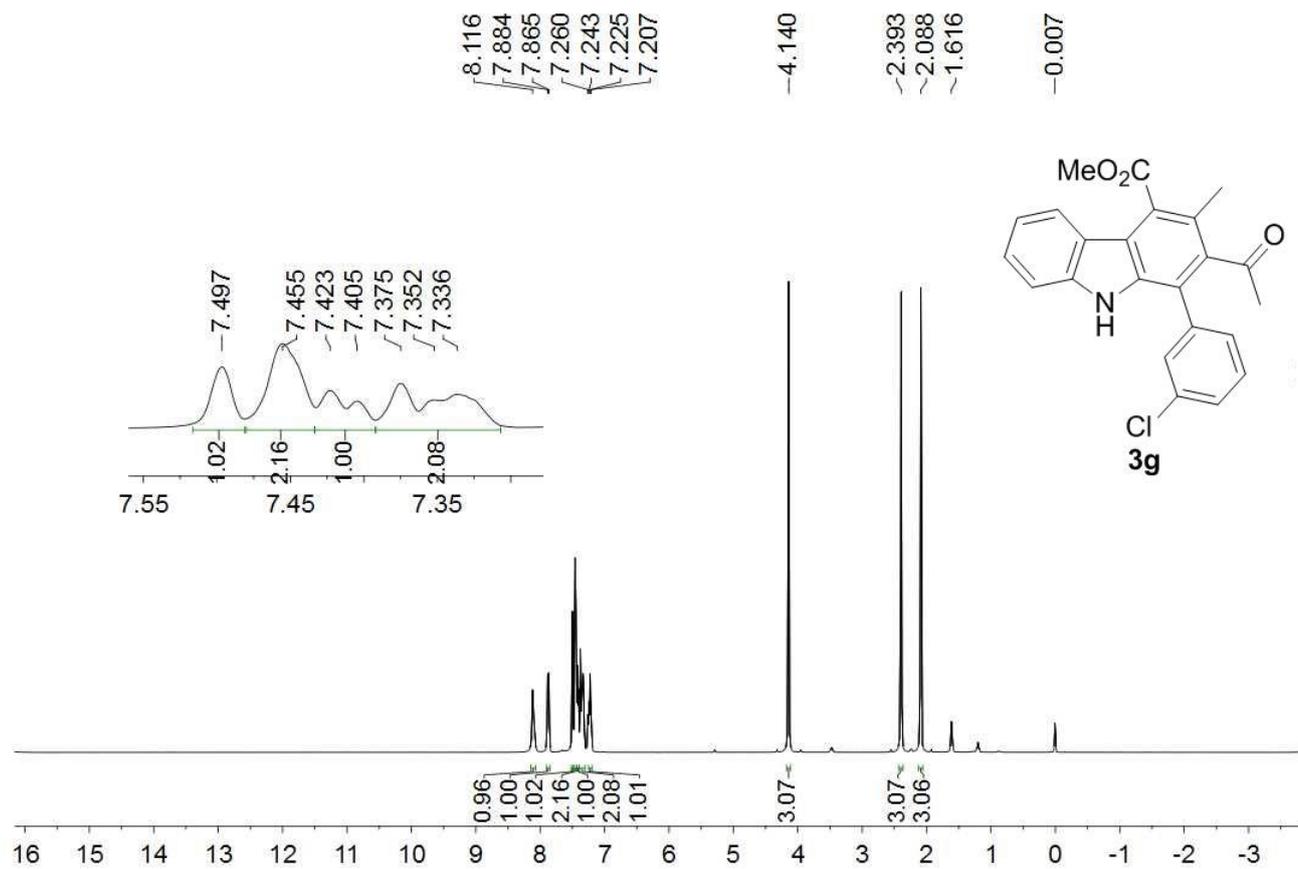
^1H NMR spectrum of the compound **3f** (400 MHz, CDCl_3)



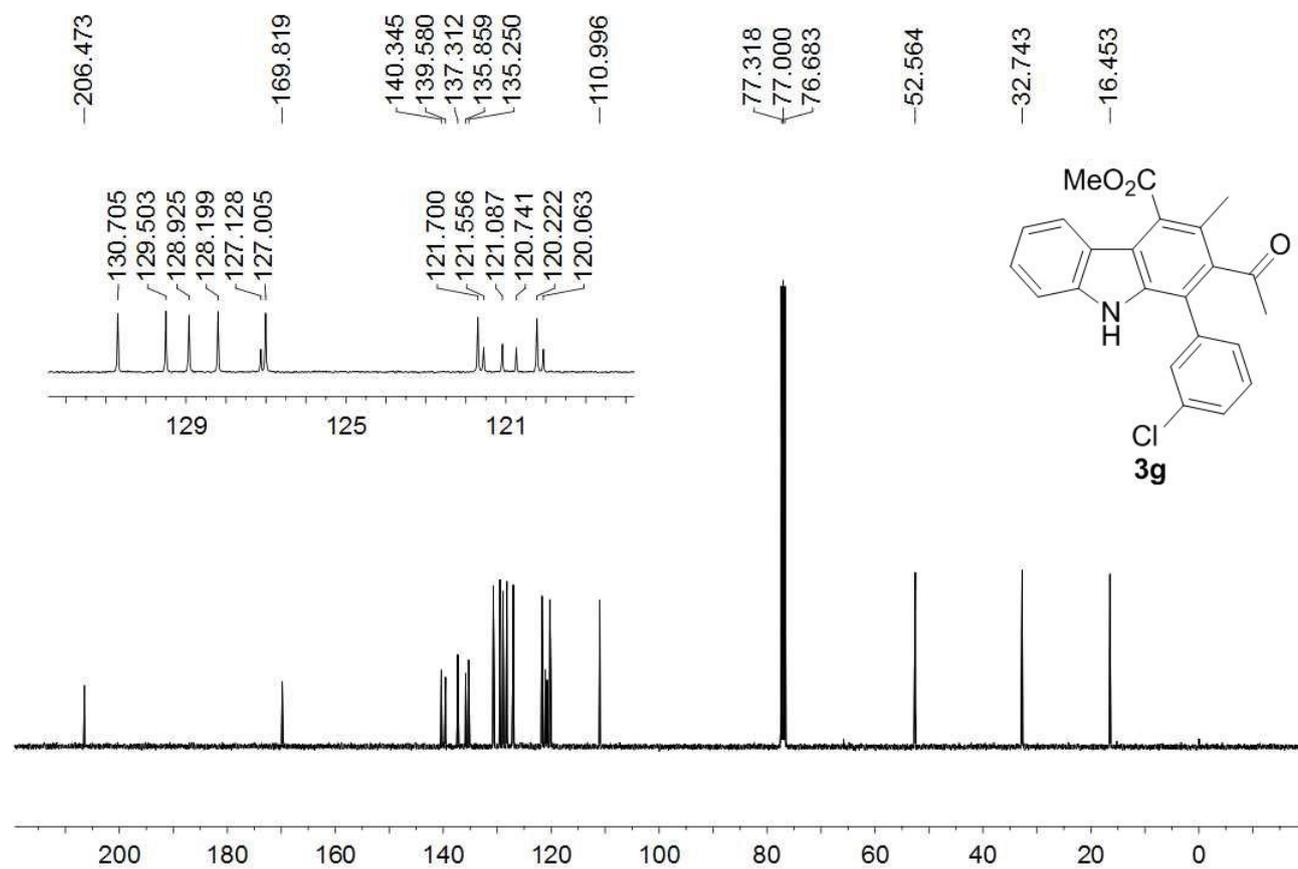
^{13}C NMR spectrum of the compound **3f** (100 MHz, CDCl_3)



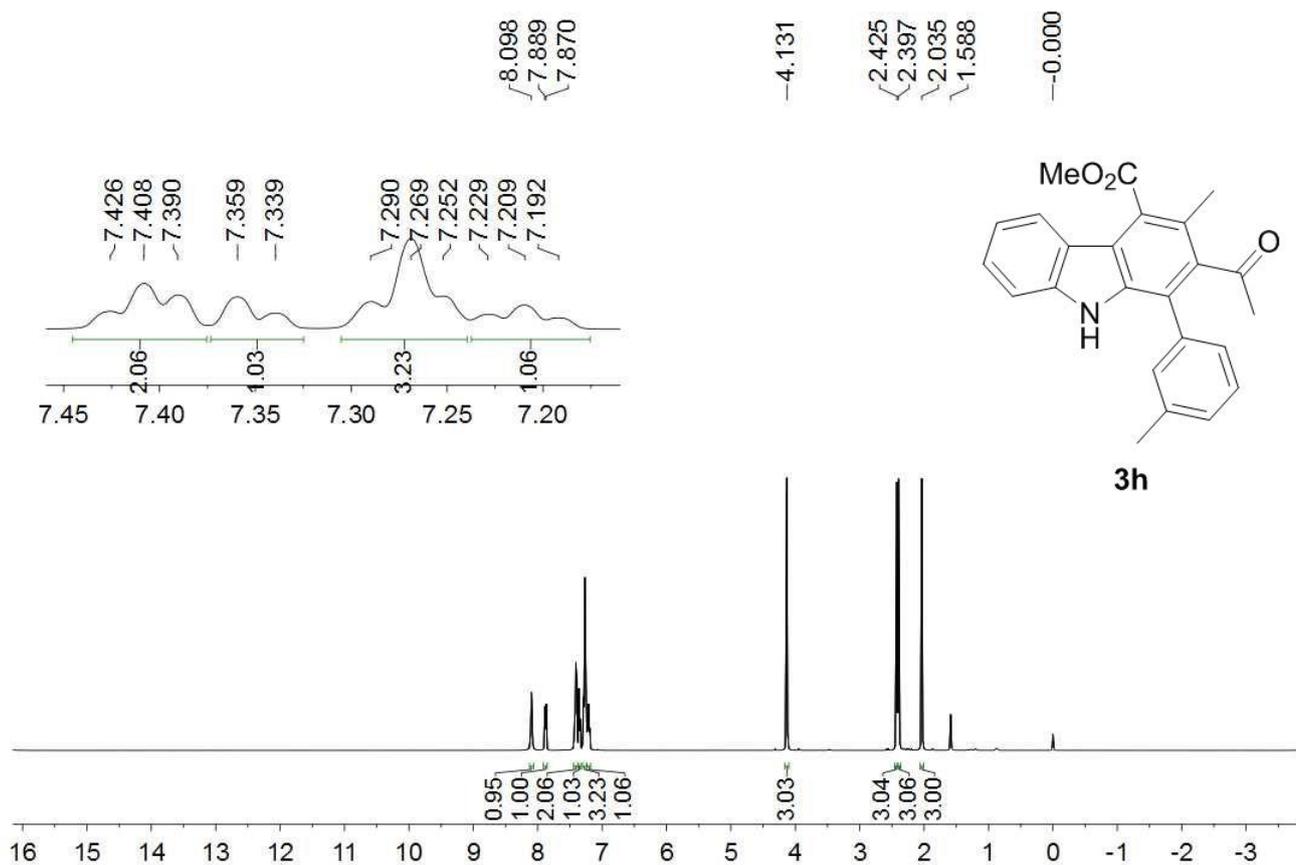
^1H NMR spectrum of the compound **3g** (400 MHz, CDCl_3)



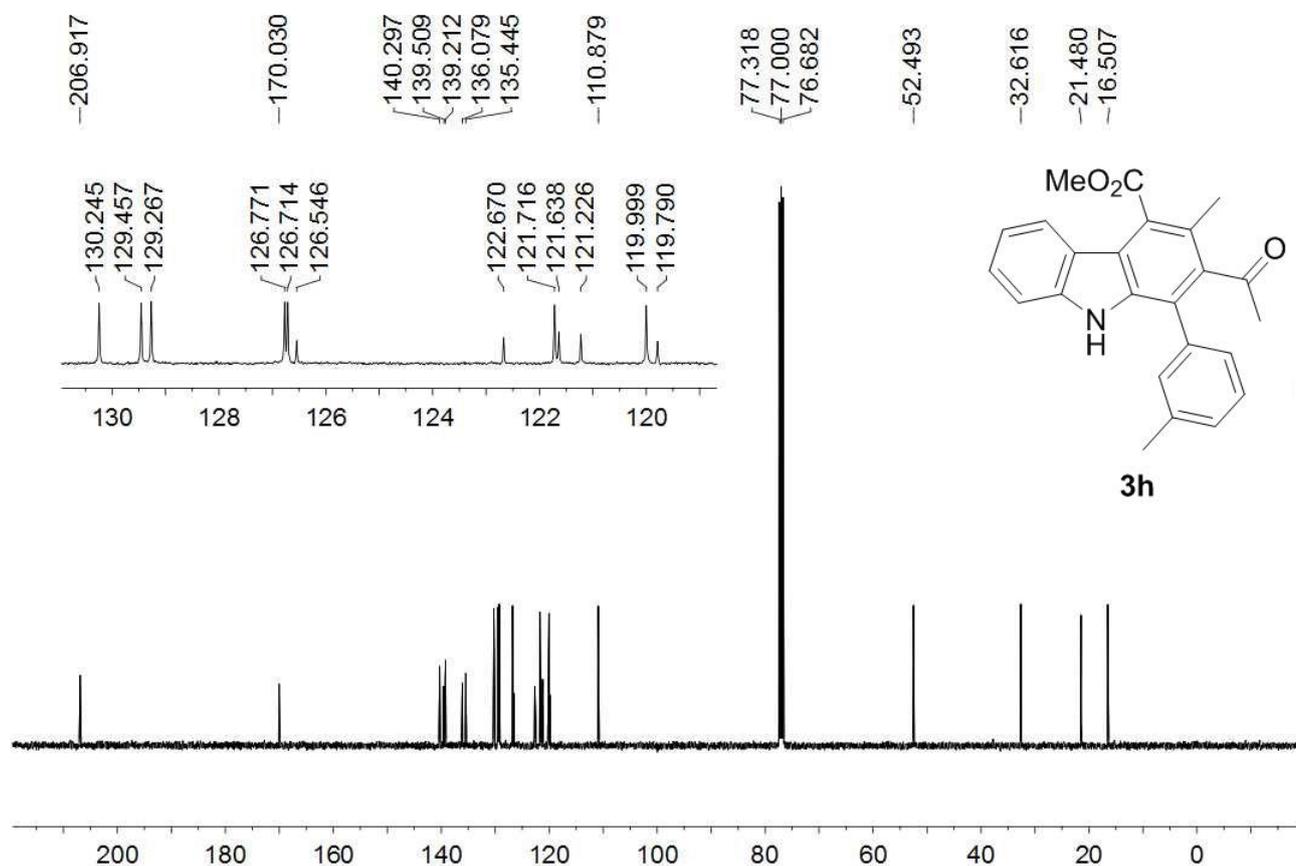
^{13}C NMR spectrum of the compound **3g** (100 MHz, CDCl_3)



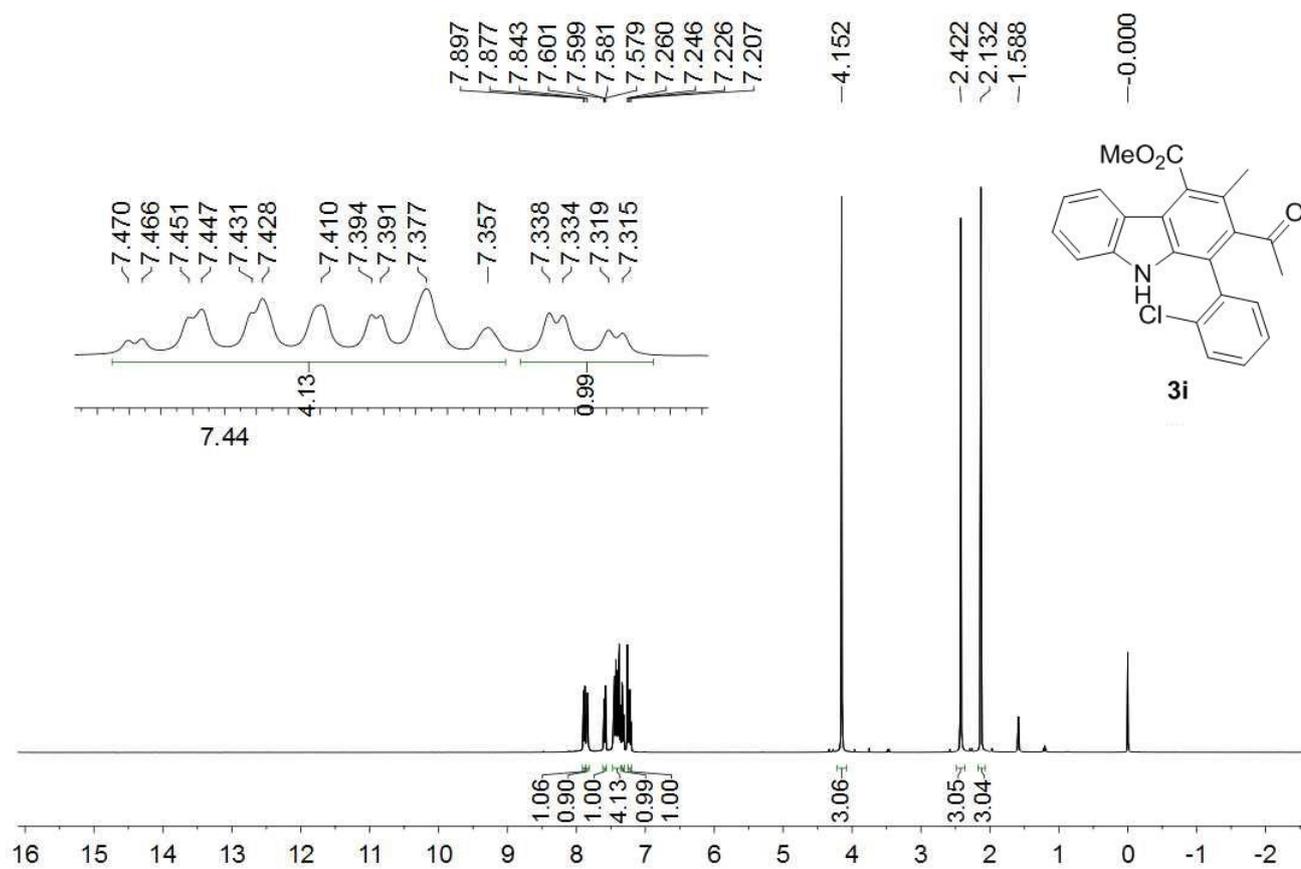
^1H NMR spectrum of the compound **3h** (400 MHz, CDCl_3)



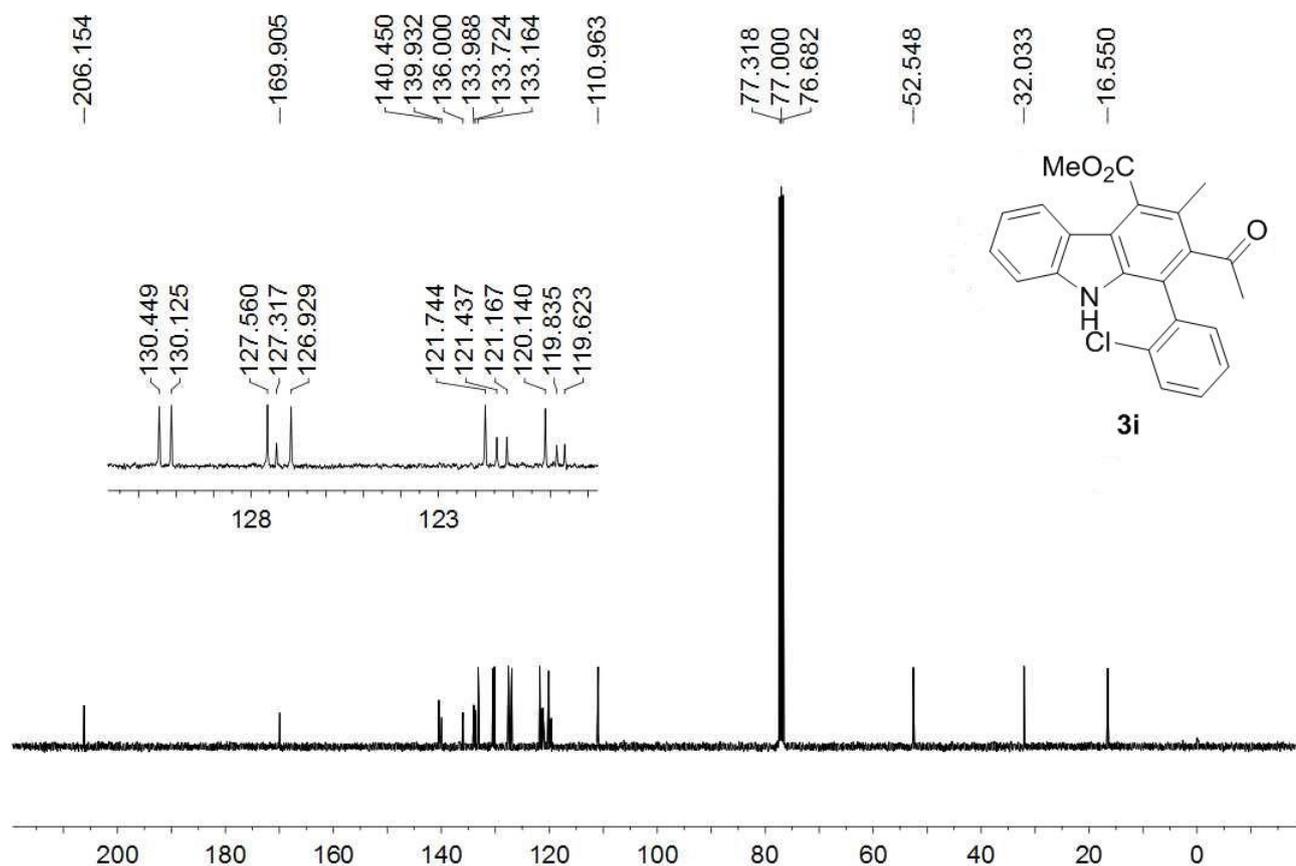
^{13}C NMR spectrum of the compound **3h** (100 MHz, CDCl_3)



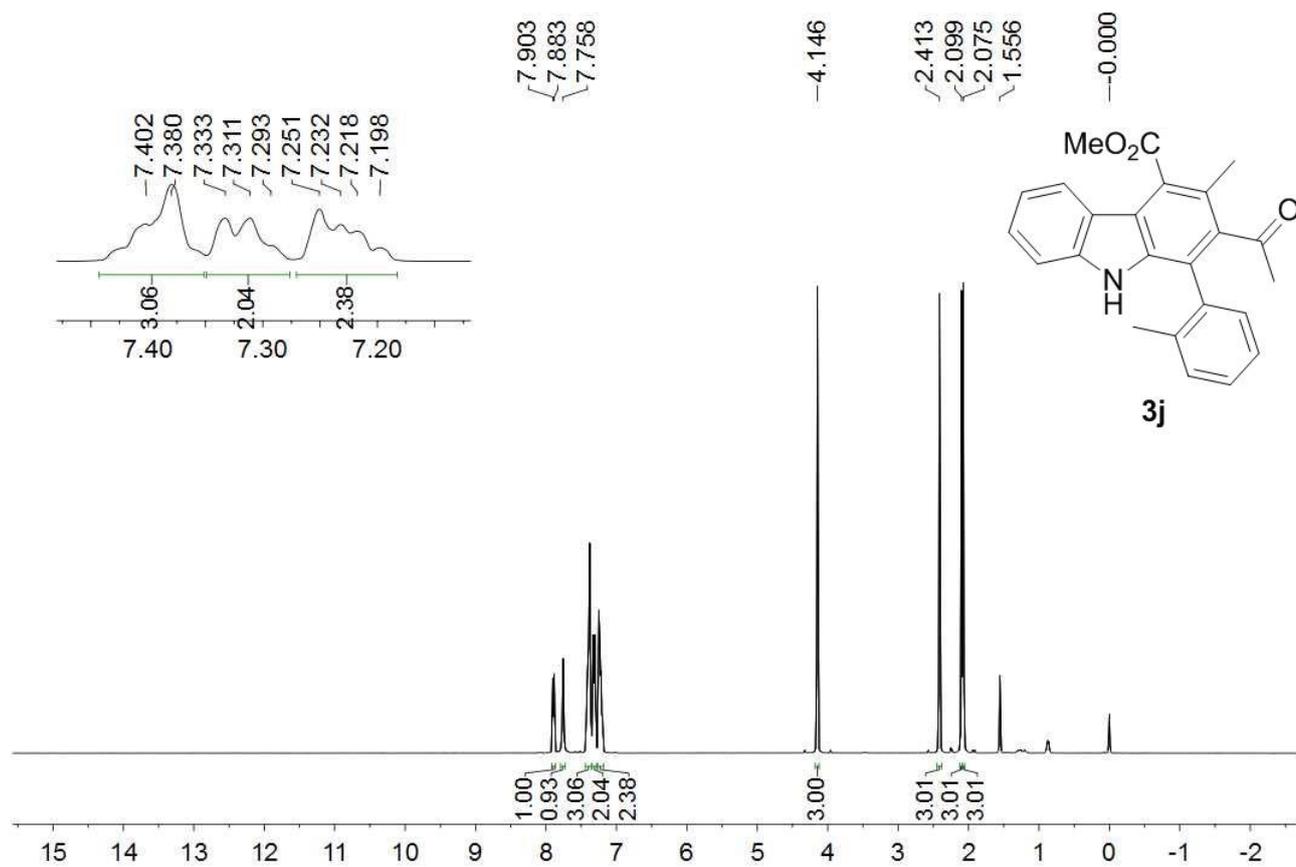
^1H NMR spectrum of the compound **3i** (400 MHz, CDCl_3)



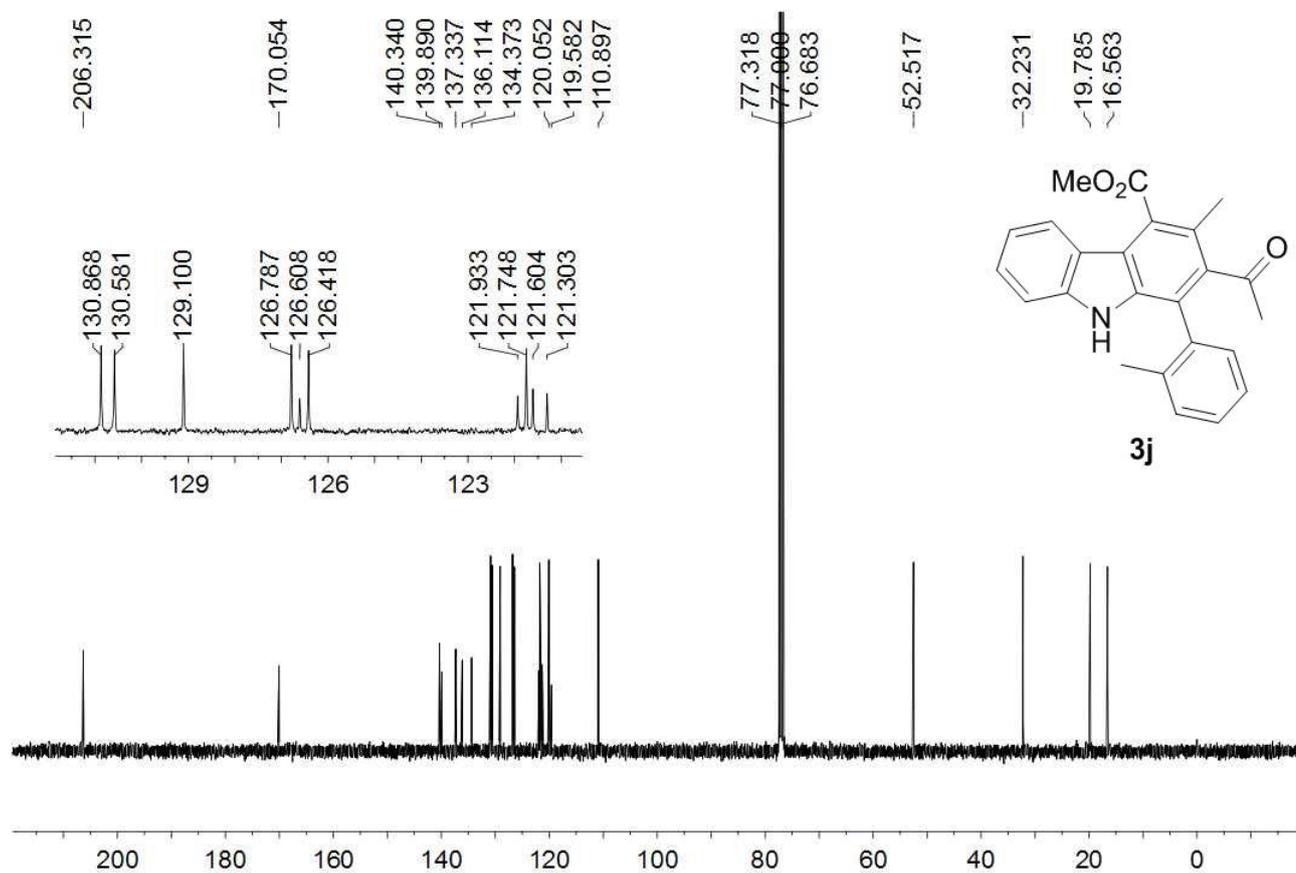
^{13}C NMR spectrum of the compound **3i** (100 MHz, CDCl_3)



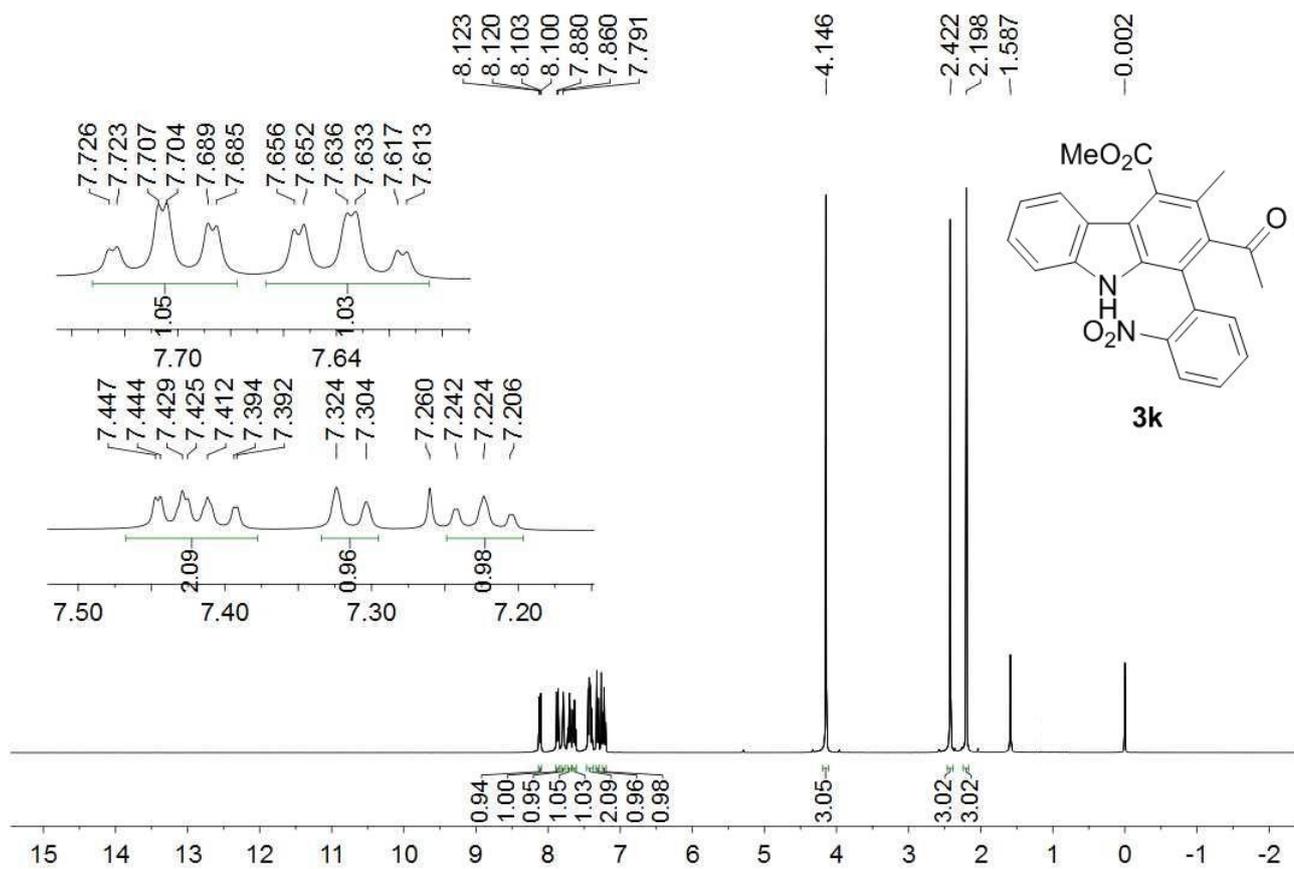
^1H NMR spectrum of the compound **3j** (400 MHz, CDCl_3)



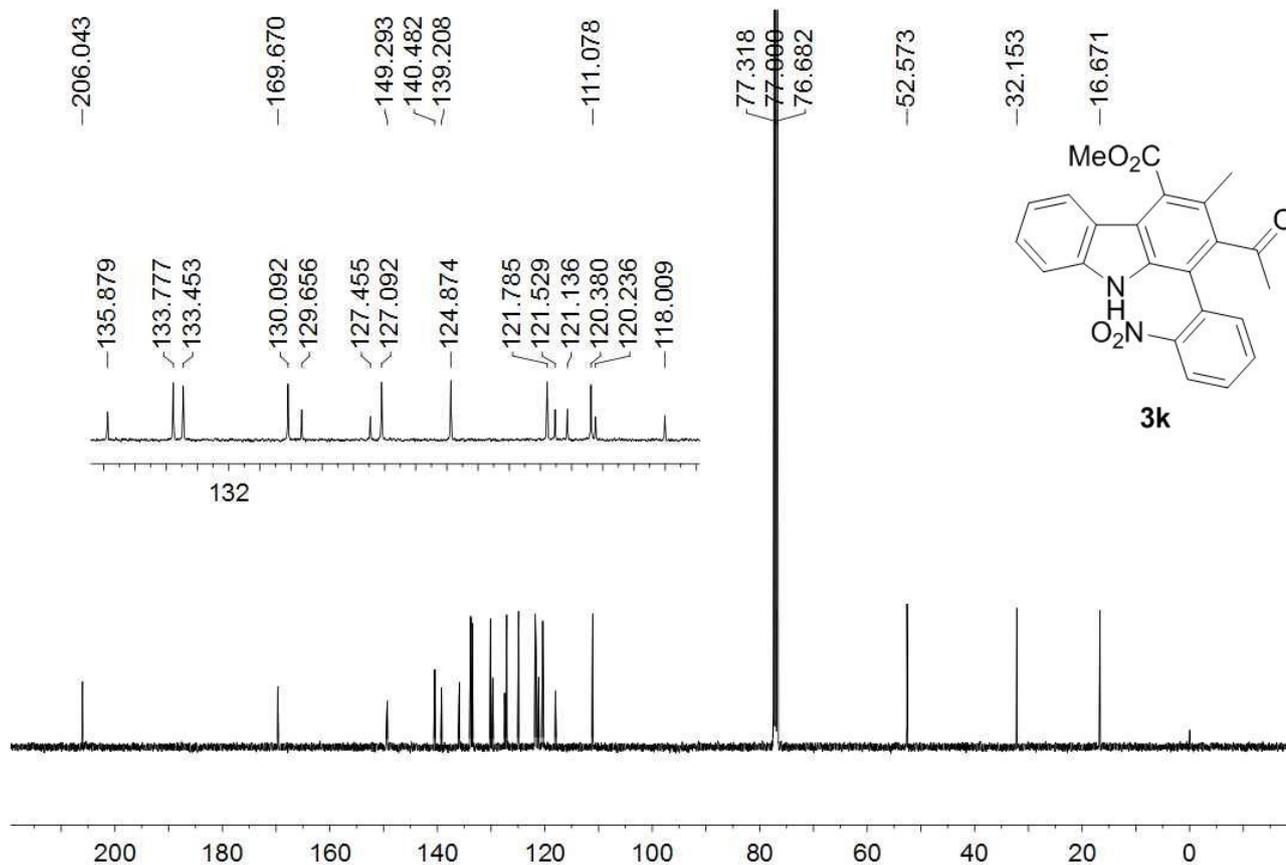
^{13}C NMR spectrum of the compound **3j** (100 MHz, CDCl_3)



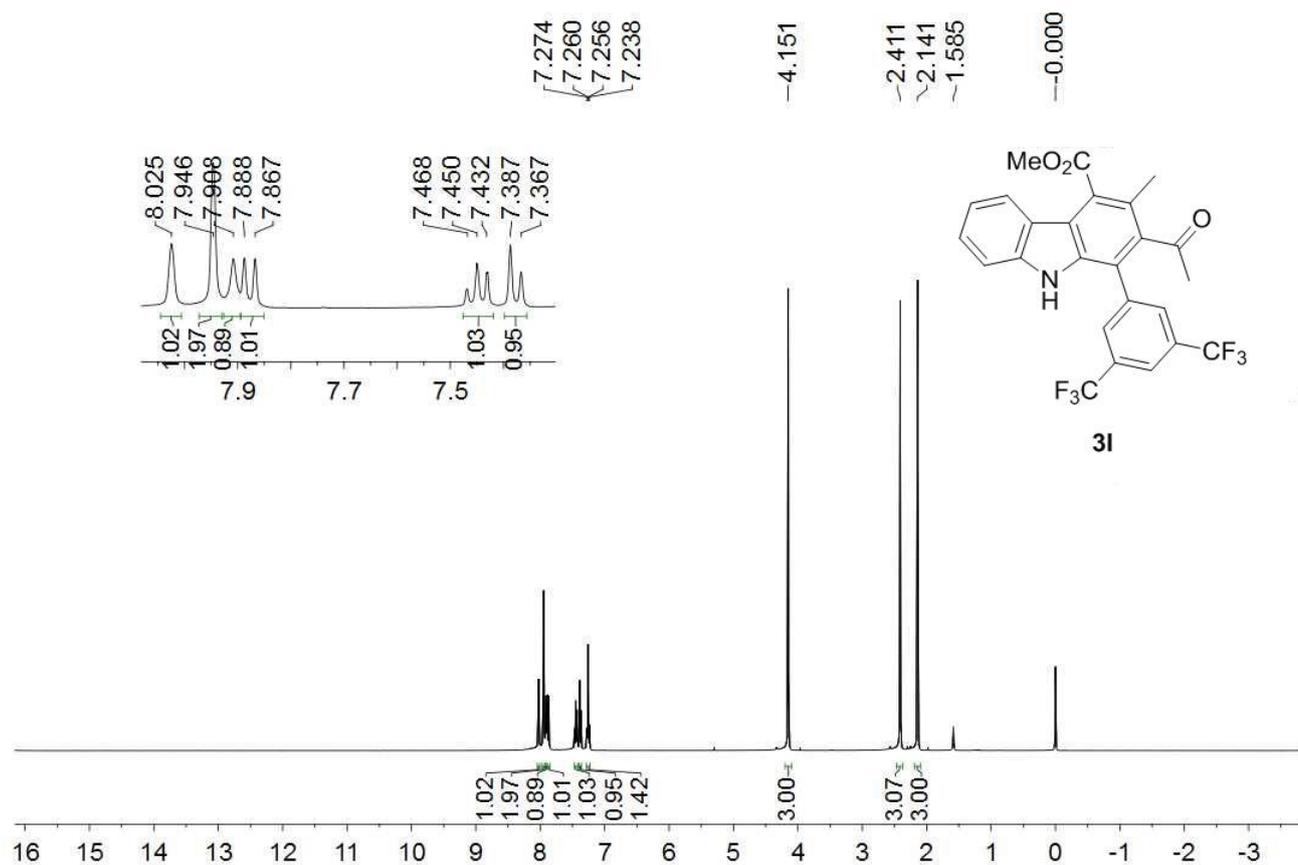
^1H NMR spectrum of the compound **3k** (400 MHz, CDCl_3)



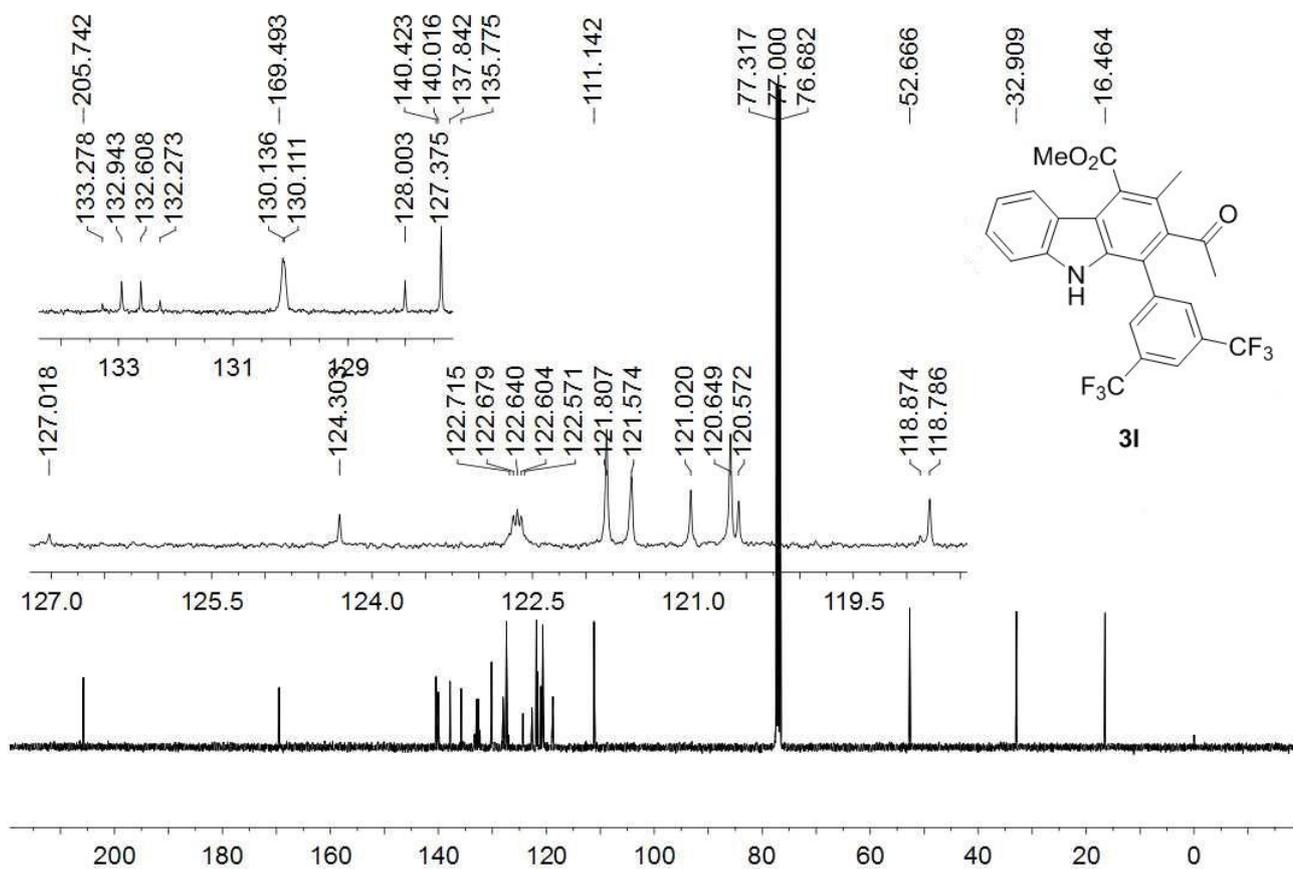
^{13}C NMR spectrum of the compound **3k** (100 MHz, CDCl_3)



