Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

A catalyst-free aqueous mediated multicomponent reaction of isocyanide: Expeditious synthesis of polyfunctionalized cyclo[*b*]fused mono-, di- and tricarbazoles

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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 Bruker 400 spectrometer, with $CDCl_3$ 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 General Synthesis

2.1.1 Synthesis of Isocyanides **1a-1l**

Isocyanides **1a-1l** were synthesized according to the known literature procedure.[1]

2.1.2 Synthesis of Tricarbaldehyde **7b**

Tricarbaldehyde **7b** was synthesized according to the known literature procedure.[2]

2.1.3 Synthesis of Compounds **4**, **6**, **8b**

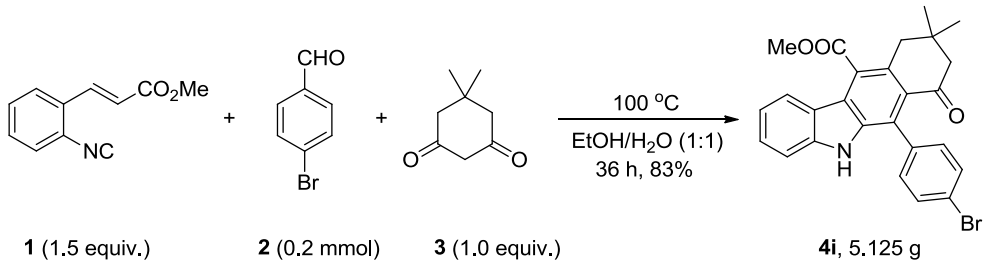
Taking the synthesis of **4a** for example: *o*-alkenyl arylisocyanide **1a** (0.3 mmol, 56.1 mg), benzaldehyde **2a** (0.2 mmol, 20.2 μL), dimedone **3a** (0.2 mmol, 28.0 mg) were added sequentially into a sealed tube and dissolved with EtOH (0.5 mL) and water (0.5 mL). Then the reaction mixture was set in a pre-heated (100 ^{o}C) metal block and kept stirring until benzaldehyde **2a** was completely consumed as indicated by TLC. Cooled to room temperature, the reaction mixture was diluted with water (2 mL) and extracted with EtOAc (3x3 mL). The combined organic layers were dried with $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by flash column chromatography (silica gel; petroleum: ethyl acetate = 25:1-15:1) to give carbazole **4a** (73.8 mg, 93% yield) as an orange solid.

2.1.4 Synthesis of Compound **8a**

o-alkenyl arylisocyanide **1a** (0.9 mmol, 168.3 mg), benzene-1,3,5-tricarboxaldehyde **7a** (0.2 mmol, 32.4 mg), dimedone **3a** (0.6 mmol, 84.0 mg) were added sequentially into a sealed tube and dissolved with EtOH (1.5 mL) and DCM (1.5 mL). Then the reaction mixture was set in a pre-heated (100 ^{o}C) metal block and kept stirring until benzene-1,3,5-tricarboxaldehyde **7a** was

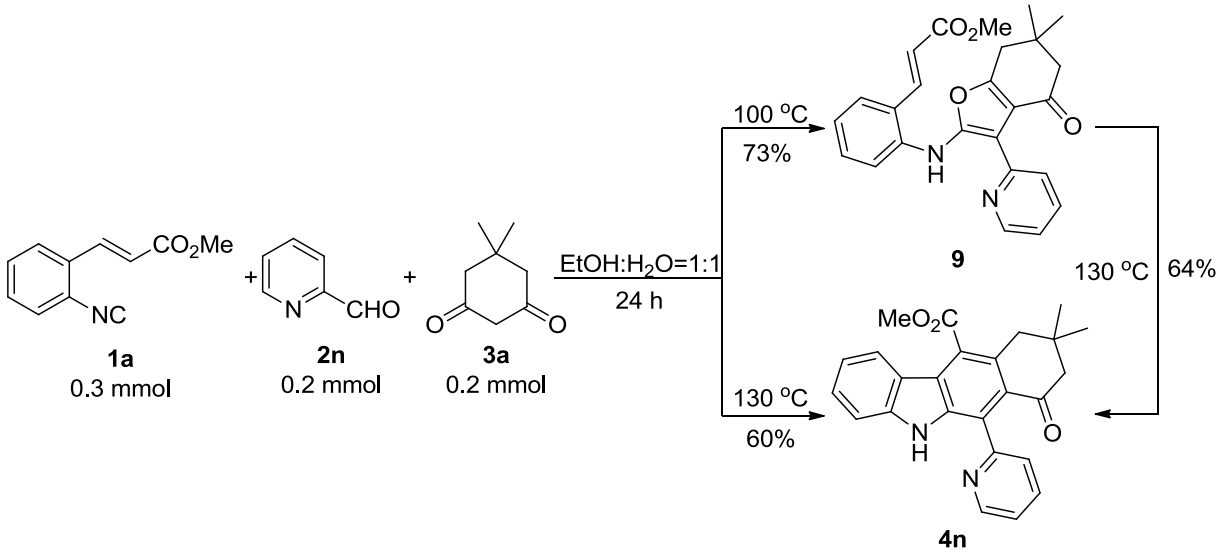
completely consumed as indicated by TLC. The reaction mixture was cooled to room temperature and filtered. The residue was washed with EtOAc (3x1 mL) to give tricarbazole **8a** (147.0 mg, 71%) as a yellow solid.

2.1.5 Multigram scale synthesis of **4i**



o-alkenyl arylisocyanide **1a** (19.5 mmol, 3.647 g), 4-bromobenzaldehyde **2i** (13 mmol, 2.392 g), dimedone **3a** (13 mmol, 1.820 g) were added sequentially into a sealed tube and dissolved with EtOH (20 mL) and water (20 mL). Then the reaction mixture was set in a pre-heated (100 ^{o}C) metal block and kept stirring until 4-bromobenzaldehyde **2i** was completely consumed as indicated by TLC. Cooled to room temperature, the reaction mixture was diluted with water (100 mL) and extracted with EtOAc (3×30 mL). The combined organic layers were dried with $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by flash column chromatography (silica gel; petroleum: ethyl acetate = 25:1-15:1) to give carbazole **4i** (5.125 g, 83% yield) as an orange solid.

2.2 Control Experiments



To shed light on the reaction mechanism of this method, control experiments were performed. When the reaction of *o*-alkenyl arylisocyanide **1a**, benzaldehyde **2n** and dimedone **3a** was

performed under optimized conditions, aminofuran **9** was obtained in 73% yield. The desired product **4n** was obtained in 60% yield when the reaction was performed at 130 ^{o}C. Furthermore, when purified aminofuran **9** was treated at 130 ^{o}C, carbazole **4n** was obtained in 64% yield. This result indicated that aminofuran **9** is most likely an intermediate of this method formed by an isocyanide-based [4+1] annulation.

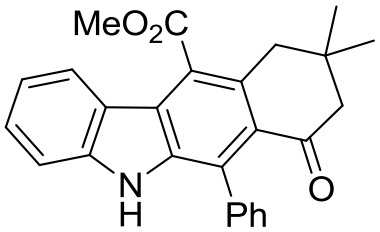
2.3 References:

1 (a) A.-H. Li, E. Ahmed, X. Chen, M. Cox, A. P. Crew, H.-Q. Dong, M.-Z. Jin, L.-F. Ma, B. Panicker, K. W. Siu, A. G. Steinig, K. M. Stolz, P. A. R. Tavares, B. Volk, Q.-H. Weng, D. Werner and M. J. Mulvihill, *Org. Biomol. Chem.*, 2007, **5**, 61; (b) M. Tobisu, H. Fujihara, K. Koh and N. Chatani, *J. Org. Chem.*, 2010, **75**, 4841; (c) Z.-Y. Hu, H.-Y. Yuan, Y. Men, Q. Liu, J.-P. Zhang and X.-X. Xu, *Angew. Chem., Int. Ed.*, 2016, **55**, 7077.

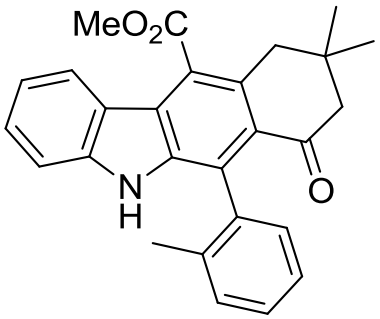
2 (a) G. Wang, X.-H. Zhang, J.-L. Geng, K. Li, D. Ding, K.-Y. Pu, L.-P. Cai, Y.-H. Lai and B. Liu, *Chem. Eur. J.*, 2012, **18**, 9705; (b) Y.-C. Zhao, T. Wang, L.-M. Zhang, Y. Cui and B.-H. Han, *ACS Appl. Mater. Interfaces*, 2012, **4**, 6975.

3 (a) A. Shaabani, M. B. Teimouri and H. R. Bijanzadeh, *Monatsh. Chem.*, 2004, **135**, 441; (b) M. Kumar, L. K. Kumawat, V. K. Gupta and A. Sharma, *ChemistryOpen*, 2015, **4**, 626; (c) Y. Men, Z.-Y. Hu, J.-H. Dong and X.-X. Xu, *Org. Lett.*, 2018, **20**, 5348.

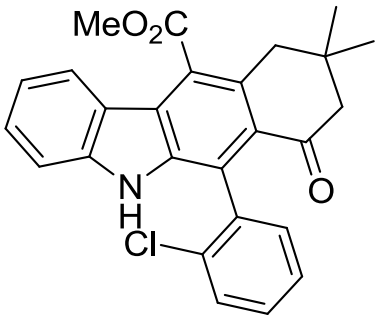
3. Analytical Data of Compounds 4, 6, 8 and 9



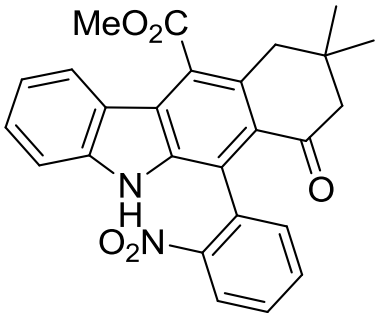
4a, Methyl 9,9-dimethyl-7-oxo-6-phenyl-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Orange solid in 93% yield, 73.8 mg. m.p. 211-213 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.13 (s, 6H), 2.50 (s, 2H), 3.04 (s, 2H), 4.18 (s, 3H), 7.22 (t, J = 7.6 Hz, 1H), 7.28-7.34 (m, 3H), 7.43-7.49 (m, 2H), 7.54 (t, J = 7.2 Hz, 2H), 7.90 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.3, 41.6, 52.7, 53.8, 111.1, 120.2, 120.7, 122.2, 122.6, 125.8, 126.7, 127.4, 127.8, 128.0, 128.3, 128.9, 131.0, 137.8, 138.2, 141.2, 169.8, 198.4. **HRMS** (ESI-TOF) m/z calculated for $C_{26}H_{23}NNaO_3^+$ ($[M+Na]^+$) 420.1570, found 420.1579.



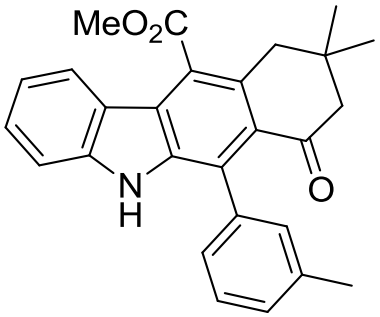
4b, Methyl 9,9-dimethyl-7-oxo-6-(*o*-tolyl)-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Light yellow solid in 80% yield, 65.7 mg, m.p. 227-229 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.11 (s, 3H), 1.14 (s, 3H), 1.96 (s, 3H), 2.49 (t, J = 17.0 Hz, 2H), 3.03 (d, J = 16.0 Hz, 1H), 3.08 (d, J = 16.4 Hz, 1H), 4.19 (s, 3H), 7.12 (d, J = 7.2 Hz, 1H), 7.20-7.25 (m, 1H), 7.30-7.39 (m, 4H), 7.42-7.47 (m, 1H), 7.80 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.7, 27.7, 28.6, 33.1, 41.6, 52.6, 53.5, 111.1, 120.2, 120.7, 122.2, 122.7, 125.7, 126.3, 126.7, 127.6, 127.7, 127.9, 130.2, 130.9, 135.8, 137.5, 137.6, 141.2, 169.8, 198.1. **HRMS** (ESI-TOF) m/z calculated for $C_{27}H_{25}NNaO_3^+$ ($[M+Na]^+$) 434.1727, found 434.1719.