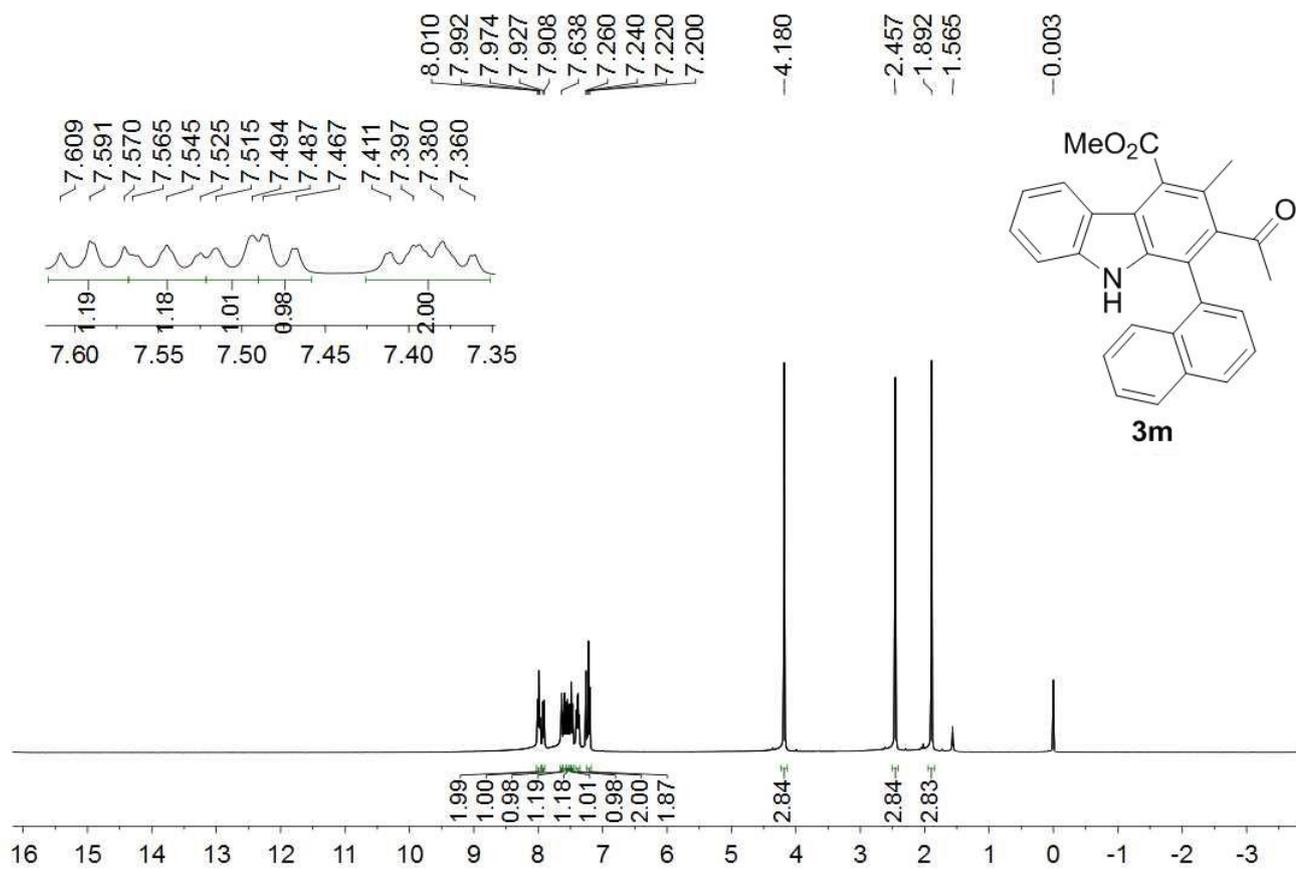
¹H NMR spectrum of the compound **3I** (400 MHz, CDCl₃)



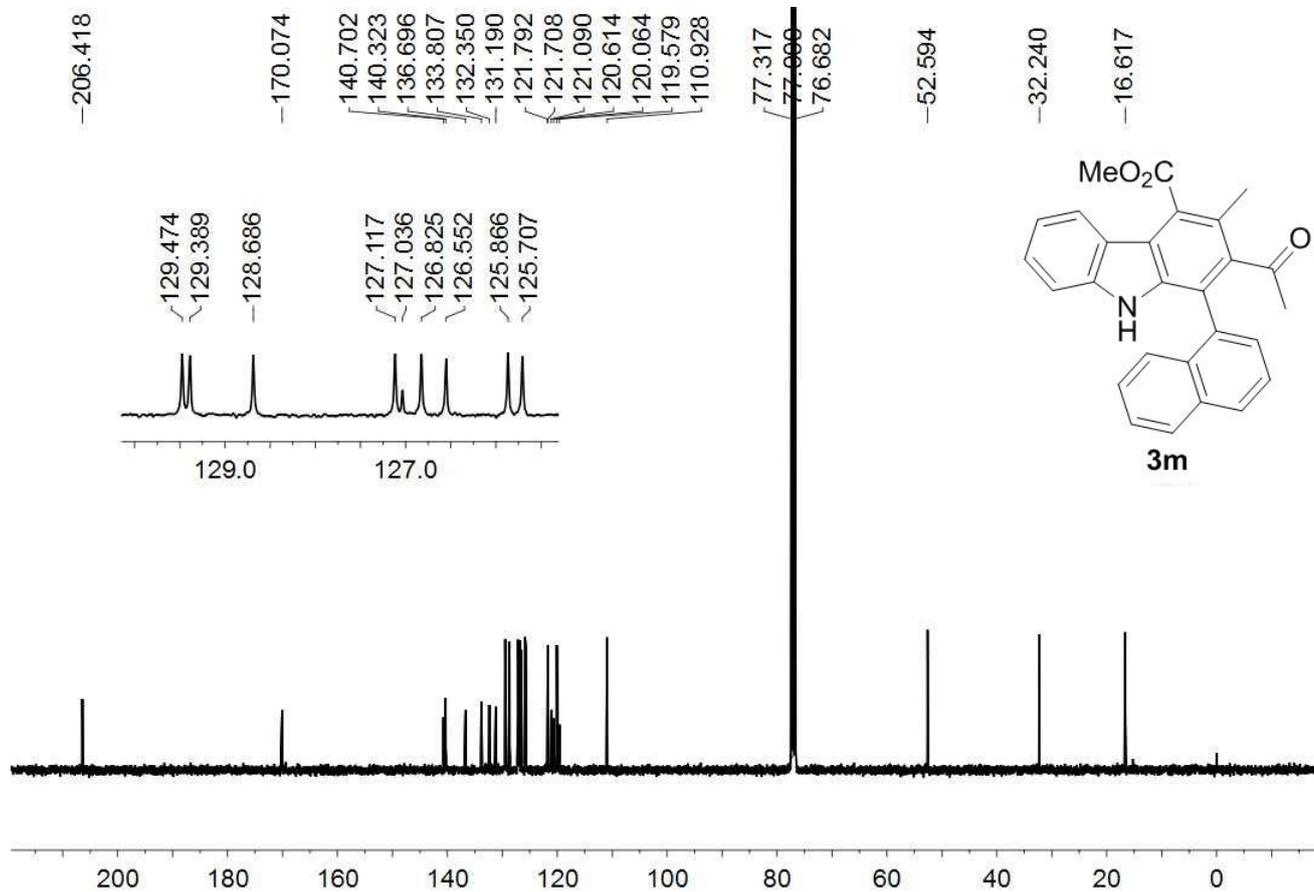
¹³C NMR spectrum of the compound **3I** (100 MHz, CDCl₃)



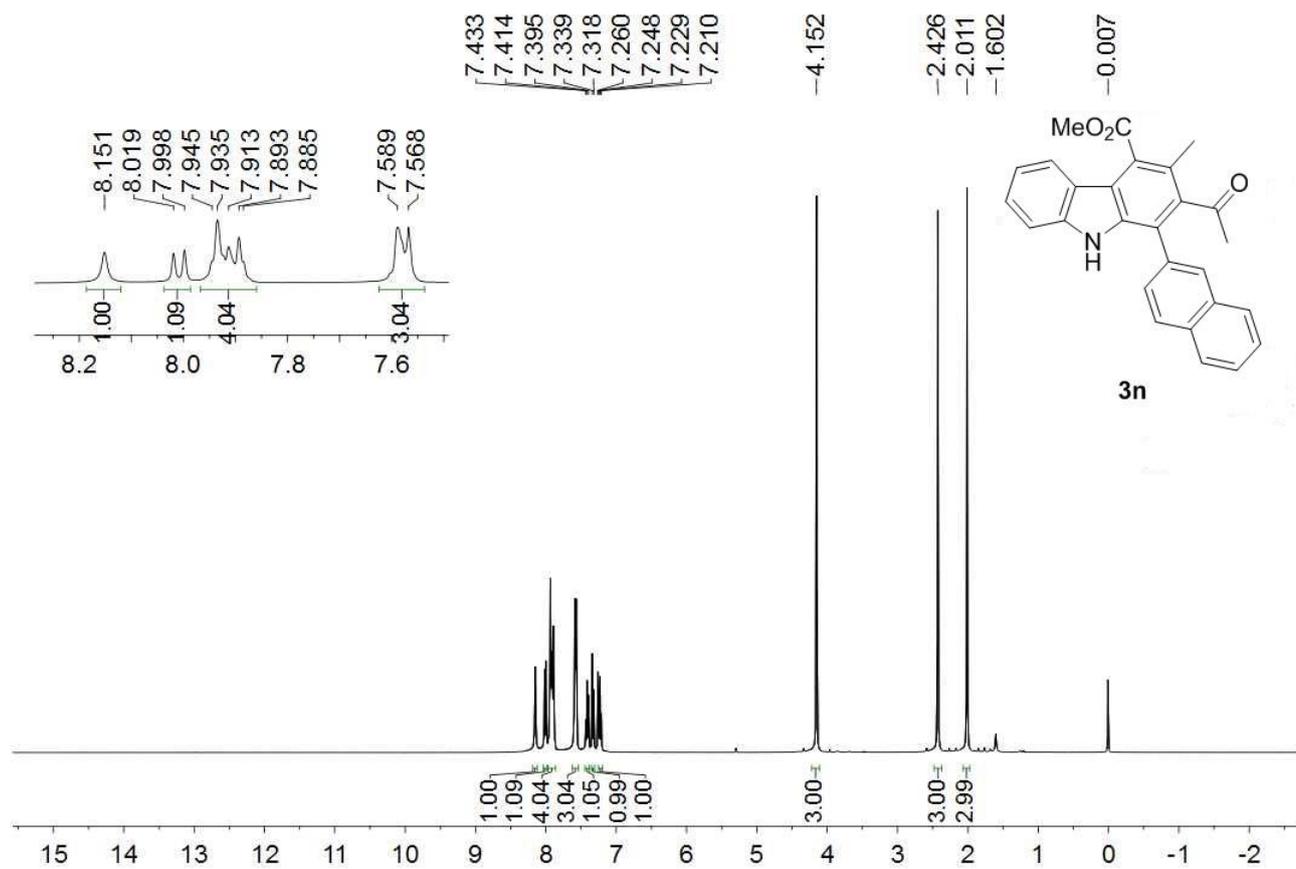
^1H NMR spectrum of the compound **3m** (400 MHz, CDCl_3)



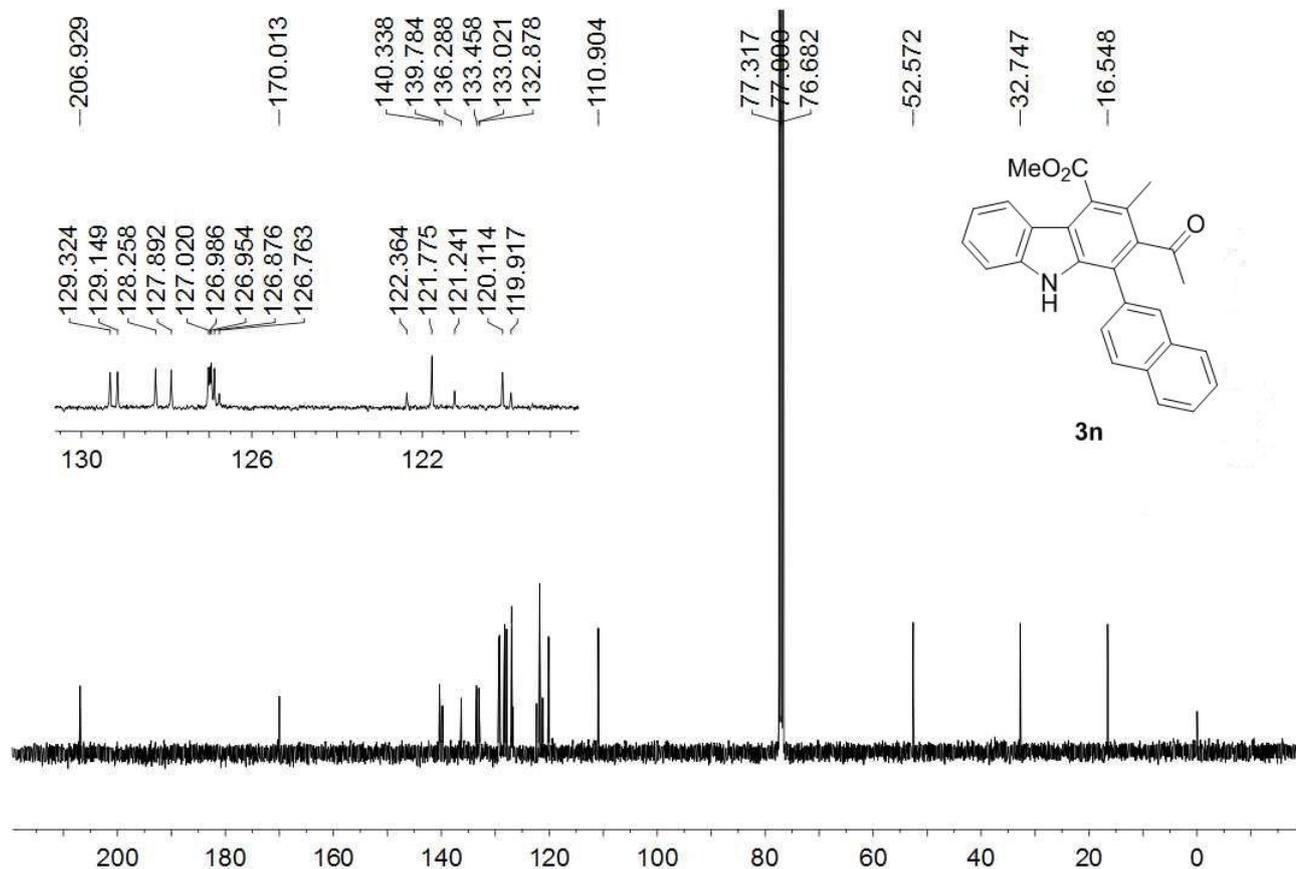
^{13}C NMR spectrum of the compound **3m** (100 MHz, CDCl_3)



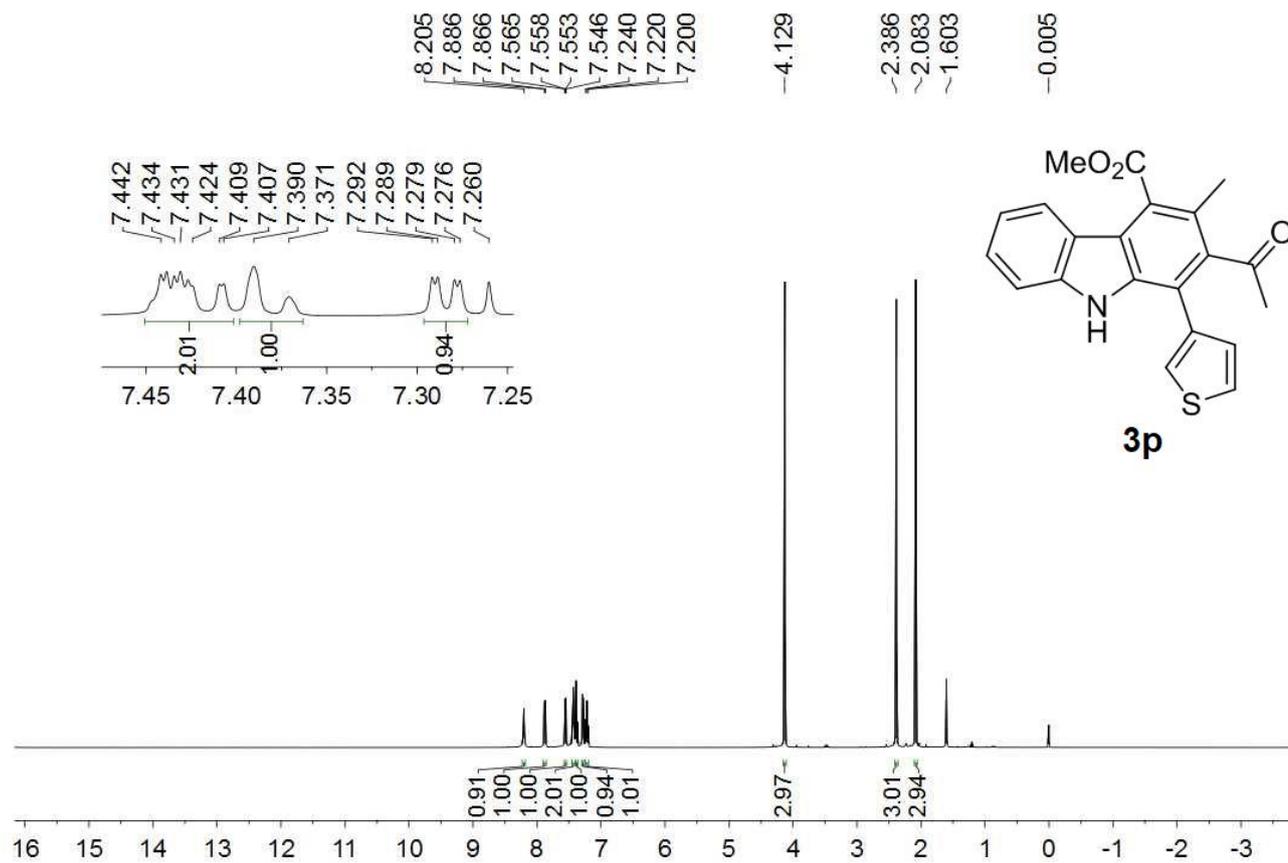
¹H NMR spectrum of the compound **3n** (400 MHz, CDCl₃)



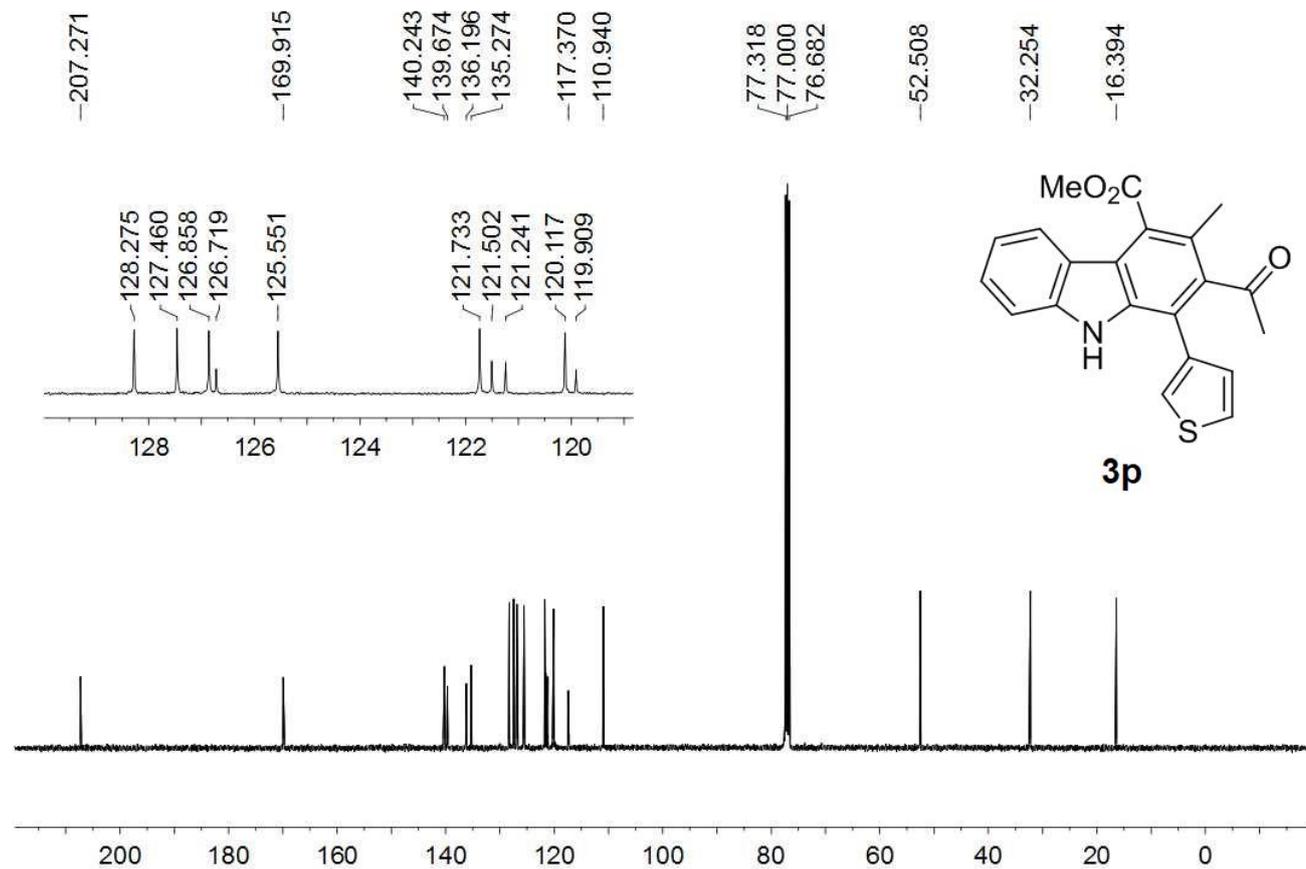
¹³C NMR spectrum of the compound **3n** (100 MHz, CDCl₃)



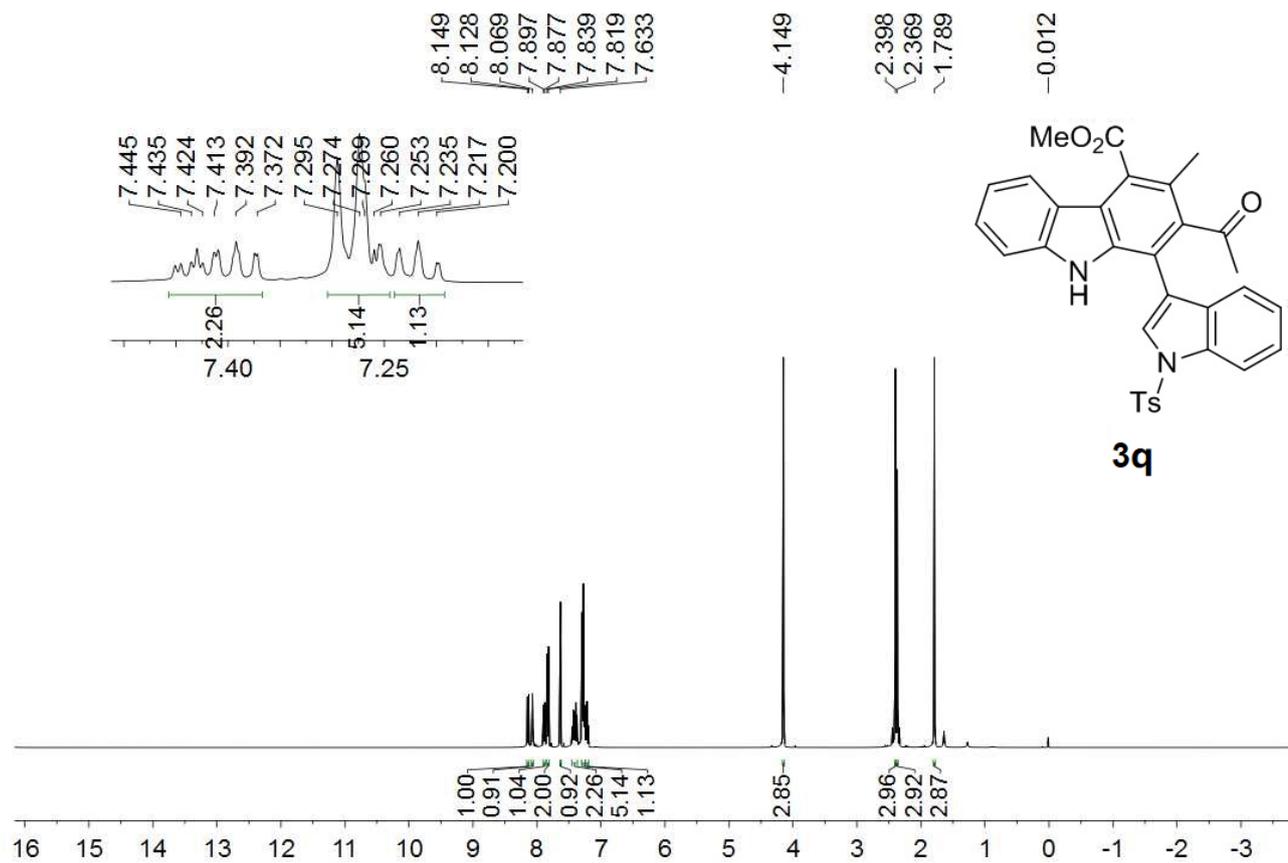
^1H NMR spectrum of the compound **3p** (400 MHz, CDCl_3)



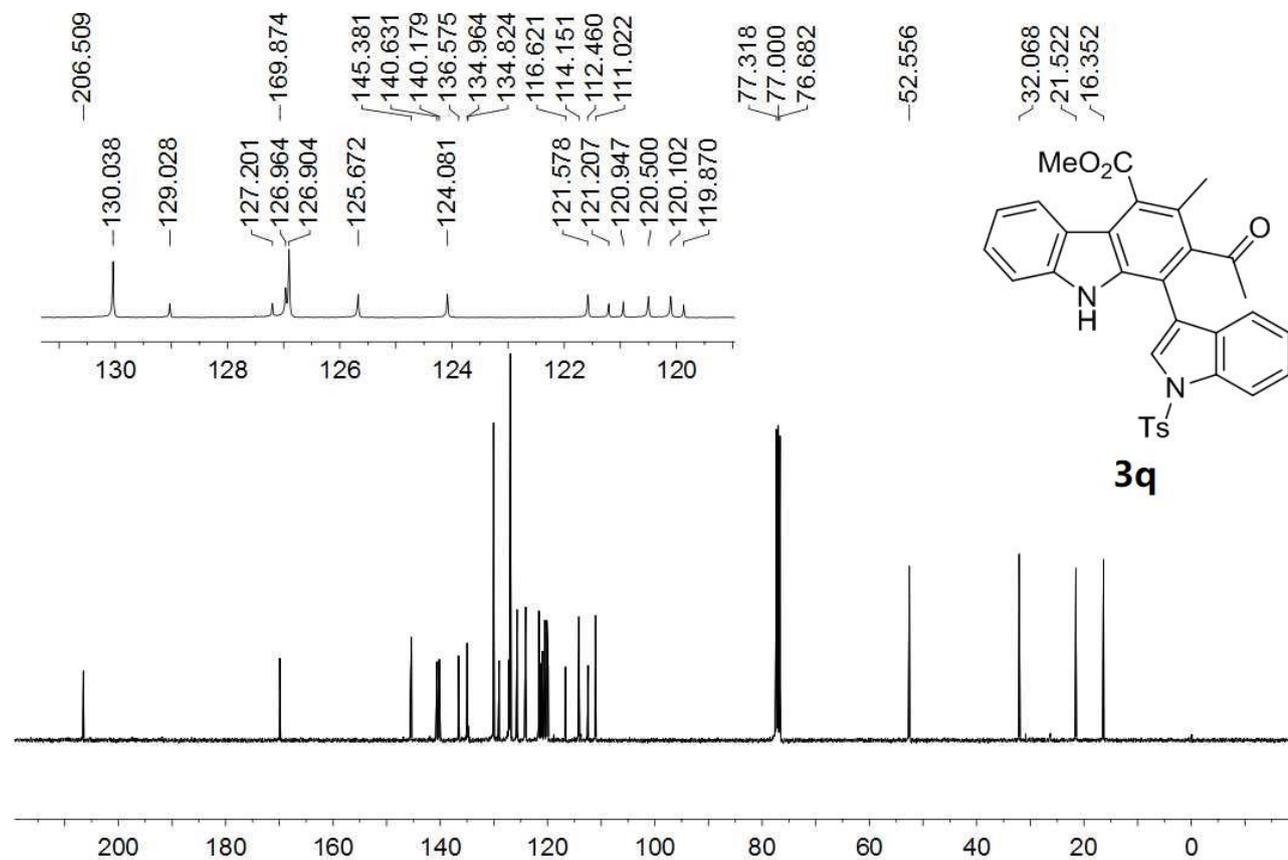
^{13}C NMR spectrum of the compound **3p** (100 MHz, CDCl_3)



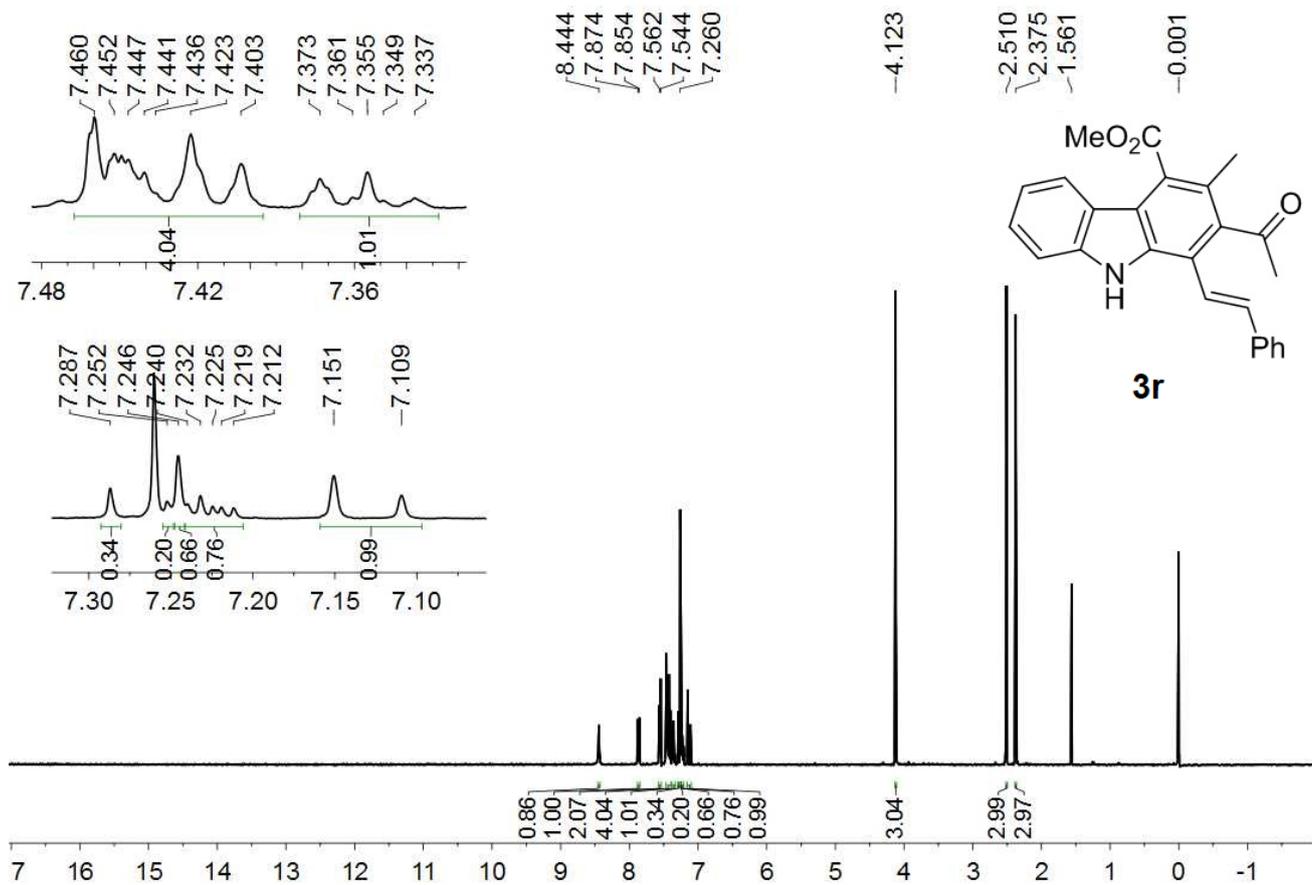
^1H NMR spectrum of the compound **3q** (400 MHz, CDCl_3)



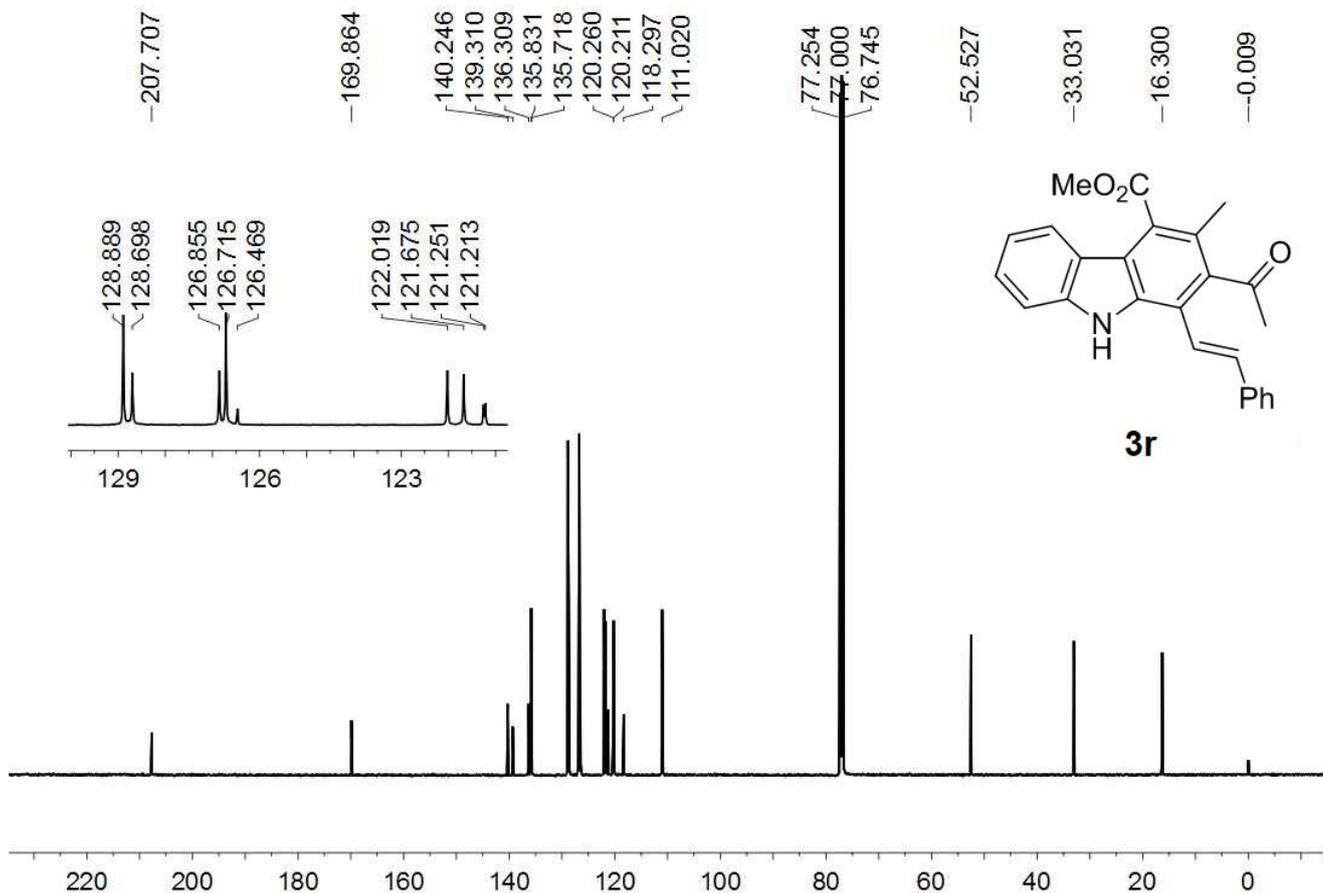
^{13}C NMR spectrum of the compound **3q** (100 MHz, CDCl_3)



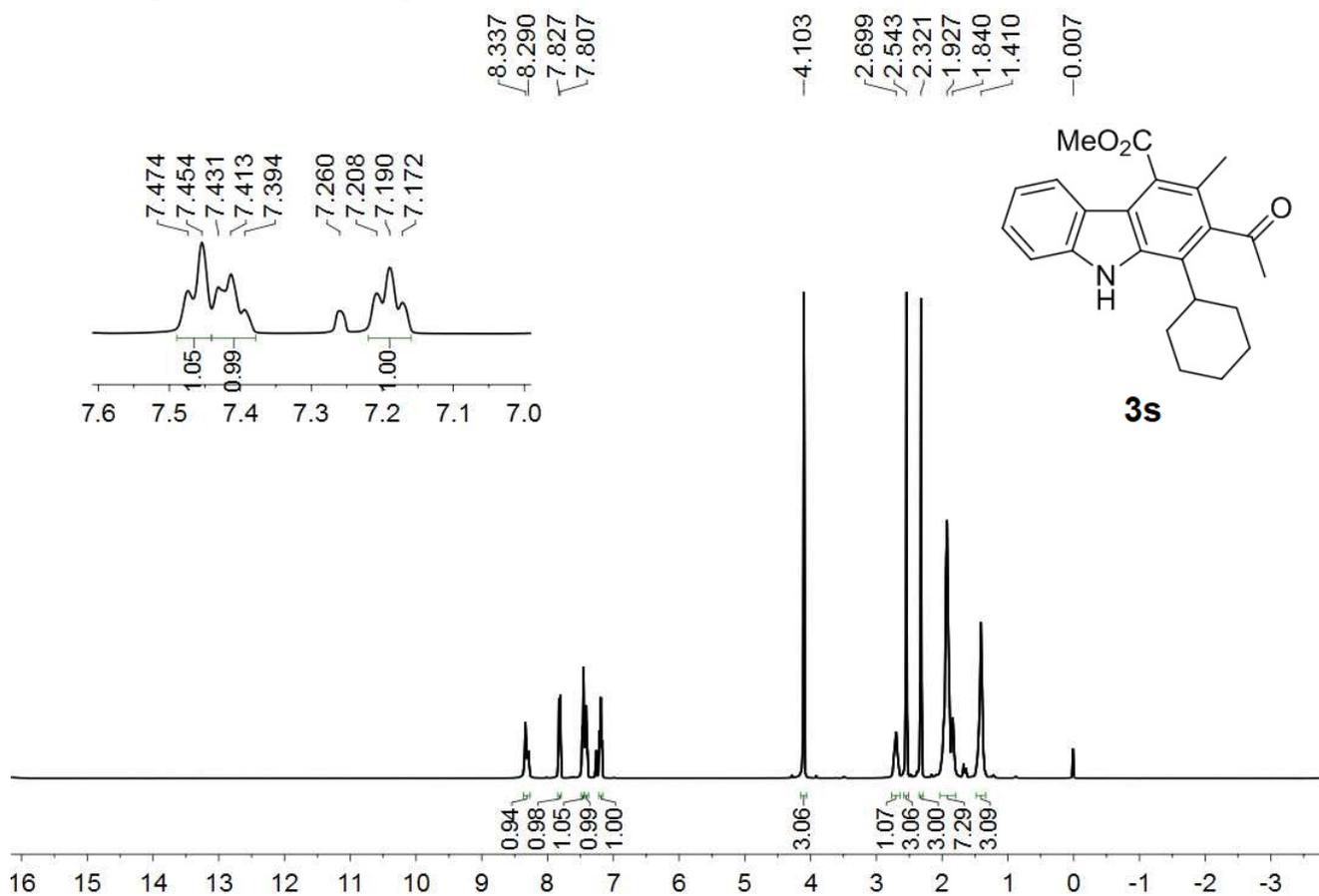
^1H NMR spectrum of the compound **3r** (400 MHz, CDCl_3)



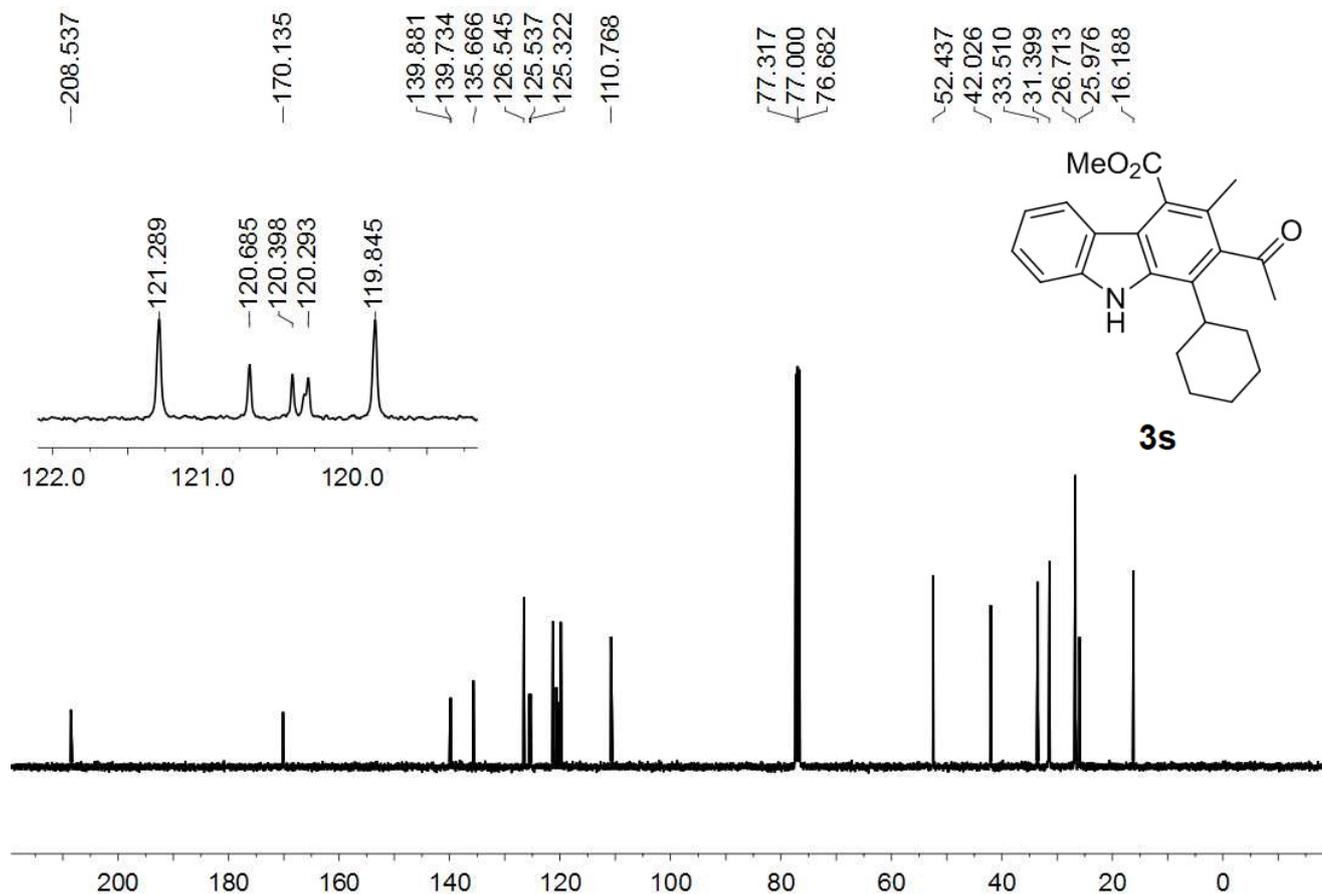
^{13}C NMR spectrum of the compound **3r** (100 MHz, CDCl_3)