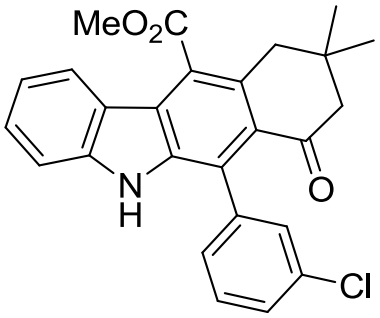
4c, Methyl 6-(2-chlorophenyl)-9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Light yellow solid in 84% yield, 72.5 mg, m.p. 227-229 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.12 (s, 3H), 1.13 (s, 3H), 2.46 (d, J = 16.4 Hz, 1H), 2.55 (d, J = 16.4 Hz, 1H), 3.04 (s, 2H), 4.19 (s, 3H), 7.23 (t, J = 7.6 Hz, 1H), 7.27-7.30 (m, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.38-7.48 (m, 3H), 7.54-7.58 (m, 1H), 7.84 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 27.8, 28.5, 33.1, 41.5, 52.7, 53.2, 111.2, 120.3, 120.7, 122.2, 123.2, 124.1, 126.3, 127.0, 127.3, 128.1, 128.9, 129.6, 129.9, 130.9, 132.9, 137.0, 137.3, 141.3, 169.7, 198.1. **HRMS** (ESI-TOF) m/z calculated for $C_{26}H_{22}ClNNaO_3^+$ ($[M+Na]^+$) 454.1180, found 454.1189.



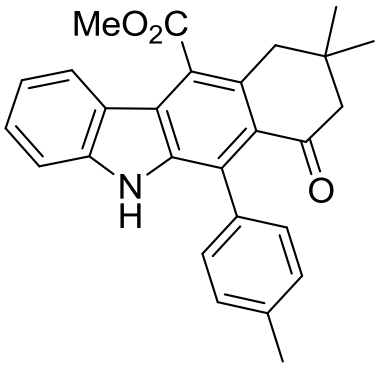
4d, Methyl 9,9-dimethyl-6-(2-nitrophenyl)-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 79% yield, 69.8 mg, m.p. 219-221 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.09 (s, 3H), 1.10 (s, 3H), 2.40 (d, J = 16.4 Hz, 1H), 2.45 (d, J = 16.4 Hz, 1H), 3.02 (s, 2H), 4.17 (s, 3H), 7.22 (t, J = 7.6 Hz, 1H), 7.25-7.31 (m, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.70 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.80 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 8.22 (dd, J_1 = 8.2 Hz, J_2 = 0.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 27.5, 28.6, 33.1, 41.4, 52.7, 53.1, 111.2, 120.5, 120.6, 122.3, 123.4, 123.6, 125.0, 126.1, 126.3, 128.2, 128.5, 130.7, 131.2, 133.8, 133.9, 136.8, 141.4, 148.0, 169.5, 198.6. **HRMS** (ESI-TOF) m/z calculated for $C_{26}H_{22}N_2NaO_5^+$ ($[M+Na]^+$) 465.1421, found 465.1418.



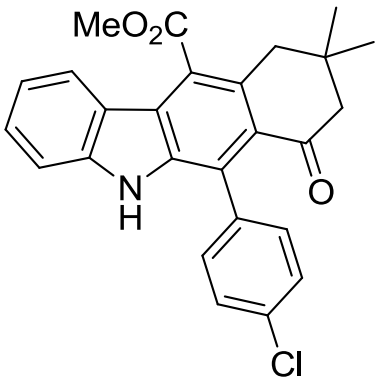
4e, Methyl 9,9-dimethyl-7-oxo-6-(*m*-tolyl)-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 86% yield, 70.7 mg, m.p. 197-199 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.13 (s, 6H), 2.43 (s, 3H), 2.51 (s, 2H), 3.04 (s, 2H), 4.18 (s, 3H), 7.08-7.12 (m, 2H), 7.19-7.24 (m, 1H), 7.27 (d, J = 6.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.39-7.47 (m, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.94 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.6, 28.2, 33.3, 41.6, 52.6, 53.8, 111.1, 120.1, 120.7, 122.2, 122.5, 125.3, 125.6, 126.7, 127.9, 128.0, 128.2, 128.7, 128.8, 130.9, 137.9, 138.1, 138.4, 141.2, 169.8, 198.3. **HRMS** (ESI-TOF) m/z calculated for $C_{27}H_{25}NNaO_3^+$ ($[M+Na]^+$) 434.1727, found 434.1747.



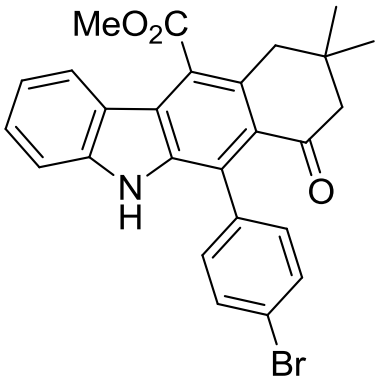
4f, Methyl 6-(3-chlorophenyl)-9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 88% yield, 75.9 mg, m.p. 228-230 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.13 (s, 6H), 2.50 (s, 2H), 3.04 (s, 2H), 4.18 (s, 3H), 7.15-7.20 (m, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.29 (s, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.38-7.48 (m, 3H), 7.90 (d, J = 8.0 Hz, 1H), 7.94 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.3, 41.5, 52.7, 53.7, 111.2, 120.3, 120.6, 122.2, 122.9, 126.0, 126.2, 126.6, 126.7, 127.6, 128.1, 128.3, 130.0, 131.0, 134.6, 137.6, 140.1, 141.3, 169.6, 198.2. **HRMS** (ESI-TOF) m/z calculated for $C_{26}H_{22}ClNNaO_3^+$ ($[M+Na]^+$) 454.1180, found 454.1186.



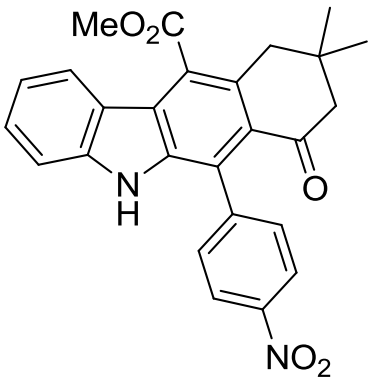
4g, Methyl 9,9-dimethyl-7-oxo-6-(p-tolyl)-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 95% yield, 78.1 mg, m.p. 165-166 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.13 (s, 6H), 2.46 (s, 3H), 2.51 (s, 2H), 3.04 (s, 2H), 4.18 (s, 3H), 7.18-7.25 (m, 3H), 7.32 (t, J = 8.2 Hz, 3H), 7.44 (t, J = 7.2 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.98 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.3, 28.2, 33.2, 41.6, 52.6, 53.8, 111.1, 120.1, 120.7, 122.2, 122.4, 125.5, 126.8, 127.8, 127.9, 128.1, 129.6, 130.9, 135.0, 137.0, 137.9, 141.2, 169.8, 198.4. **HRMS** (ESI-TOF) m/z calculated for $C_{27}H_{25}NNaO_3^+$ ($[M+Na]^+$) 434.1727, found 434.1734.



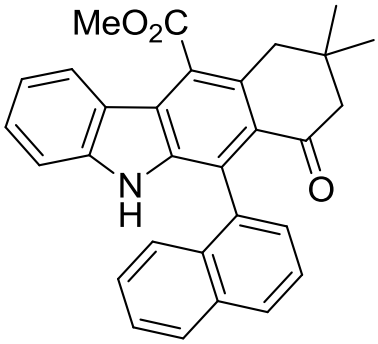
4h, Methyl 6-(4-chlorophenyl)-9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. White solid in 91% yield, 78.5 mg, m.p. 211-213 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.13 (s, 6H), 2.50 (s, 2H), 3.03 (s, 2H), 4.18 (s, 3H), 7.20-7.26 (m, 3H), 7.34 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.86 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.3, 41.5, 52.7, 53.7, 111.1, 120.4, 120.6, 122.3, 122.8, 126.1, 126.3, 126.6, 128.2, 129.1, 129.7, 131.1, 133.4, 136.6, 137.7, 141.2, 169.6, 198.4. **HRMS** (ESI-TOF) m/z calculated for $C_{26}H_{22}ClNNaO_3^+$ ($[M+Na]^+$) 454.1180, found 454.1186.



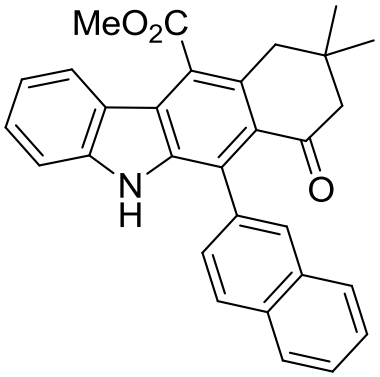
4i, Methyl 6-(4-bromophenyl)-9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 92% yield, 87.2 mg, m.p. 178-181 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.13 (s, 6H), 2.50 (s, 2H), 3.04 (s, 2H), 4.18 (s, 3H), 7.15-7.19 (m, 2H), 7.20-7.25 (m, 1H), 7.43-7.48 (m, 1H), 7.62-7.65 (m, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.92 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.3, 41.5, 52.7, 53.7, 111.1, 120.3, 120.6, 121.5, 122.2, 122.8, 126.1, 126.3, 126.5, 128.1, 130.1, 131.0, 132.0, 137.1, 137.6, 141.3, 169.6, 198.3. **HRMS** (ESI-TOF) m/z calculated for $C_{26}H_{22}BrNNaO_3^+$ ($[M+Na]^+$) 498.0675, found 498.0692.



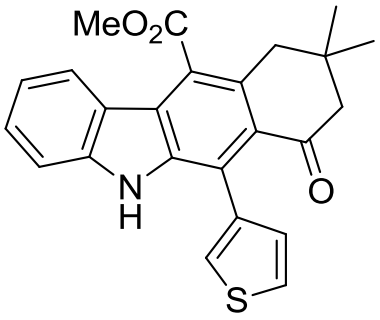
4j, Methyl 9,9-dimethyl-6-(4-nitrophenyl)-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 99% yield, 87.5 mg, m.p. 274-276 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.14 (s, 6H), 2.50 (s, 2H), 3.05 (s, 2H), 4.19 (s, 3H), 7.25 (t, J = 7.4 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.45-7.53 (m, 3H), 7.91 (d, J = 8.0 Hz, 1H), 7.98 (s, 1H), 8.35 (d, J = 8.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.3, 41.5, 52.8, 53.5, 111.3, 120.5, 120.6, 122.3, 123.4, 124.1, 125.0, 126.3, 126.8, 128.5, 129.5, 131.2, 137.1, 141.5, 146.1, 147.0, 169.4, 198.3. **HRMS** (ESI-TOF) m/z calculated for $C_{26}H_{22}N_2NaO_5^+$ ($[M+Na]^+$) 465.1421, found 465.1428.



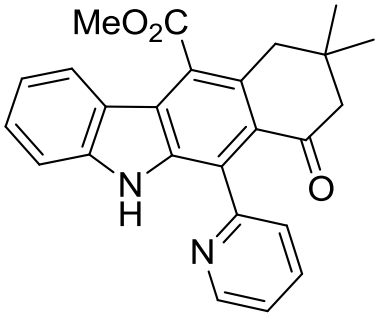
4k, Methyl 9,9-dimethyl-6-(naphthalen-1-yl)-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 92% yield, 82.2 mg, m.p. 233-235 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.12 (s, 6H), 2.38 (s, 2H), 3.08 (s, 2H), 4.19 (s, 3H), 7.07 (d, J = 8.0 Hz, 1H), 7.16-7.25 (m, 3H), 7.29 (d, J = 6.8 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.40-7.45 (m, 1H), 7.51-7.56 (m, 1H), 7.74 (s, 1H), 7.91 (t, J = 7.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.0, 28.4, 33.1, 41.6, 52.7, 53.3, 111.1, 120.1, 120.5, 122.1, 122.8, 124.8, 125.3, 125.7 (2C), 126.0 (2C), 126.2, 127.6, 127.8, 127.9, 128.4, 130.9, 131.6, 133.7, 135.9, 138.2, 141.2, 169.8, 197.5. **HRMS** (ESI-TOF) m/z calculated for $C_{30}H_{25}NNaO_3^+$ ($[M+Na]^+$) 470.1727, found 470.1743.