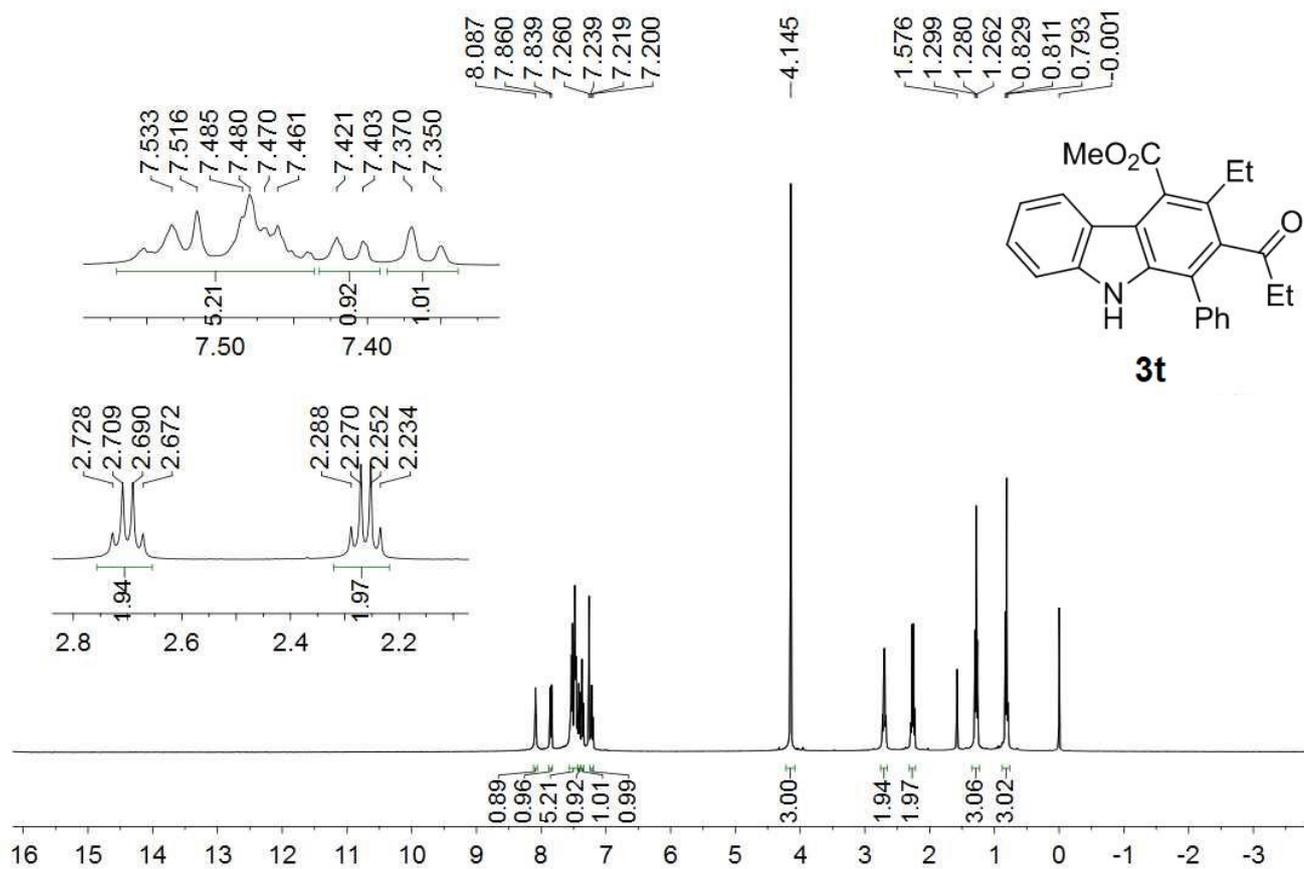
^1H NMR spectrum of the compound **3s** (400 MHz, CDCl_3)



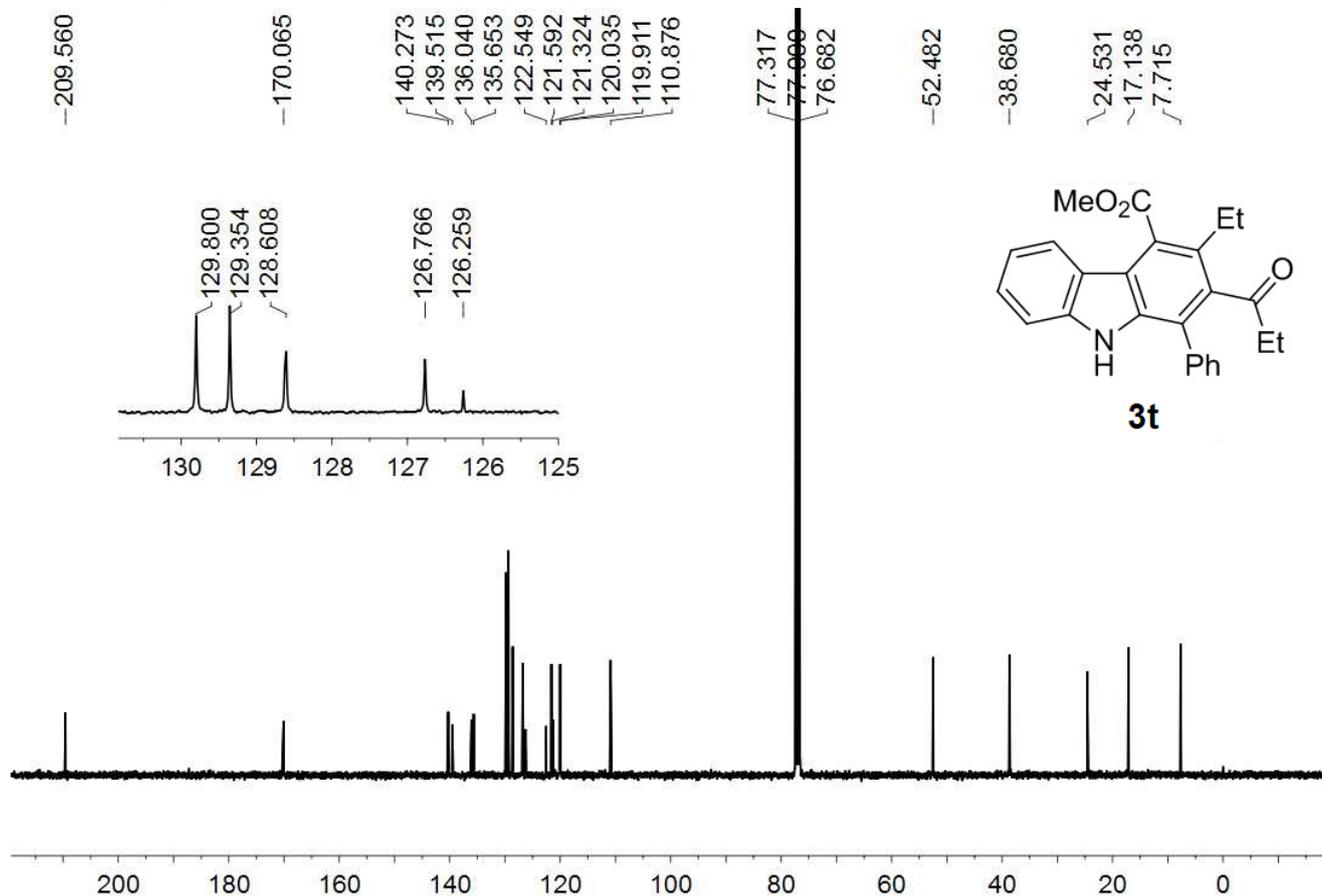
^{13}C NMR spectrum of the compound **3s** (100 MHz, CDCl_3)



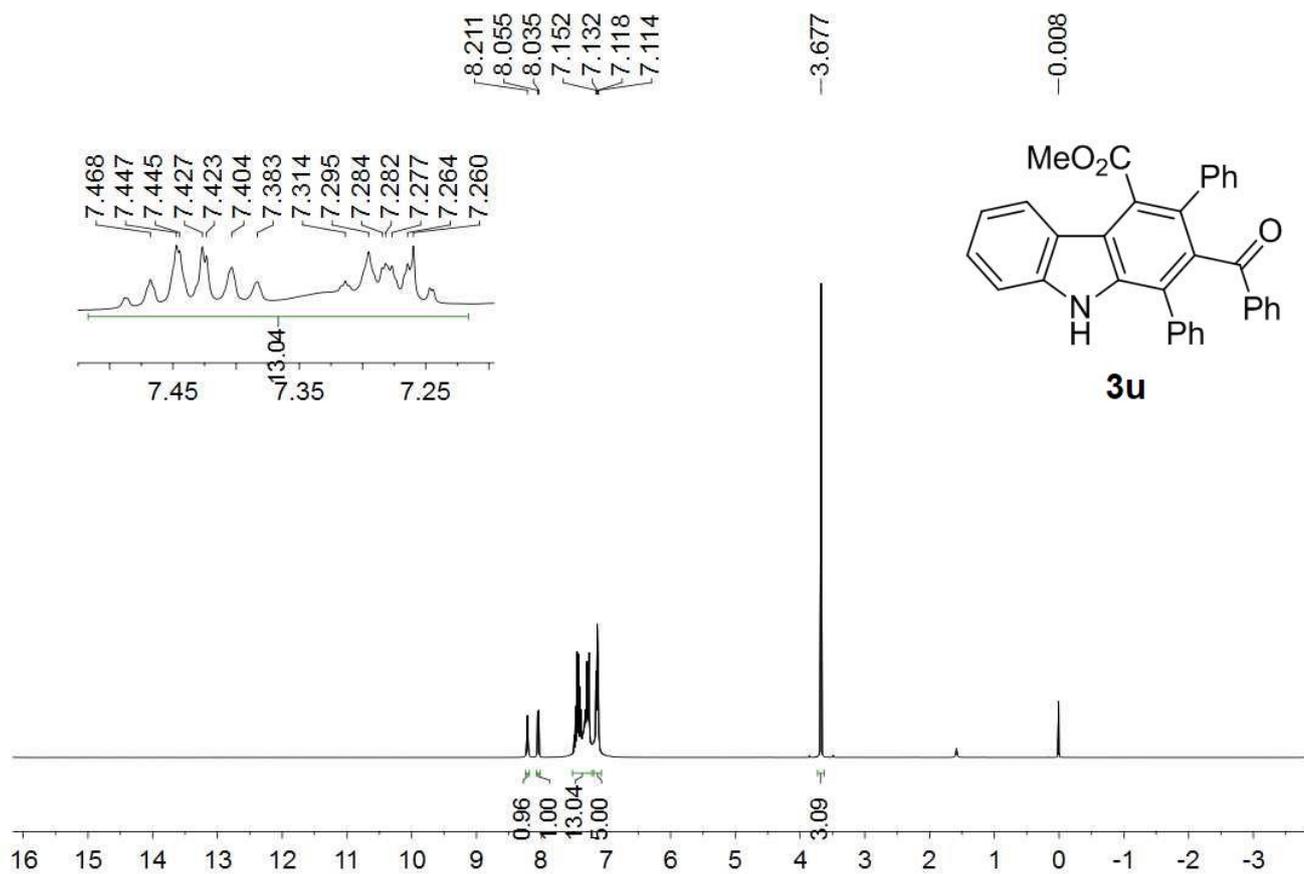
^1H NMR spectrum of the compound **3t** (400 MHz, CDCl_3)



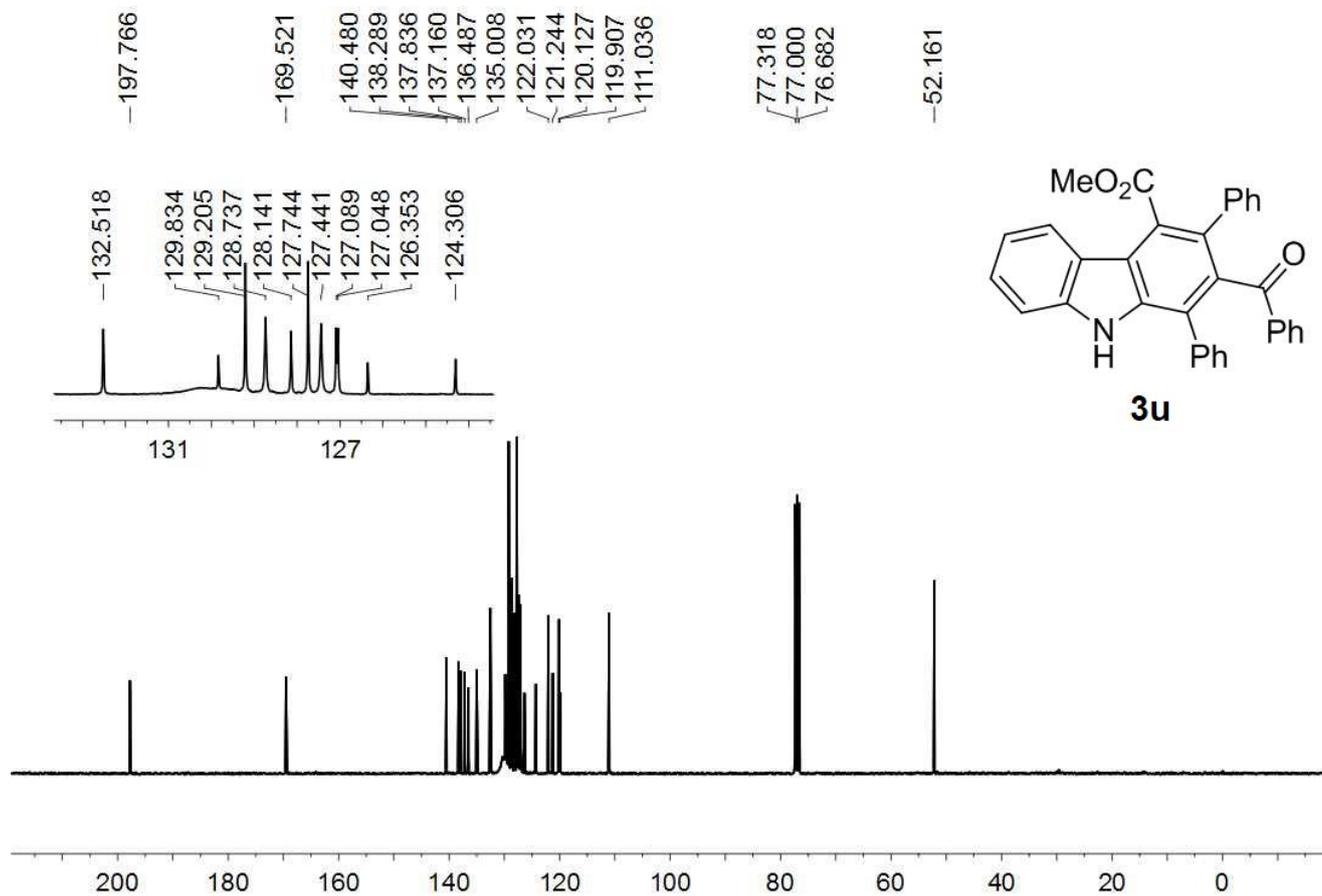
^{13}C NMR spectrum of the compound **3t** (100 MHz, CDCl_3)



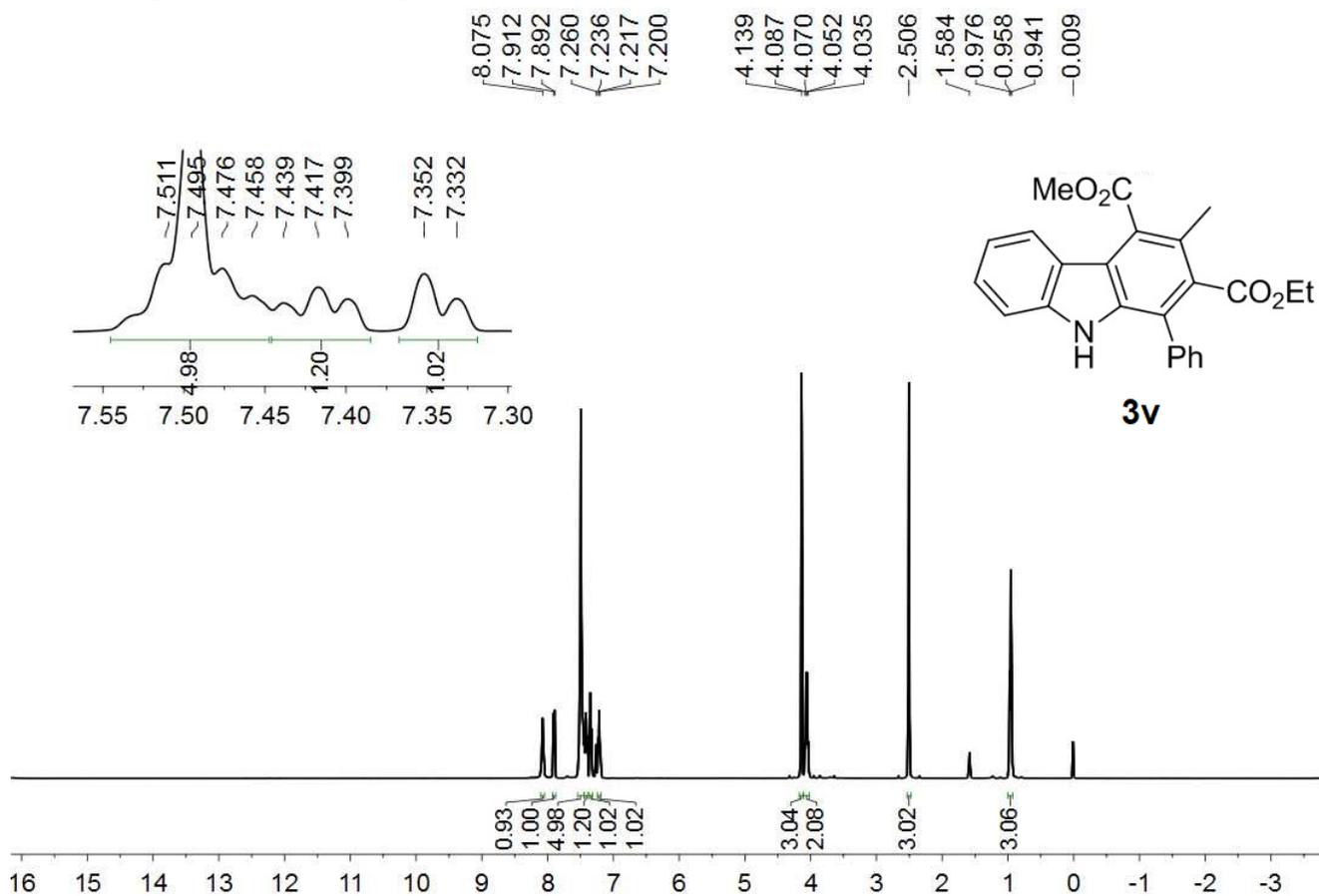
^1H NMR spectrum of the compound **3u** (400 MHz, CDCl_3)



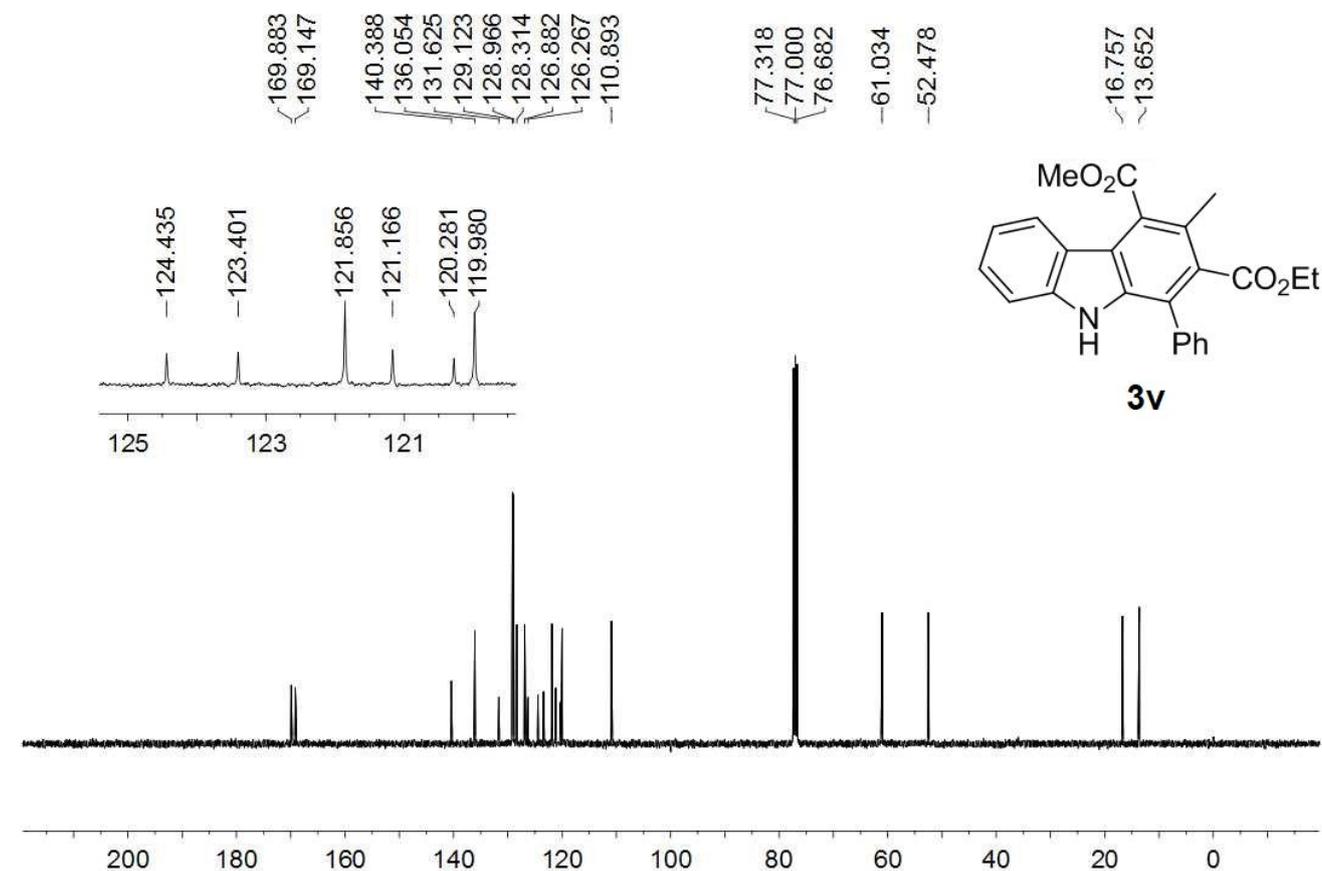
^{13}C NMR spectrum of the compound **3u** (100 MHz, CDCl_3)



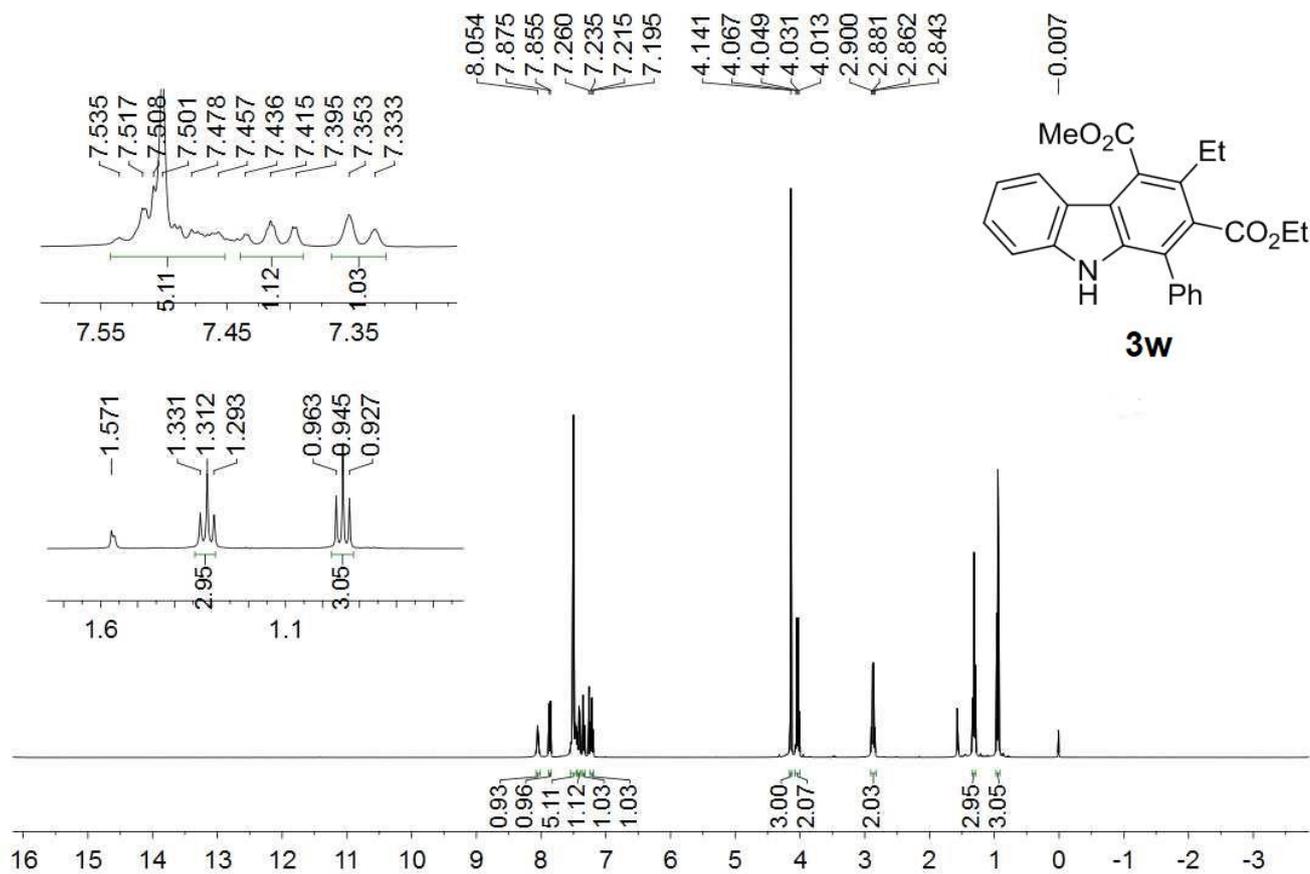
^1H NMR spectrum of the compound **3v** (400 MHz, CDCl_3)



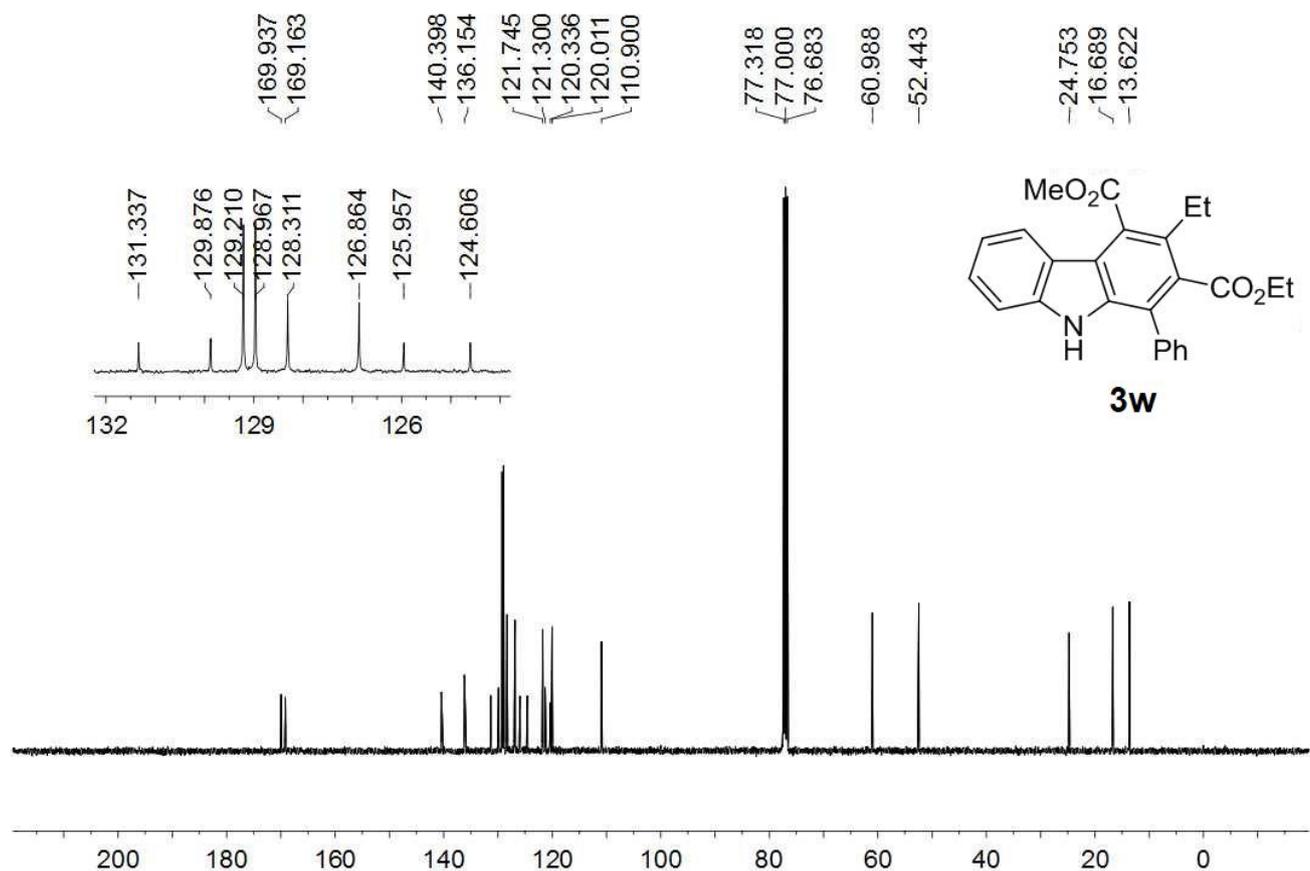
^{13}C NMR spectrum of the compound **3v** (100 MHz, CDCl_3)



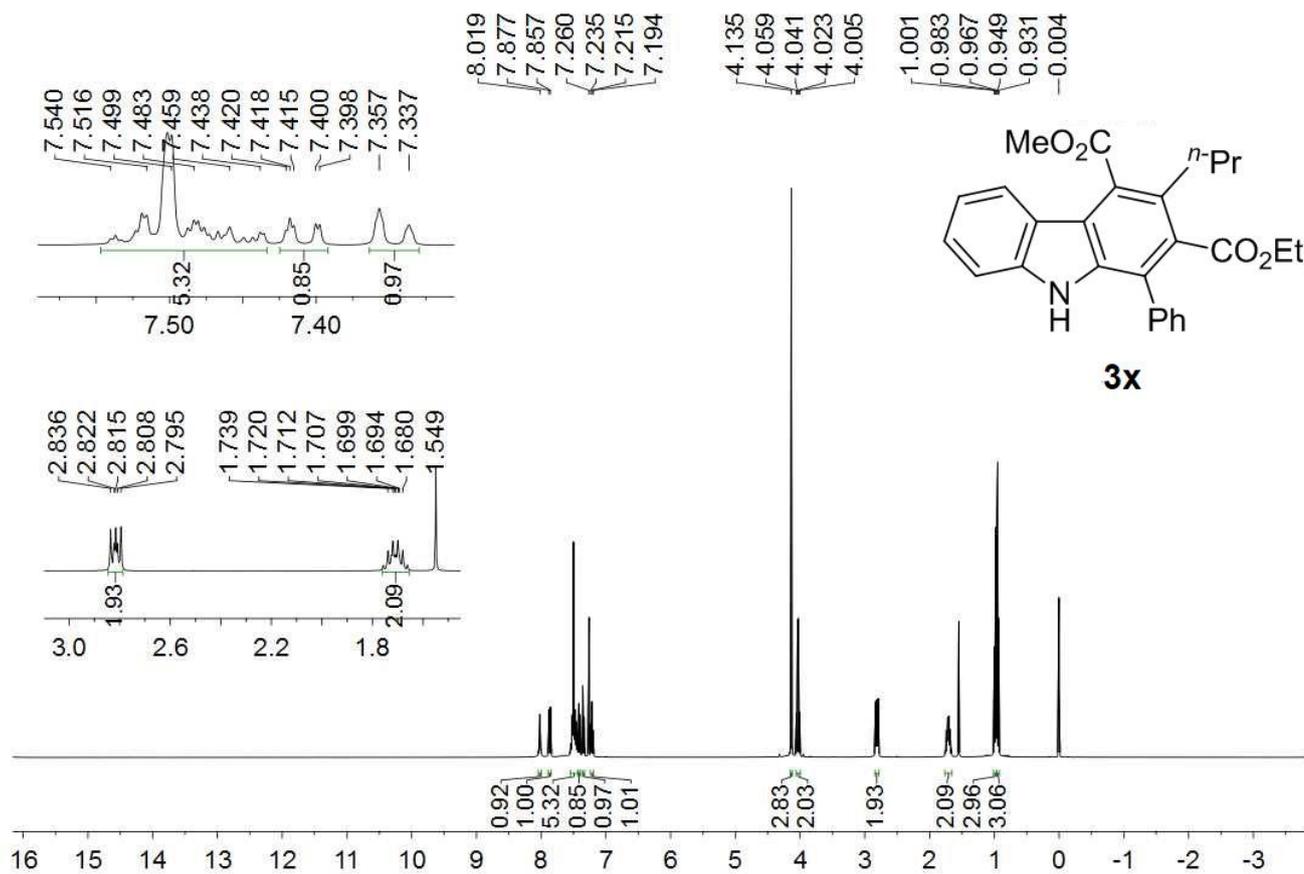
^1H NMR spectrum of the compound **3w** (400 MHz, CDCl_3)



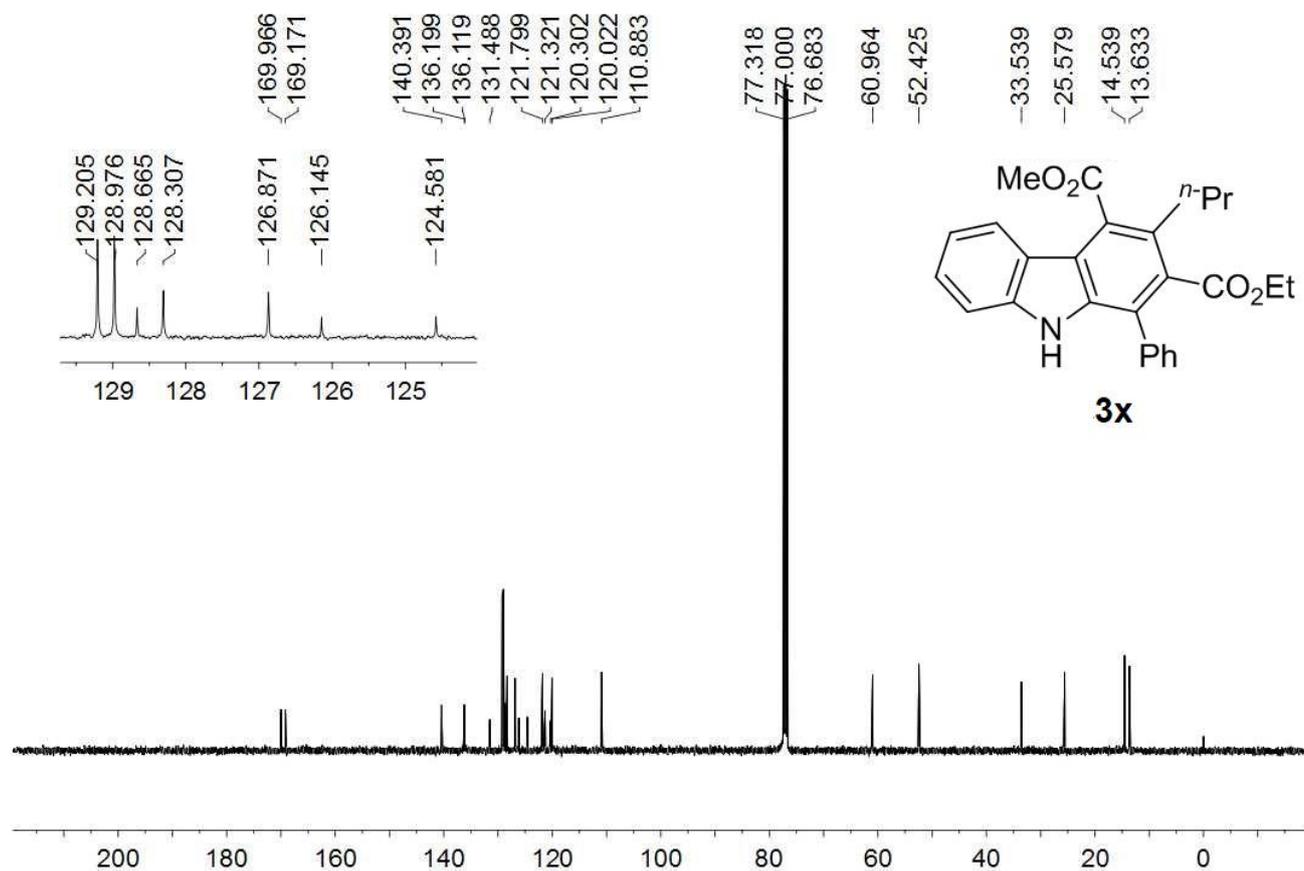
^{13}C NMR spectrum of the compound **3w** (100 MHz, CDCl_3)



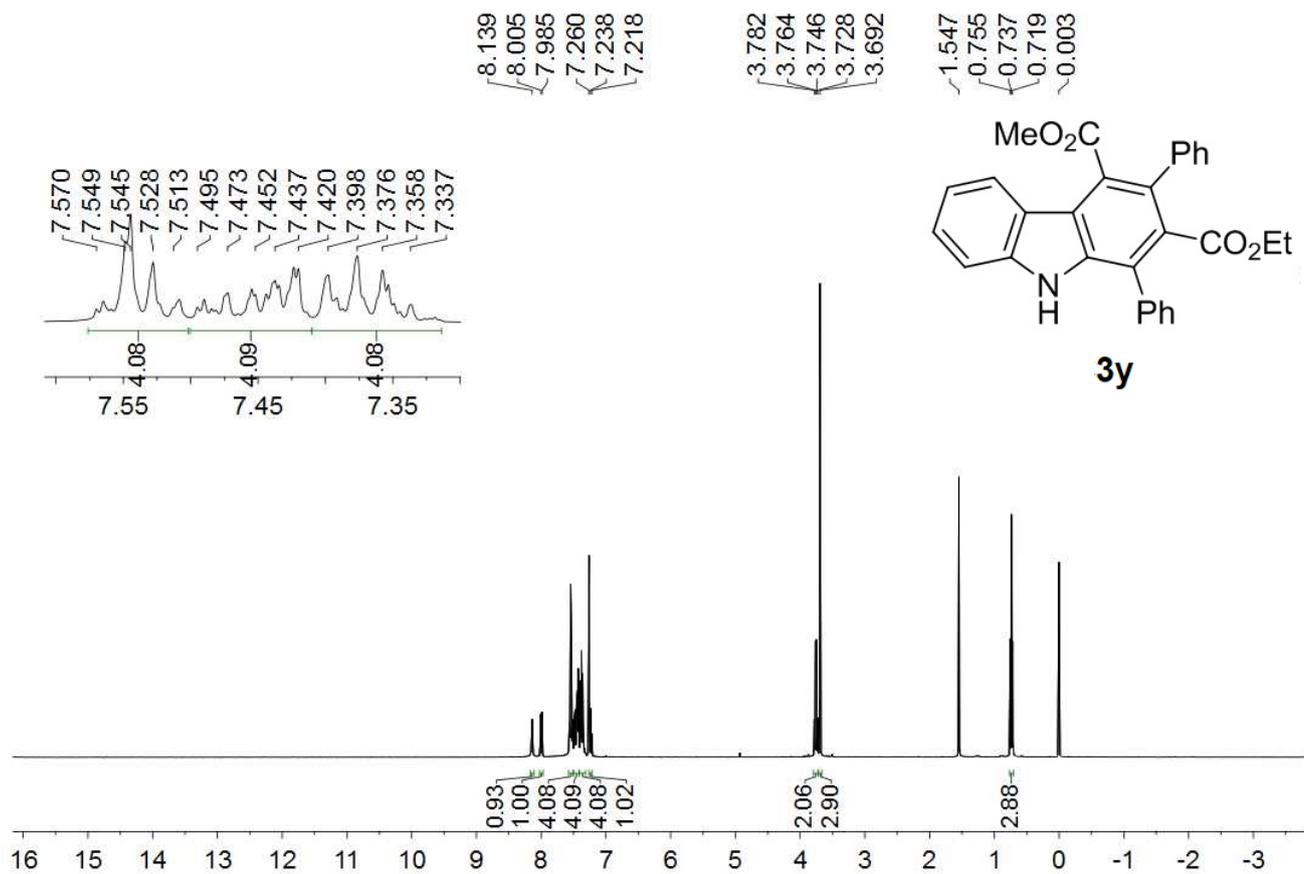
^1H NMR spectrum of the compound **3x** (400 MHz, CDCl_3)



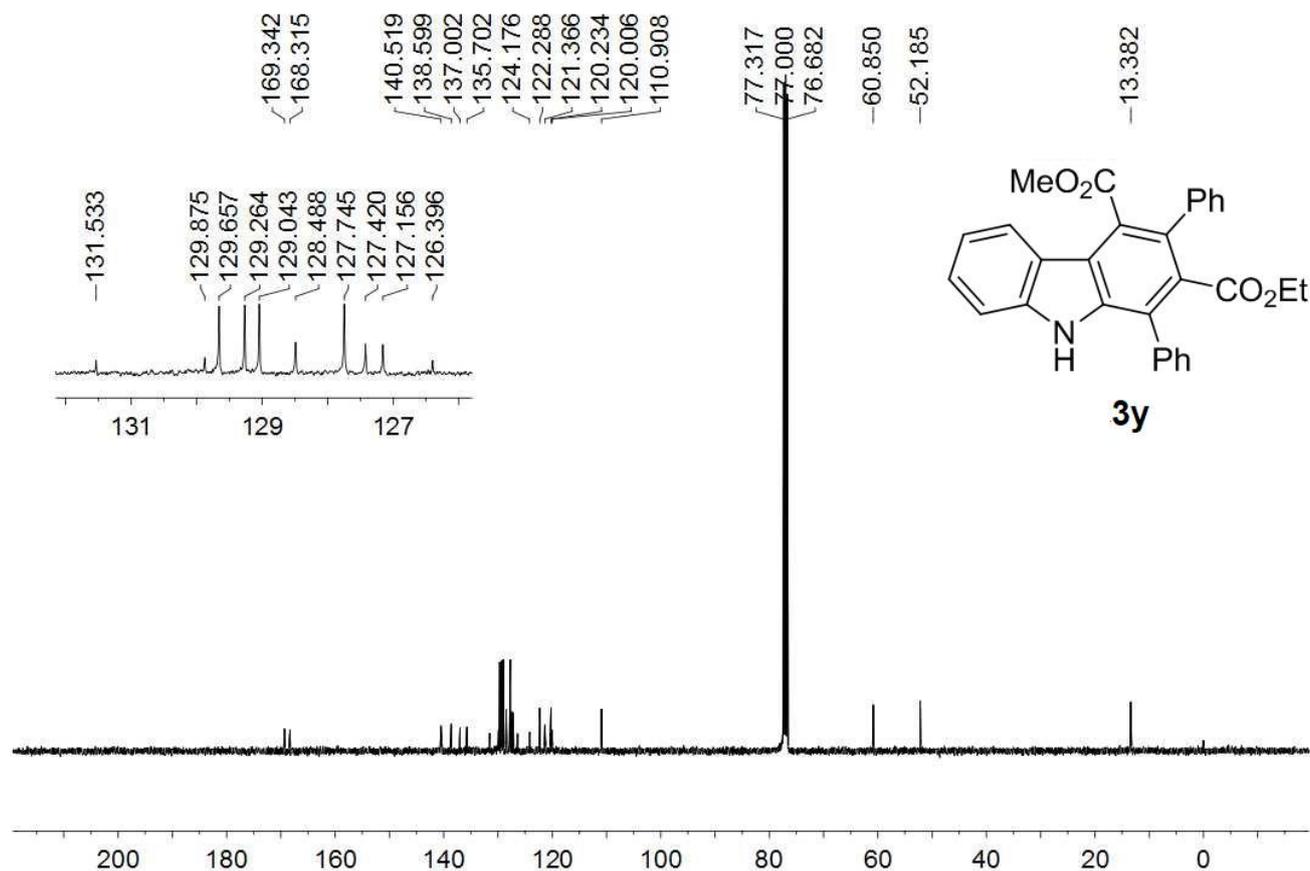
^{13}C NMR spectrum of the compound **3x** (100 MHz, CDCl_3)



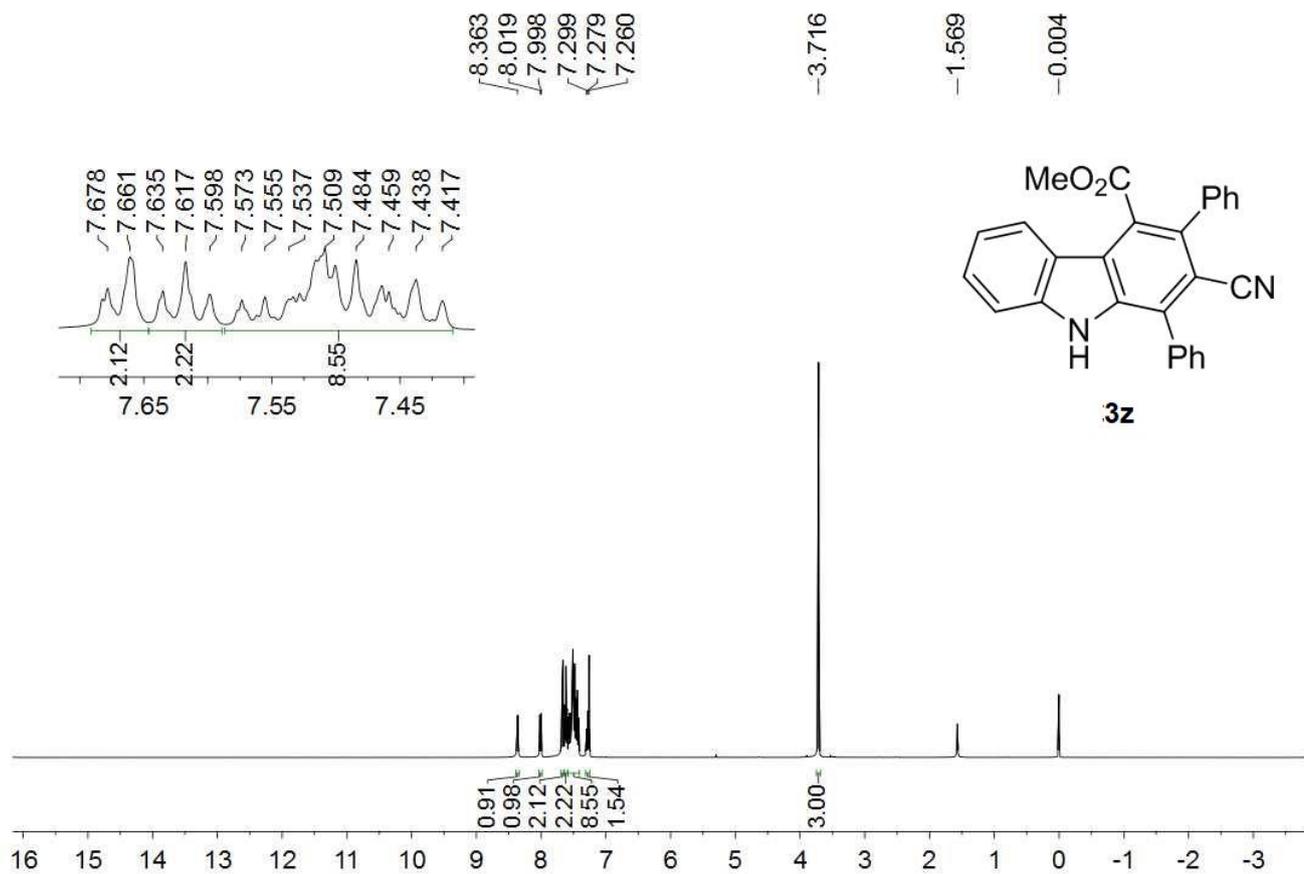
^1H NMR spectrum of the compound **3y** (400 MHz, CDCl_3)