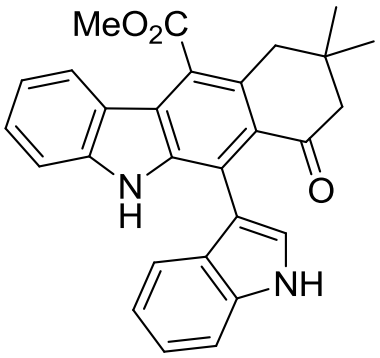
4l, Methyl 9,9-dimethyl-6-(naphthalen-2-yl)-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 86% yield, 76.9 mg, m.p. 231-233 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.14 (s, 3H), 1.16 (s, 3H), 2.48 (d, J = 16 Hz, 1H), 2.53 (d, J = 16 Hz, 1H), 3.07 (s, 2H), 4.19 (s, 3H), 7.22 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.38 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.41-7.46 (m, 1H), 7.51-7.57 (m, 2H), 7.80 (s, 1H), 7.85-7.95 (m, 4H), 7.98 (d, J = 8.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 28.3, 33.3, 41.6, 52.7, 53.7, 111.1, 120.2, 120.7, 122.3, 122.7, 125.9, 126.1, 126.2, 126.7, 127.4, 127.6, 127.9, 128.0, 128.4, 131.1, 133.5, 135.9, 141.2, 169.8, 198.3. **HRMS** (ESI-TOF) m/z calculated for $C_{30}H_{25}NNaO_3^+$ ($[M+Na]^+$) 470.1727, found 470.1724.



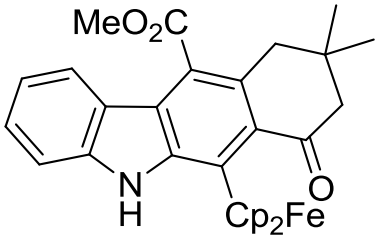
4m, Methyl 9,9-dimethyl-7-oxo-6-(thiophen-3-yl)-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Orange solid in 91% yield, 73.3 mg, m.p. 181-183 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.13 (s, 6H), 2.52 (s, 2H), 3.03 (s, 2H), 4.17 (s, 3H), 7.04 (dd, J_1 = 5.0 Hz, J_2 = 0.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.49-7.52 (m, 1H), 7.89 (d, J = 8.0 Hz, 1H), 8.13 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.3, 41.6, 52.7, 53.8, 111.1, 120.2, 120.7, 121.6, 122.2, 122.5 (2C), 125.9, 127.1, 128.0, 129.0, 130.9, 137.5, 138.2, 141.1, 169.7, 198.4. **HRMS** (ESI-TOF) m/z calculated for $C_{24}H_{21}NNaO_3S^+$ ($[M+Na]^+$) 426.1134, found 426.1137.



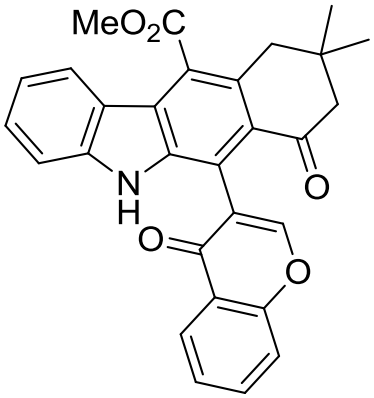
4n, Methyl 9,9-dimethyl-7-oxo-6-(pyridin-2-yl)-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 60% yield, 47.8 mg, m.p. 208-211 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.11 (s, 6H), 2.52 (s, 2H), 2.92 (s, 2H), 4.15 (s, 3H), 7.17 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.0 Hz, 2H), 7.31-7.35 (m, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.74-7.78 (m, 1H), 7.82 (d, J = 8.0 Hz, 1H), 8.62 (d, J = 4.4 Hz, 1H), 9.40 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.4, 41.4, 52.5, 53.6, 111.5, 119.9, 120.4, 122.1, 123.8, 125.2, 125.5, 126.3, 127.0, 127.7, 130.7, 136.3, 137.7, 142.1, 149.1, 157.7, 169.5, 198.6. **HRMS** (ESI-TOF) m/z calculated for $C_{25}H_{22}N_2NaO_3^+$ ($[M+Na]^+$) 421.1523, found 421.1530.



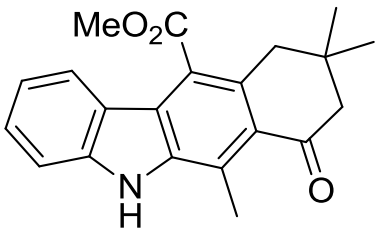
4o, Methyl 6-(1*H*-indol-3-yl)-9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 72% yield, 62.8 mg, m.p. 257-258 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.16 (s, 3H), 1.17 (s, 3H), 2.49 (d, J = 16.0 Hz, 1H), 2.59 (d, J = 16.0 Hz, 1H), 3.08 (s, 2H), 4.20 (s, 3H), 7.05 (t, J = 7.4 Hz, 1H), 7.14-7.25 (m, 5H), 7.35 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 8.18 (s, 1H), 8.69 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.4 (2C), 33.2, 41.8, 52.6, 53.9, 111.1, 111.6, 112.0, 119.4, 120.0, 120.2, 120.3, 120.9, 122.2, 122.4, 123.3, 125.4, 126.7, 127.7, 128.3, 131.0, 136.3, 139.0, 141.1, 170.0, 198.7. **HRMS** (ESI-TOF) m/z calculated for $C_{28}H_{24}N_2NaO_3^+$ ($[M+Na]^+$) 459.1679, found 459.1691.



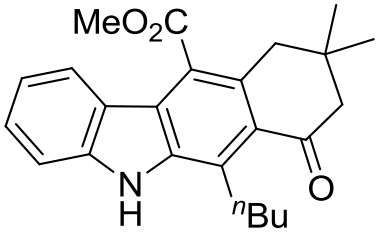
4p, Methyl 9,9-dimethyl-7-oxo-6-ferrocenyl-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Red solid in 92% yield, 92.9 mg, m.p. > 300 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.11 (s, 6H), 2.58 (s, 2H), 2.96 (s, 2H), 4.16 (brs, 8H), 4.53 (brd, J = 36.0 Hz, 4H), 7.26 (s, 1H), 7.55 (s, 2H), 7.91 (s, 1H), 10.15 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.4, 33.9, 41.6, 52.6, 54.3, 68.6, 69.3, 70.2, 110.9, 120.1, 120.8, 121.9, 122.2, 123.1, 124.7, 127.8, 129.8, 130.8, 137.6, 140.4, 169.9, 199.4. **HRMS** (ESI-TOF) m/z calculated for $C_{30}H_{27}FeNNaO_3^+$ ($[M+Na]^+$) 528.1233, found 528.1237.



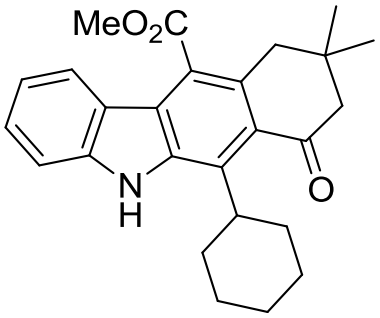
4q, Methyl 9,9-dimethyl-7-oxo-6-(4-oxo-4*H*-chromen-3-yl)-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 72% yield, 62.8 mg, m.p. 257-258 ^{o}C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 1.05 (s, 3H), 1.06 (s, 3H), 2.42-2.52 (m, 2H), 2.96 (s, 2H), 4.13 (s, 3H), 7.22 (t, J = 6.8 Hz, 1H), 7.46-7.51 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.89 (t, J = 7.6 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.37 (s, 1H), 11.55 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 28.1, 28.3, 33.4, 41.2, 53.3, 53.4, 112.2, 117.6, 118.9, 120.0, 120.2, 122.0, 122.3, 123.4, 124.3, 125.7, 126.0, 126.7, 128.1, 128.5, 129.8, 134.6, 139.1, 142.4, 153.1, 156.8, 169.6, 175.9, 198.1. **HRMS** (ESI-TOF) m/z calculated for $C_{29}H_{23}NNaO_5^+$ ($[M+Na]^+$) 488.1468, found 488.1470.



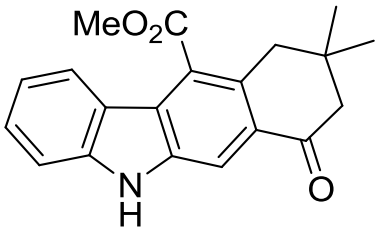
4r, Methyl 6,9,9-trimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Light yellow solid in 59% yield, 39.5 mg, m.p. 259-262 ^{o}C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 1.01 (s, 6H), 2.54 (s, 2H), 2.87 (s, 3H), 2.88 (s, 2H), 4.07 (s, 3H), 7.18 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 11.66 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 16.7, 28.2, 33.2, 41.4, 53.1, 54.2, 112.2, 119.9, 120.3, 121.2, 122.0, 124.4, 125.4, 127.2, 128.0, 130.1, 138.8, 142.2, 169.9, 200.4. **HRMS** (ESI-TOF) m/z calculated for $C_{21}H_{21}NNaO_3^+$ ([M+Na]$^+$) 358.1414, found 358.1407.



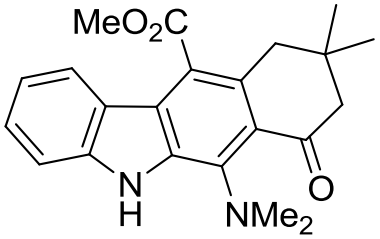
4s, Methyl 6-butyl-9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Orange crystal in 72% yield, 54.3 mg, m.p. 152-154 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.98 (t, J = 7.4 Hz, 3H), 1.09 (s, 6H), 1.48-1.58 (m, 2H), 1.63-1.73 (m, 2H), 2.57 (s, 2H), 2.96 (s, 2H), 3.34 (t, J = 8.0 Hz, 2H), 4.14 (s, 3H), 7.18-7.22 (m, 1H), 7.45 (d, J = 3.6 Hz, 2H), 7.85 (d, J = 8.0 Hz, 1H), 8.51 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.0, 23.4, 28.1, 29.2, 32.0, 32.9, 41.8, 52.6, 54.5, 111.1, 120.0, 121.0, 122.0, 122.2, 124.3, 126.8, 127.7, 130.1, 131.3, 137.9, 141.1, 170.1, 200.5. **HRMS** (ESI-TOF) m/z calculated for $C_{24}H_{27}NNaO_3^+$ ([M+Na]$^+$) 400.1883, found 400.1903.



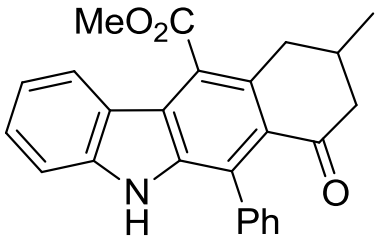
4t, Methyl 6-cyclohexyl-9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. White crystal in 53% yield, 42.7 mg, m.p. 212-213 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.10 (s, 6H), 1.43 (t, J = 12.4 Hz, 1H), 1.47-1.57 (m, 2H), 1.80-2.05 (m, 7H), 2.61 (s, 2H), 2.92 (s, 2H), 4.07-4.17 (m, 1H), 4.13 (s, 3H), 7.17-7.22 (m, 1H), 7.43-7.51 (m, 2H), 7.82 (d, J = 8.0 Hz, 1H), 8.50 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 26.4, 26.9, 28.4, 31.5, 33.2, 38.9, 41.7, 52.6, 54.9, 110.9, 120.0, 120.1, 121.8, 122.7, 124.4, 127.7, 129.2, 130.7, 133.6, 137.2, 140.7, 170.1, 201.8. **HRMS** (ESI-TOF) m/z calculated for $C_{26}H_{29}NNaO_3^+$ ([M+Na]$^+$) 426.2040, found 426.2048.



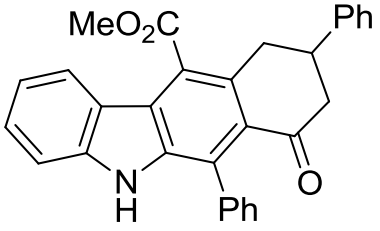
4u, Methyl 9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 20% yield, 12.8 mg, m.p. 233-235 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.11 (s, 6H), 2.59 (s, 2H), 2.98 (2H), 4.15 (s, 3H), 7.20-7.25 (m, 1H), 7.45-7.50 (m, 2H), 7.91 (d, J = 8.0 Hz, 1H), 8.27 (s, 1H), 8.50 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.3, 33.6, 40.9, 52.3, 52.6, 110.9, 111.1, 120.2, 120.6, 122.4, 124.3, 126.3, 128.1, 129.4, 130.5, 137.9, 141.7, 169.7, 198.4. **HRMS** (ESI-TOF) m/z calculated for $C_{20}H_{19}NNaO_3^+$ ([M+Na]$^+$) 344.1257, found 344.1266.



4v, Methyl 6-(dimethylamino)-9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 57% yield, 41.5 mg, m.p. 180-182 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.10 (s, 6H), 2.56 (s, 2H), 2.92 (s, 2H), 2.94 (s, 6H), 4.11 (s, 3H), 7.17-7.21 (m, 1H), 7.41-7.47 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H), 8.65 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.3, 33.4, 41.7, 42.4, 52.4, 54.1, 111.1, 119.9, 121.3, 121.6, 122.0, 123.1, 124.6, 127.3, 132.0, 135.9, 140.3, 140.5, 170.1, 198.8. **HRMS** (ESI-TOF) m/z calculated for $C_{22}H_{24}N_2NaO_3^+$ ($[M+Na]^+$) 387.1679, found 387.1675.

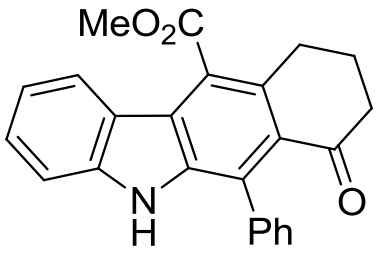


4w, Methyl 9-methyl-7-oxo-6-phenyl-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Light yellow solid in 79% yield, 60.5 mg, m.p. 210-212 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.18 (d, J = 6.0 Hz, 3H), 2.30-2.44 (m, 2H), 2.68 (d, J = 14.4 Hz, 1H), 2.86 (dd, J_1 = 16.0 Hz, J_2 = 10.8 Hz, 1H), 3.19 (dd, J_1 = 16.0 Hz, J_2 = 3.6 Hz, 1H) 4.18 (s, 3H), 7.23 (t, J = 7.4 Hz, 1H), 7.31 (dd, J_1 = 7.6 Hz, J_2 = 3.6 Hz, 3H), 7.45 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.96 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.4, 30.1, 36.1, 48.4, 52.7, 111.1, 120.1, 120.6, 122.2, 122.4, 125.0, 127.1, 127.4, 127.9 (2C), 128.2, 128.8, 132.1, 137.8, 138.1, 141.2, 169.8, 198.3. **HRMS** (ESI-TOF) m/z calculated for $C_{25}H_{21}NNaO_3^+$ ($[M+Na]^+$) 406.1414, found 406.1416.

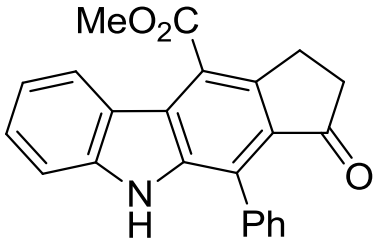


4x, Methyl 7-oxo-6,9-diphenyl-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Light yellow solid in 82% yield, 73.0 mg, m.p. 259-261 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.88-2.94 (m, 2H), 3.39 (d, J = 8.0 Hz, 2H), 3.48-3.57 (m, 1H), 7.24 (t, J = 8.0 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.34 (d, J = 8.4 Hz, 5H), 7.40 (t, J = 7.6 Hz, 2H), 7.45-7.52 (m, 2H), 7.55 (t, J = 7.2 Hz, 2H), 7.92 (d, J = 8.0 Hz, 1H), 7.95 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 35.7,

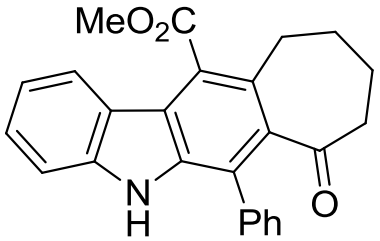
40.9, 47.4, 52.8, 111.2, 120.3, 120.6, 122.4, 122.7, 125.2, 126.8, 126.9, 127.0, 127.5, 128.1, 128.2 (2C), 128.8, 128.9, 131.7, 138.0, 141.3, 143.4, 169.6, 197.5. **HRMS** (ESI-TOF) m/z calculated for $C_{30}H_{23}NNaO_3^+$ ($[M+Na]^+$) 468.1570, found 468.1569.



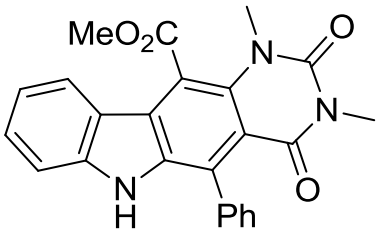
4y, Methyl 7-oxo-6-phenyl-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 82% yield, 56.9 mg, m.p. 256-258 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.15-2.23 (m, 2H), 2.65 (t, J = 6.6 Hz, 2H), 3.16 (t, J = 6.0 Hz, 2H), 4.17 (s, 3H), 7.22 (t, J = 7.4 Hz, 1H), 7.29-7.35 (m, 3H), 7.43-7.49 (m, 2H), 7.53 (t, J = 7.2 Hz, 2H), 7.89 (s, 1H), 7.91 (d, J = 8.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 23.0, 27.9, 40.4, 52.6, 111.1, 120.2, 120.7, 122.4 (2C), 125.0, 127.4, 127.7, 128.0, 128.1, 128.2, 128.9, 132.9, 137.9, 138.2, 141.3, 169.7, 198.2. **HRMS** (ESI-TOF) m/z calculated for $C_{24}H_{20}NO_3^+$ ($[M+H]^+$) 370.1438, found 370.1443.



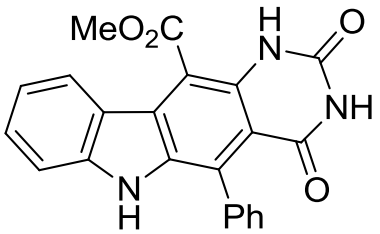
4z, Methyl 3-oxo-4-phenyl-1,2,3,5-tetrahydrocyclopenta[*b*]carbazole-10-carboxylate. Yellow solid in 27% yield, 19.2 mg, m.p. 217-220 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.75-2.78 (m, 2H), 3.45 (t, J = 6.2 Hz, 2H), 4.16 (s, 3H), 7.26 (t, J = 7.4 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.47-7.60 (m, 6H), 8.19 (s, 1H), 8.36 (d, J = 8.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 25.1, 37.5, 52.2, 111.0, 120.2, 121.0, 122.1, 124.7, 125.9, 126.3, 128.4, 128.6, 128.7, 129.4, 130.3, 133.7, 138.6, 142.1, 146.5, 168.2, 205.4. **HRMS** (ESI-TOF) m/z calculated for $C_{23}H_{17}NNaO_3^+$ ($[M+Na]^+$) 378.1101, found 378.1119.



4aa, Methyl 7-oxo-6-phenyl-5,7,8,9,10,11-hexahydrocyclohepta[*b*]carbazole-12-carboxylate. Yellow solid in 43% yield, 32.9 mg, m.p. 252-254 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.85-1.98 (m, 4H), 2.57 (t, J = 5.8 Hz, 2H), 2.90 (t, J = 6.4 Hz, 2H), 4.15 (s, 3H), 7.20-7.25 (m, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.35-7.39 (m, 2H), 7.40-7.45 (m, 2H), 7.47-7.52 (m, 2H), 7.91 (d, J = 8.0 Hz, 1H), 8.12 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.4, 25.7, 28.4, 42.4, 52.5, 111.0, 120.0, 120.5, 121.2, 121.8, 124.5, 124.8, 126.1, 127.0, 128.1, 129.0, 129.2, 136.0, 137.0, 137.7, 140.3, 169.7, 209.4. **HRMS** (ESI-TOF) m/z calculated for $C_{25}H_{21}NNaO_3^+$ ($[M+Na]^+$) 406.1414, found 406.1425.

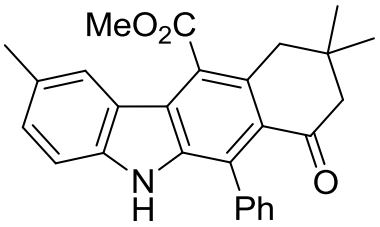


4ab, Methyl 1,3-dimethyl-2,4-dioxo-5-phenyl-2,3,4,6-tetrahydro-1*H*-pyrimido[5,4-*b*]carbazole-11-carboxylate. Yellow solid in 70% yield, 57.8 mg, m.p. 291-293 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.35 (s, 3H), 3.72 (s, 3H), 4.18 (s, 3H), 7.21-7.27 (m, 1H), 7.33-7.37 (m, 3H), 7.46-7.60 (m, 4H), 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.

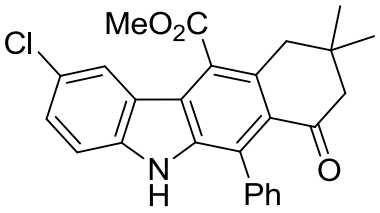


4ac, Methyl 2,4-dioxo-5-phenyl-2,3,4,6-tetrahydro-1*H*-pyrimido[5,4-*b*]carbazole-11-carboxylate.

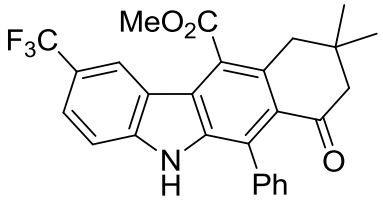
Yellow solid in 84% yield, 64.6 mg, m.p. 274-276 ^{o}C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 4.13 (s, 3H), 7.17 (t, J = 7.2 Hz, 1H), 7.33 (d, J = 6.0 Hz, 2H), 7.43-7.57 (m, 5H), 8.03 (d, J = 8.0 Hz, 1H), 10.48 (s, 1H), 10.69 (s, 1H), 11.13 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 53.5, 110.0, 110.7, 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.



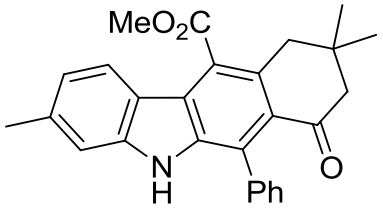
4ad, Methyl 2,9,9-trimethyl-7-oxo-6-phenyl-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 70% yield, 57.6 mg, m.p. 222-224 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.11 (s, 6H), 2.48 (brs, 5H), 3.01 (s, 2H), 4.16 (s, 3H), 7.19 (d, J = 8.4 Hz, 1H), 7.25 (d, J = 8.8 Hz, 1H), 7.28 (d, J = 7.2 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.63 (s, 1H), 7.81 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.6, 28.2, 33.3, 41.6, 52.6, 53.8, 110.8, 120.8, 121.8, 122.4, 125.6, 126.5, 127.3, 127.7, 128.3, 128.8, 129.4, 129.5, 130.6, 138.1, 138.3, 139.6, 169.9, 198.3. **HRMS** (ESI-TOF) m/z calculated for $C_{27}H_{25}NNaO_3^+$ ([M+Na]$^+$) 434.1727, found 434.1735.



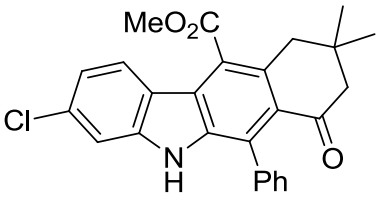
4ae, Methyl 2-chloro-9,9-dimethyl-7-oxo-6-phenyl-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 70% yield, 60.4 mg, m.p. 222-224 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.13 (s, 6H), 2.50 (s, 2H), 3.04 (s, 2H), 4.19 (s, 3H), 7.24 (d, J = 8.8 Hz, 1H), 7.27-7.30 (m, 2H), 7.39 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.43-7.70 (m, 1H), 7.48-7.54 (m, 2H), 7.85 (d, J = 2.0 Hz, 1H), 7.98 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.2, 41.6, 52.7, 53.7, 112.1, 121.7, 121.8, 121.9, 125.5, 125.9, 127.3, 127.5, 128.1, 128.2, 128.9, 131.4, 137.8, 138.4, 139.4, 169.3, 198.3. **HRMS** (ESI-TOF) m/z calculated for $C_{26}H_{22}ClNNaO_3^+$ ([M+Na]$^+$) 454.1180, found 454.1215.



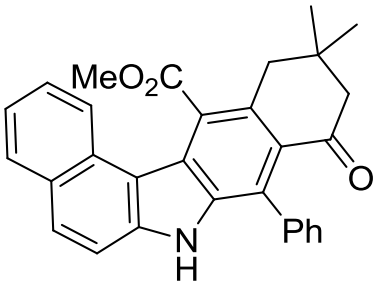
4af, methyl 9,9-dimethyl-7-oxo-6-phenyl-2-(trifluoromethyl)-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Light yellow crystal in 61% yield, 56.7 mg, m.p. 247-248 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.14 (s, 6H), 2.51 (s, 2H), 3.07 (s, 2H), 4.20 (s, 3H), 7.28-7.31 (m, 2H), 7.39 (d, J = 8.8 Hz, 1H), 7.43-7.48 (m, 1H), 7.49-7.54 (m, 2H), 7.67 (dd, J_1 = 8.8 Hz, J_2 = 1.2 Hz, 1H), 8.15 (s, 1H), 8.19 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.2, 41.6, 52.7, 53.7, 111.5, 120.0 (q, J = 4.3 Hz), 120.4, 122.3, 122.4 (q, J = 32.1 Hz), 124.6 (q, J = 3.2 Hz), 124.8 (q, J = 269.9 Hz), 126.0, 127.6, 127.7, 128.2, 128.3, 128.9, 132.1, 137.6, 138.4, 142.5, 169.2, 198.2. **HRMS** (ESI-TOF) m/z calculated for $C_{27}H_{22}F_3NNaO_3^+$ ([M+Na]$^+$) 488.1444, found 488.1444.