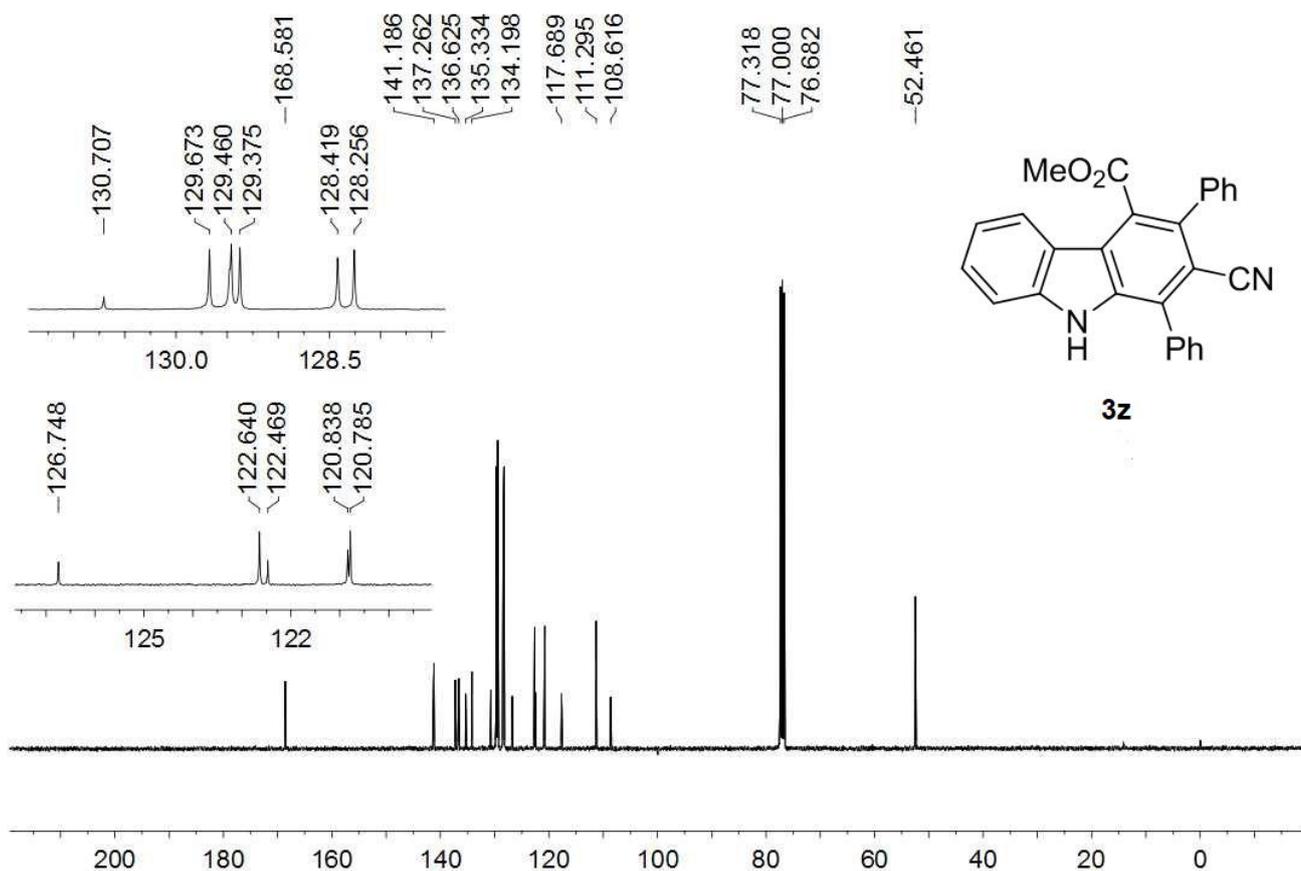
^{13}C NMR spectrum of the compound **3y** (100 MHz, CDCl_3)



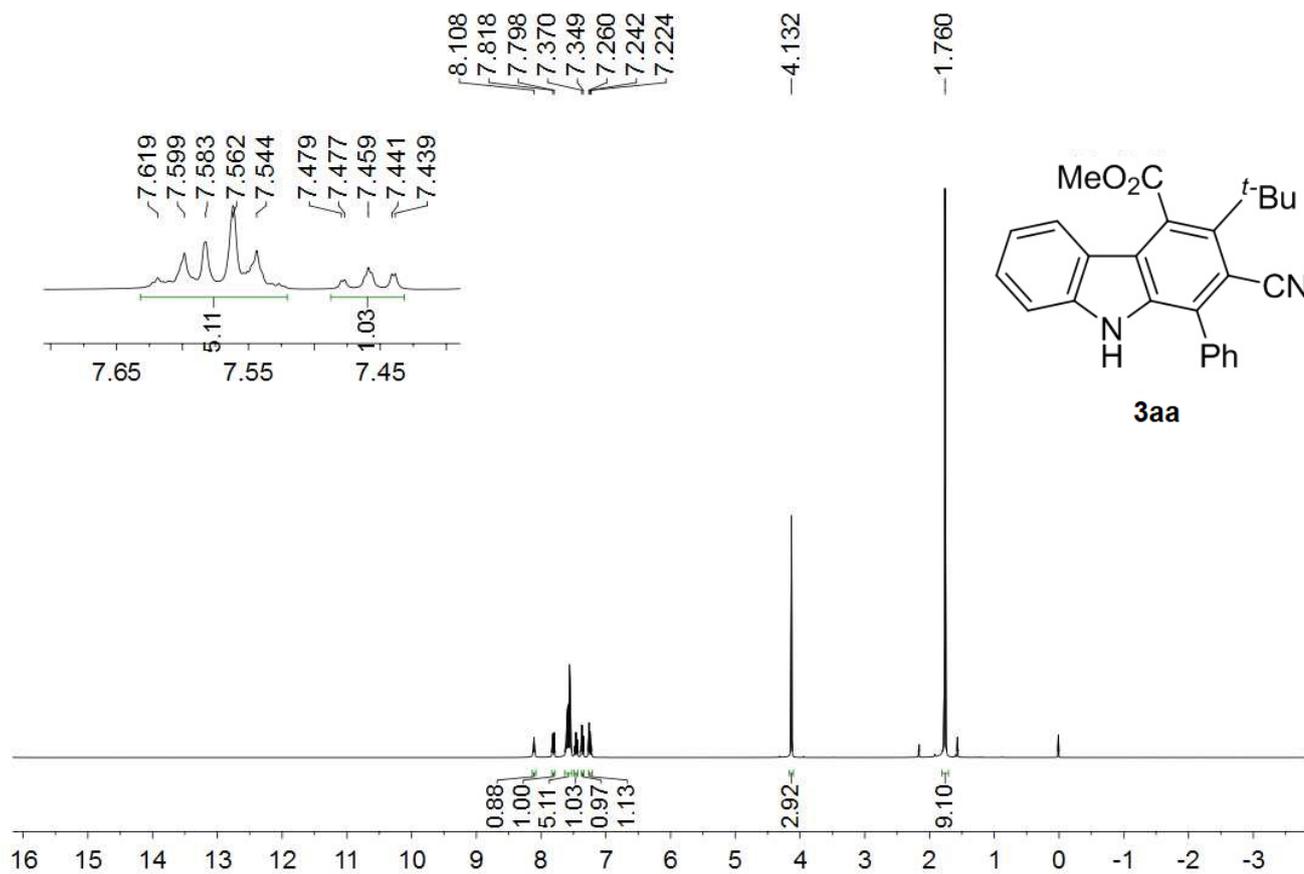
^1H NMR spectrum of the compound **3z** (400 MHz, CDCl_3)



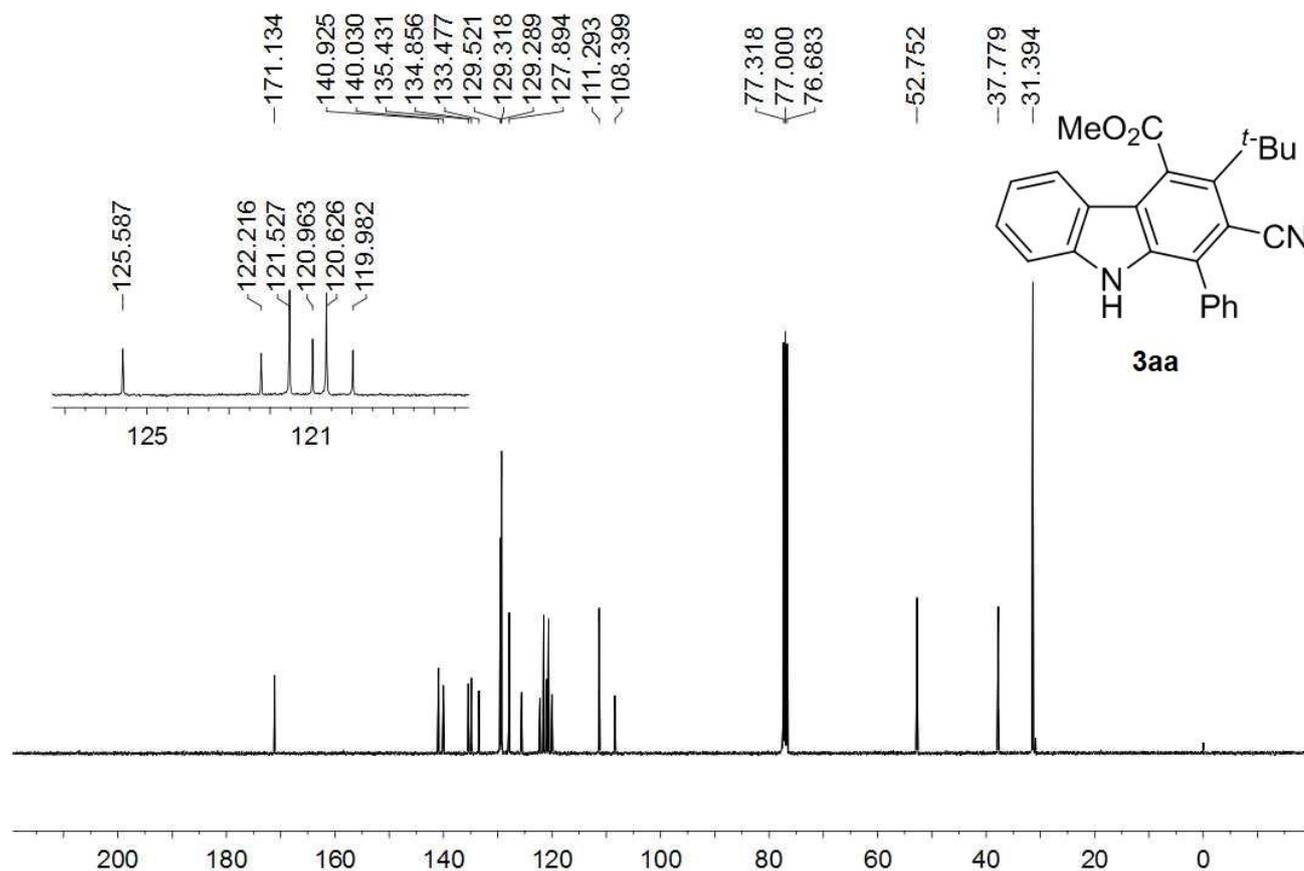
^{13}C NMR spectrum of the compound **3z** (100 MHz, CDCl_3)



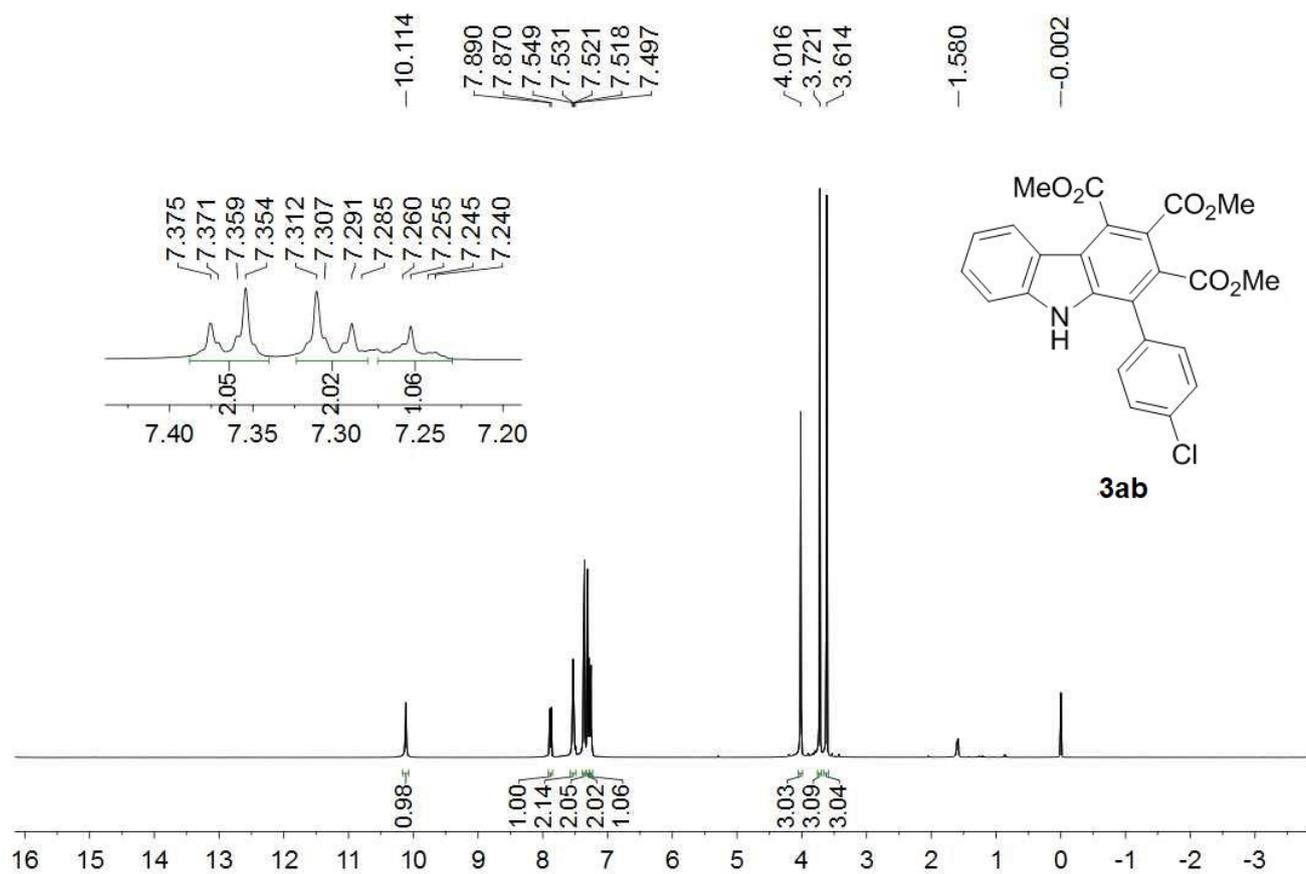
^1H NMR spectrum of the compound **3aa** (400 MHz, CDCl_3)



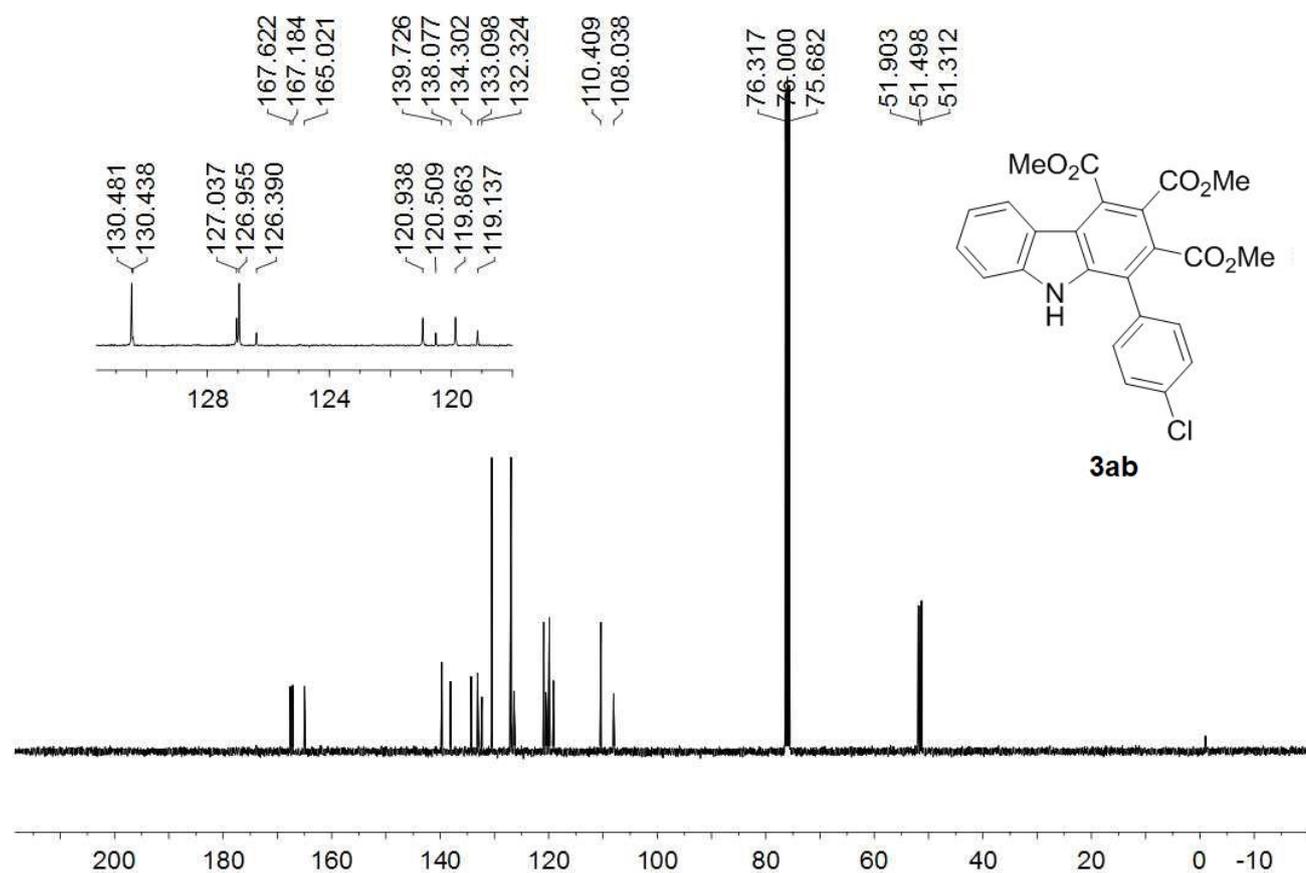
^{13}C NMR spectrum of the compound **3aa** (400 MHz, CDCl_3)



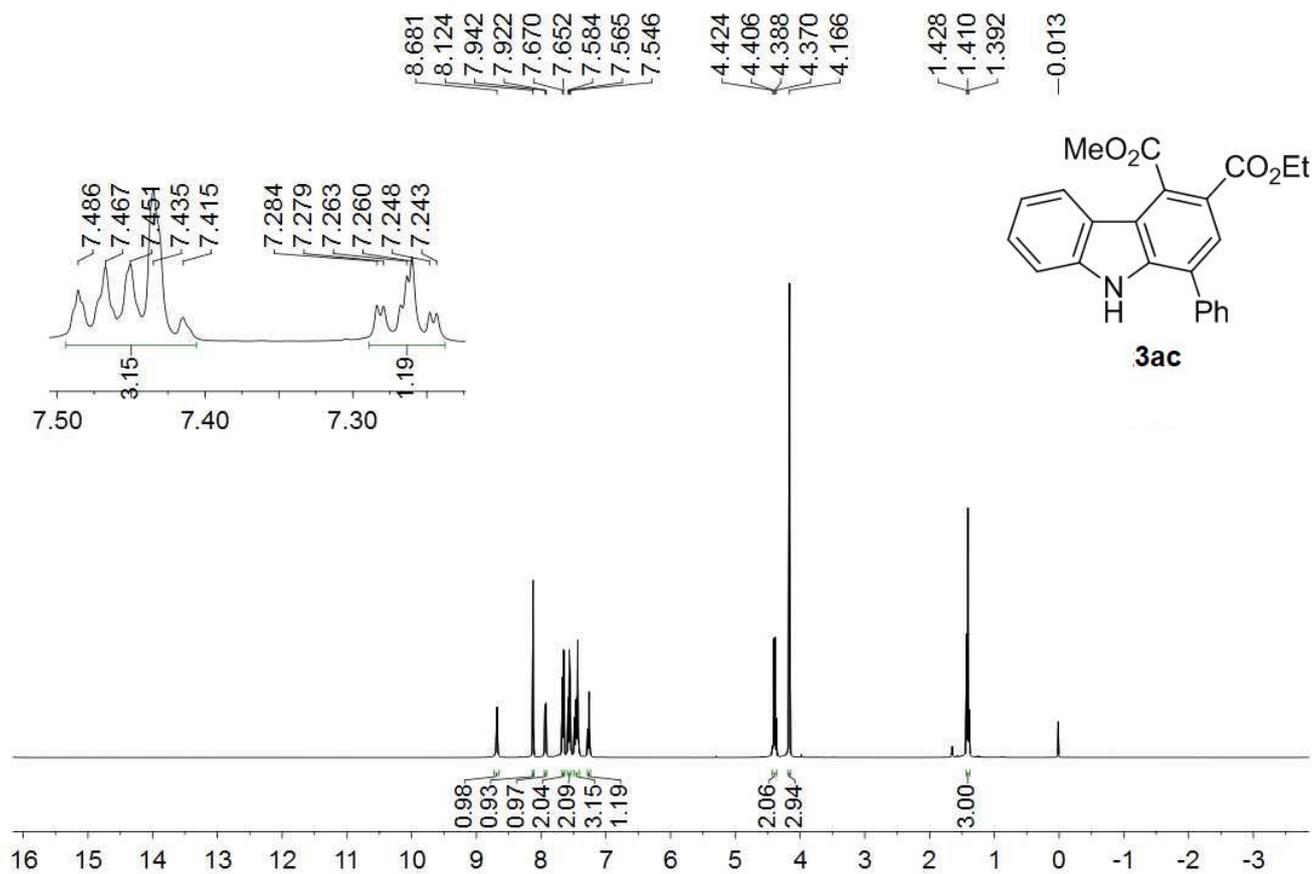
^1H NMR spectrum of the compound **3ab** (400 MHz, CDCl_3)



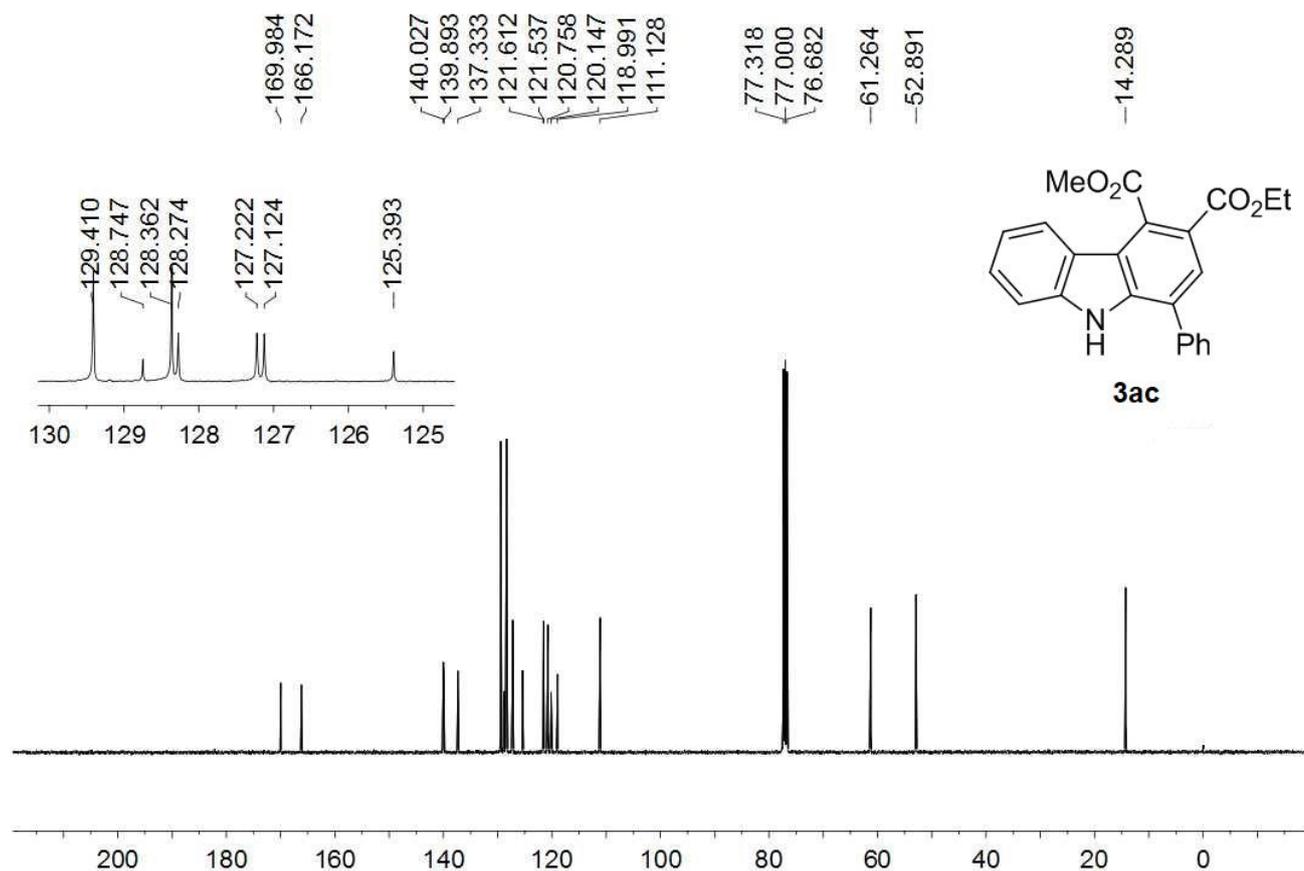
^{13}C NMR spectrum of the compound **3ab** (400 MHz, CDCl_3)



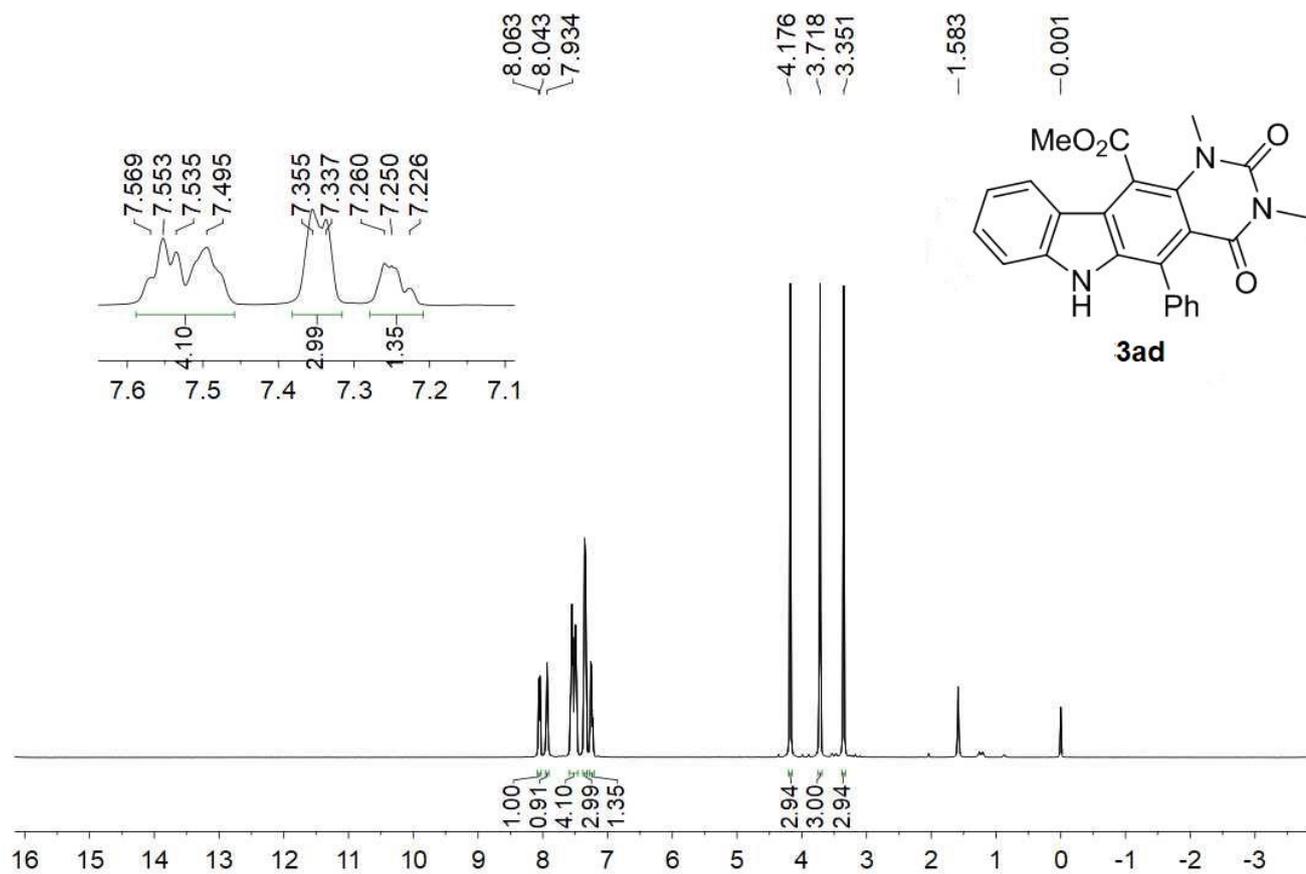
^1H NMR spectrum of the compound **3ac** (400 MHz, CDCl_3)



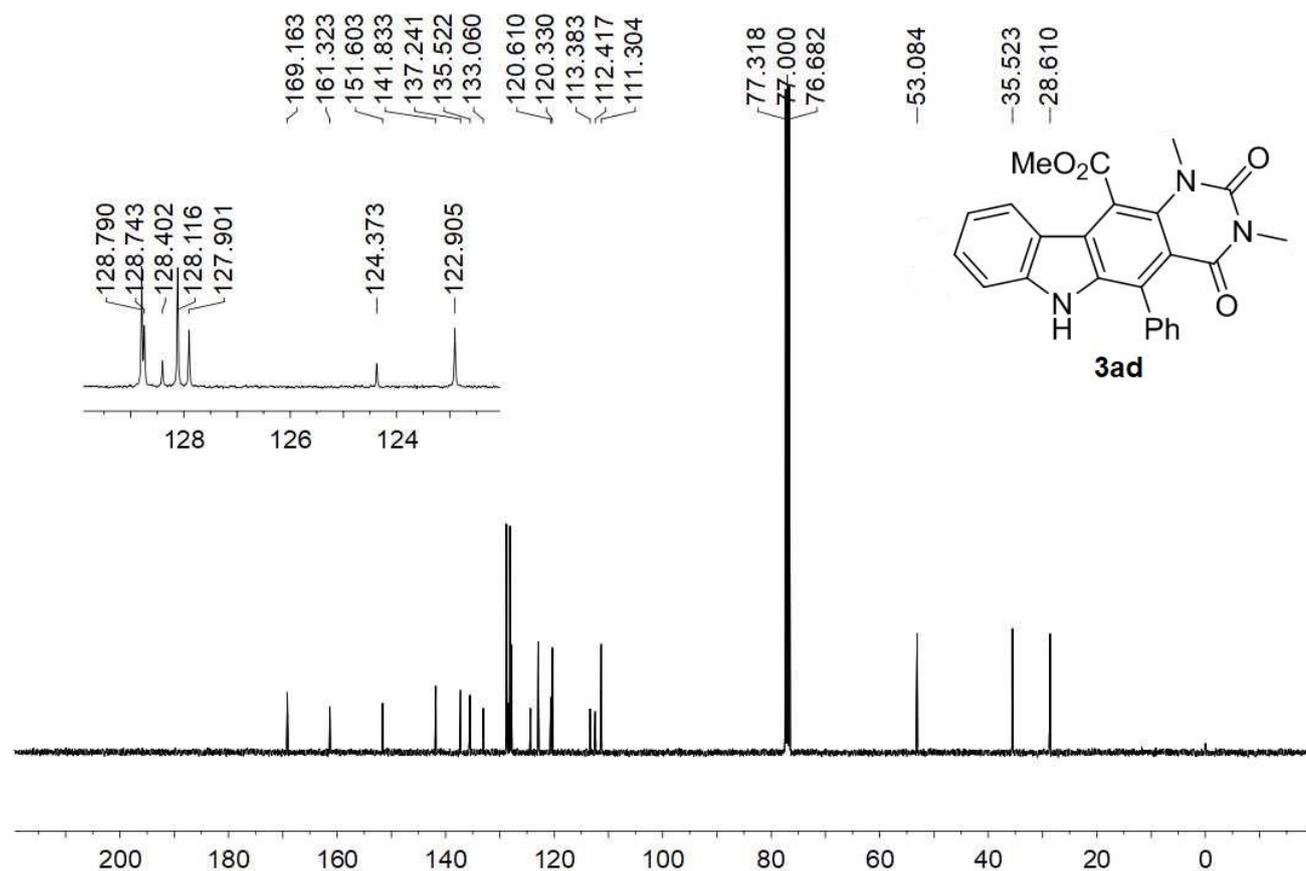
^{13}C NMR spectrum of the compound **3ac** (100 MHz, CDCl_3)



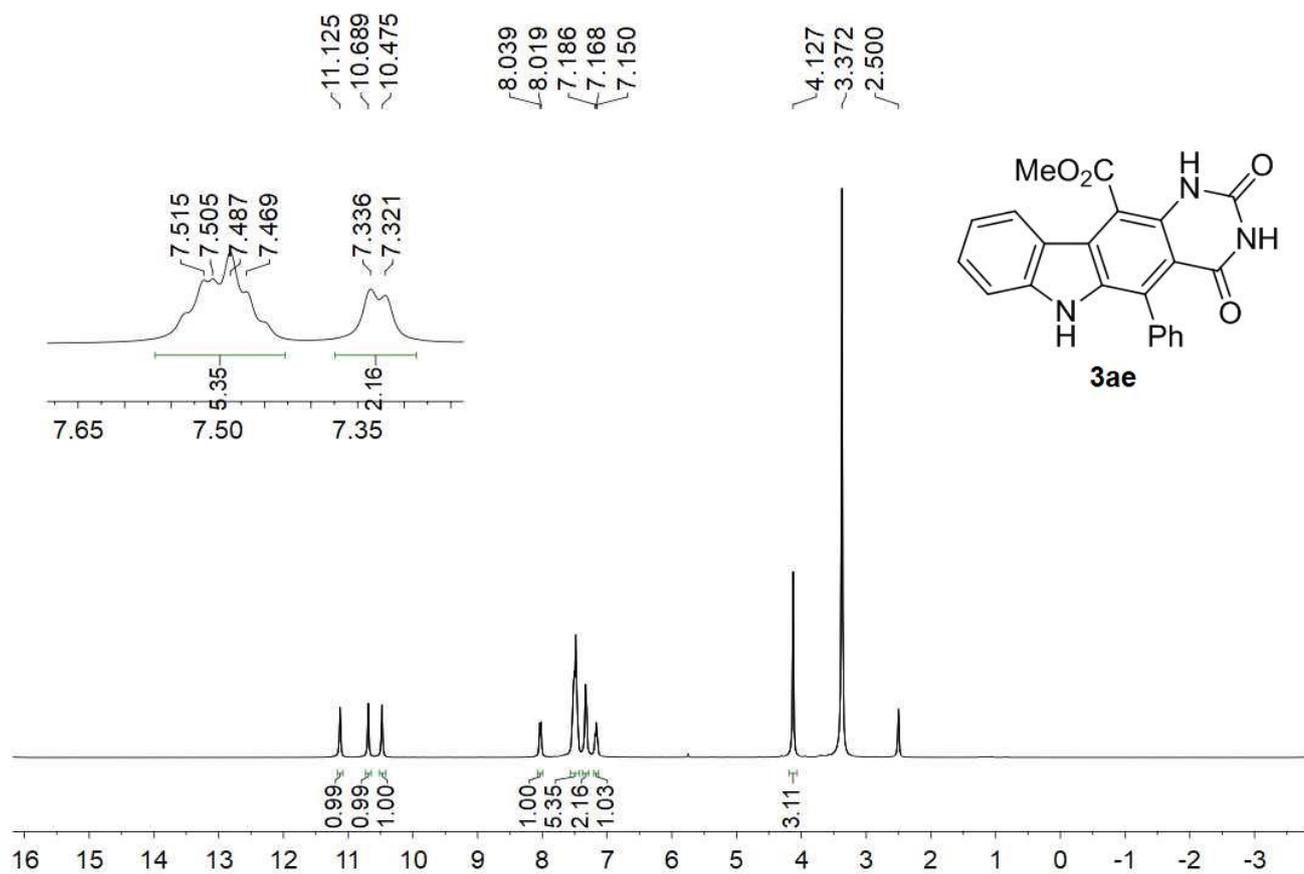
^1H NMR spectrum of the compound **3ad** (400 MHz, CDCl_3)



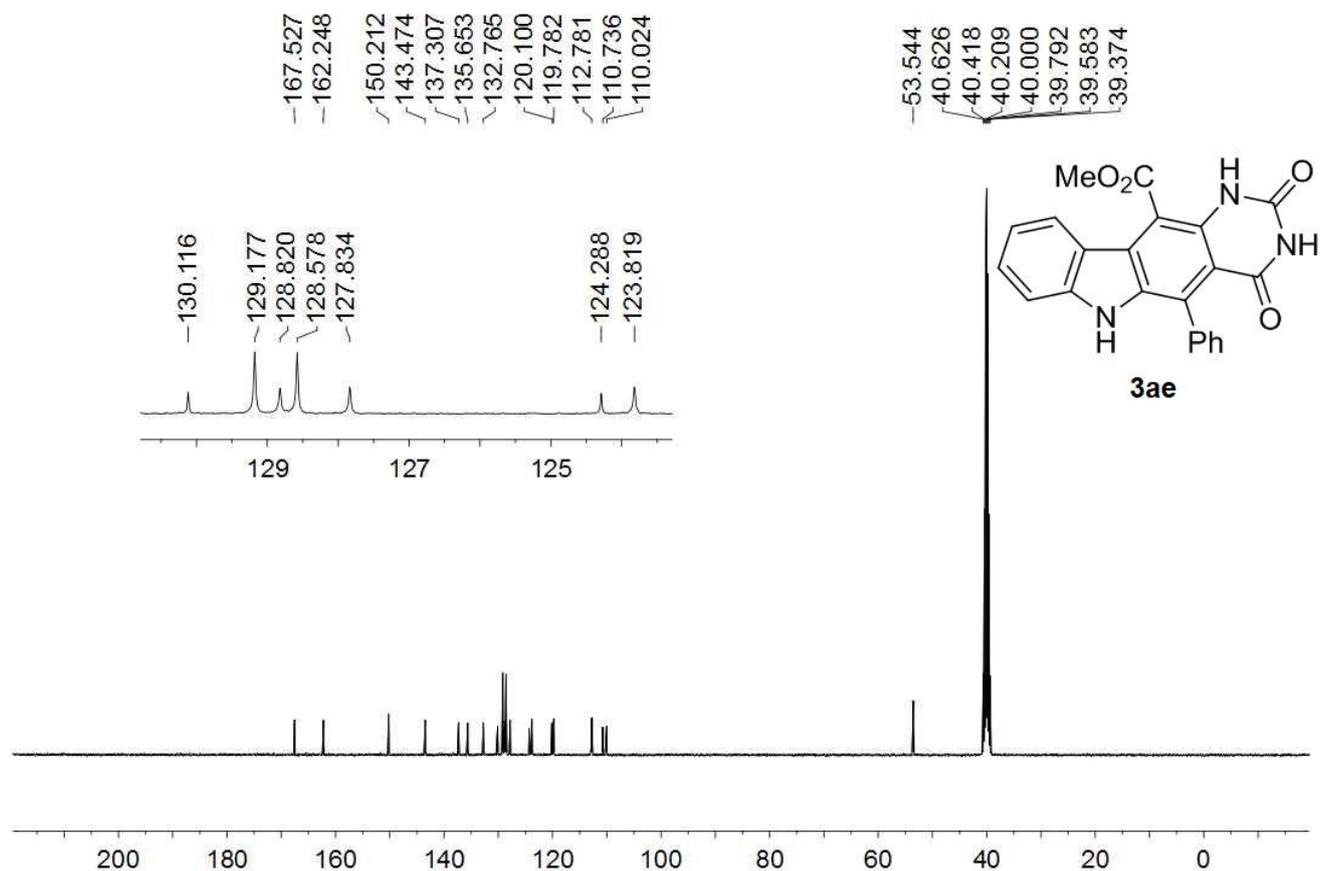
^{13}C NMR spectrum of the compound **3ad** (100 MHz, CDCl_3)



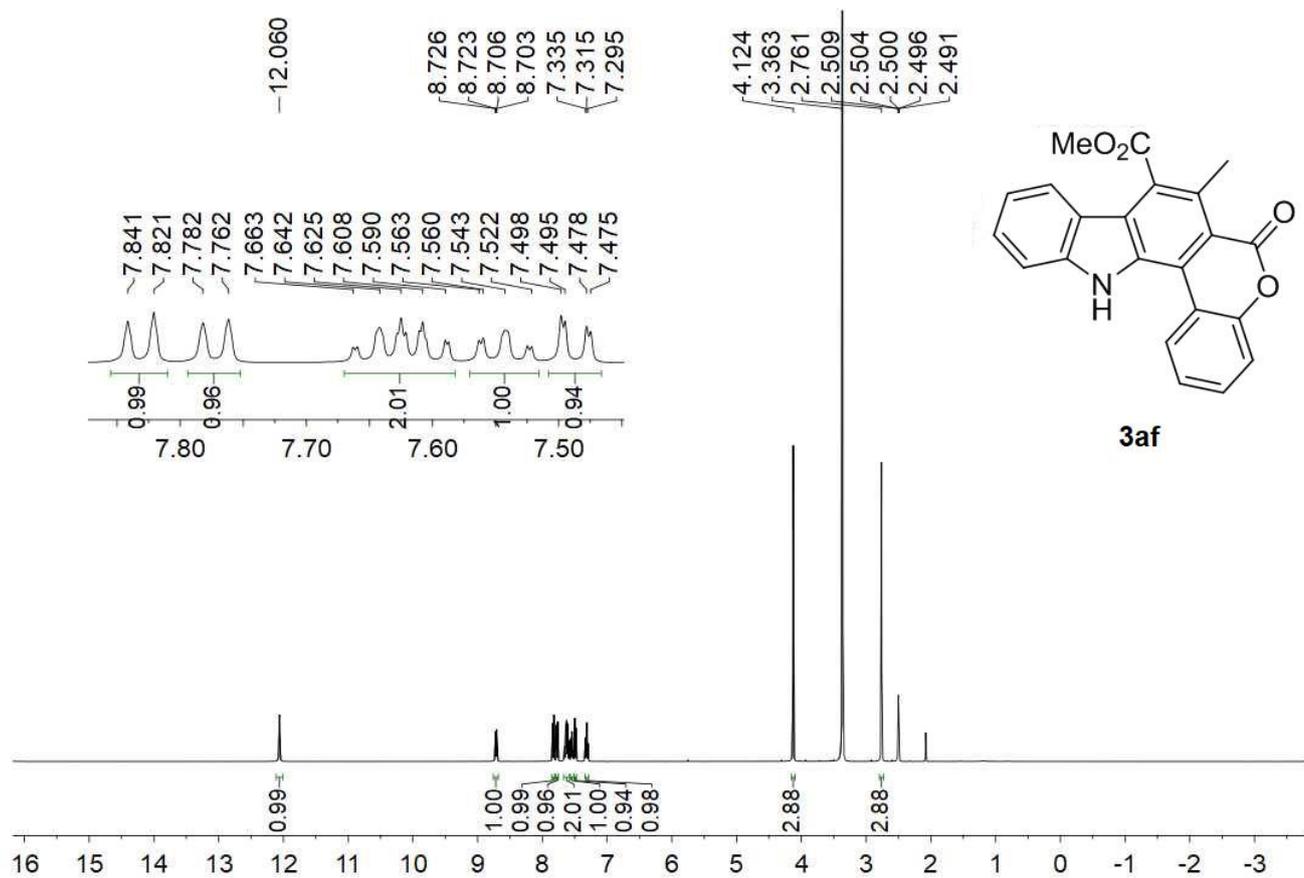
^1H NMR spectrum of the compound **3ae** (400 MHz, DMSO- d_6)