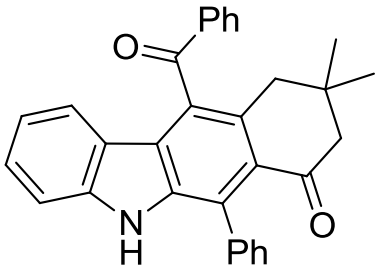
4ag, methyl 3,9,9-trimethyl-7-oxo-6-phenyl-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. White solid in 79% yield, 64.9 mg, m.p. 219-221 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.12 (s, 6H), 2.48 (s, 3H), 2.49 (s, 2H), 3.03 (s, 2H), 4.16 (s, 3H), 7.04 (dd, J_1 = 8.4 Hz, J_2 = 0.4 Hz, 1H), 7.11 (s, 1H), 7.28-7.31 (m, 2H), 7.43-7.49 (m, 1H), 7.50-7.55 (m, 2H), 7.77 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 22.1, 28.3, 33.3, 41.7, 52.6, 53.8, 111.1, 118.5, 121.9, 122.0, 122.9, 125.3, 126.3, 127.3, 127.7, 128.3, 128.8, 131.1, 137.8, 138.3, 138.6, 141.8, 169.8, 198.3. **HRMS** (ESI-TOF) m/z calculated for $C_{27}H_{25}NNaO_3^+$ ([M+Na]$^+$) 434.1727, found 434.1744.



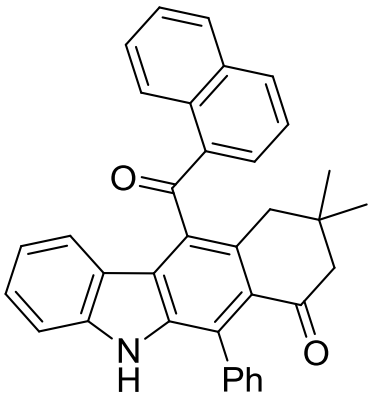
4ah, Methyl 3-chloro-9,9-dimethyl-7-oxo-6-phenyl-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate. Yellow solid in 65% yield, 56.1 mg, m.p. 252-254 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.12 (s, 6H), 2.49 (s, 2H), 3.03 (s, 2H), 4.16 (s, 3H), 7.17 (dd, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 1H), 7.27 (s, 1H), 7.29-7.31 (m, 2H), 7.44-7.47 (m, 1H), 7.49-7.54 (m, 2H), 7.80 (d, J = 8.8 Hz, 1H), 7.97 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.2, 41.7, 52.7, 53.7, 111.1, 119.3, 120.9, 122.1, 123.2, 125.6, 127.0, 127.5, 128.0, 128.2, 128.9, 131.6, 133.8, 137.8, 138.1, 141.7, 169.5, 198.2. **HRMS** (ESI-TOF) m/z calculated for $C_{26}H_{22}ClNNaO_3^+$ ($[M+Na]^+$) 454.1180, found 454.1208.



4ai, Methyl 11,11-dimethyl-9-oxo-8-phenyl-9,10,11,12-tetrahydro-7*H*-dibenzo[*b*,*g*]carbazole-13-carboxylate. Yellow crystal in 87% yield, 77.8 mg, m.p. 200-201 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.17 (s, 6H), 2.52 (s, 2H), 3.16 (s, 2H), 4.07 (s, 3H), 7.33-7.36 (m, 2H), 7.42 (d, J = 8.4 Hz, 1H), 7.48 (t, J = 7.0 Hz, 2H), 7.54 (t, J = 7.2 Hz, 2H), 7.66 (t, J = 7.2 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.40 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.3, 33.0, 41.9, 52.3, 53.5, 112.6, 114.4, 123.3, 123.4, 124.1, 125.4, 126.1, 126.9, 127.5, 128.3, 128.4, 128.8, 129.4, 129.5, 129.6, 130.4, 131.9, 136.9, 138.1, 140.2, 171.3, 198.3. **HRMS** (ESI-TOF) m/z calculated for $C_{30}H_{25}NNaO_3^+$ ($[M+Na]^+$) 470.1727, found 470.1721.

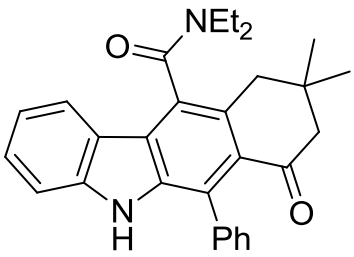


4aj, 11-benzoyl-9,9-dimethyl-6-phenyl-9,10-dihydro-5*H*-benzo[*b*]carbazol-7(8*H*)-one. Light yellow solid in 54% yield, 47.8 mg, m.p. 230-233 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.03 (s, 6H), 2.50 (s, 2H), 2.72 (s, 1H), 2.96 (s, 1H), 6.98 (t, J = 7.4 Hz, 1H), 7.27-7.37 (m, 3H), 7.42-7.60 (m, 7H), 7.65 (t, J = 7.4 Hz, 1H), 7.97 (s, 1H), 8.03 (d, J = 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 27.6, 28.6, 33.6, 41.4, 54.0, 110.9, 120.1, 120.8, 122.8 (2C), 126.7, 127.1, 127.4, 127.6, 128.4, 128.9, 129.1, 129.8, 130.4, 132.4, 134.4, 136.6, 137.7, 138.3, 141.1, 198.5, 199.1. **HRMS** (ESI-TOF) m/z calculated for $C_{31}H_{25}NNaO_2^+$ ($[M+Na]^+$) 466.1778, found 466.1764.



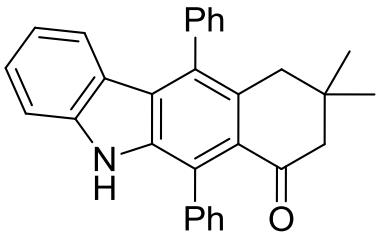
4ak,

11-(1-naphthoyl)-9,9-dimethyl-6-phenyl-9,10-dihydro-5*H*-benzo[*b*]carbazol-7(8*H*)-one. Yellow solid in 85% yield, 83.8 mg, m.p. 171-172 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.00 (s, 6H), 2.49 (s, 2H), 2.79 (s, 1H), 3.02 (s, 1H), 6.90 (t, J = 7.2 Hz, 1H), 7.27-7.39 (m, 4H), 7.45-7.61 (m, 5H), 7.72 (t, J = 7.4 Hz, 1H), 7.89 (t, J = 7.8 Hz, 2H), 7.99 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 9.69 (d, J = 8.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 27.6, 28.4, 33.5, 41.3, 54.0, 110.9, 120.1, 121.1, 122.9, 123.1, 124.7, 126.3, 126.8, 126.9, 127.0, 127.4, 127.6, 128.4, 128.9, 129.5, 130.6, 131.1, 132.3, 134.2, 134.3, 134.4, 135.5, 137.8, 138.4, 141.1, 198.6, 201.0. **HRMS** (ESI-TOF) m/z calculated for $C_{35}H_{27}NNaO_2^+$ ($[M+Na]^+$) 516.1934, found 516.1928.

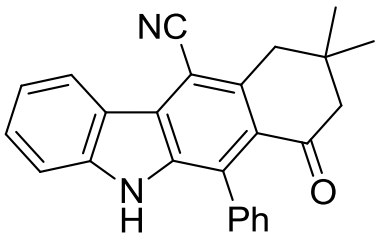


4al,

***N*,*N*-diethyl-9,9-dimethyl-7-oxo-6-phenyl-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxamide.** Light yellow solid in 52% yield, 45.6 mg, m.p. 199-200 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.2 Hz, 3H), 1.11 (s, 3H), 1.14 (s, 3H), 1.49 (t, *J* = 7.0 Hz, 3H), 2.45 (d, *J* = 15.6 Hz, 1H), 2.55 (d, *J* = 16.0 Hz, 1H), 2.80 (d, *J* = 16.0 Hz, 1H), 3.15 (d, *J* = 16.0 Hz, 1H), 3.29 (q, *J* = 7.2 Hz, 2H), 3.66-3.78 (m, 1H), 3.95-4.05 (m, 1H), 7.15-7.23 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.38-7.47 (m, 3H), 7.48-7.57 (m, 2H), 7.93 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 12.8, 14.1, 27.8, 28.7, 33.4, 38.8, 40.9, 42.7, 54.0, 110.9, 120.1, 121.1, 122.1, 122.4, 126.4, 126.9, 127.3, 127.6, 128.2, 128.5, 128.7, 128.9, 129.2, 129.7, 137.8, 138.3, 141.0, 169.1, 198.7. **HRMS** (ESI-TOF) m/z calculated for $C_{29}H_{30}N_2NaO_2^+$ ($[M+Na]^+$) 461.2199, found 461.2201.

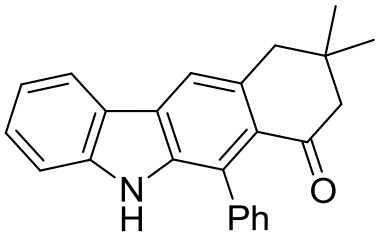


4am, 9,9-dimethyl-6,11-diphenyl-9,10-dihydro-5*H*-benzo[*b*]carbazol-7(8*H*)-one. Yellow solid in 54% yield, 44.8 mg, m.p. 222-223 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.04 (s, 6H), 2.48 (s, 2H), 2.75 (s, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 6.0 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.37-7.43 (m, 4H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.53-7.64 (m, 5H), 7.84 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.3, 33.3, 41.9, 53.9, 110.5, 119.4, 122.6, 123.0, 125.3 (2C), 126.9, 127.0, 127.1, 127.7, 128.5, 128.8, 129.2, 131.9, 135.5, 137.4, 139.0, 139.6, 141.0, 199.5. **HRMS** (ESI-TOF) m/z calculated for $C_{30}H_{25}NNaO^+$ ($[M+Na]^+$) 438.1828, found 438.1827.

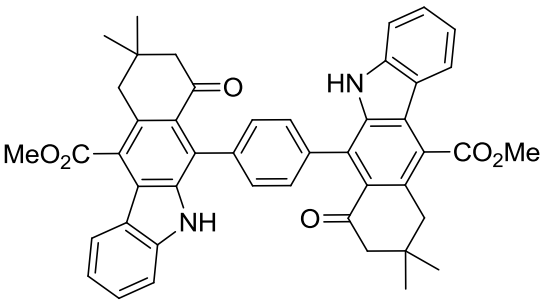


4an,

9,9-dimethyl-7-oxo-6-phenyl-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carbonitrile. Yellow solid in 88% yield, 64.1 mg, m.p. 232-234 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.17 (s, 6H), 2.54 (s, 2H), 3.33 (s, 2H), 7.28-7.32 (m, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.46-7.52 (m, 1H), 7.55 (t, J = 7.6 Hz, 3H), 8.02 (s, 1H), 8.67 (d, J = 8.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.4, 42.7, 53.7, 103.1, 111.2, 117.4, 120.5, 120.8, 122.6, 126.4, 126.8, 127.9, 128.0, 129.0, 129.2, 130.6, 137.2, 137.6, 139.1, 141.4, 197.4. **HRMS** (ESI-TOF) m/z calculated for $C_{25}H_{20}N_2NaO^+$ ($[M+Na]^+$) 387.1468, found 387.1468.

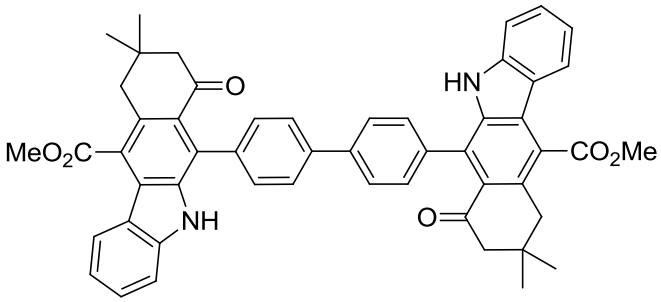


4ao, 9,9-dimethyl-6-phenyl-9,10-dihydro-5*H*-benzo[*b*]carbazol-7(8*H*)-one. Light yellow solid in 29% yield, 19.7 mg, m.p. 201-202 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.13 (s, 6H), 2.50 (s, 2H), 3.11 (s, 2H), 7.24 (t, J = 7.4 Hz, 1H), 7.30-7.36 (m, 3H), 7.41-7.47 (m, 2H), 7.53 (t, J = 7.4 Hz, 2H), 7.77 (s, 1H), 7.93 (s, 1H), 8.10 (d, J = 8.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.7, 45.2, 54.3, 110.9, 119.6, 119.7, 121.3, 122.3, 126.1, 126.6, 127.1, 127.5, 128.5, 128.8, 134.6, 138.0, 138.8, 141.1, 199.0. **HRMS** (ESI-TOF) m/z calculated for $C_{24}H_{21}NNaO^+$ ($[M+Na]^+$) 362.1515, found 362.1522 .