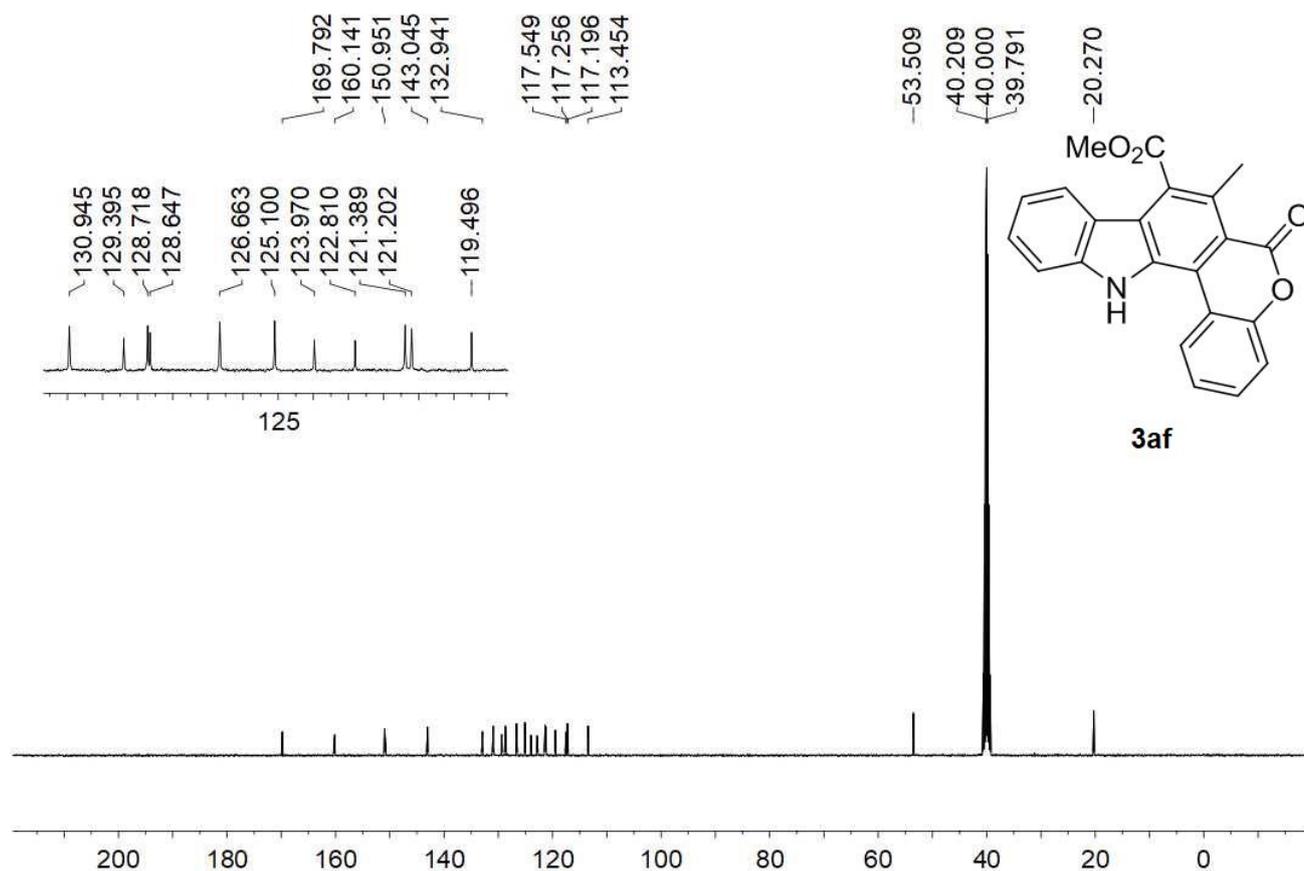
^{13}C NMR spectrum of the compound **3ae** (100 MHz, DMSO- d_6)



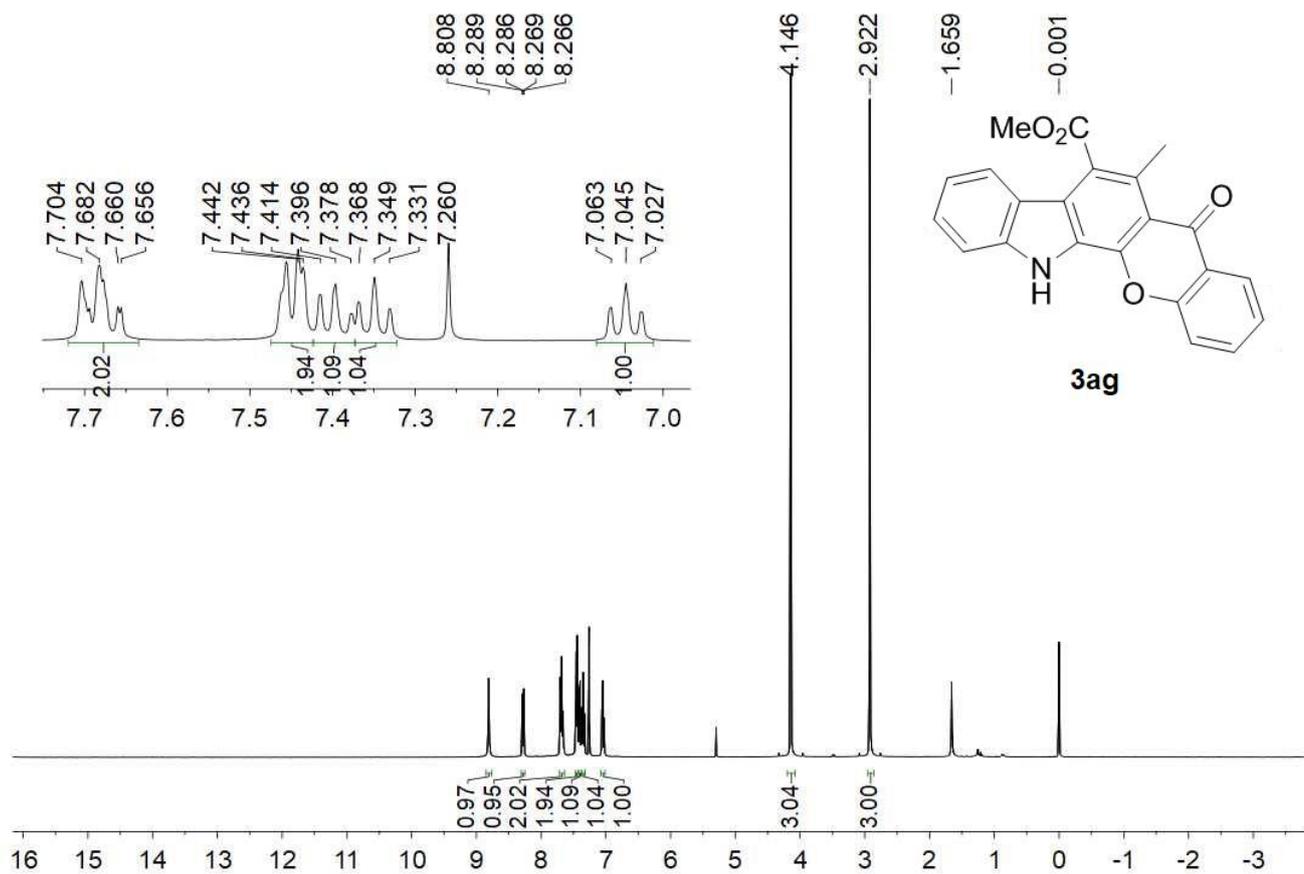
¹H NMR spectrum of the compound **3af** (400 MHz, DMSO-*d*₆)



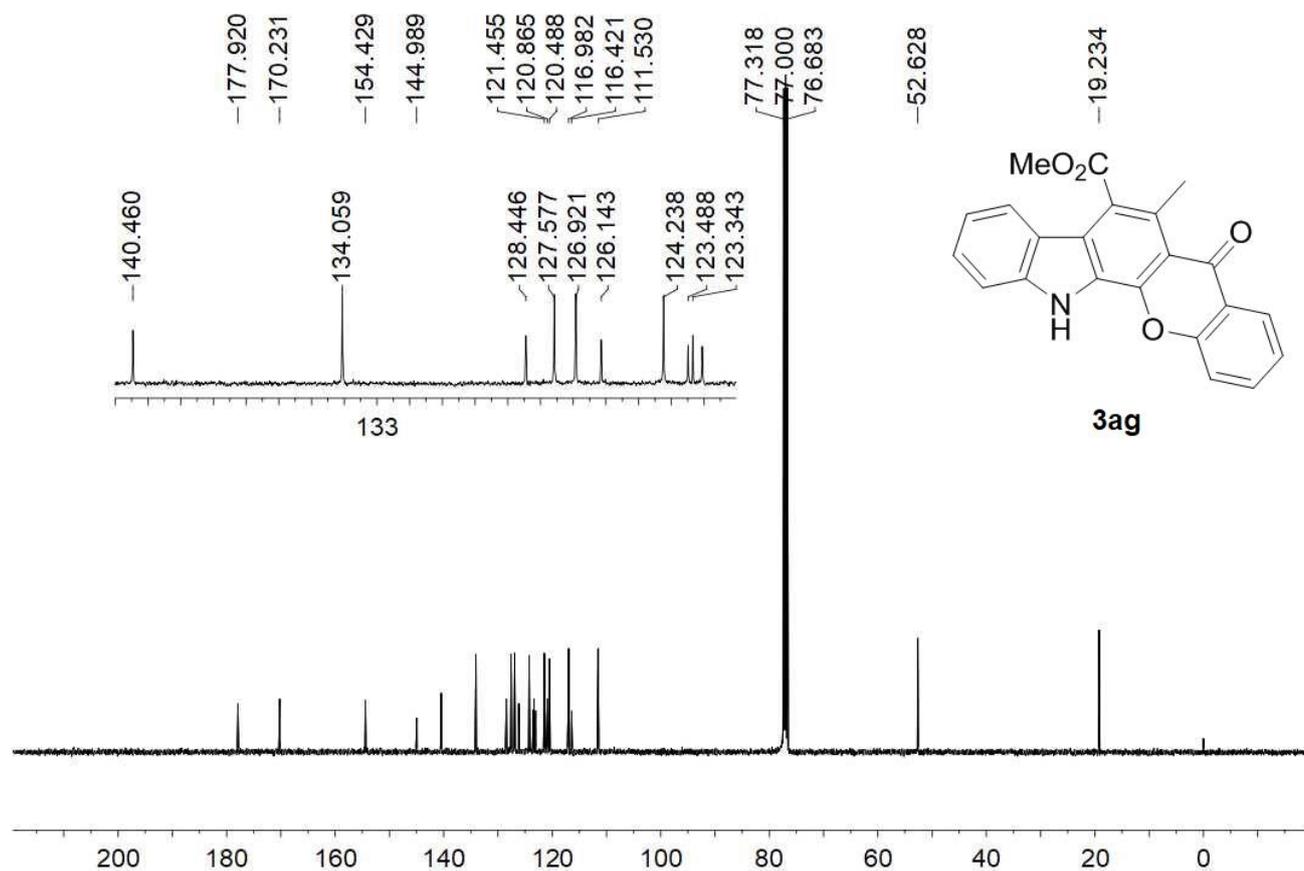
¹³C NMR spectrum of the compound **3af** (100 MHz, DMSO-*d*₆)



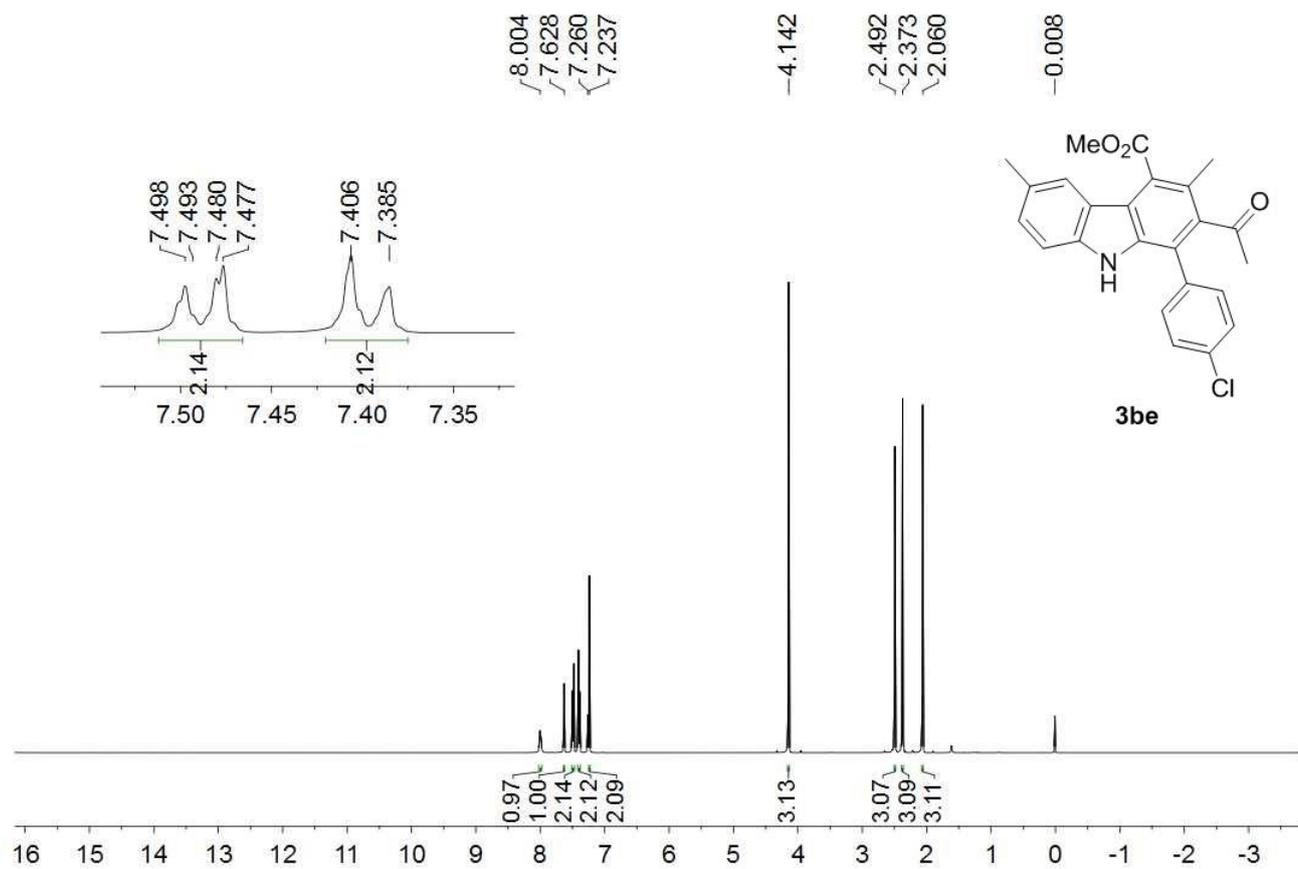
^1H NMR spectrum of the compound **3ag** (400 MHz, CDCl_3)



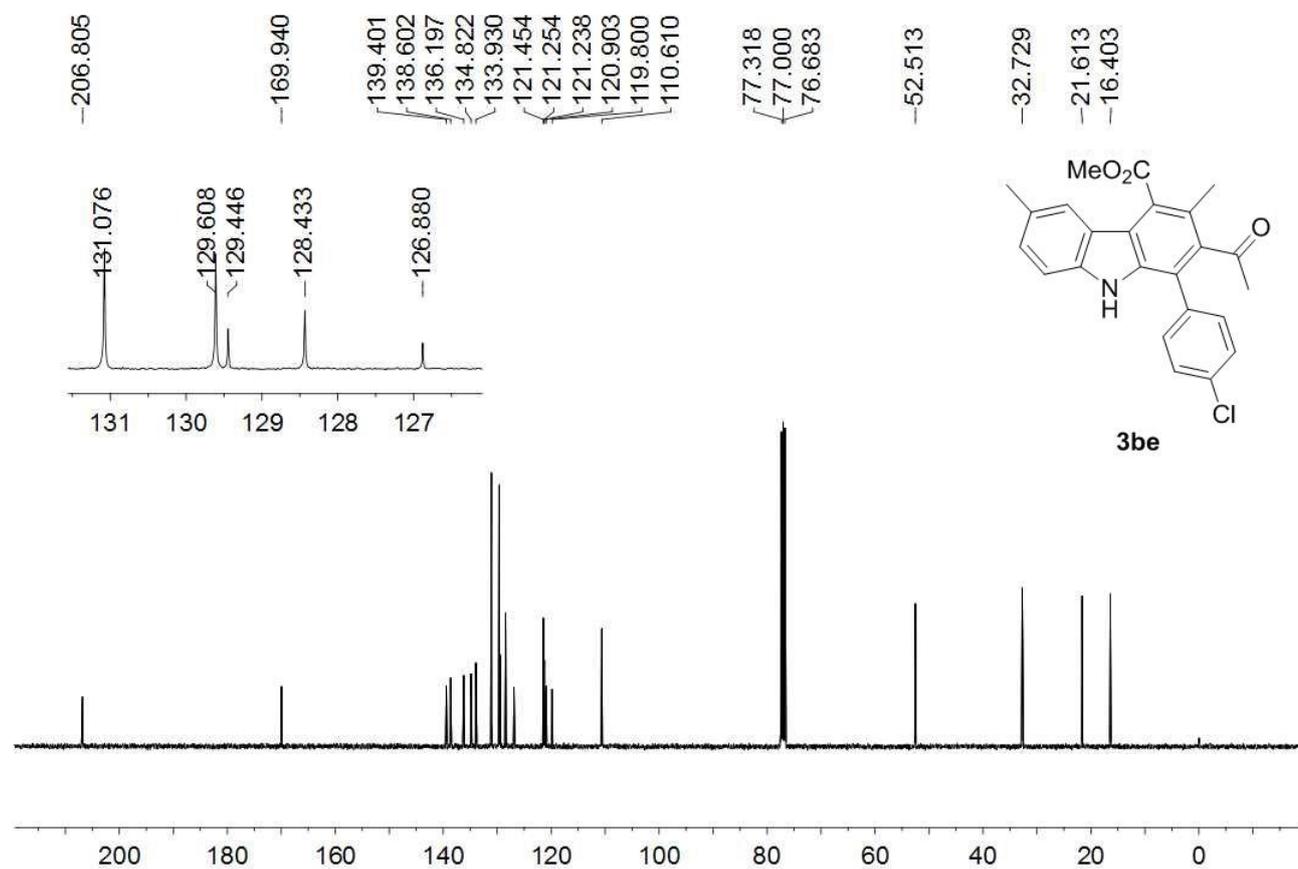
^{13}C NMR spectrum of the compound **3ag** (100 MHz, CDCl_3)



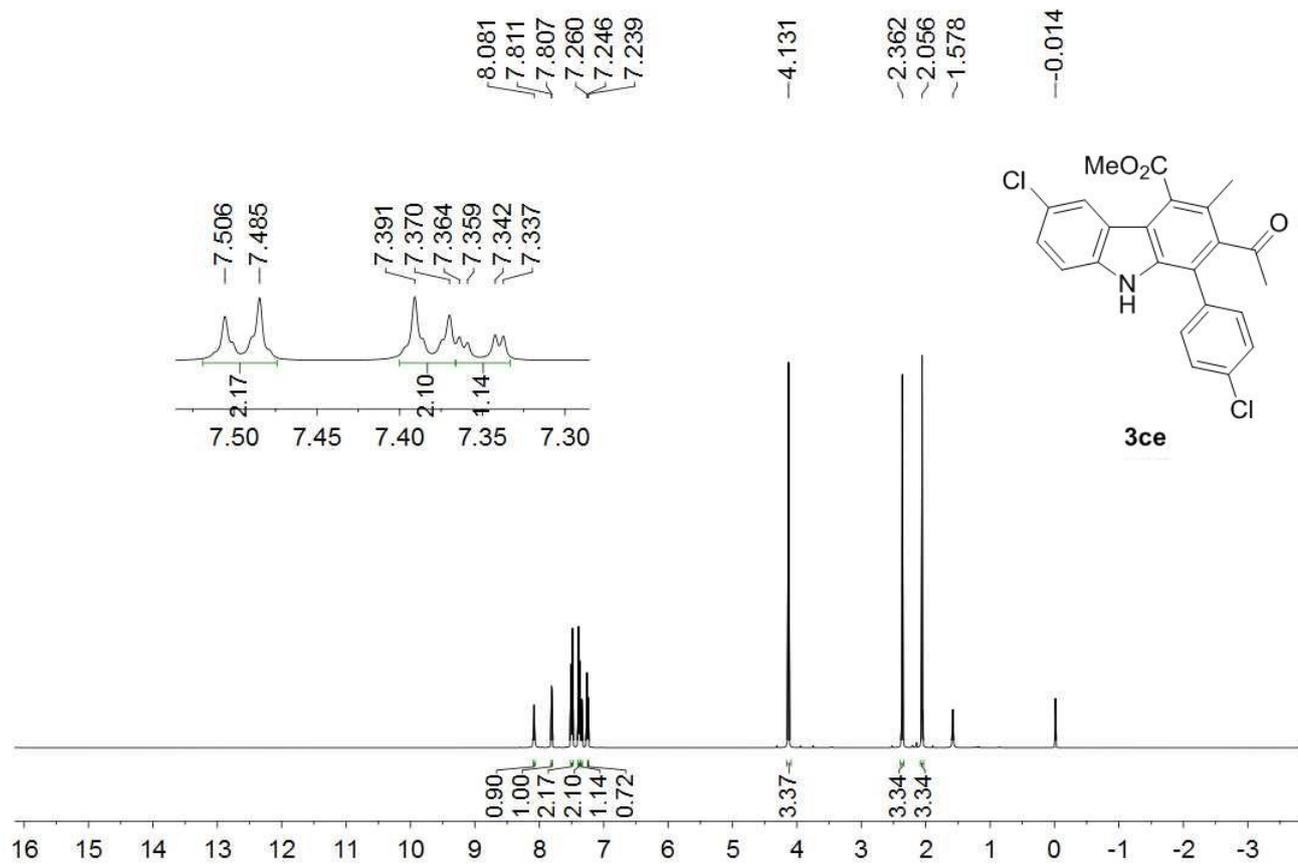
¹H NMR spectrum of the compound **3be** (400 MHz, CDCl₃)



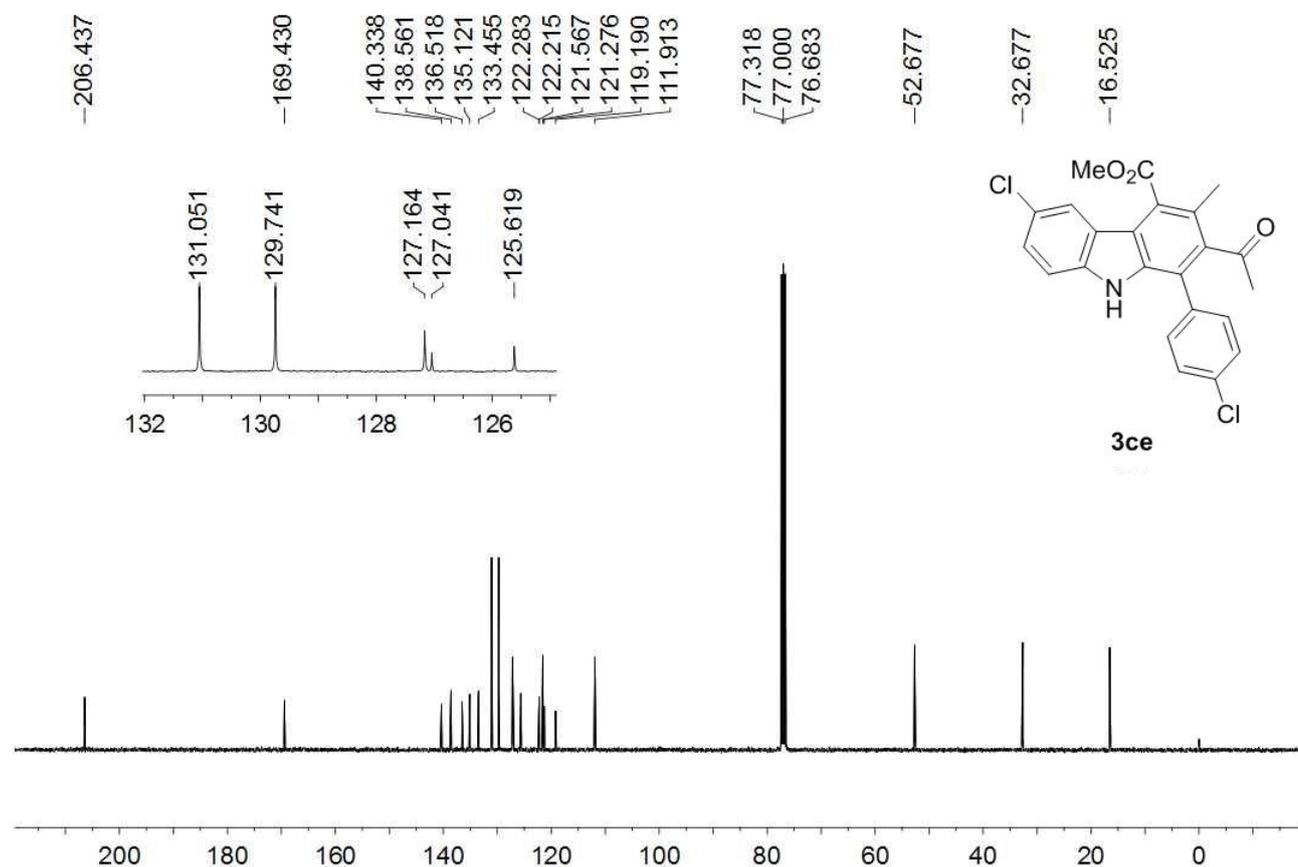
¹³C NMR spectrum of the compound **3be** (100 MHz, CDCl₃)



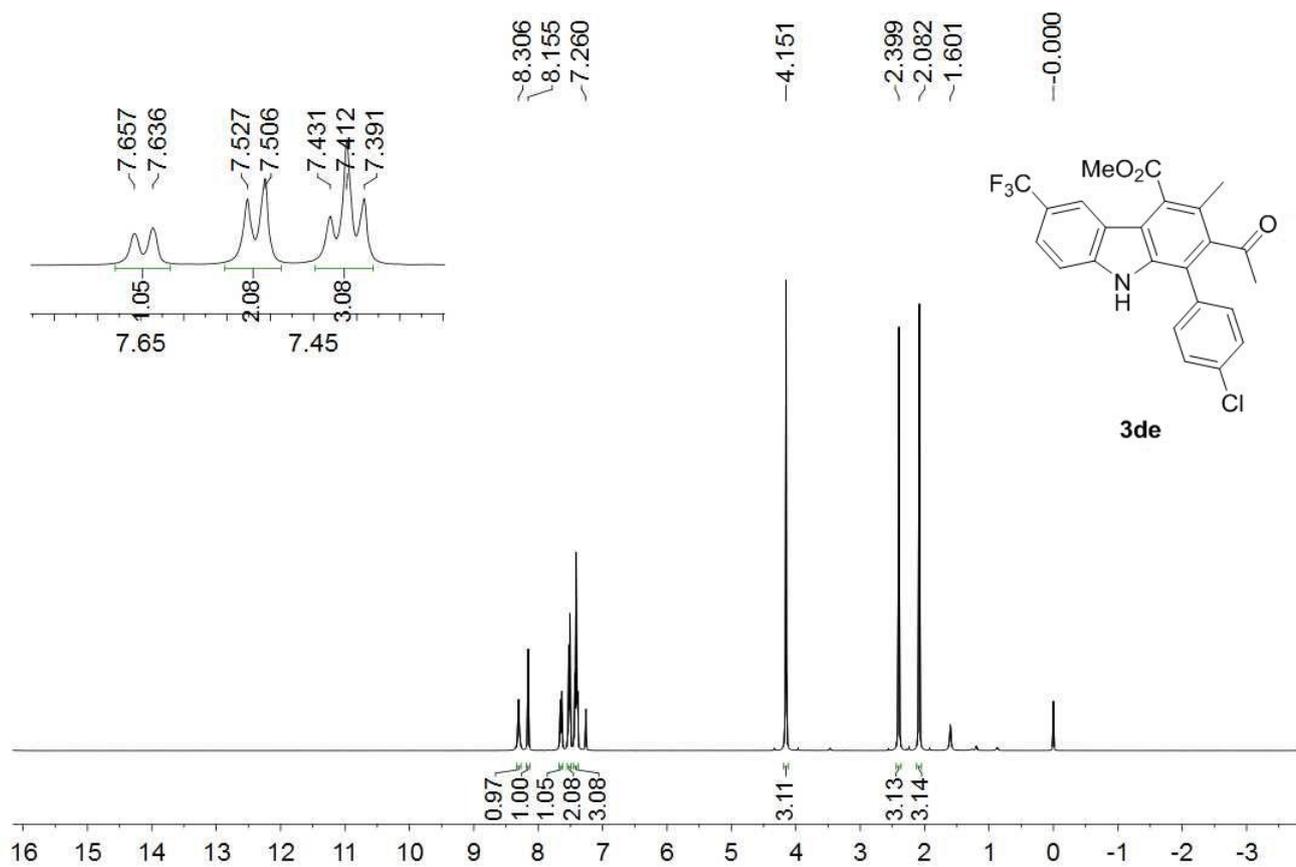
^1H NMR spectrum of the compound **3ce** (400 MHz, CDCl_3)



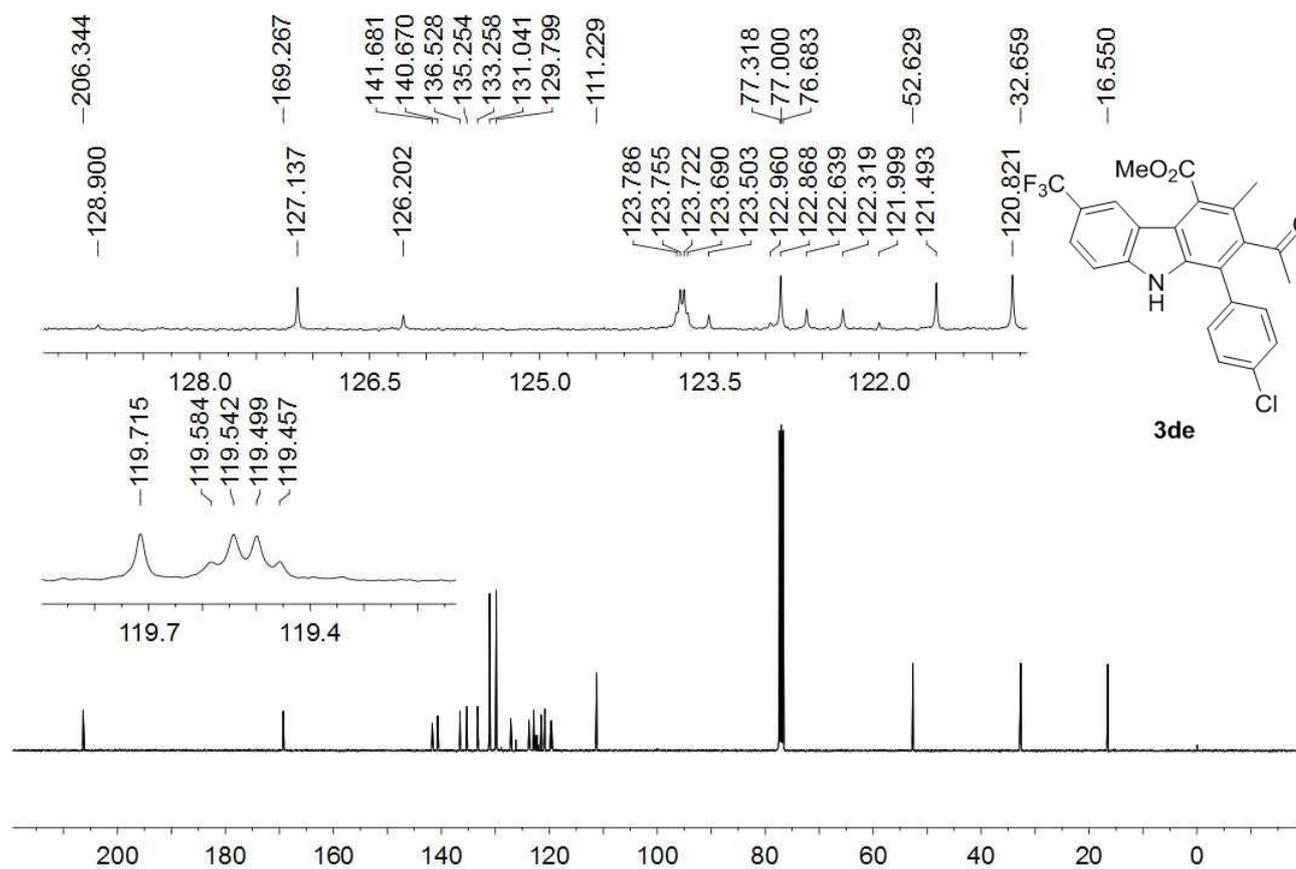
^{13}C NMR spectrum of the compound **3ce** (100 MHz, CDCl_3)



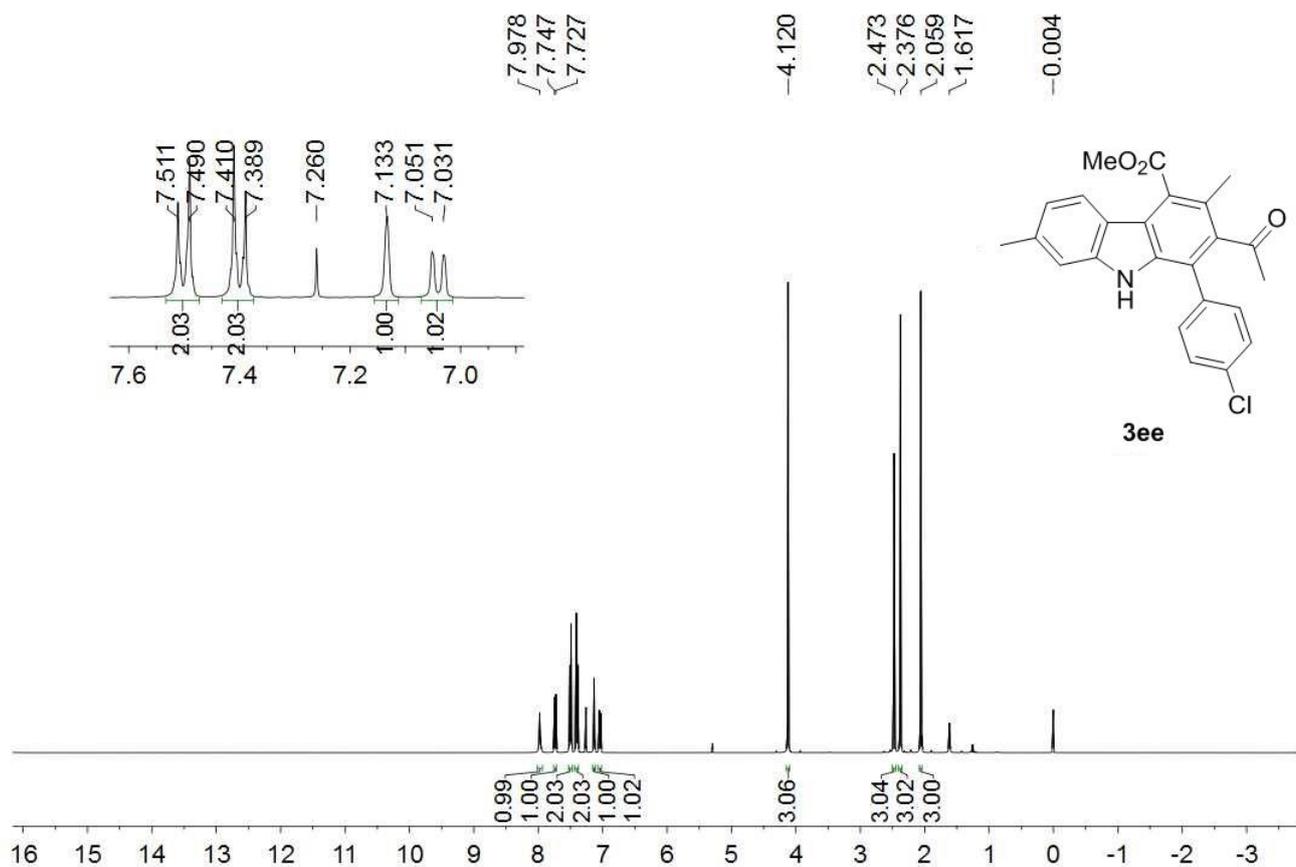
^1H NMR spectrum of the compound **3de** (400 MHz, CDCl_3)



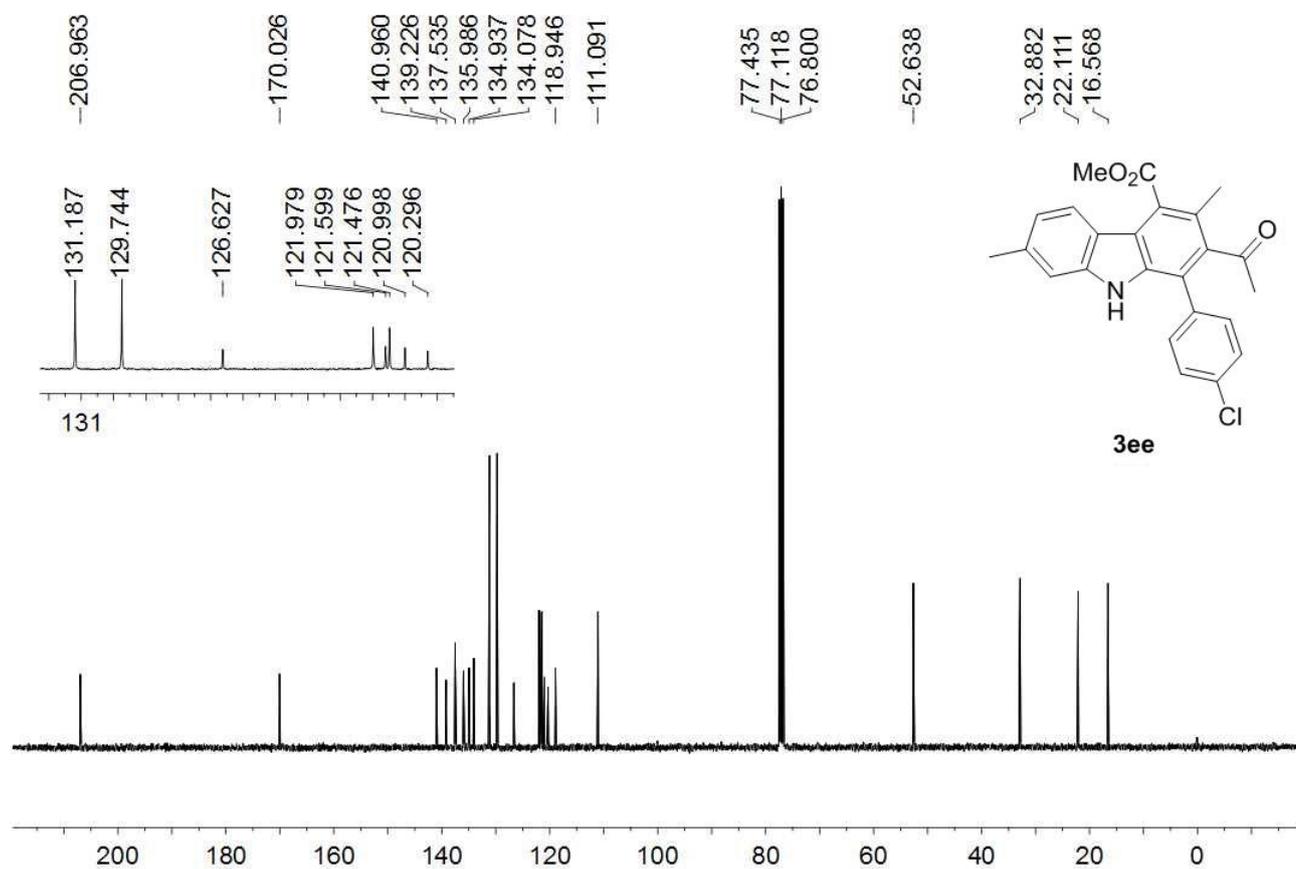
^{13}C NMR spectrum of the compound **3de** (100 MHz, CDCl_3)



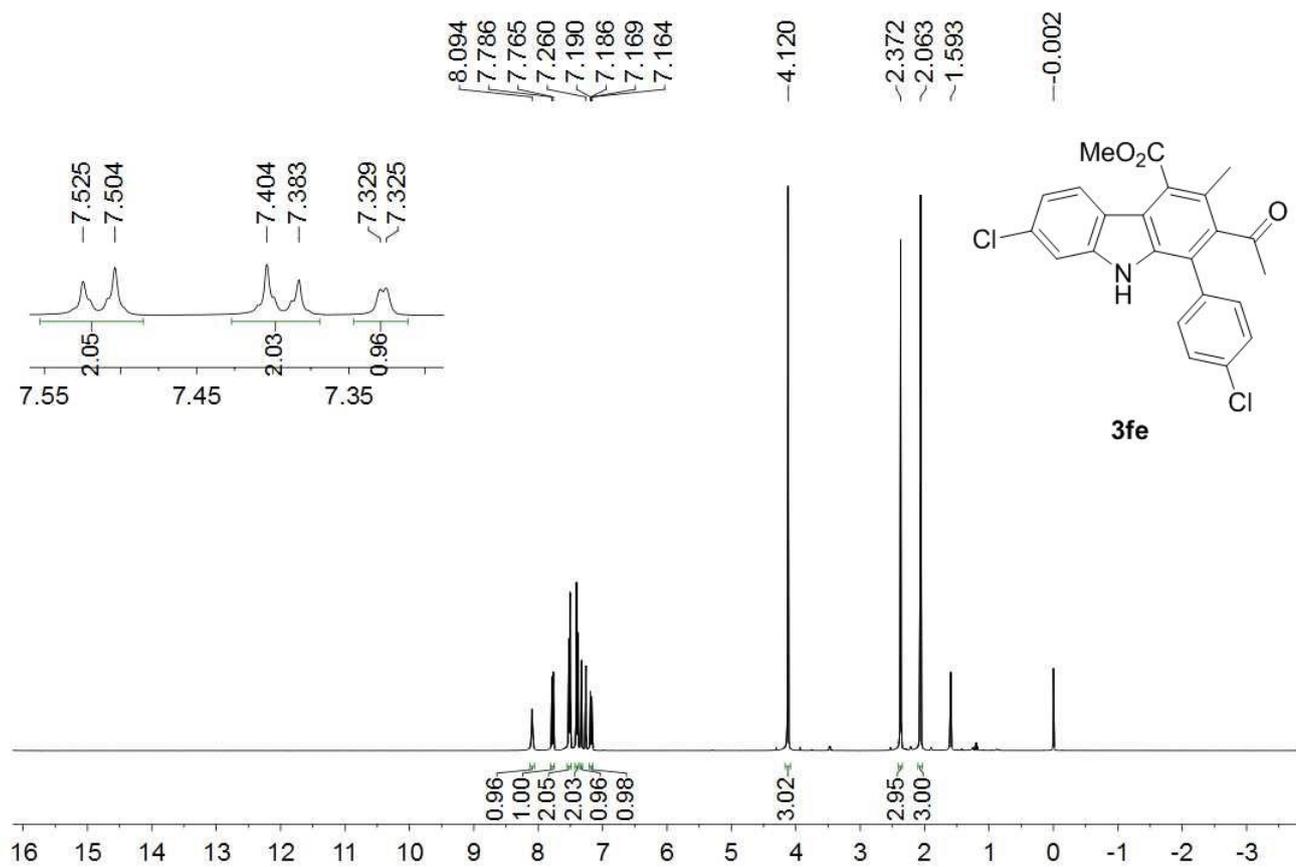
^1H NMR spectrum of the compound **3ee** (400 MHz, CDCl_3)