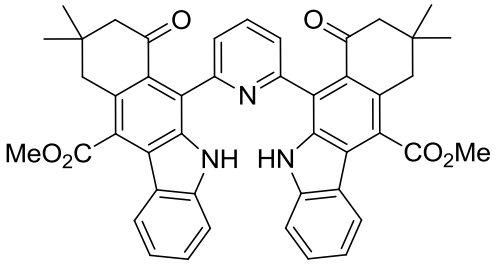


6a, Dimethyl

6,6'-(1,4-phenylene)bis(9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate). White solid in 65% yield, 92.7 mg, m.p. > 300 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.17 (s, 12H), 2.57 (s, 4H), 3.09 (s, 4H), 4.20 (s, 6H), 7.24 (t, J = 7.4 Hz, 2H), 7.43-7.51 (m, 8H), 7.92 (d, J = 8.0 Hz, 2H), 8.51 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.4, 41.6, 52.7, 54.1, 111.5, 120.1, 120.5, 122.1, 122.9, 125.9, 126.4, 127.6, 128.1, 128.8, 130.9, 137.3, 138.0, 141.5, 169.8, 199.3. **HRMS** (ESI-TOF) m/z calculated for $C_{46}H_{40}N_2NaO_6^+$ ($[M+Na]^+$) requires m/z 739.2779, found 739.2808.

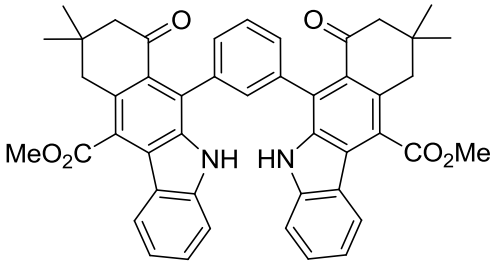


6b, Dimethyl 6,6'-([1,1'-biphenyl]-4,4'-diyl)bis(9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate). Light yellow solid in 58% yield, 91.9 mg, m.p. > 300 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.16 (s, 12H), 2.55 (s, 4H), 3.07 (s, 4H), 4.19 (s, 6H), 7.24 (t, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 4H), 7.47 (t, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 4H), 7.92 (d, J = 8.0 Hz, 2H), 8.03 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.3, 33.3, 41.7, 52.7, 53.9, 111.2, 120.2, 120.7, 122.3, 122.7, 125.9, 126.8, 127.4, 127.6, 128.0, 128.9, 131.1, 137.3, 137.9, 139.8, 141.3, 169.8, 198.5. **HRMS** (ESI-TOF) m/z calculated for $C_{52}H_{44}N_2NaO_6^+$ ($[M+Na]^+$) requires m/z 815.3092, found 815.3104.

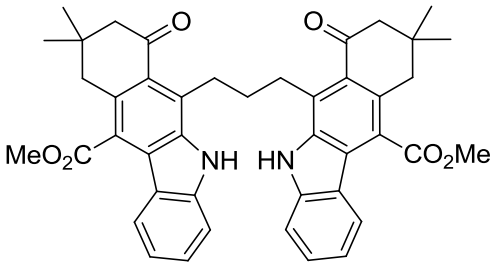


6c, Dimethyl 6,6'-(pyridine-2,6-diyl)bis(9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate). Light yellow solid in 56% yield, 80.3 mg, m.p. > 300 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.15 (s, 12H), 2.62 (s, 4H), 3.06 (s, 4H), 4.15 (s, 3H), 7.20 (t, J = 7.6 Hz, 2H),

7.43 (d, *J* = 7.6 Hz, 4H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.97 (t, *J* = 7.8 Hz, 1H), 9.33 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.7, 41.5, 52.6, 54.1, 111.4, 119.9, 120.3, 122.3, 122.7, 124.1, 126.0, 126.1, 126.6, 128.2, 130.9, 137.2, 138.3, 142.3, 157.5, 169.6, 200.4. **HRMS** (ESI-TOF) m/z calculated for $C_{45}H_{39}N_3NaO_6^+$ ($[M+Na]^+$) requires m/z 740.2731, found 740.2748.

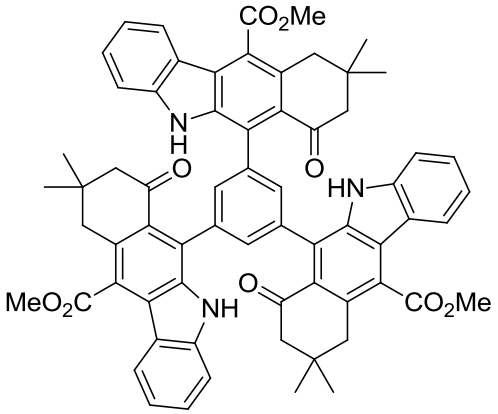


6d, Dimethyl 6,6'-(1,3-phenylene)bis(9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate). Yellow solid in 77% yield, 110.3 mg, m.p. 266-268 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.12 (s, 6H), 1.19 (s, 3H), 2.55 (d, *J* = 16.0 Hz, 2H), 2.67 (d, *J* = 16.0 Hz, 2H), 3.05 (d, *J* = 16.0 Hz, 2H), 3.10 (d, *J* = 16.4 Hz, 2H), 4.18 (s, 6H), 7.21-7.25 (m, 2H), 7.39 (dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 2H), 7.45-7.53 (m, 5H), 7.67 (t, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 9.23 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.1, 28.3, 33.3, 41.6, 52.6, 54.2, 111.4, 119.9, 120.4, 122.1, 123.0, 125.7, 125.8, 127.4, 127.6, 128.1, 129.1, 130.1, 130.9, 138.2, 138.3, 141.9, 169.7, 199.9. **HRMS** (ESI-TOF) m/z calculated for $C_{46}H_{40}N_2NaO_6^+$ ($[M+Na]^+$) requires m/z 739.2779, found 739.2775.

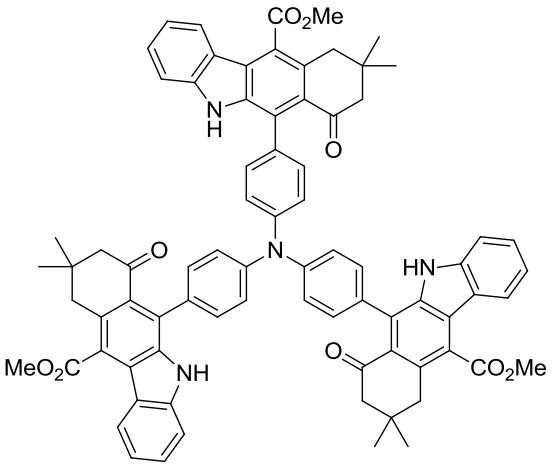


6e, Dimethyl 6,6'-(propane-1,3-diyl)bis(9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate). Light yellow solid in 60% yield, 81.8 mg, m.p. 260-263 ^{o}C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 0.98 (s, 12H), 1.94-2.02 (m, 2H), 2.52 (s, 4H), 2.84 (s, 4H), 3.66 (t, *J* = 7.6 Hz, 4H), 4.05 (s, 6H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 11.54 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 28.2, 29.5, 30.3,

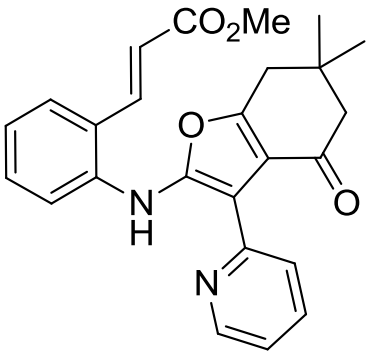
33.1, 41.5, 53.1, 54.3, 112.2, 119.9, 120.3, 121.4, 121.9, 124.6, 126.9, 128.1, 129.9, 130.3, 138.5, 142.0, 169.9, 200.2. **HRMS** (ESI-TOF) m/z calculated for $C_{43}H_{42}N_2NaO_6^+$ ($[M+Na]^+$) requires m/z 705.2935, found 705.2927.



8a, Trimethyl 6,6',6''-(benzene-1,3,5-triyl)tris(9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate). Yellow solid in 71% yield, 147.0 mg, m.p. > 300 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.08 (s, 6H), 1.14 (s, 6H), 1.15 (s, 6H), 2.54 (d, J = 16.0 Hz, 2H), 2.65 (d, J = 9.2 Hz, 2H), 2.67 (d, J = 6.8 Hz, 2H), 3.00 (d, J = 16.4 Hz, 2H), 3.05 (d, J = 16.0 Hz, 4H), 4.16 (s, 6H), 4.17 (s, 3H), 7.18-7.24 (m, 3H), 7.32-7.34 (m, 1H), 7.44-7.51 (m, 6H), 7.53 (d, J = 7.2 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.88 (dd, J_1 = 7.8 Hz, J_2 = 5.0 Hz, 3H), 9.16 (s, 2H), 10.33 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 27.8, 28.2, 28.8, 33.3, 33.4, 41.6, 52.7, 54.0, 54.8, 111.4, 111.8, 119.7, 120.0, 120.2, 120.5, 122.2, 122.9, 123.4, 124.9, 125.9 (2C), 126.2, 127.2, 127.6, 128.0 (2C), 128.2, 129.3, 137.9, 138.1, 138.2, 138.7, 140.4, 141.8, 142.6, 169.8, 199.0, 201.6. **HRMS** (ESI-TOF) m/z calculated for $C_{66}H_{57}N_3NaO_9^+$ ($[M+Na]^+$) 1058.3987, found 1058.3990.



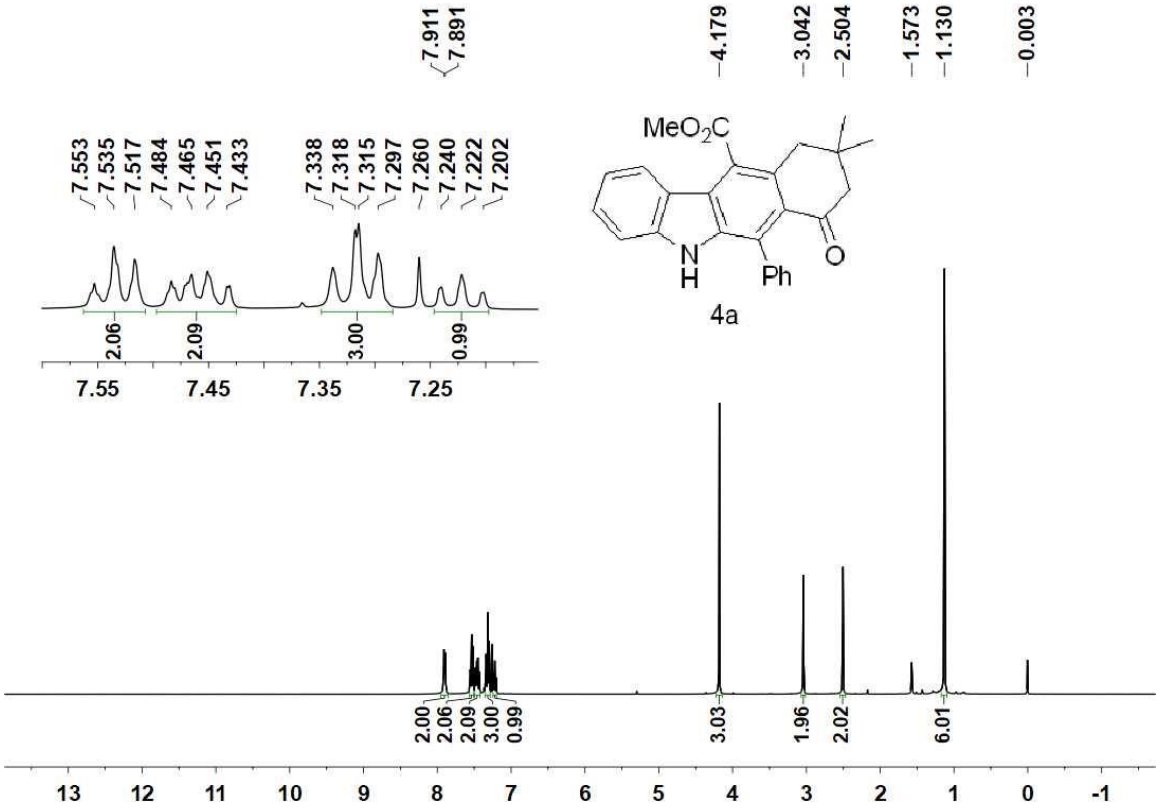
8b, Trimethyl 6,6',6''-(nitrilotris(benzene-4,1-diyl))tris(9,9-dimethyl-7-oxo-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-11-carboxylate). Yellow solid in 70% yield, 168.3 mg, m.p. 273-276 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.12 (s, 18H), 2.51 (s, 6H), 3.02 (s, 6H), 4.16 (s, 9H), 7.15-7.25 (m, 9H), 7.35-7.47 (m, 12H), 7.88 (d, J = 8.0 Hz, 3H), 8.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.2, 33.3, 41.6, 52.6, 54.0, 111.3, 120.1, 120.6, 122.1, 122.5, 124.6, 125.6, 126.8, 127.5, 127.9, 129.5, 130.9, 132.4, 137.9, 141.3, 146.7, 169.8, 198.7. **HRMS** (ESI-TOF) m/z calculated for $C_{78}H_{66}N_4NaO_9^+$ ($[M+Na]^+$) 1225.4722, found 1225.4734.