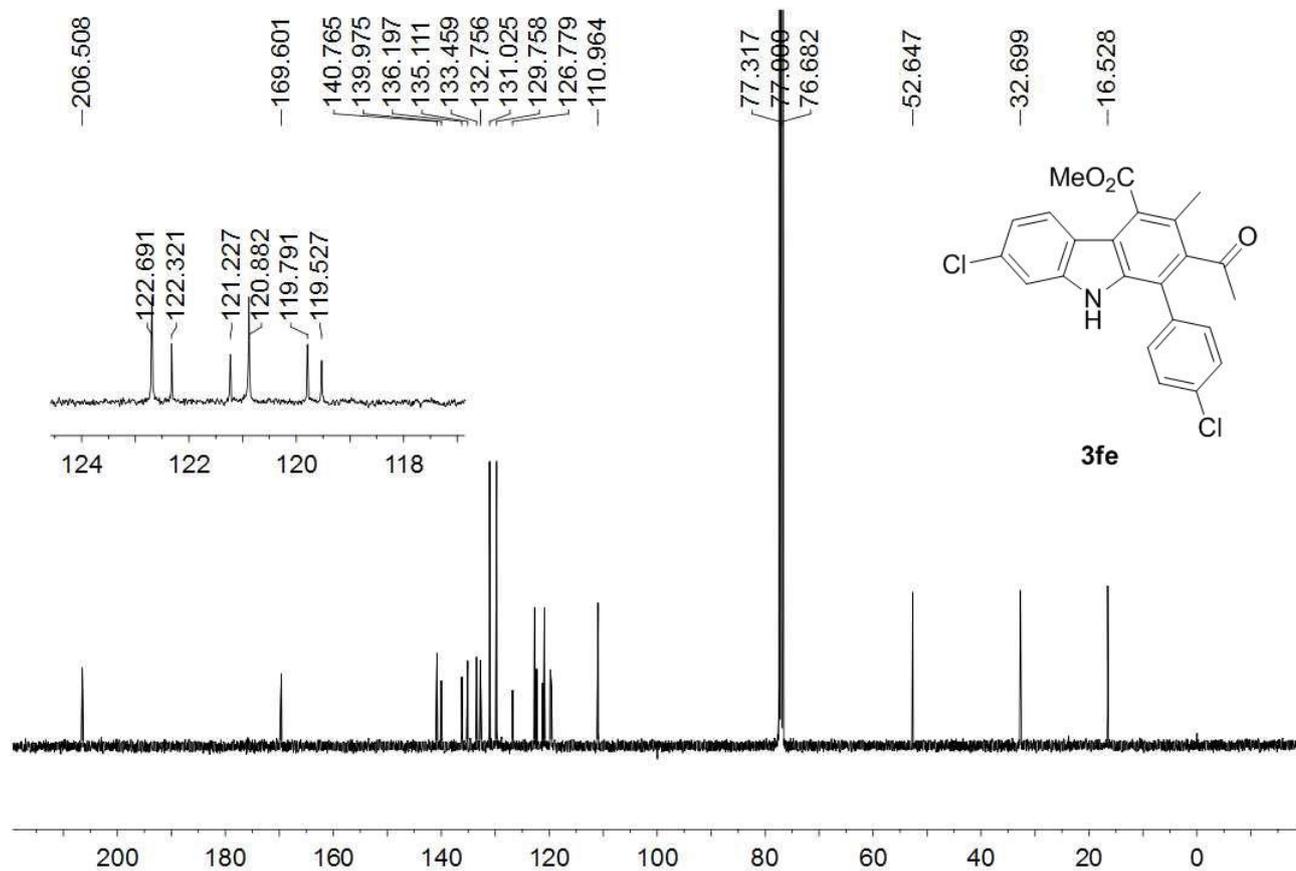
^{13}C NMR spectrum of the compound **3ee** (100 MHz, CDCl_3)



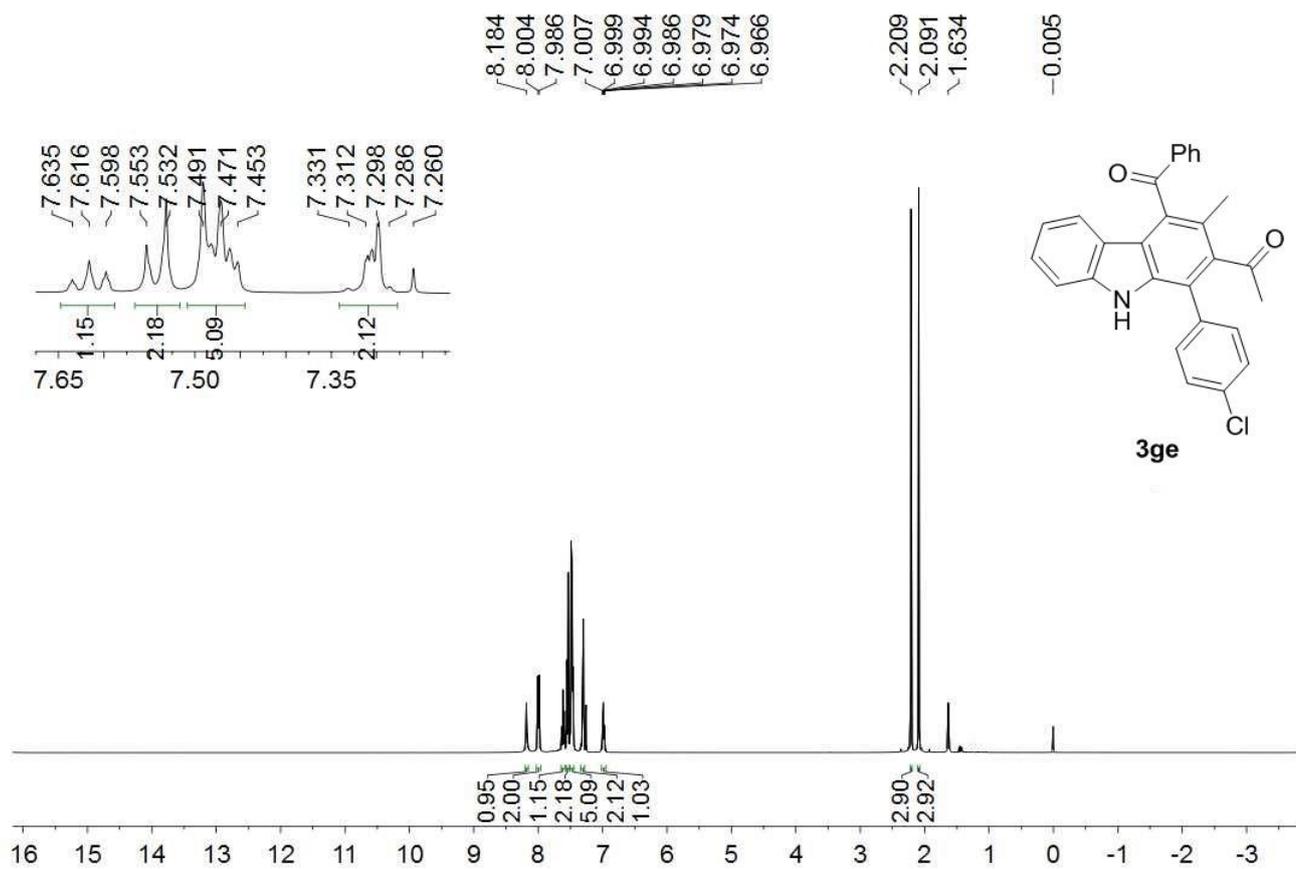
^1H NMR spectrum of the compound **3fe** (400 MHz, CDCl_3)



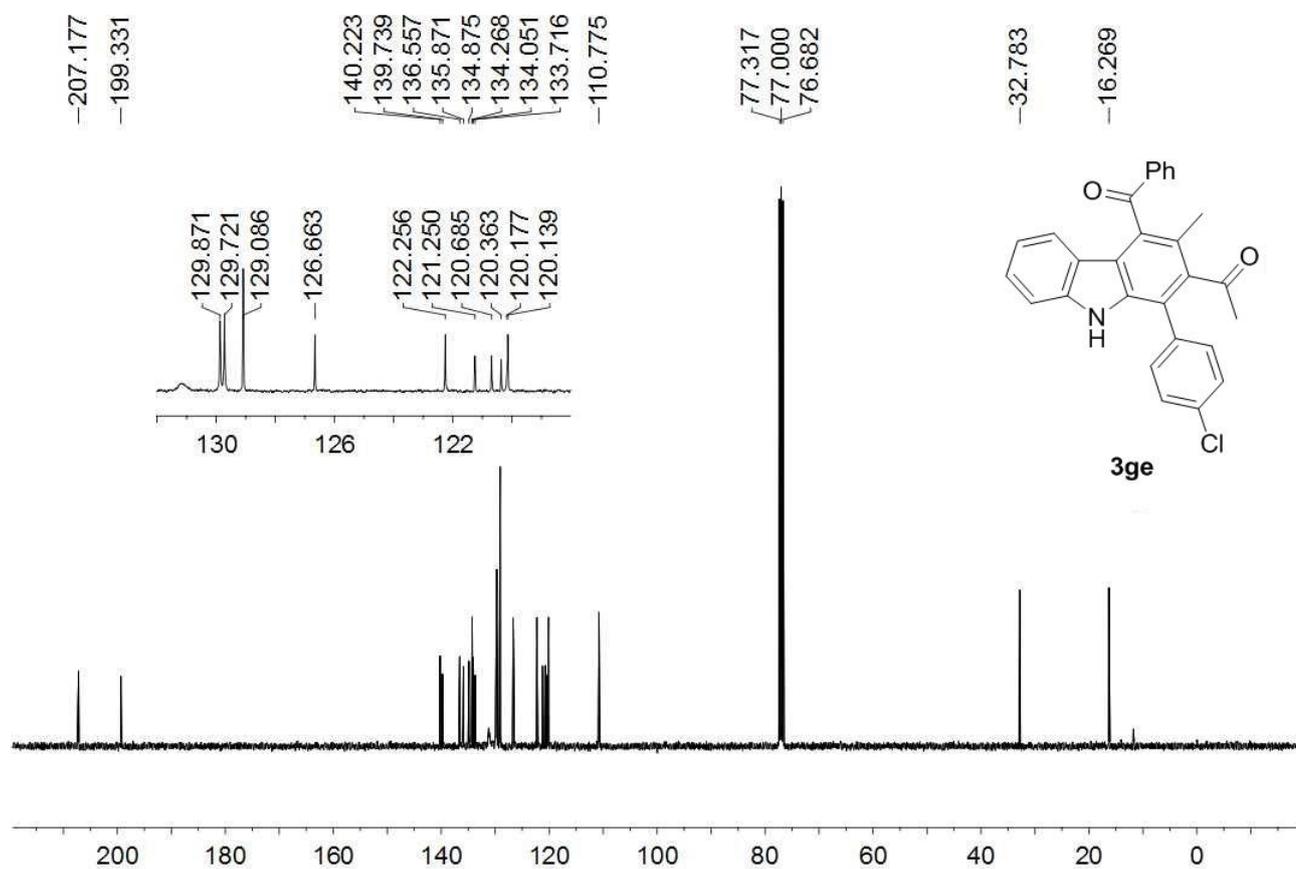
^{13}C NMR spectrum of the compound **3fe** (100 MHz, CDCl_3)



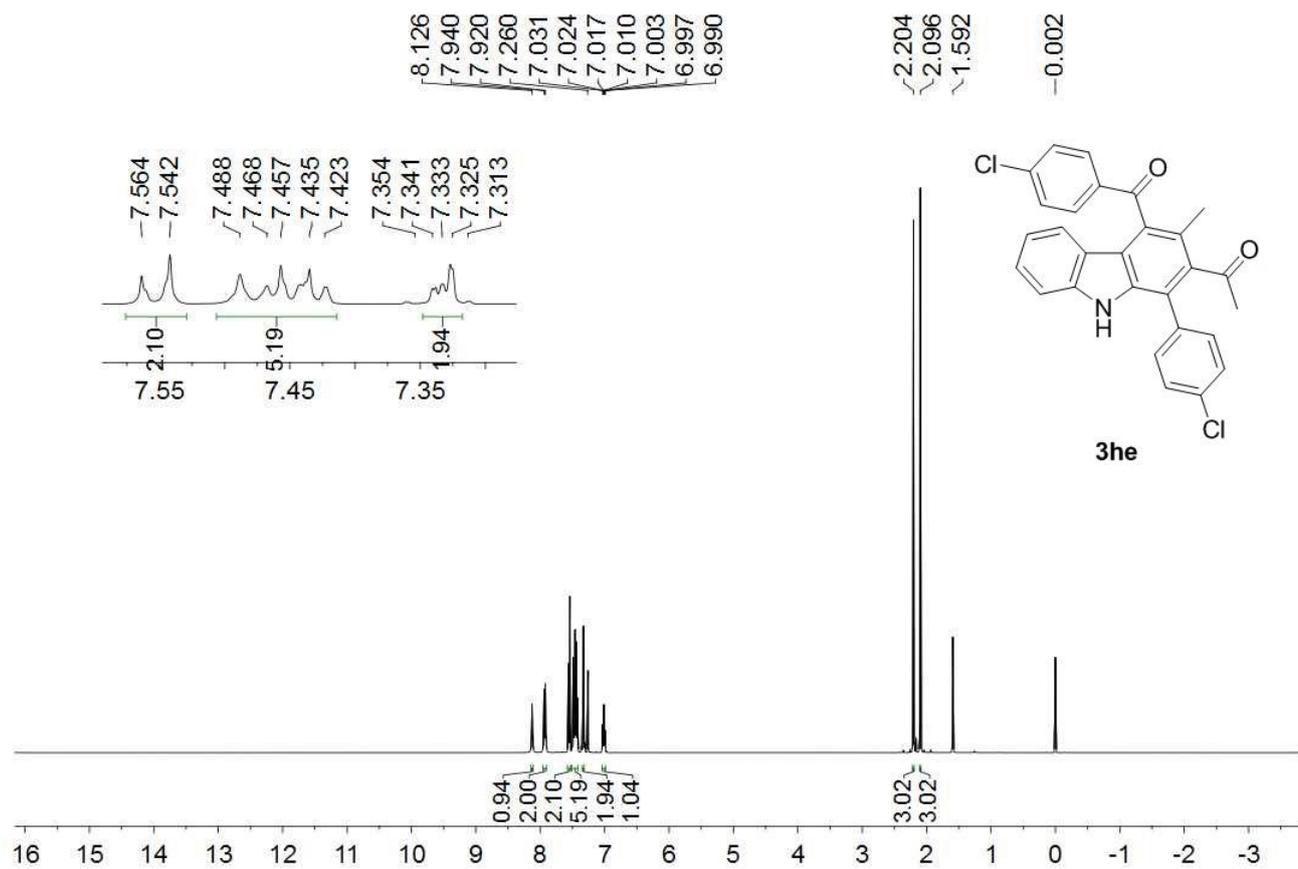
^1H NMR spectrum of the compound **3ge** (400 MHz, CDCl_3)



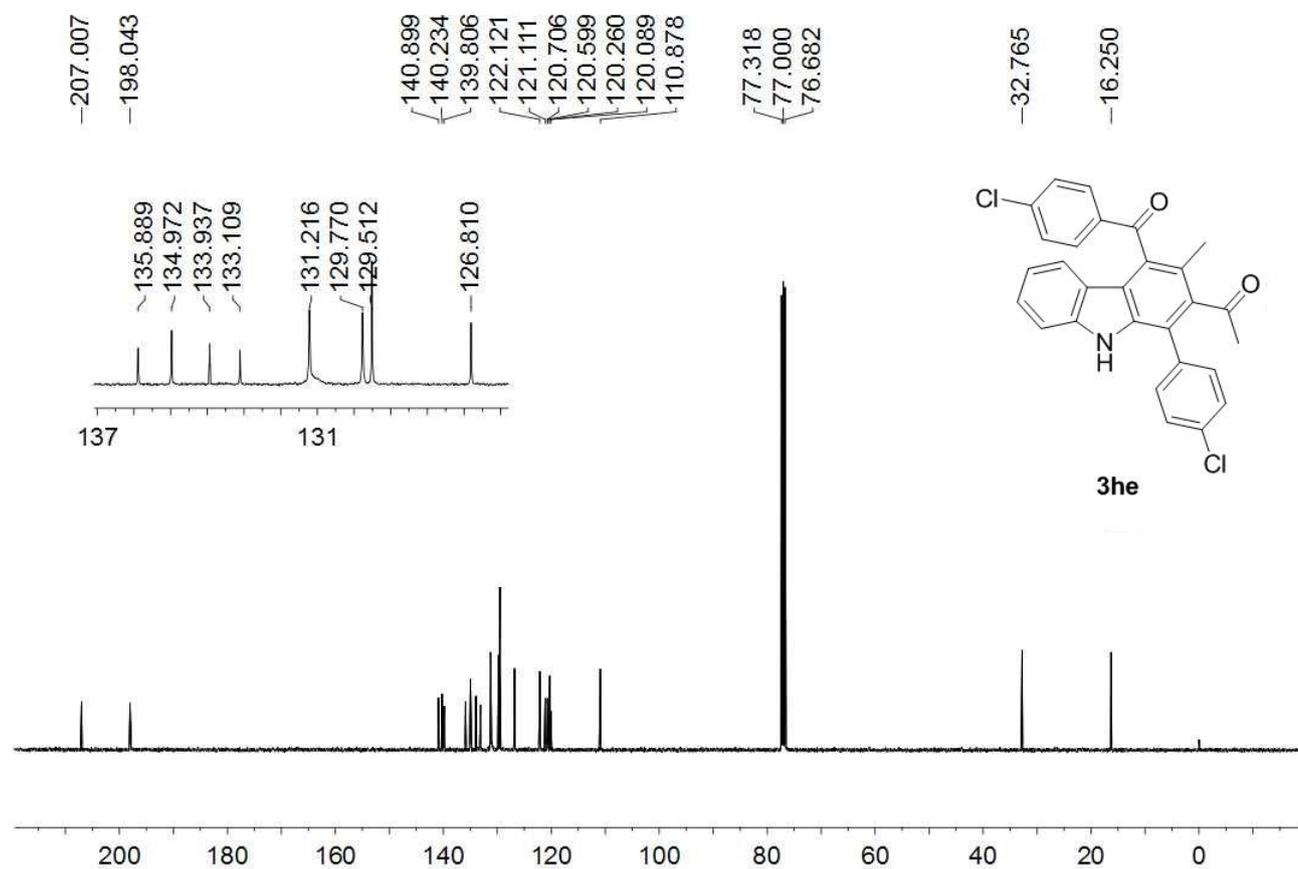
^{13}C NMR spectrum of the compound **3ge** (100 MHz, CDCl_3)



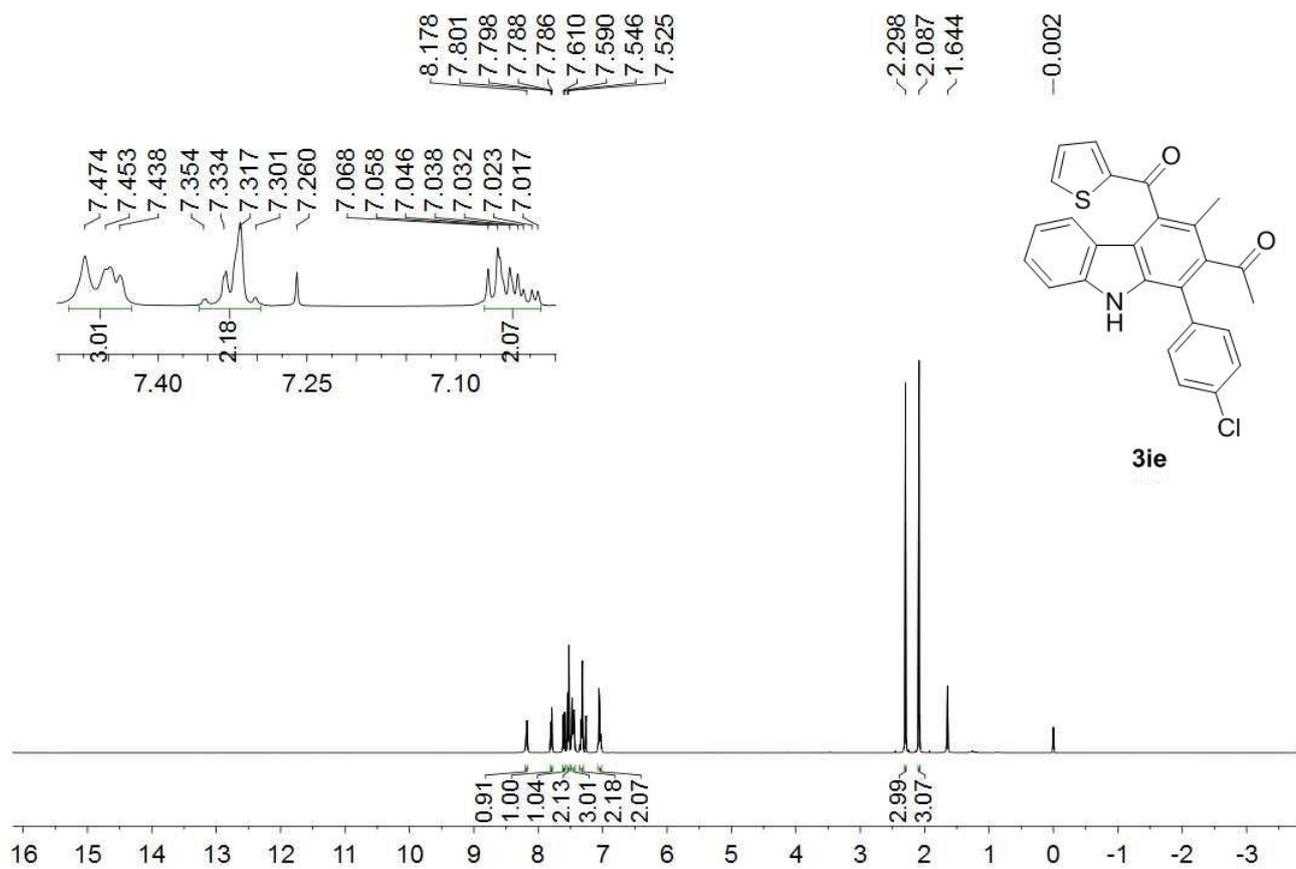
^1H NMR spectrum of the compound **3he** (400 MHz, CDCl_3)



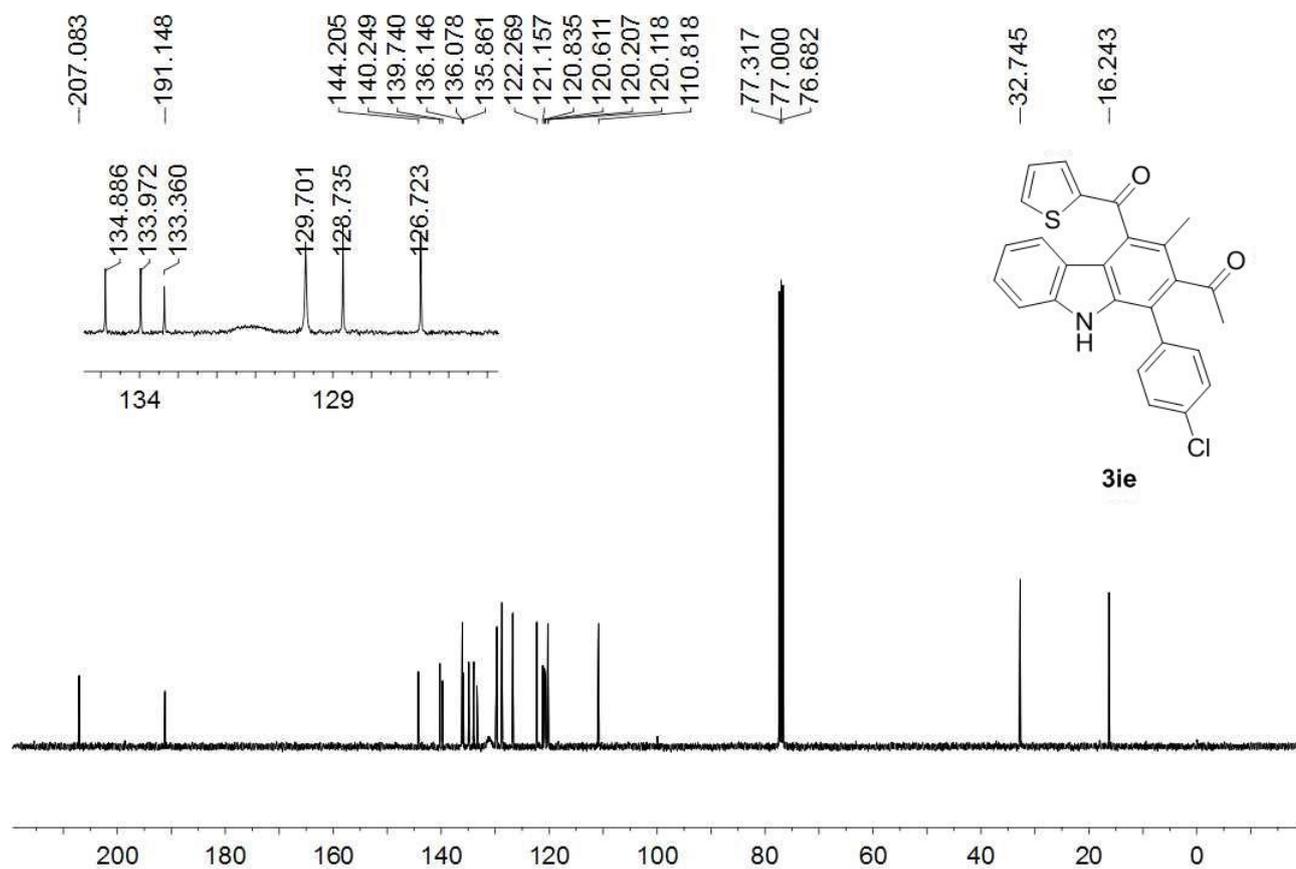
^{13}C NMR spectrum of the compound **3he** (100 MHz, CDCl_3)



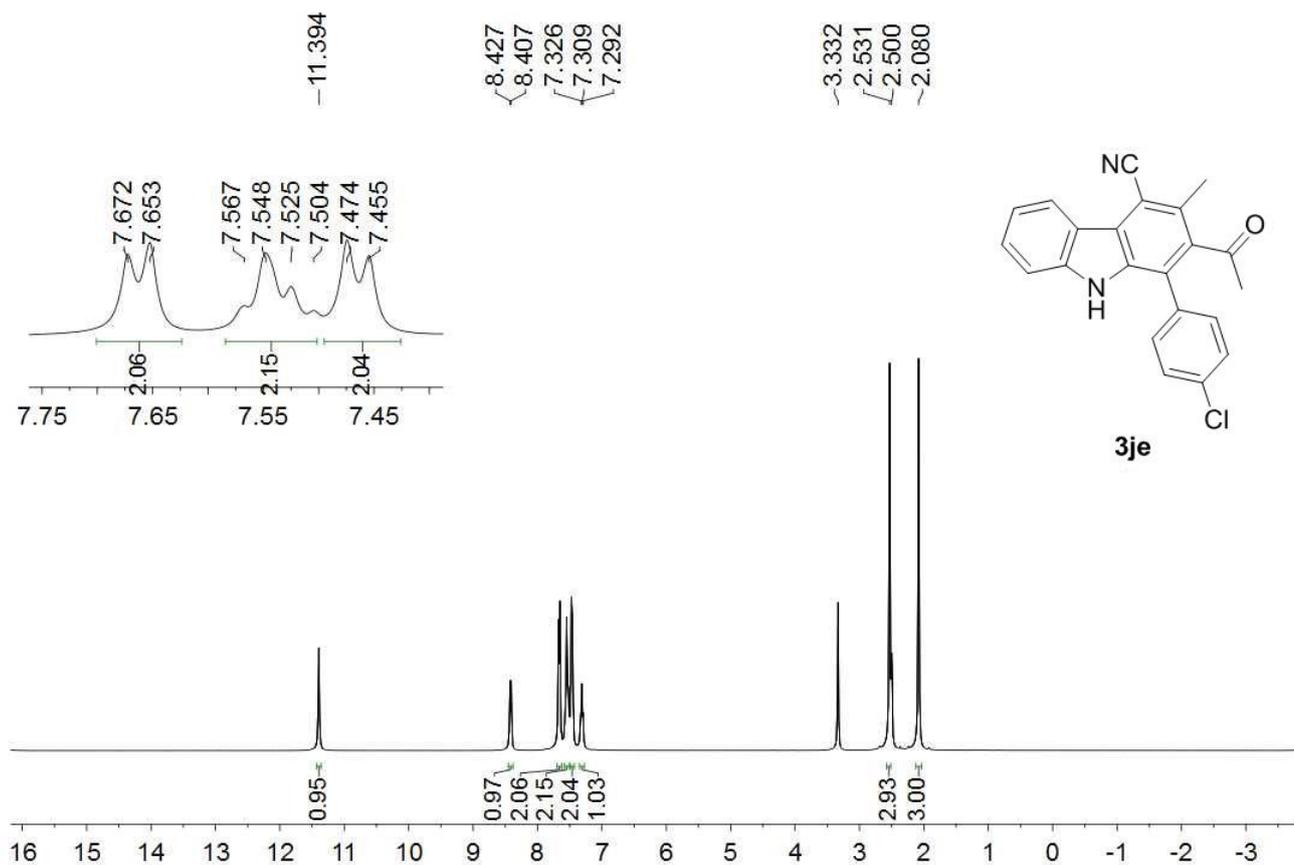
^1H NMR spectrum of the compound **3ie** (400 MHz, CDCl_3)



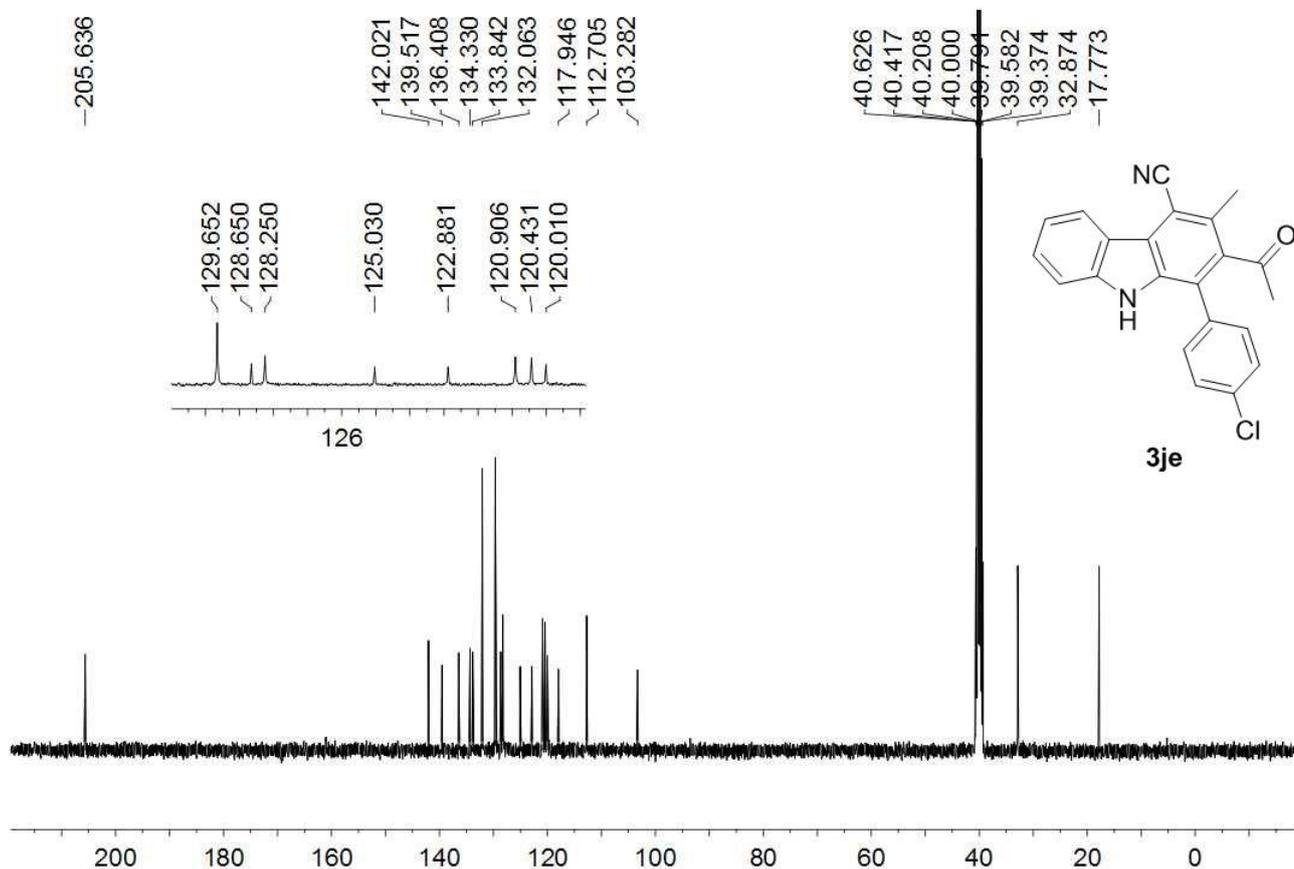
^{13}C NMR spectrum of the compound **3ie** (100 MHz, CDCl_3)



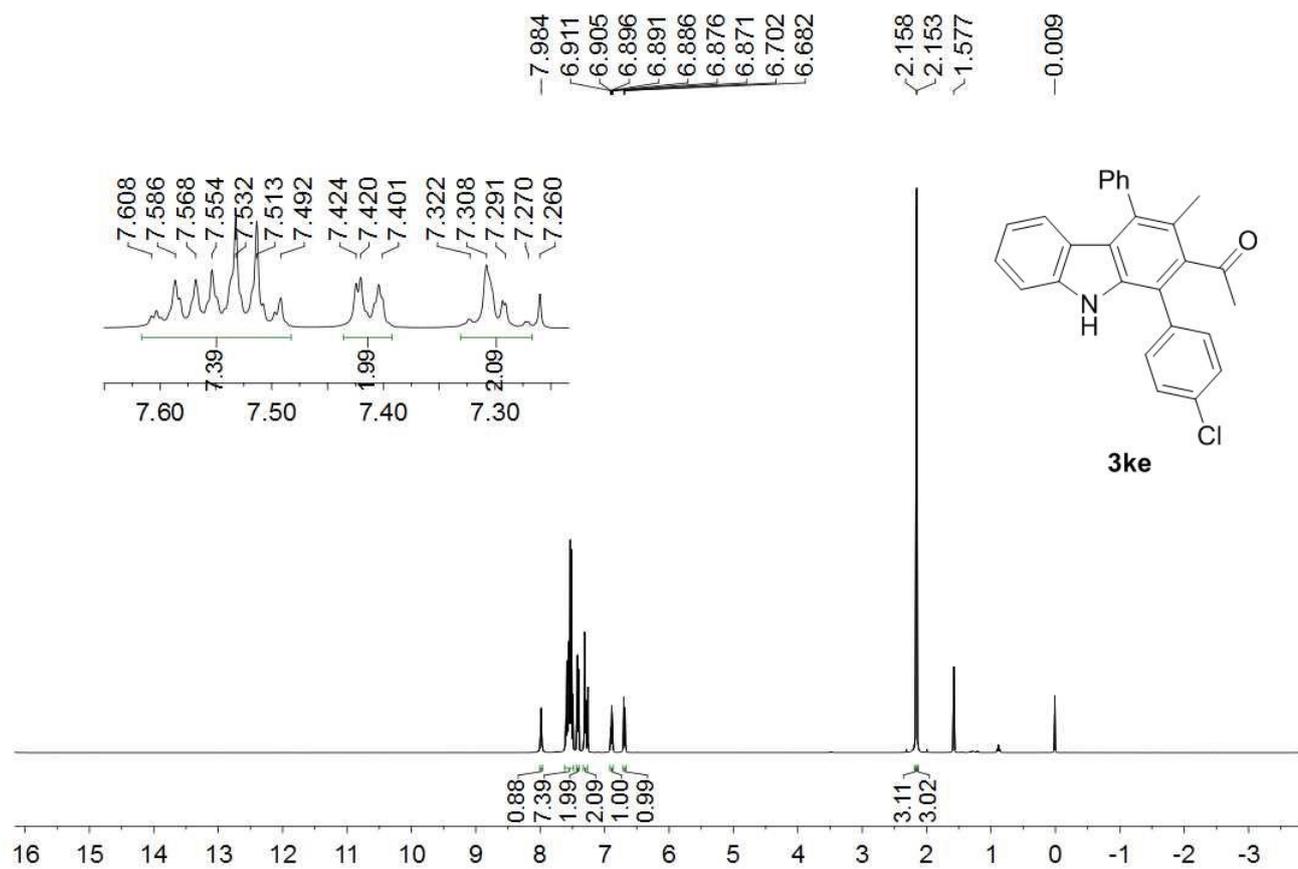
¹H NMR spectrum of the compound 3je (400 MHz, DMSO-*d*₆)



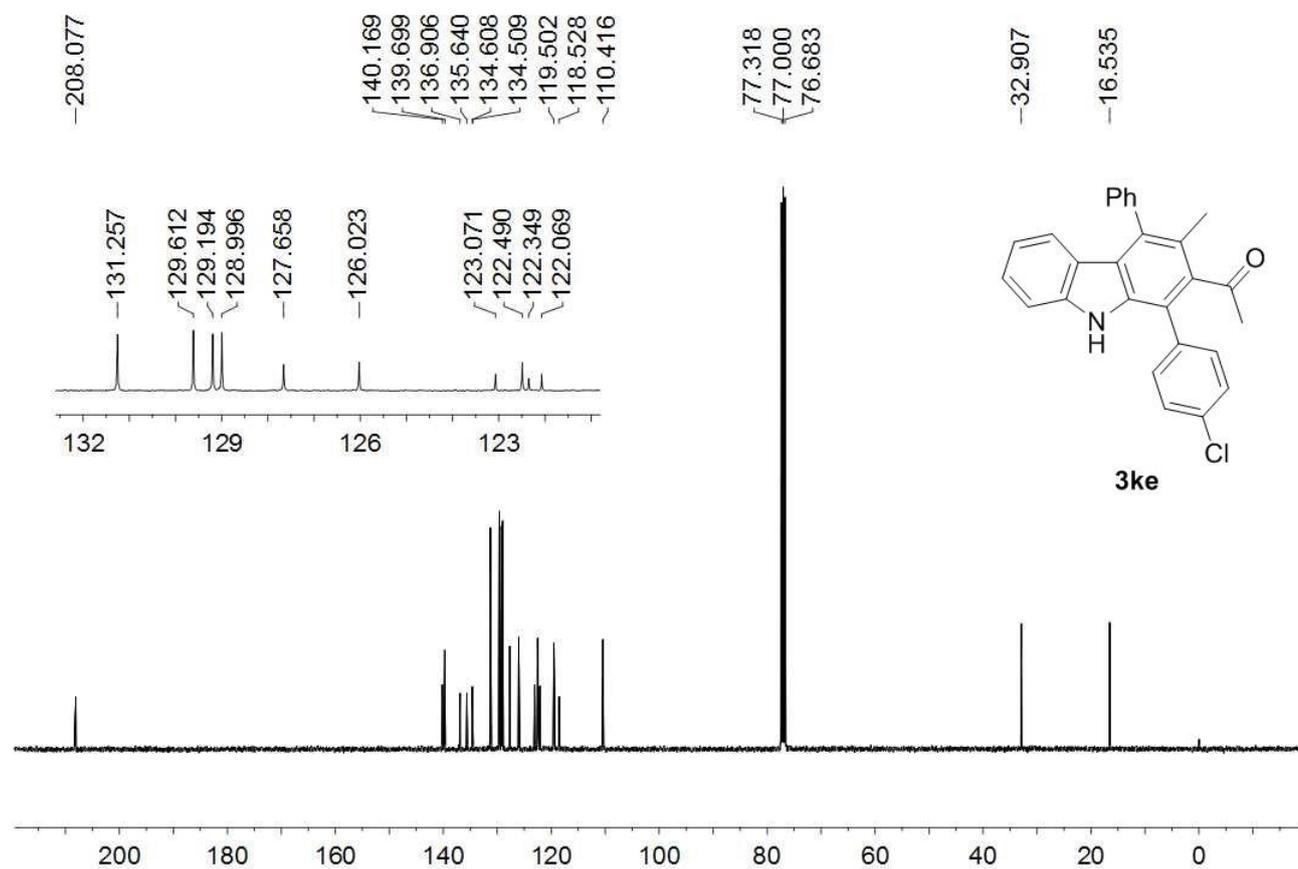
¹³C NMR spectrum of the compound 3je (100 MHz, DMSO-*d*₆)



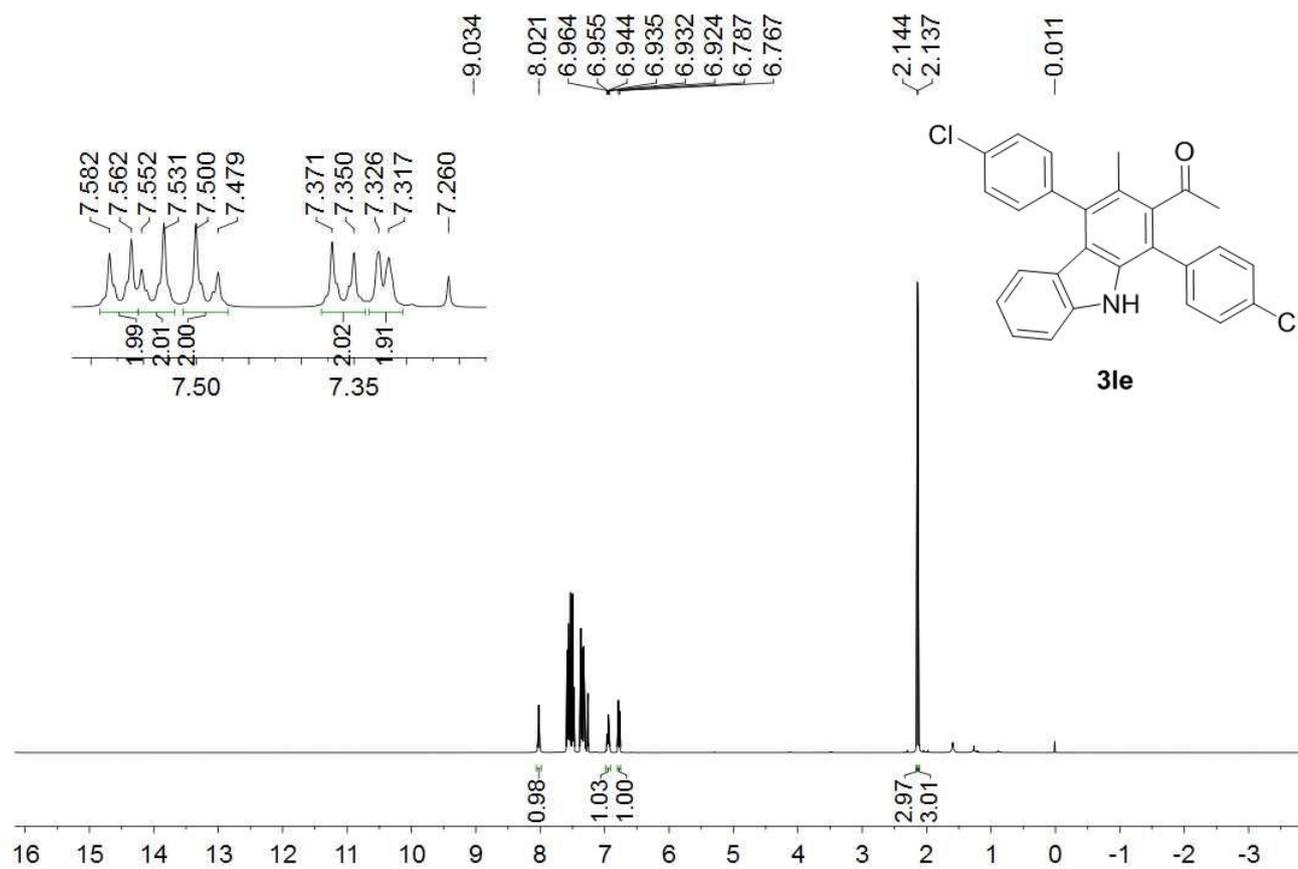
^1H NMR spectrum of the compound **3ke** (400 MHz, CDCl_3)