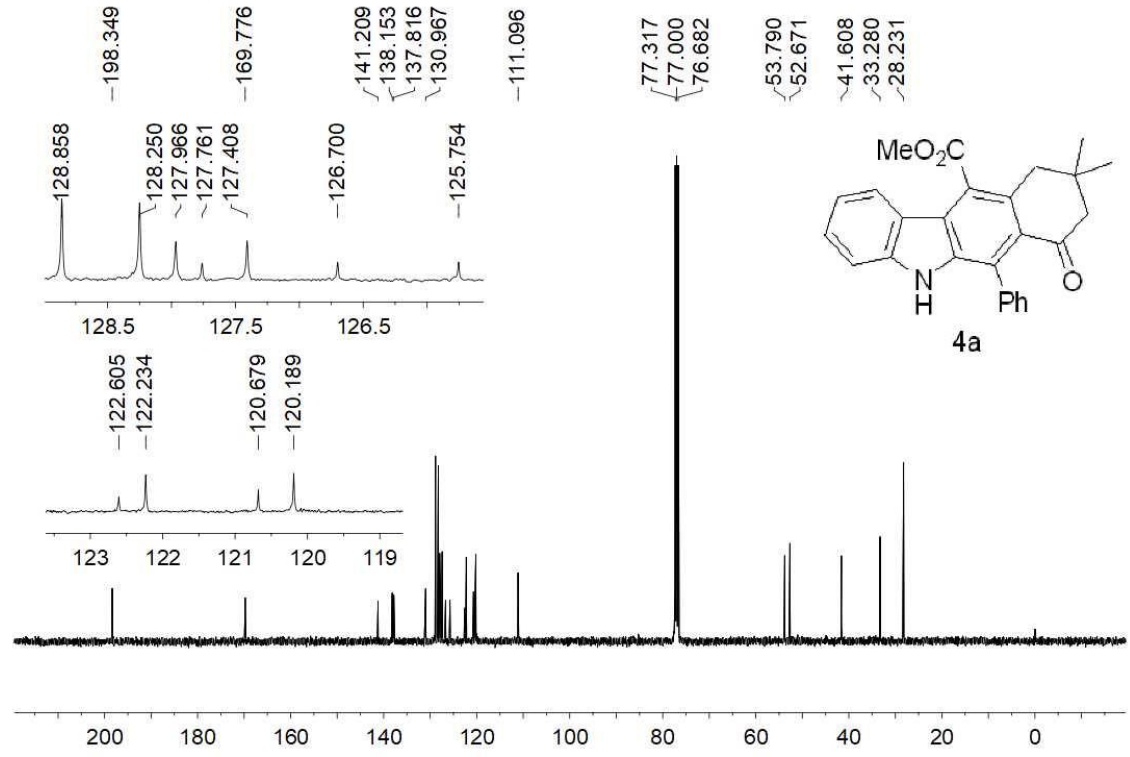
9, (*E*)-methyl 3-(2-((6,6-dimethyl-4-oxo-3-(pyridin-2-yl)-4,5,6,7-tetrahydrobenzofuran-2-yl)amino)phenyl)acrylate. Orange solid in 73% yield, 60.7mg, m.p. 169-171 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.19 (s, 6H), 2.49 (s, 2H), 2.83 (s, 2H), 3.85 (s, 3H), 6.47 (d, J = 15.6 Hz, 1H), 6.98 (t, J = 7.4 Hz, 1H), 7.03-7.07 (m, 1H), 7.32-7.38 (m, 1H), 7.53 (dd, d, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 1H), 7.67-7.72 (m, 1H), 7.74 (d, J = 7.8 Hz, 1H), 8.25 (d, J = 15.6 Hz, 1H), 8.66-8.69 (m, 1H), 8.74 (d, J = 8.4 Hz, 1H), 12.14 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.4, 34.6, 37.6, 51.7, 53.5, 95.2, 117.7, 118.3, 119.3, 119.5, 121.5, 123.1, 123.2, 127.7, 131.2, 136.6, 139.0, 140.1, 147.1, 152.7, 153.1, 158.6, 167.3, 193.9. **HRMS** (ESI-TOF) m/z calculated for $C_{25}H_{24}N_2NaO_4^+$ ($[M+Na]^+$) 439.1628, found 439.1642.

4. Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds 4, 6, 8 and 9

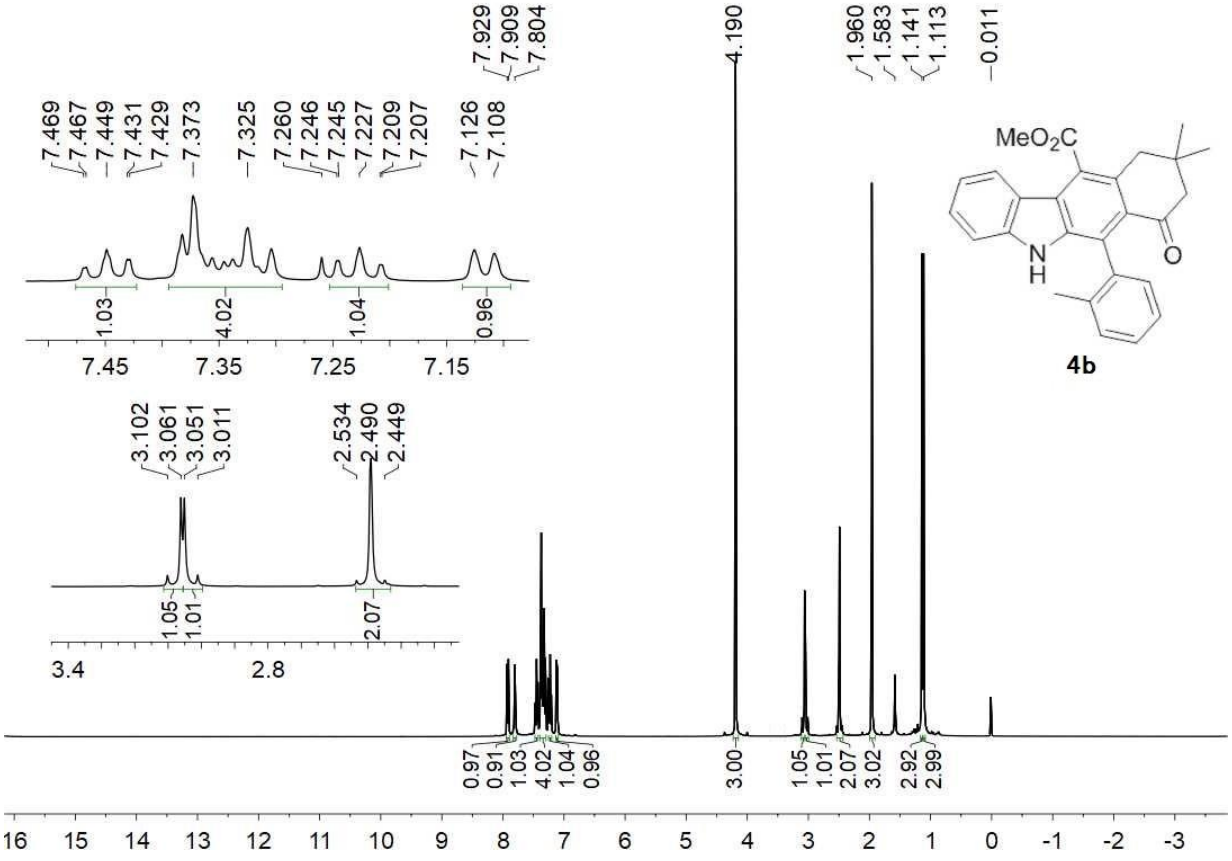
^{1}H NMR spectrum of the compound **4a** (400 MHz, $CDCl_3$)



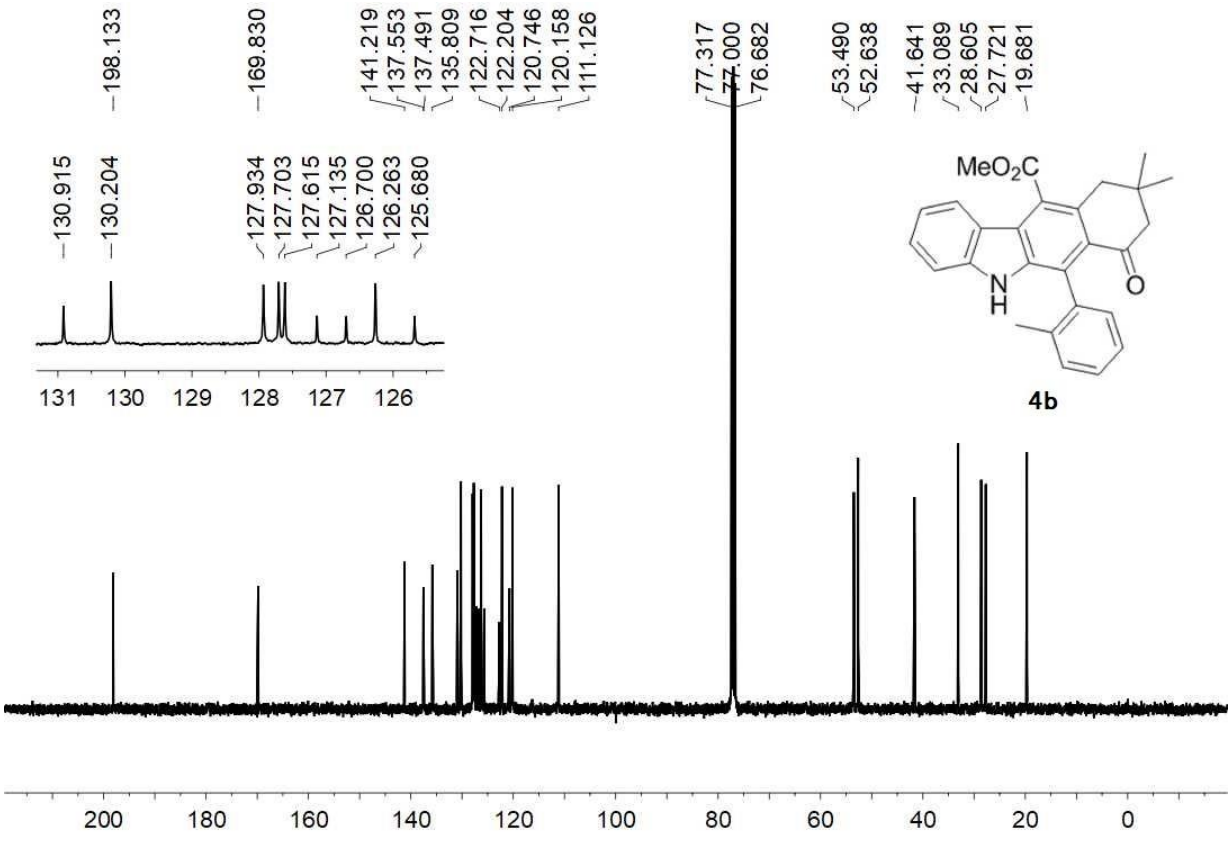
^{13}C NMR spectrum of the compound **4a** (100 MHz, $CDCl_3$)