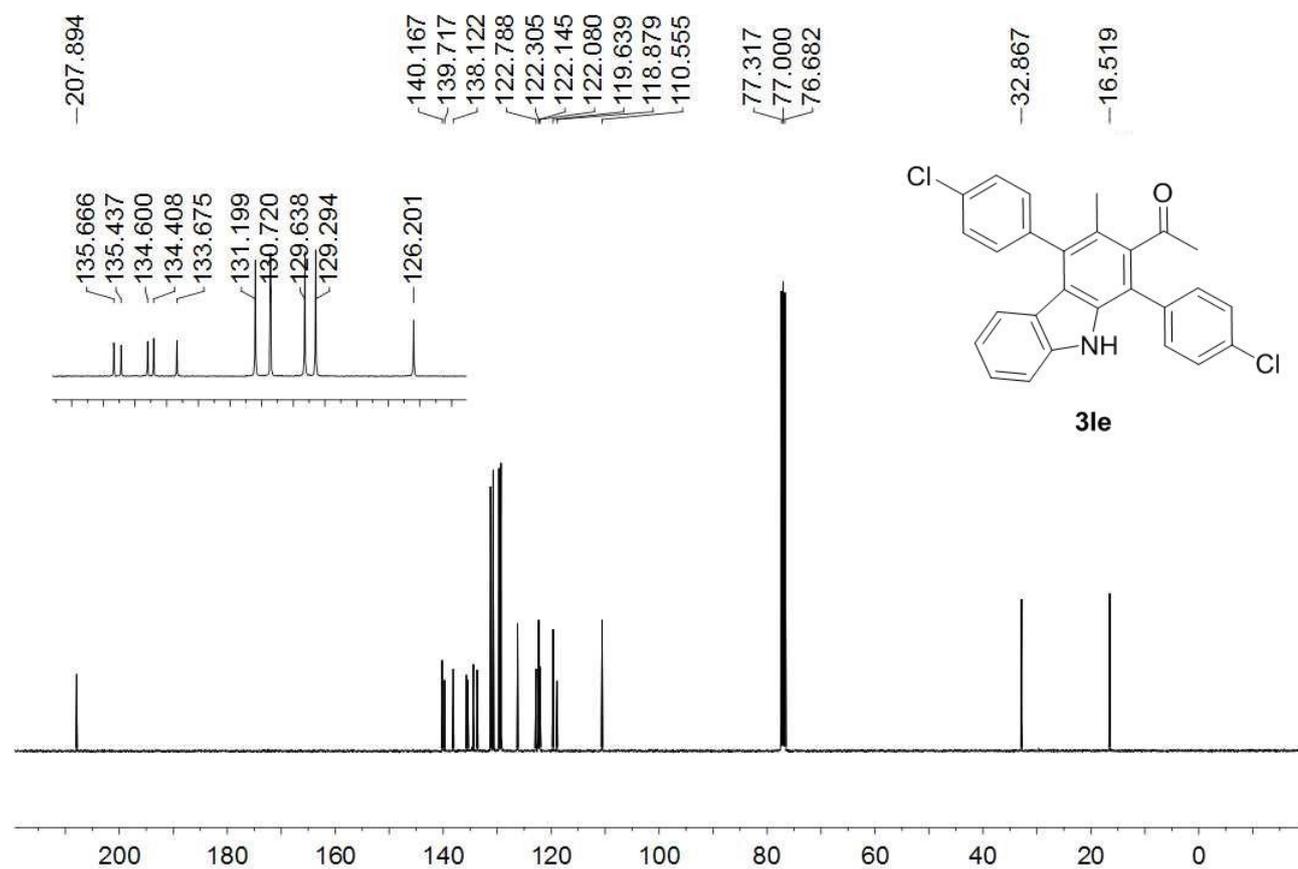
^{13}C NMR spectrum of the compound **3ke** (100 MHz, CDCl_3)



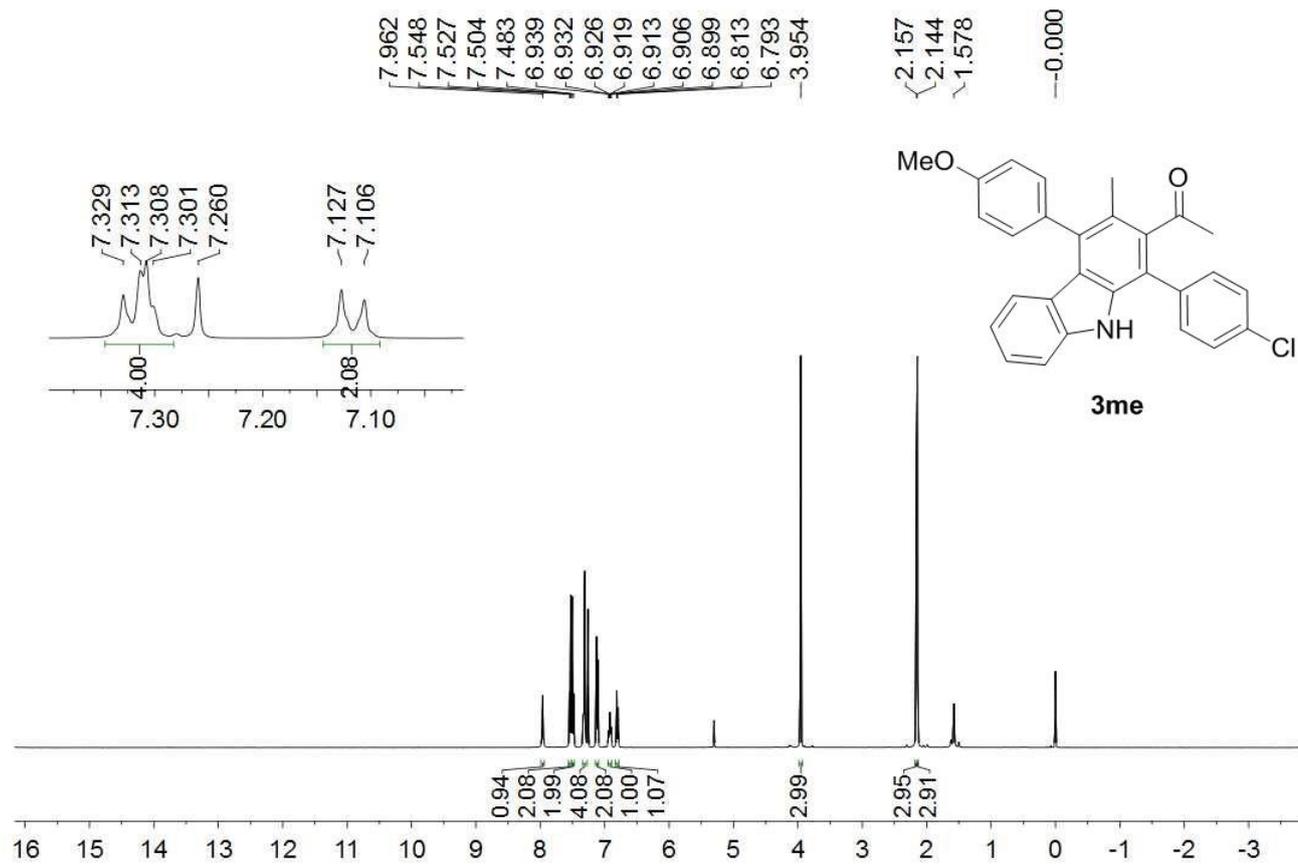
^1H NMR spectrum of the compound **3le** (400 MHz, CDCl_3)



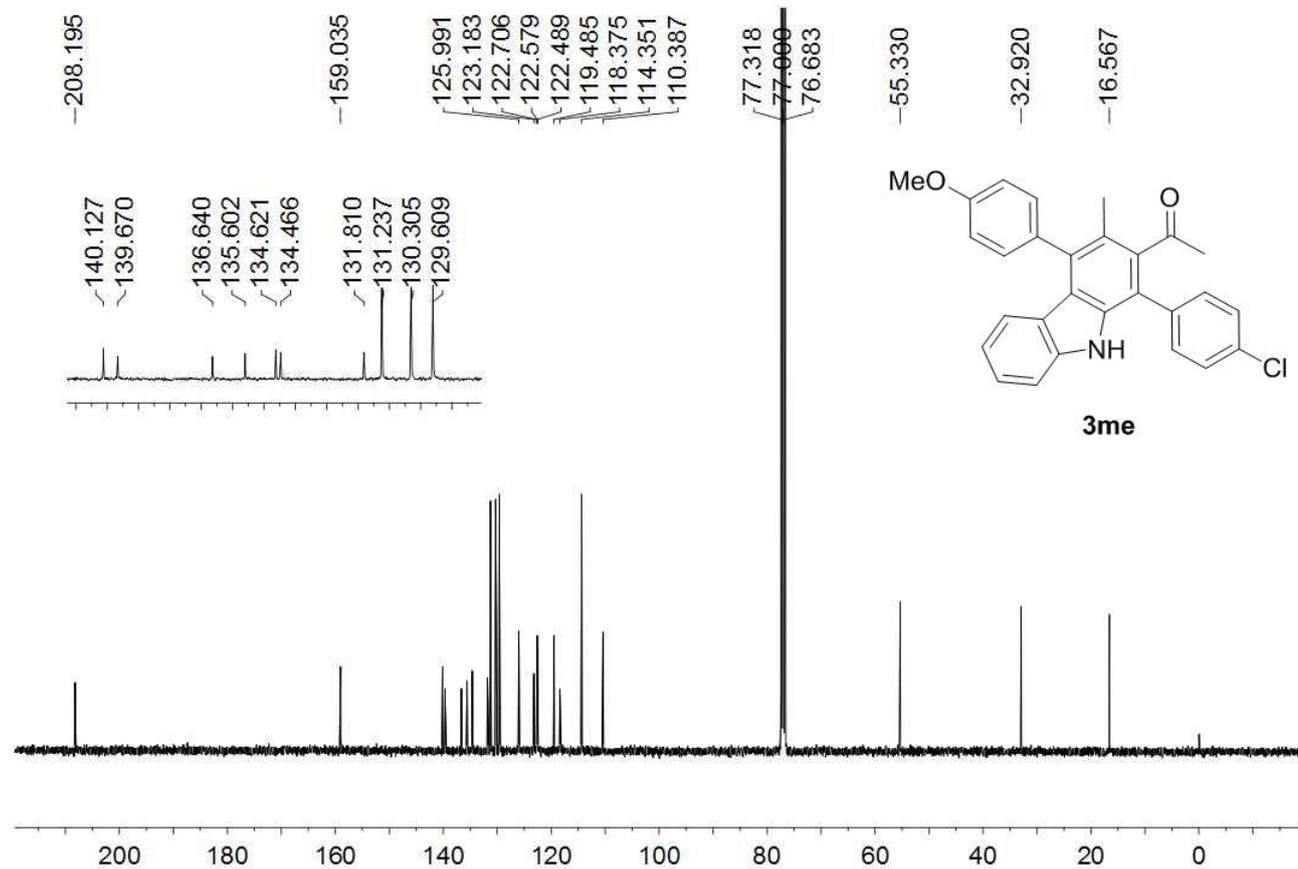
^{13}C NMR spectrum of the compound **3le** (100 MHz, CDCl_3)



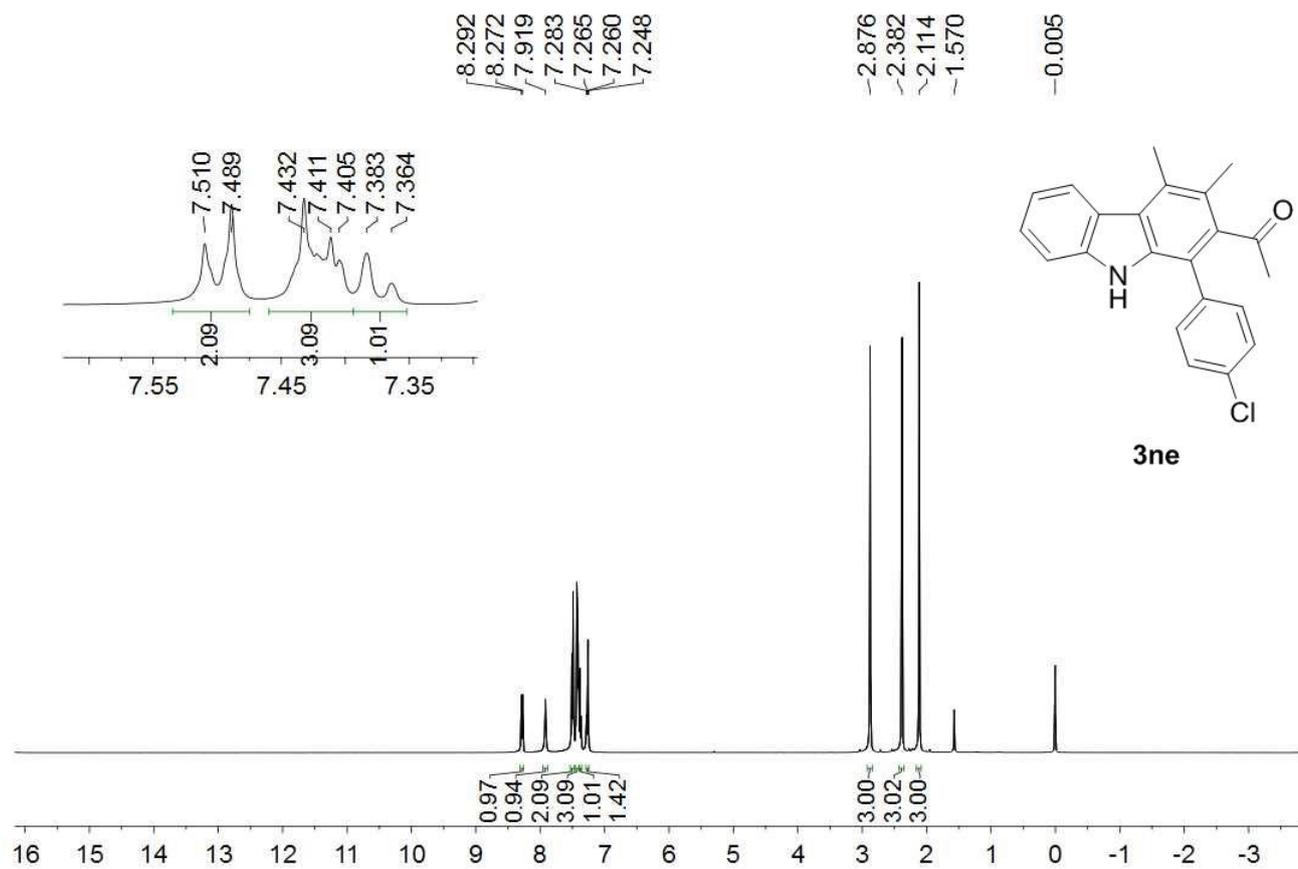
^1H NMR spectrum of the compound **3me** (400 MHz, CDCl_3)



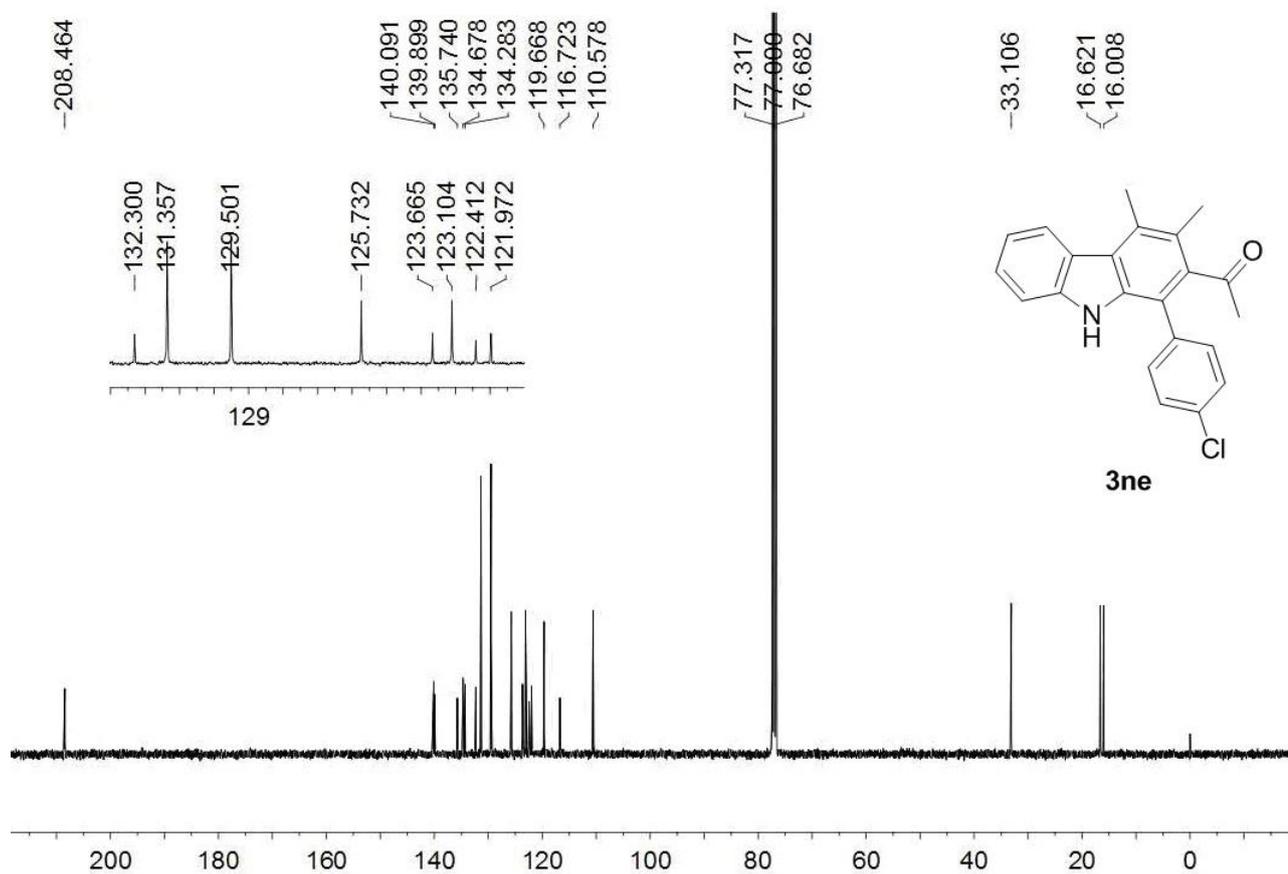
^{13}C NMR spectrum of the compound **3me** (100 MHz, CDCl_3)



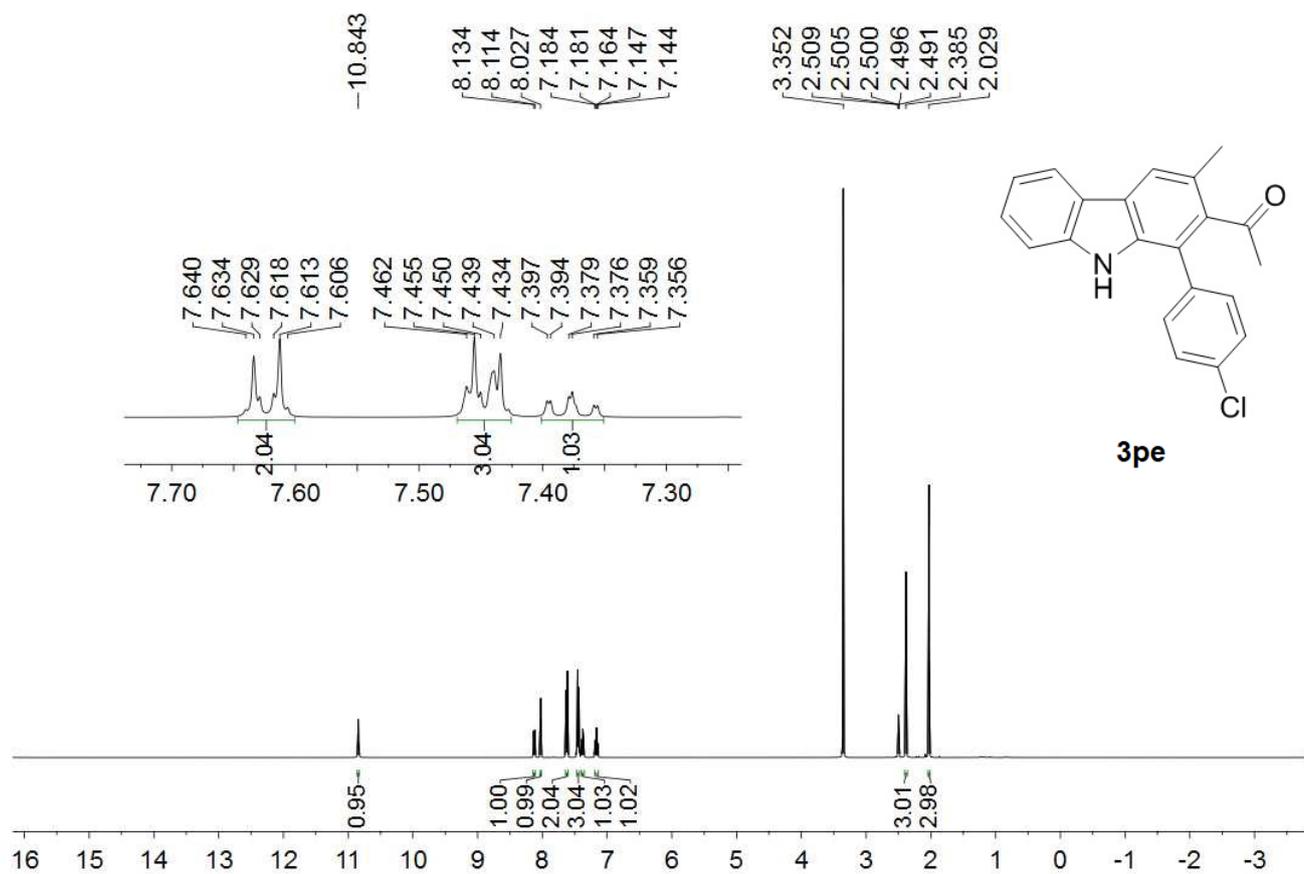
^1H NMR spectrum of the compound **3ne** (400 MHz, CDCl_3)



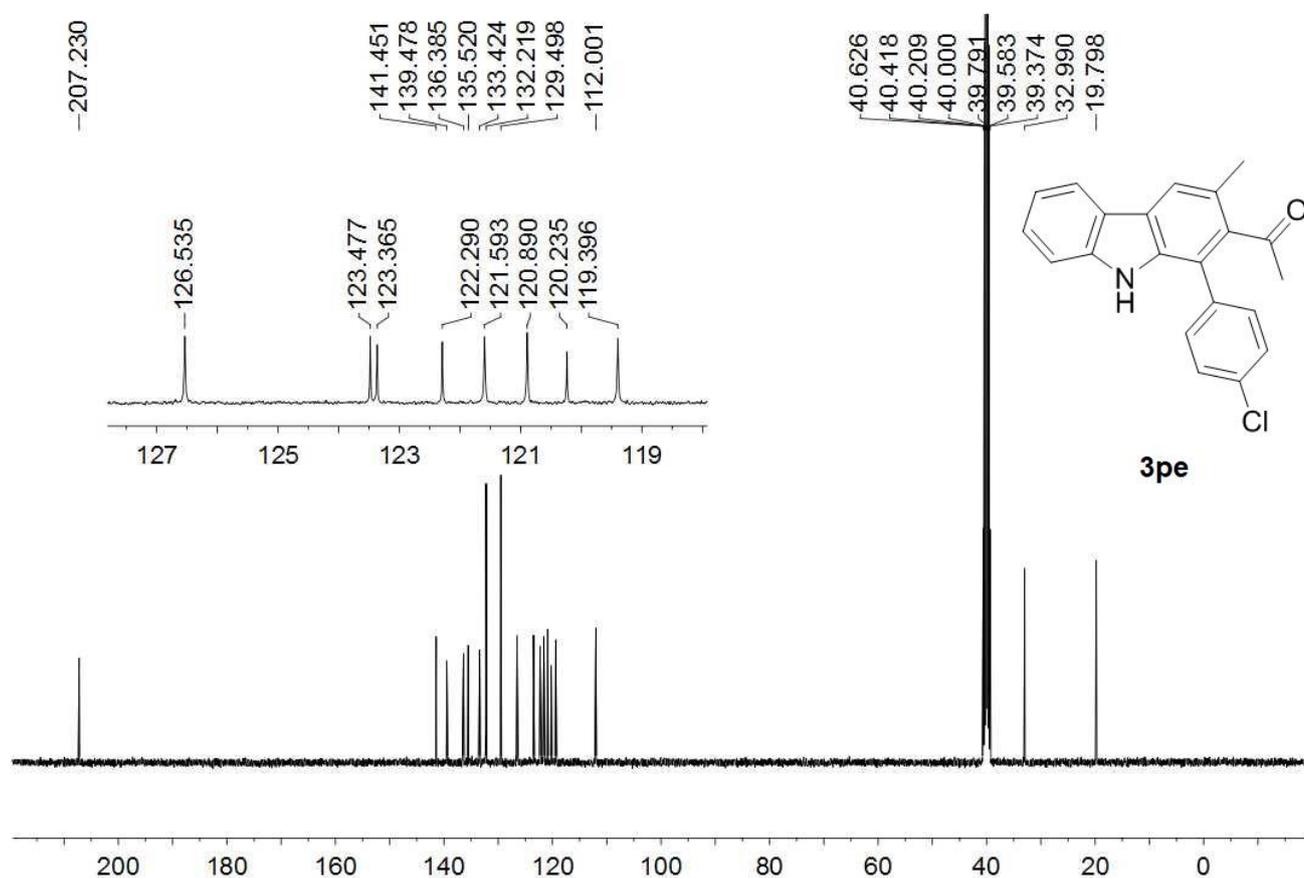
^{13}C NMR spectrum of the compound **3ne** (100 MHz, CDCl_3)



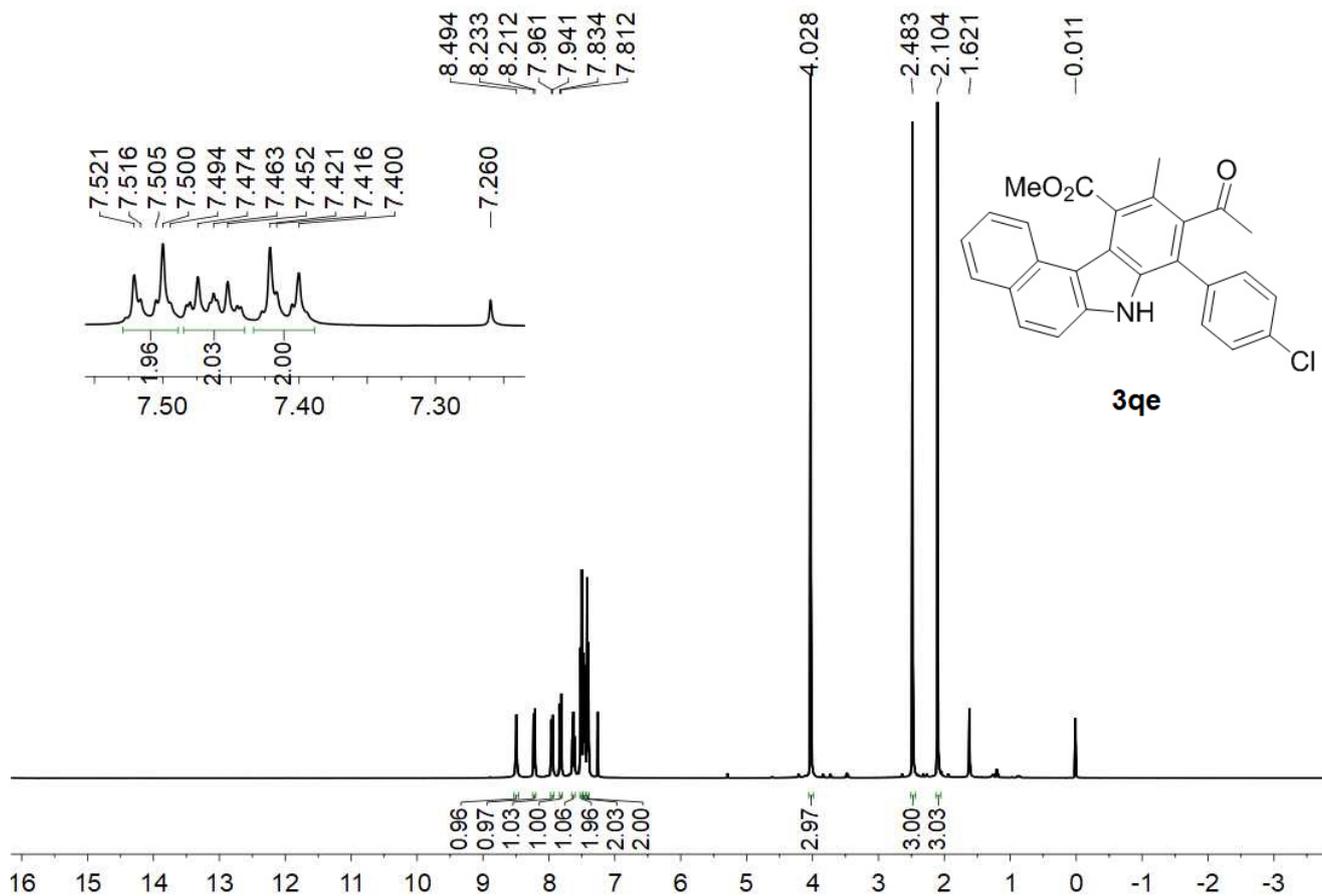
^1H NMR spectrum of the compound **3pe** (400 MHz, CDCl_3)



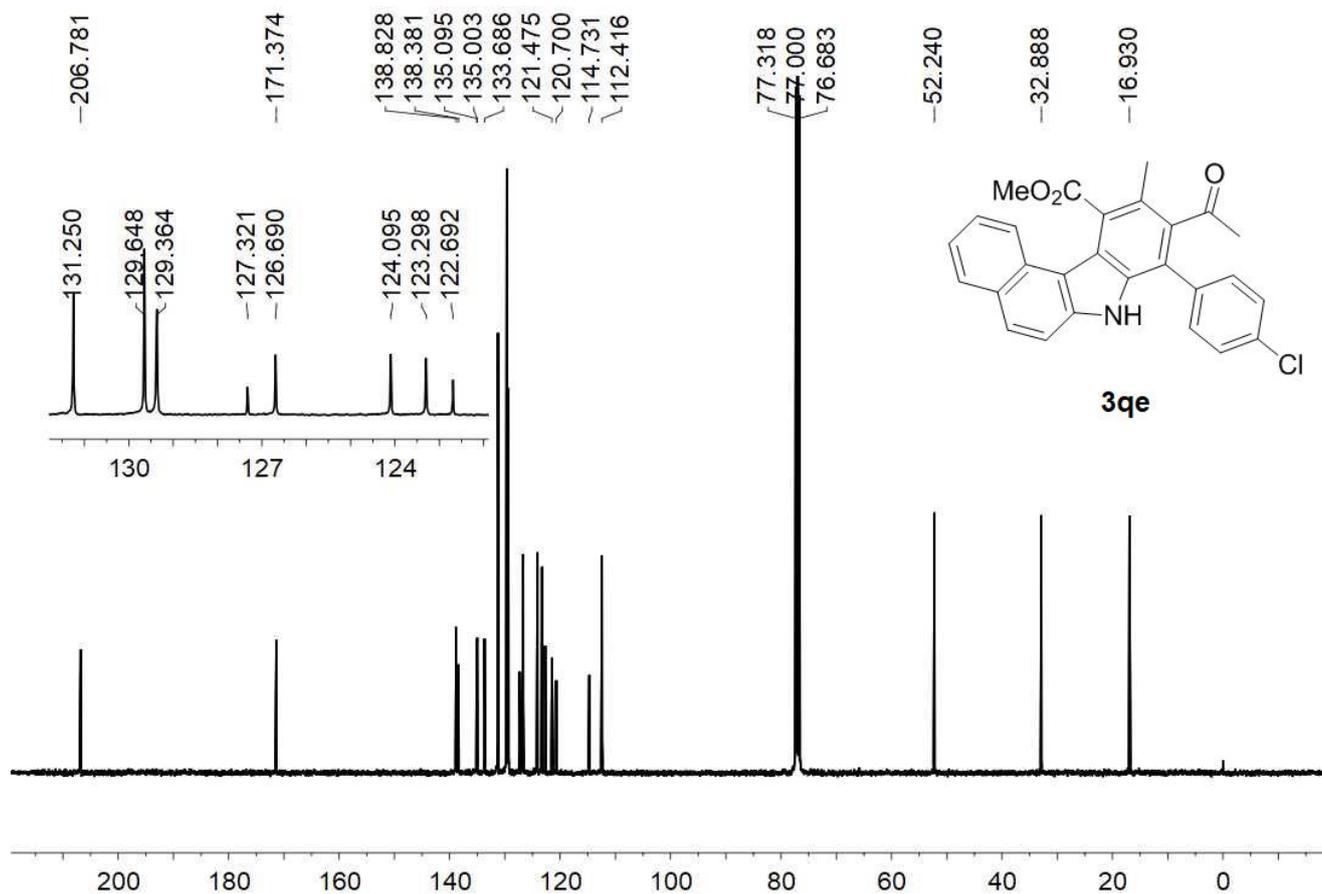
^{13}C NMR spectrum of the compound **3pe** (100 MHz, CDCl_3)



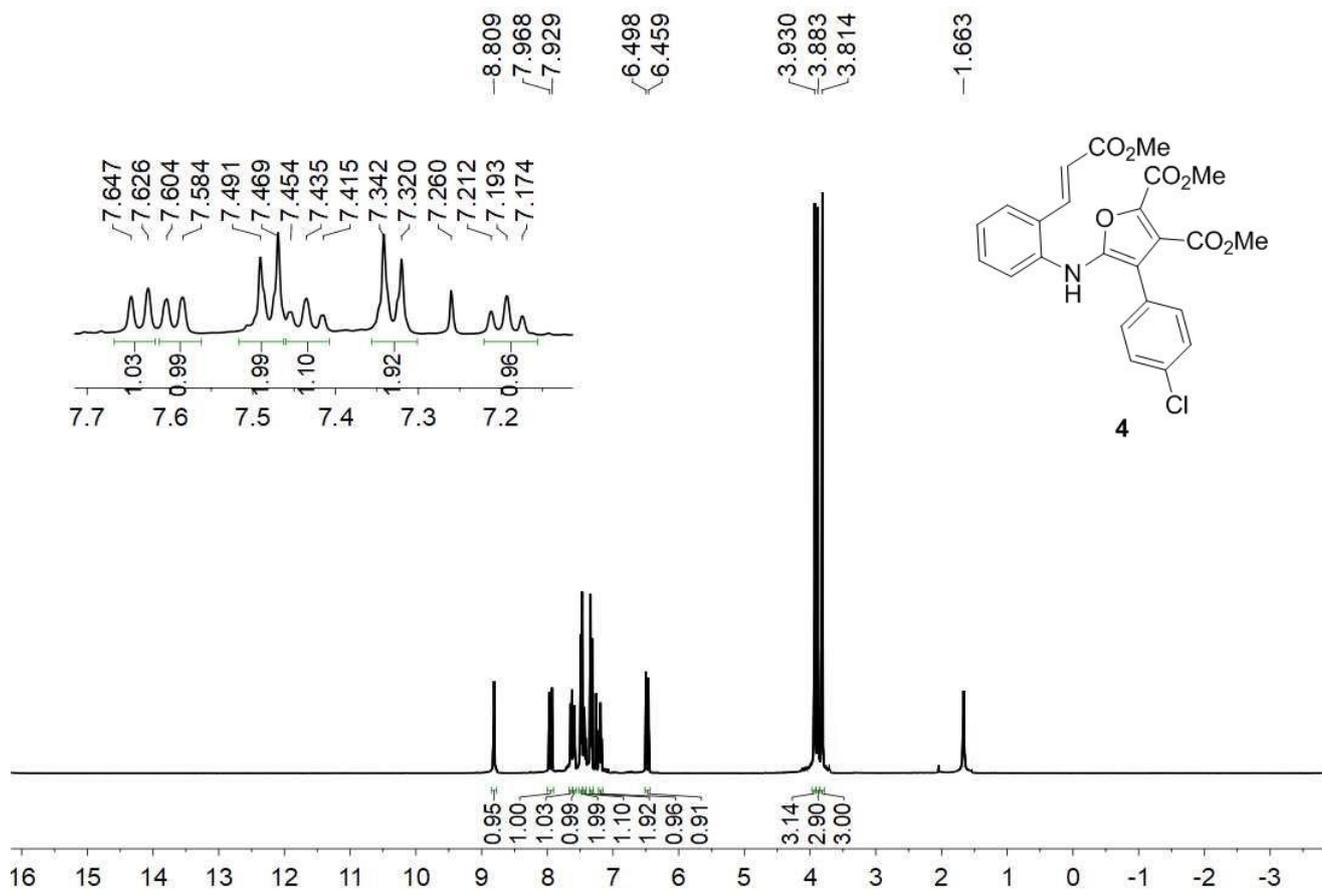
¹H NMR spectrum of the compound **3qe** (400 MHz, CDCl₃)



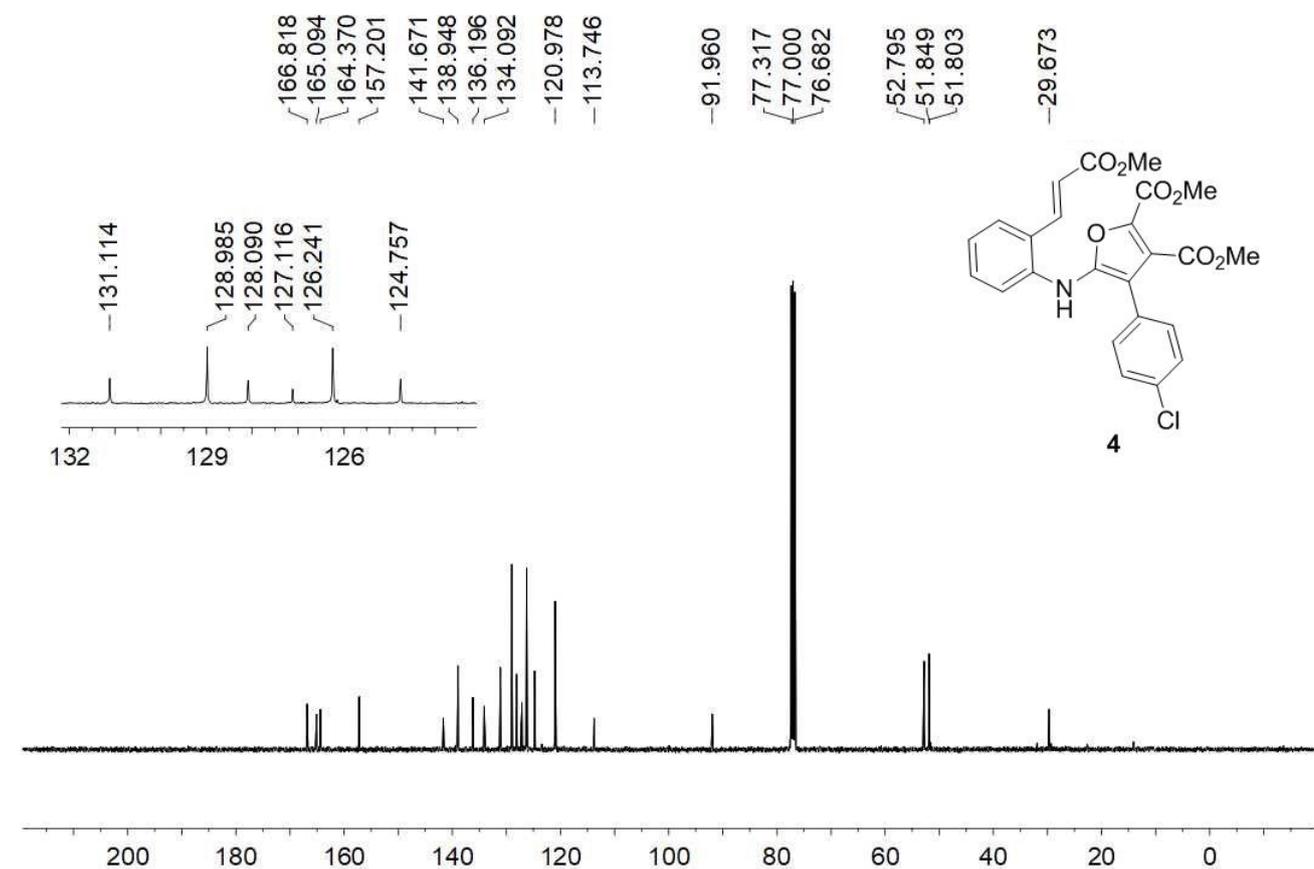
¹³C NMR spectrum of the compound **3qe** (100 MHz, CDCl₃)



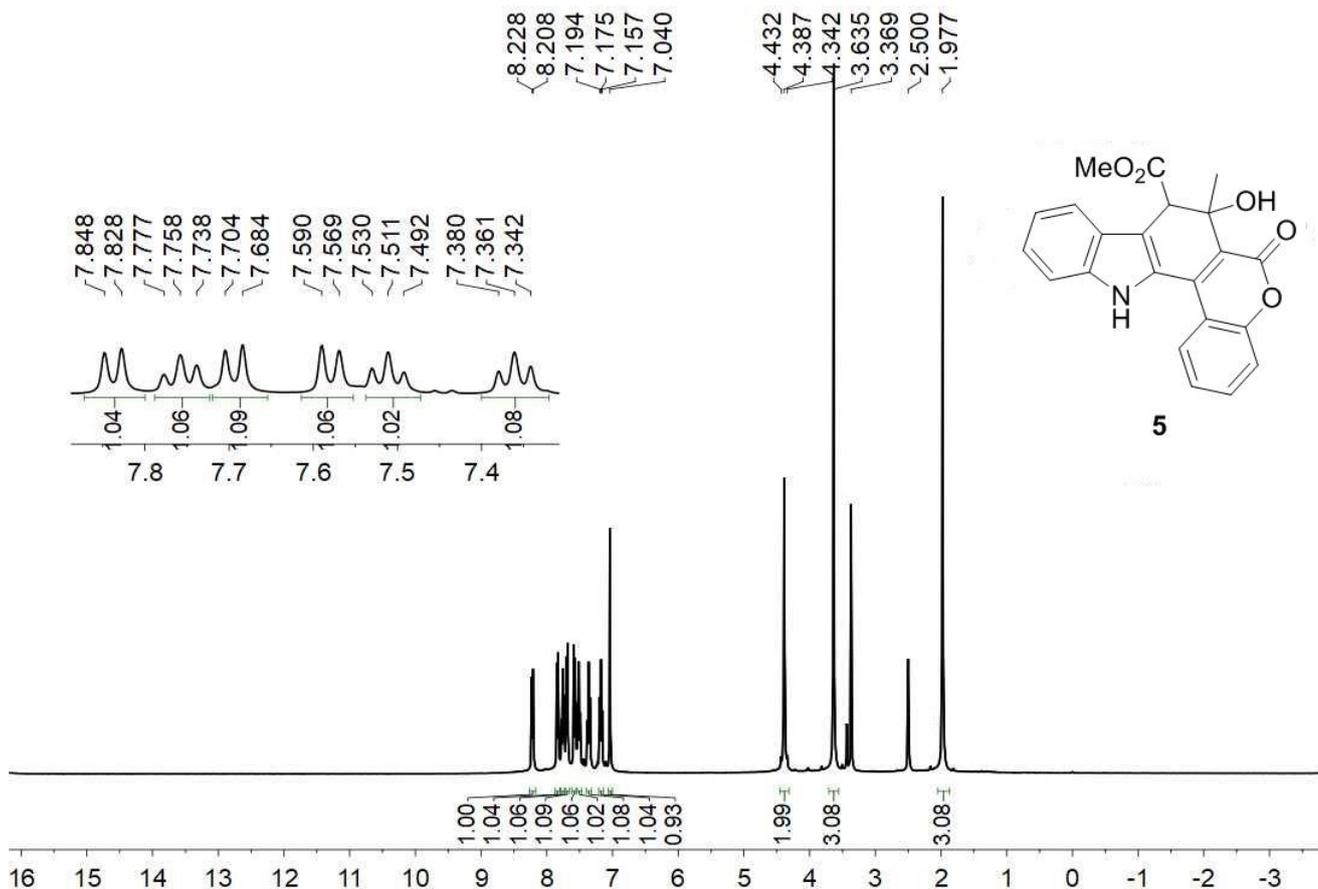
^1H NMR spectrum of the compound **4** (400 MHz, CDCl_3)



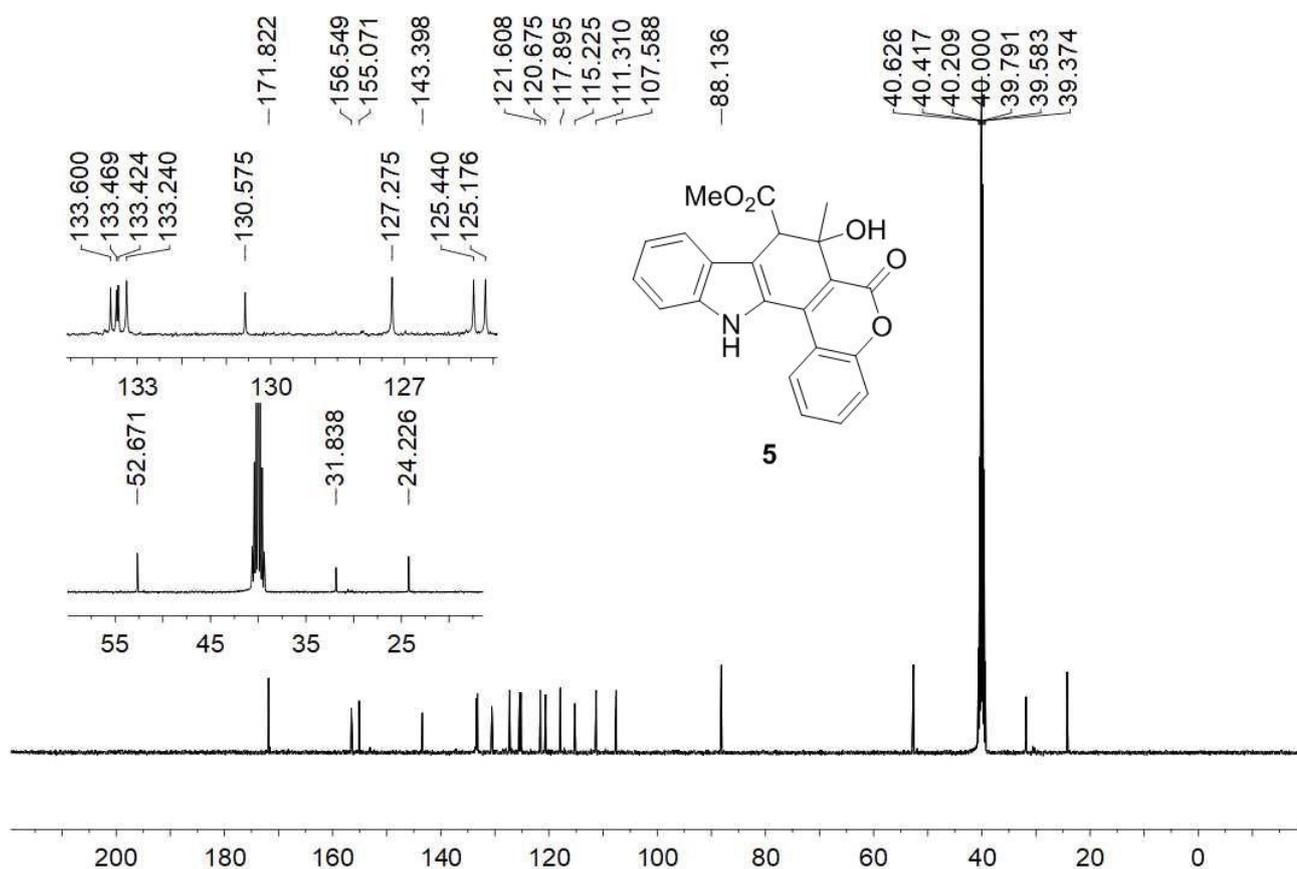
^{13}C NMR spectrum of the compound **4** (400 MHz, CDCl_3)



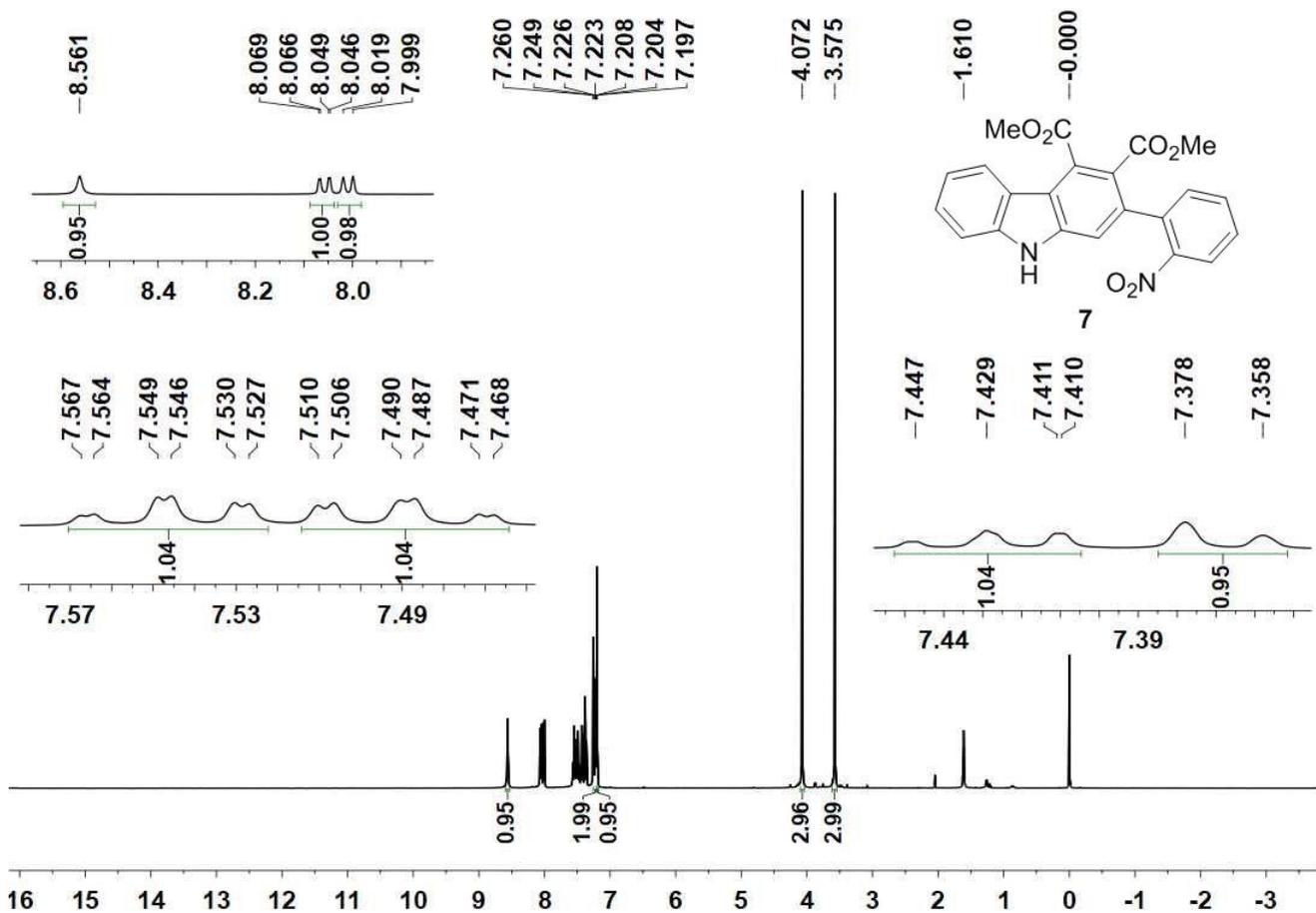
^1H NMR spectrum of the compound **5** (400 MHz, DMSO- d_6)



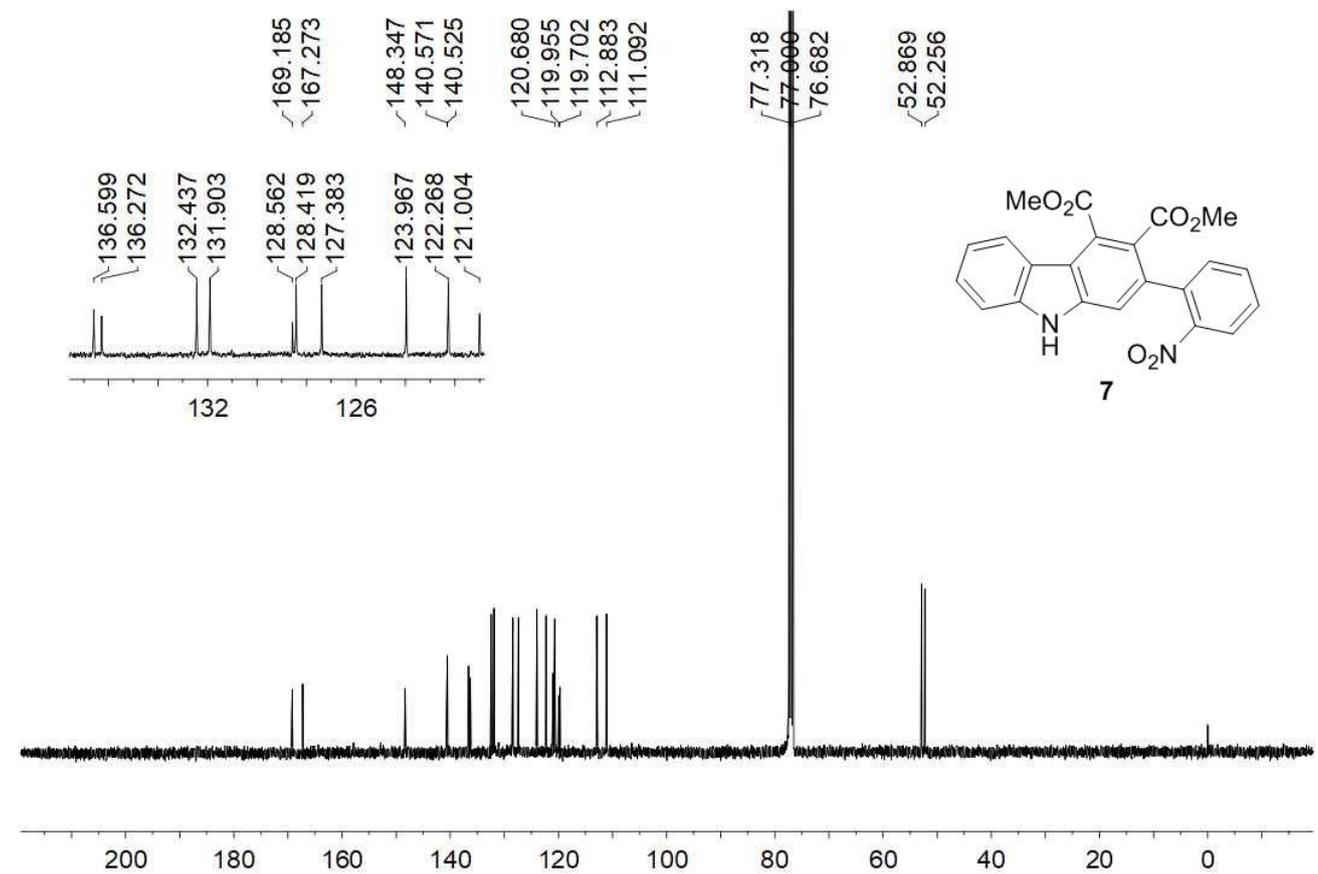
^{13}C NMR spectrum of the compound **5** (100 MHz, DMSO- d_6)



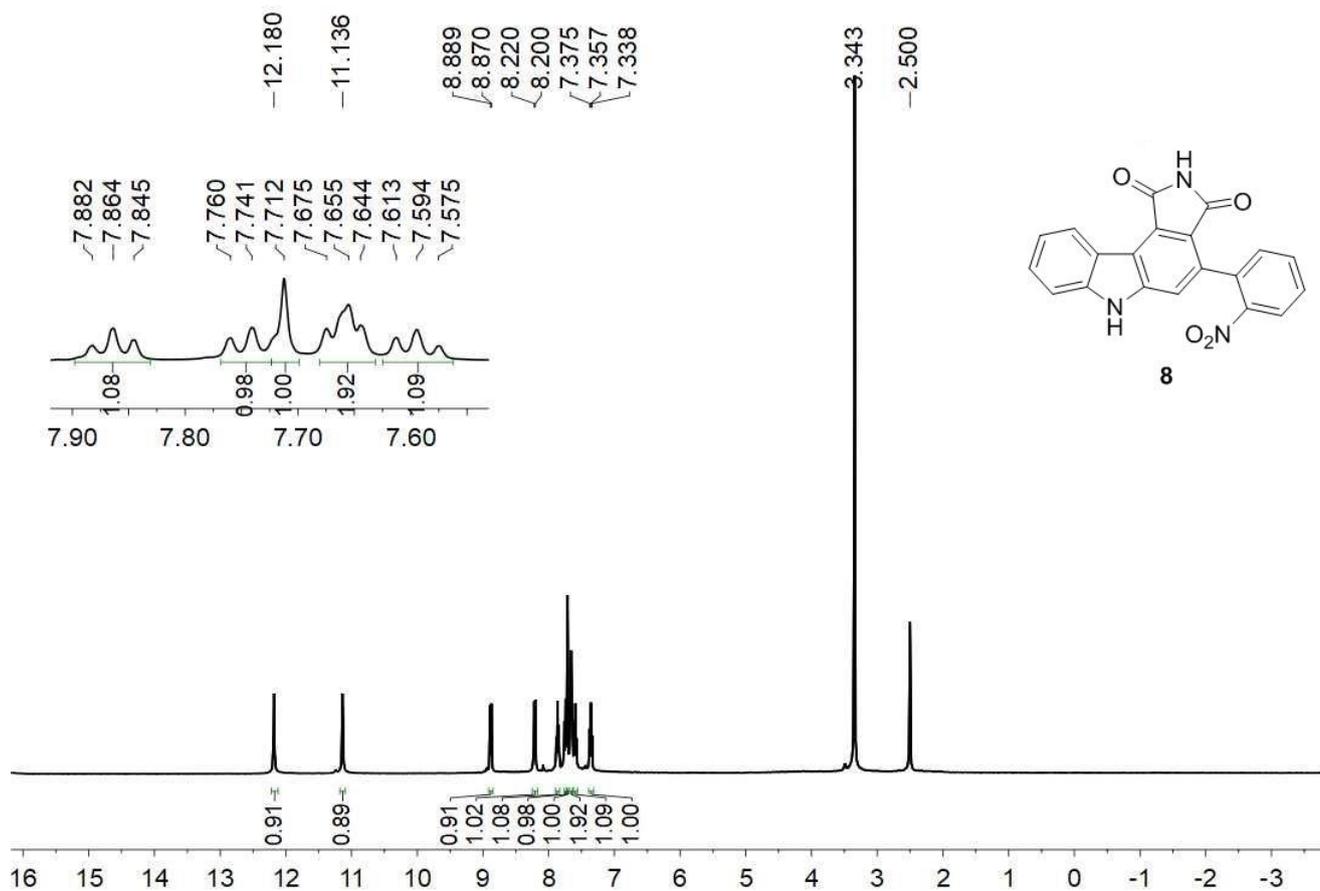
^1H NMR spectrum of the compound **7** (400 MHz, CDCl_3)



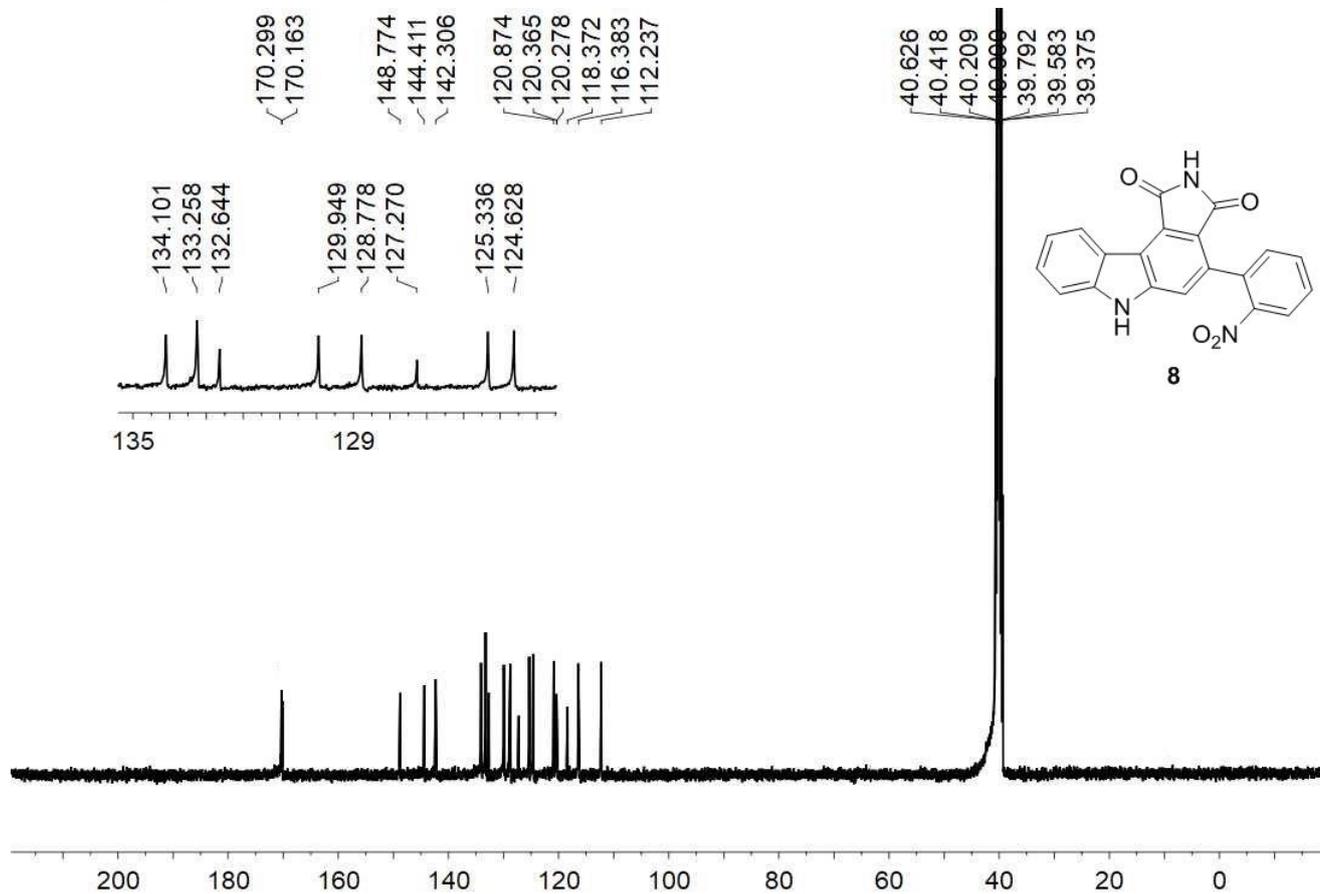
^{13}C NMR spectrum of the compound **7** (100 MHz, CDCl_3)



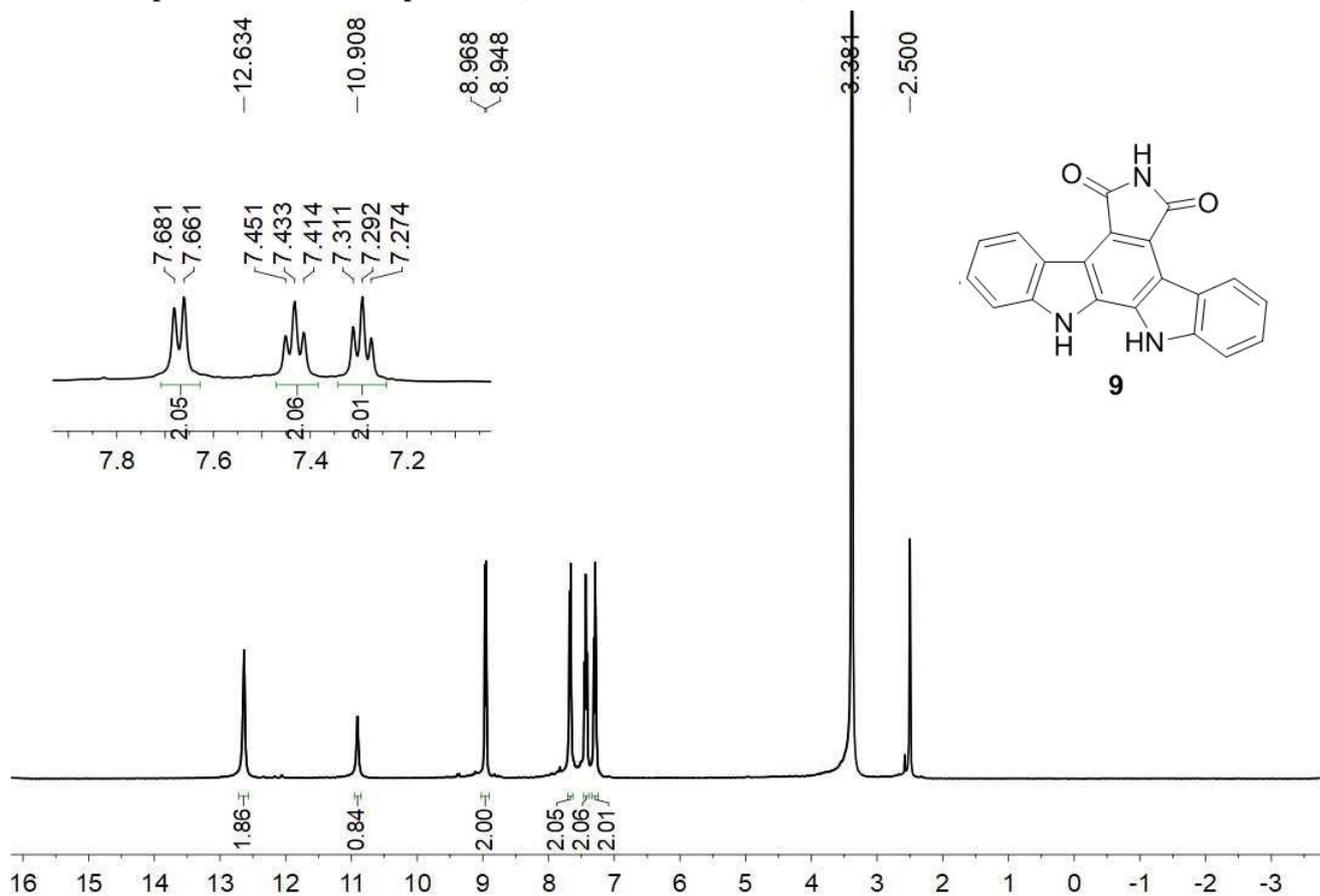
^1H NMR spectrum of the compound **8** (400 MHz, DMSO-*d*₆)



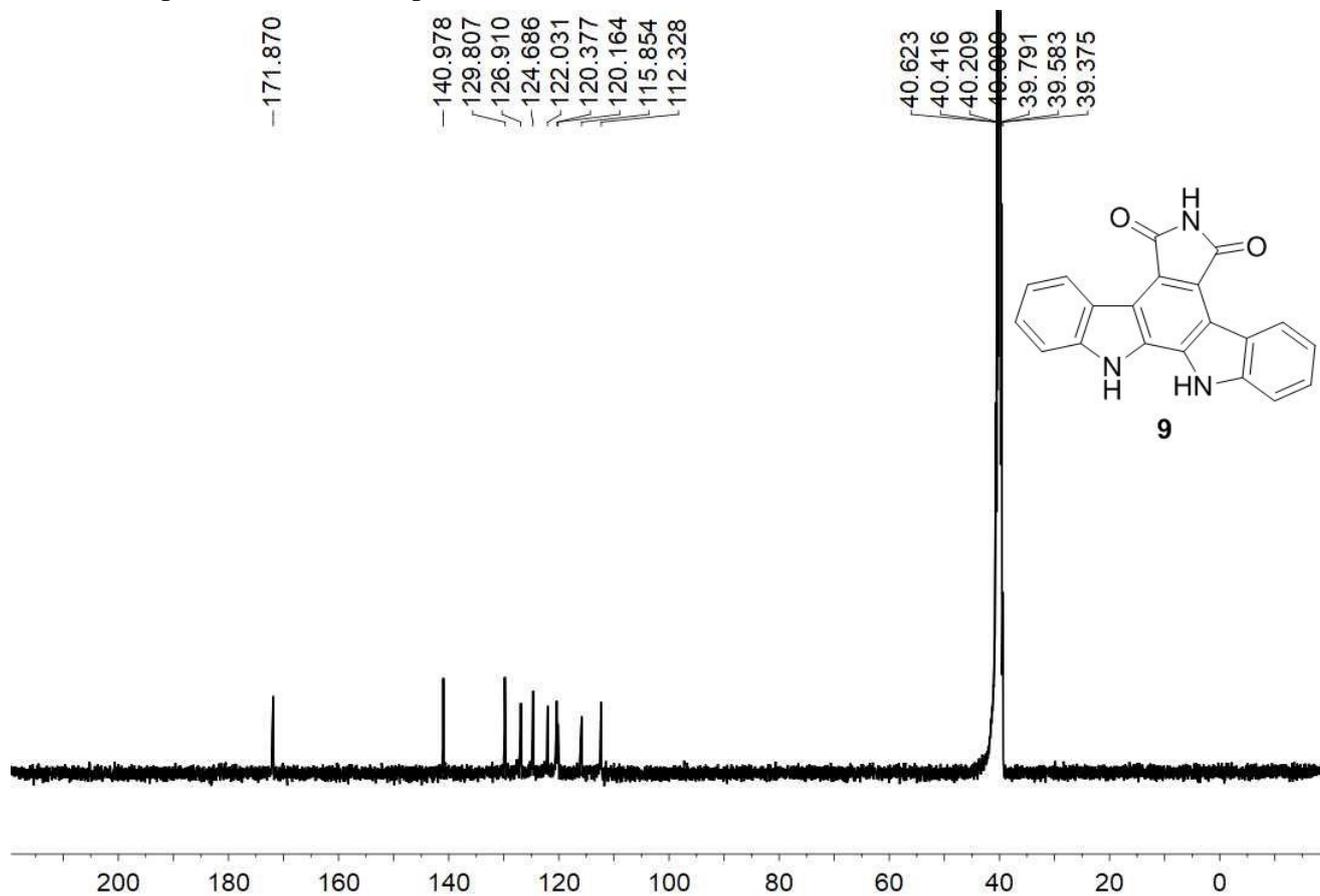
^{13}C NMR spectrum of the compound **8** (100 MHz, DMSO-*d*₆)



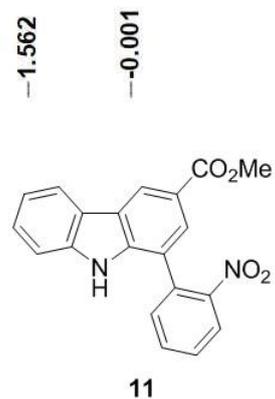
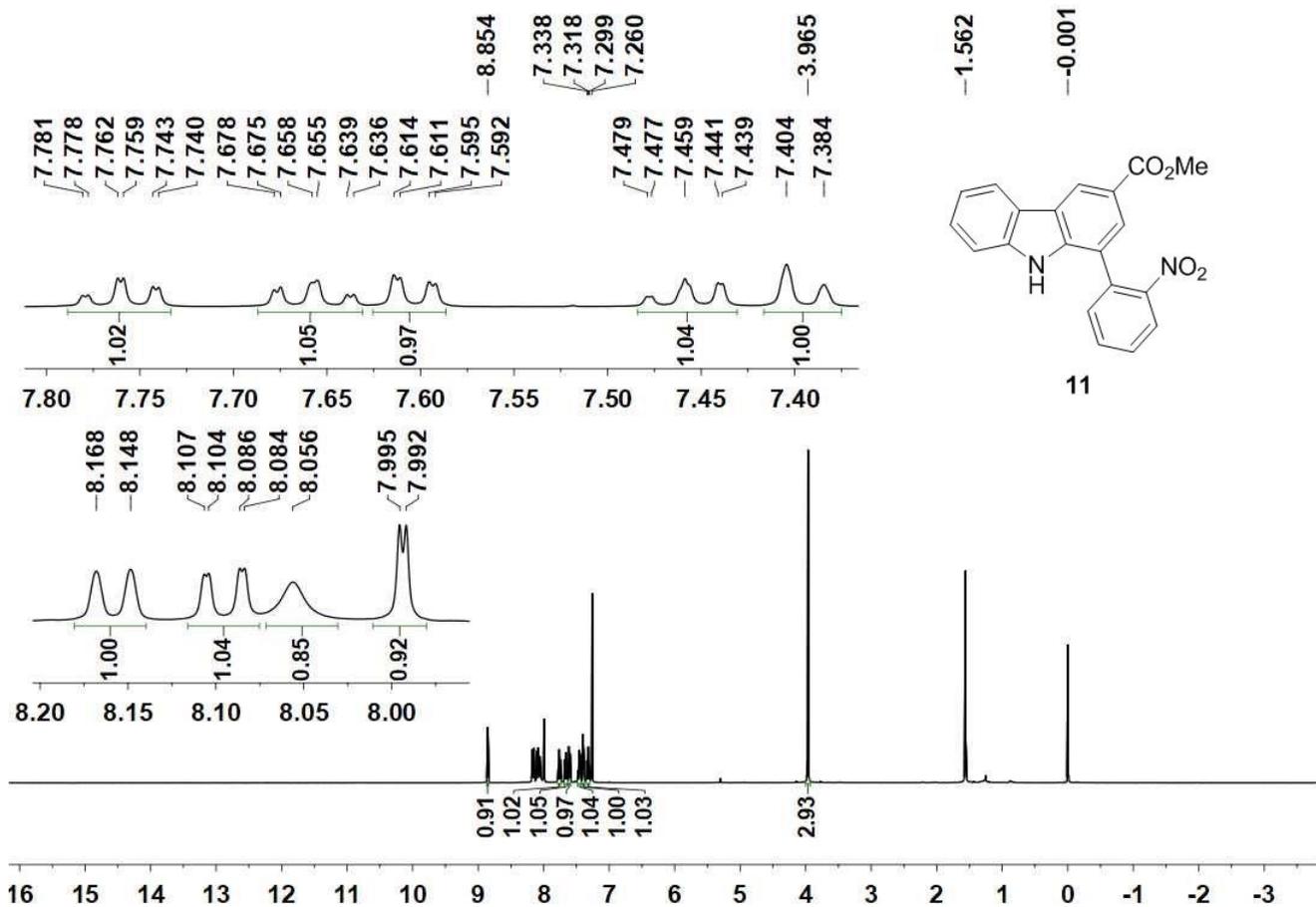
^1H NMR spectrum of the compound **9** (400 MHz, DMSO-*d*₆)



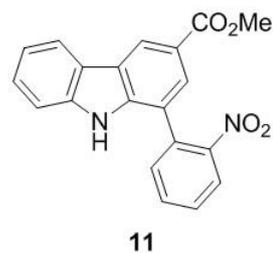
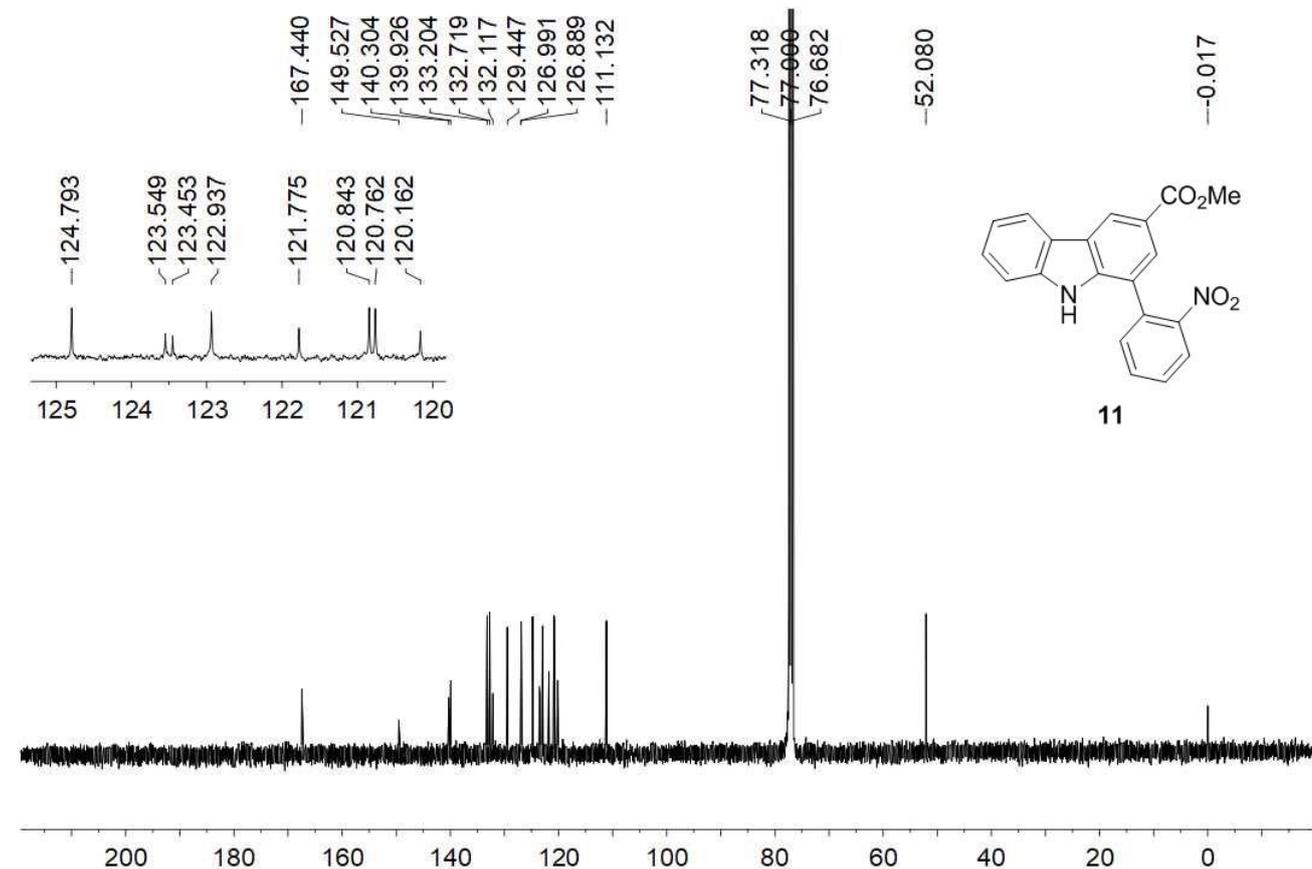
^{13}C NMR spectrum of the compound **9** (100 MHz, DMSO-*d*₆)



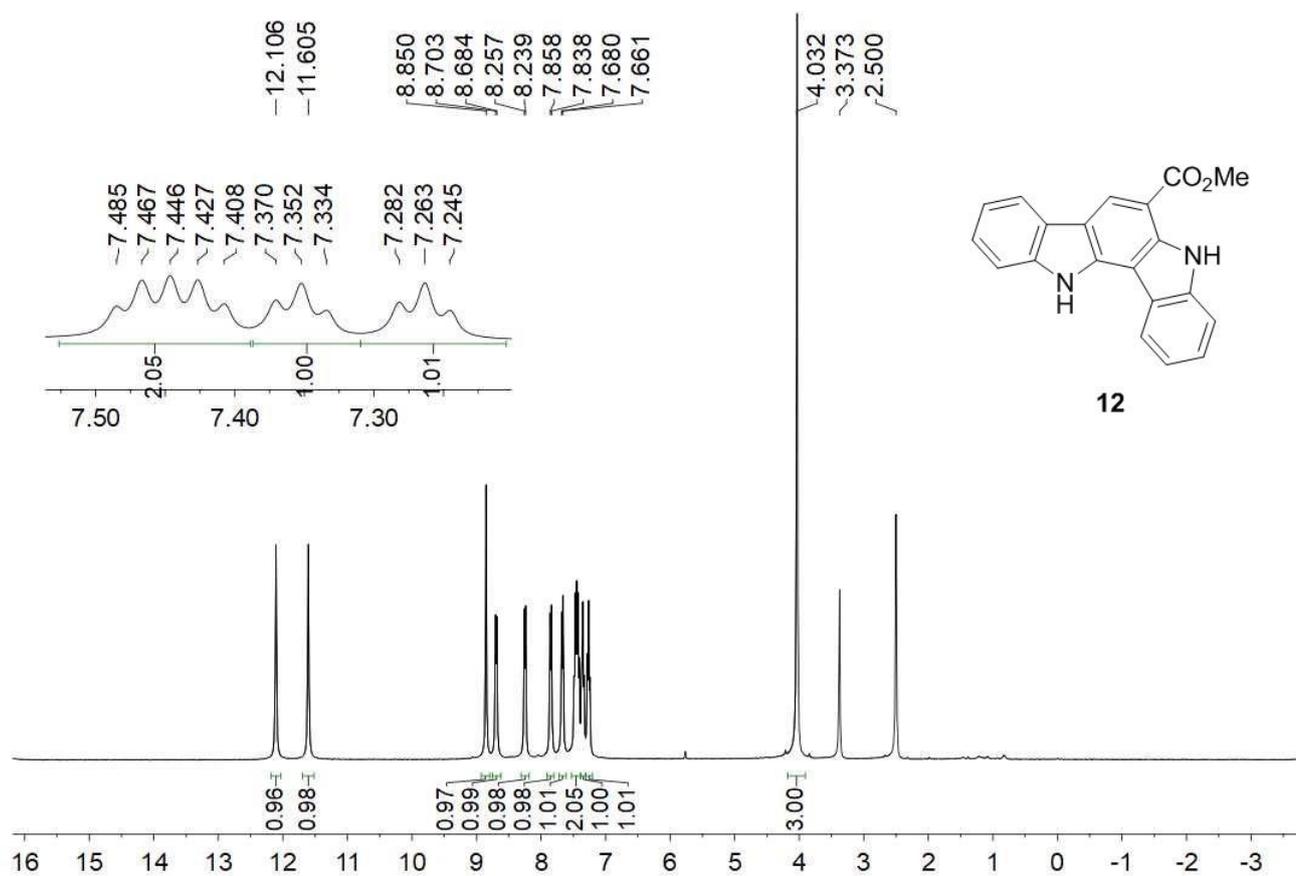
^1H NMR spectrum of the compound **11** (400 MHz, CDCl_3)



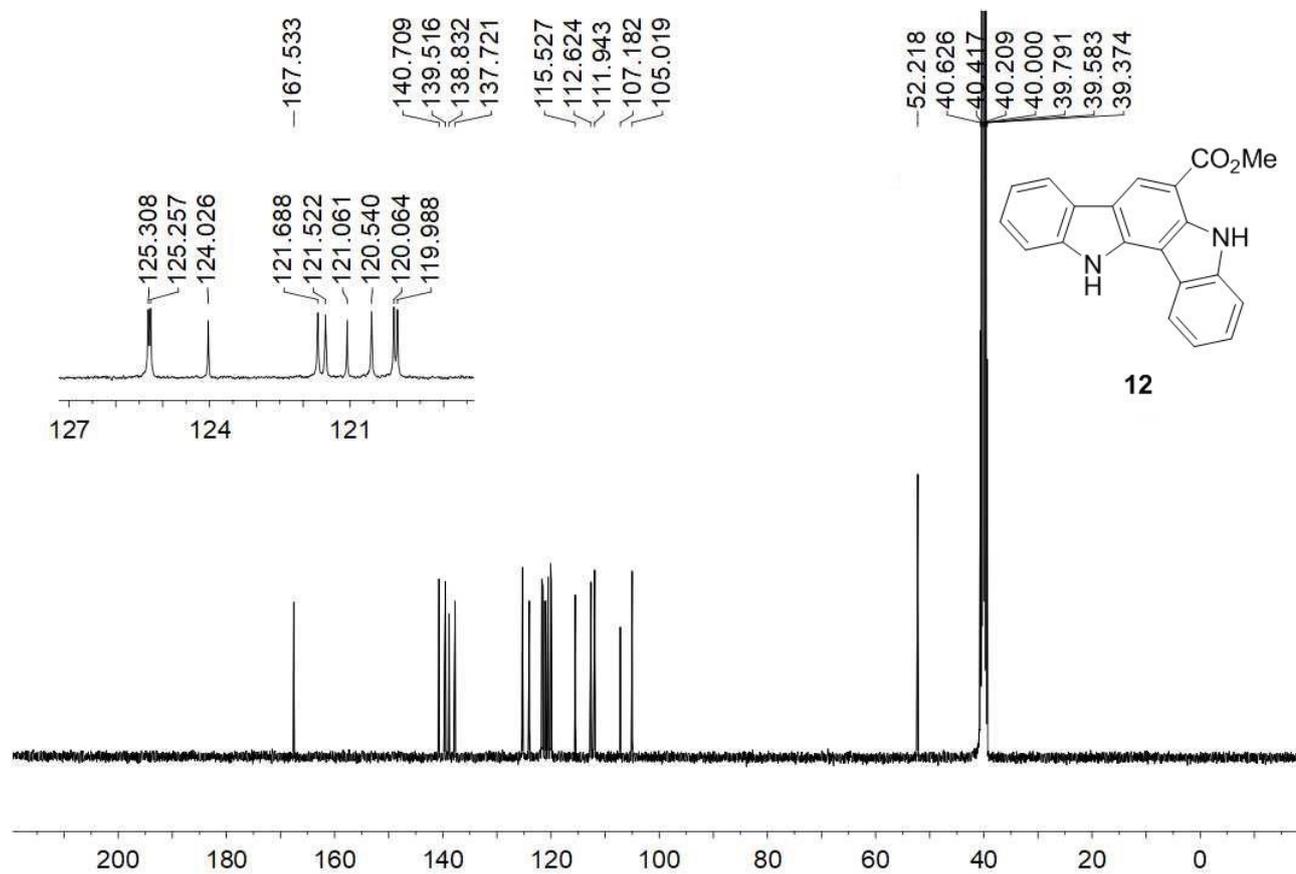
^{13}C NMR spectrum of the compound **11** (100 MHz, CDCl_3)



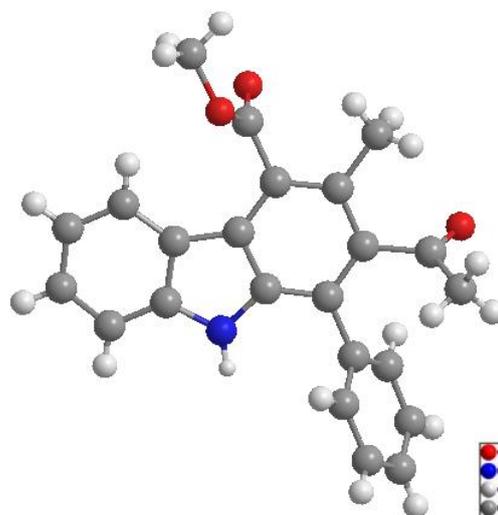
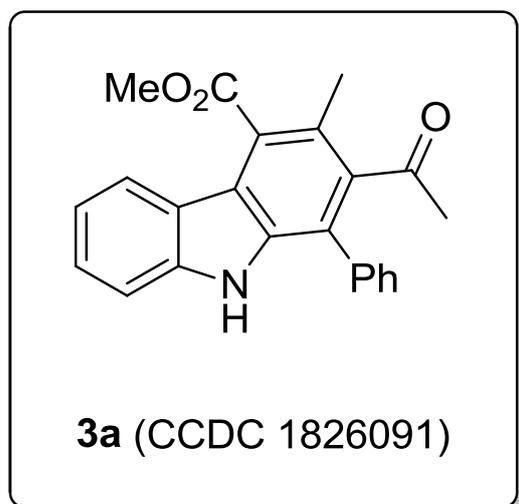
^1H NMR spectrum of the compound **12** (400 MHz, DMSO-*d*₆)



^{13}C NMR spectrum of the compound **12** (100 MHz, DMSO-*d*₆)



5. X-ray Crystallographic Data of compound 3a.



Crystal data:

Empirical formula	C ₂₃ H ₁₉ NO ₃
Formula weight	357.39
Temperature/K	293(2)
Crystal system	monoclinic
Space group	Cc
a/Å	12.566(14)
b/Å	13.358(13)
c/Å	11.423(11)
α /°	90.00
β /°	96.74(5)
γ /°	90.00
Volume/Å ³	1904(3)
Z	4
Mu (mm ⁻¹)	0.083
ρ_{calc} /cm ³	1.247
F(000)	752
Crystal size/mm ³	0.19 × 0.16 × 0.12
Radiation	MoK α
Index ranges	-15 ≤ h ≤ 15, -14 ≤ k ≤ 14, -13 ≤ l ≤ 13
Reflections collected	12503
Independent reflections	3215 [R _{int} = 0.0369, R _{sigma} = 0.0436]
Data/restraints/parameters	3215/2/248
Goodness-of-fit on F ²	1.109
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0424, wR ₂ = 0.1285
Final R indexes [all data]	R ₁ = 0.0555, wR ₂ = 0.1168