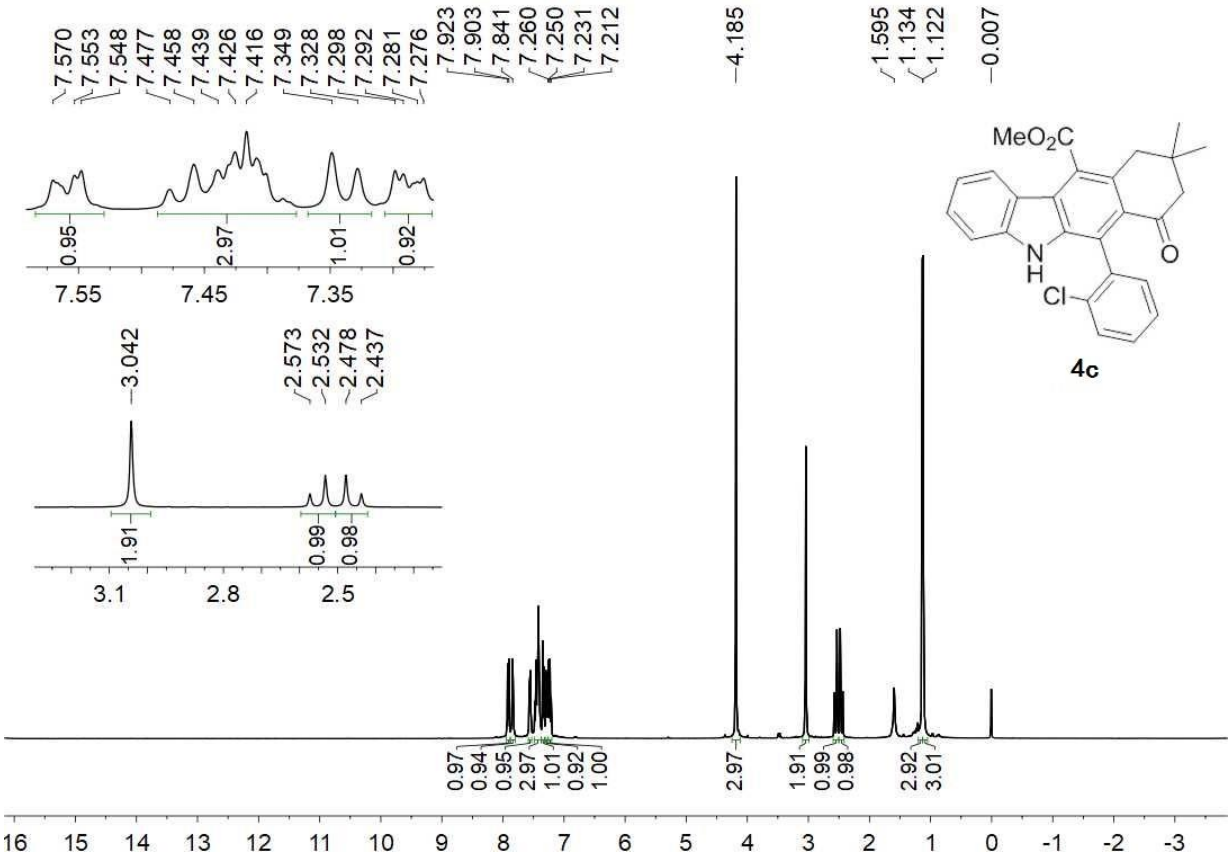
^{1}H NMR spectrum of the compound **4b** (400 MHz, $CDCl_3$)



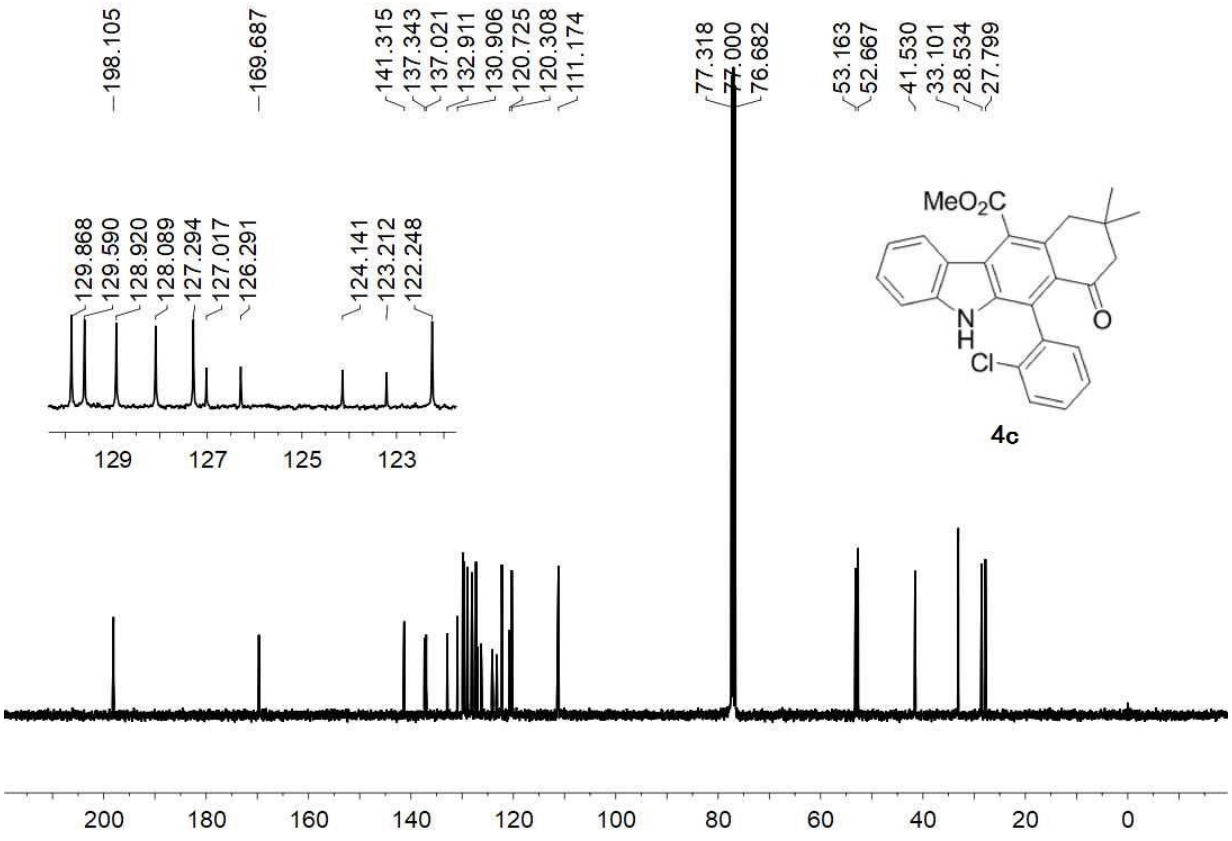
^{13}C NMR spectrum of the compound **4b** (100 MHz, $CDCl_3$)



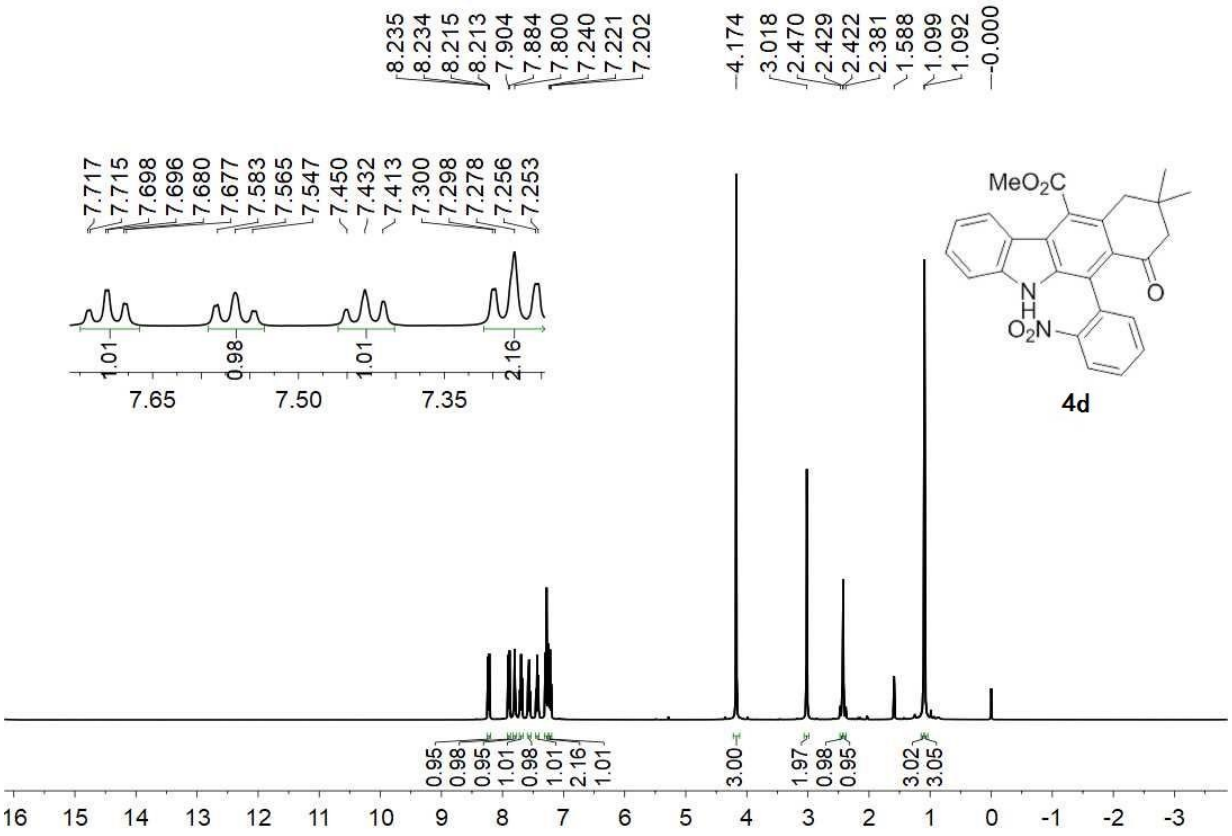
^{1}H NMR spectrum of the compound **4c** (400 MHz, $CDCl_3$)



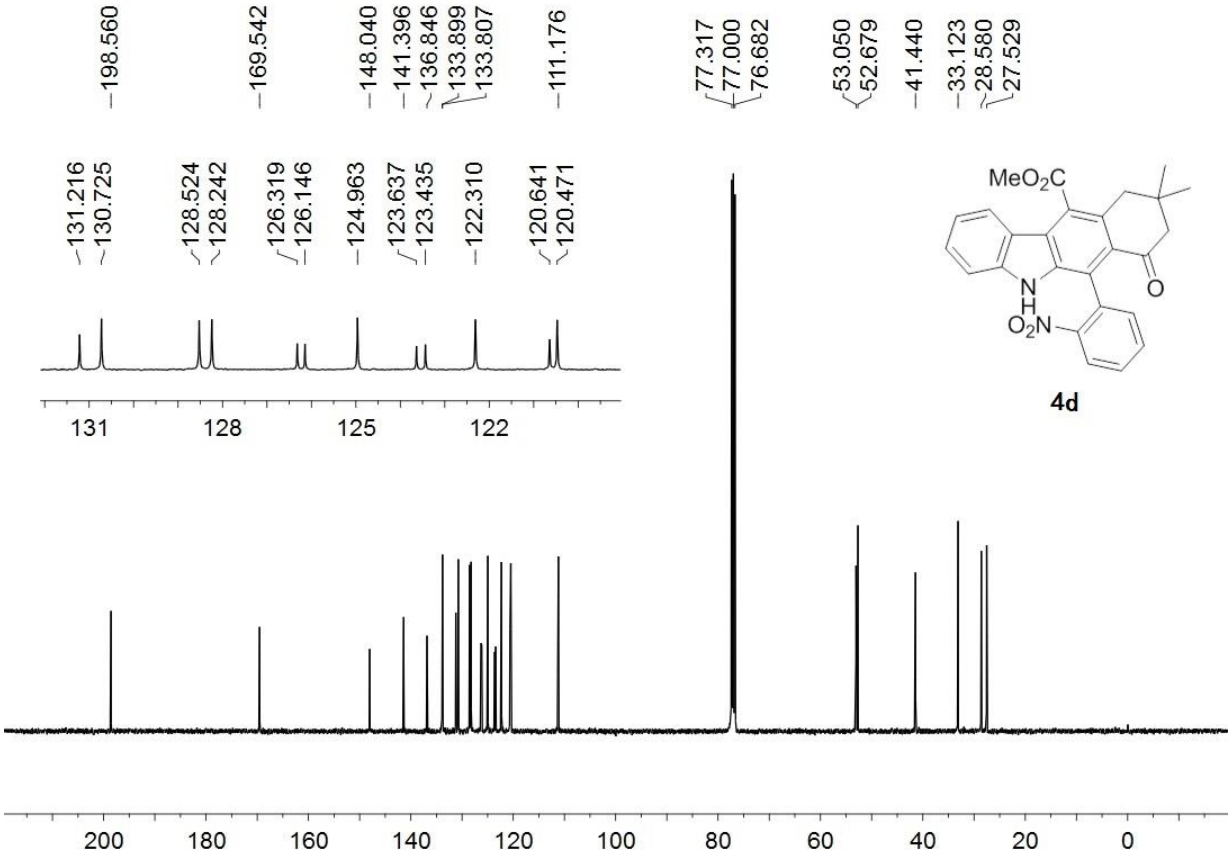
^{13}C NMR spectrum of the compound **4c** (100 MHz, $CDCl_3$)



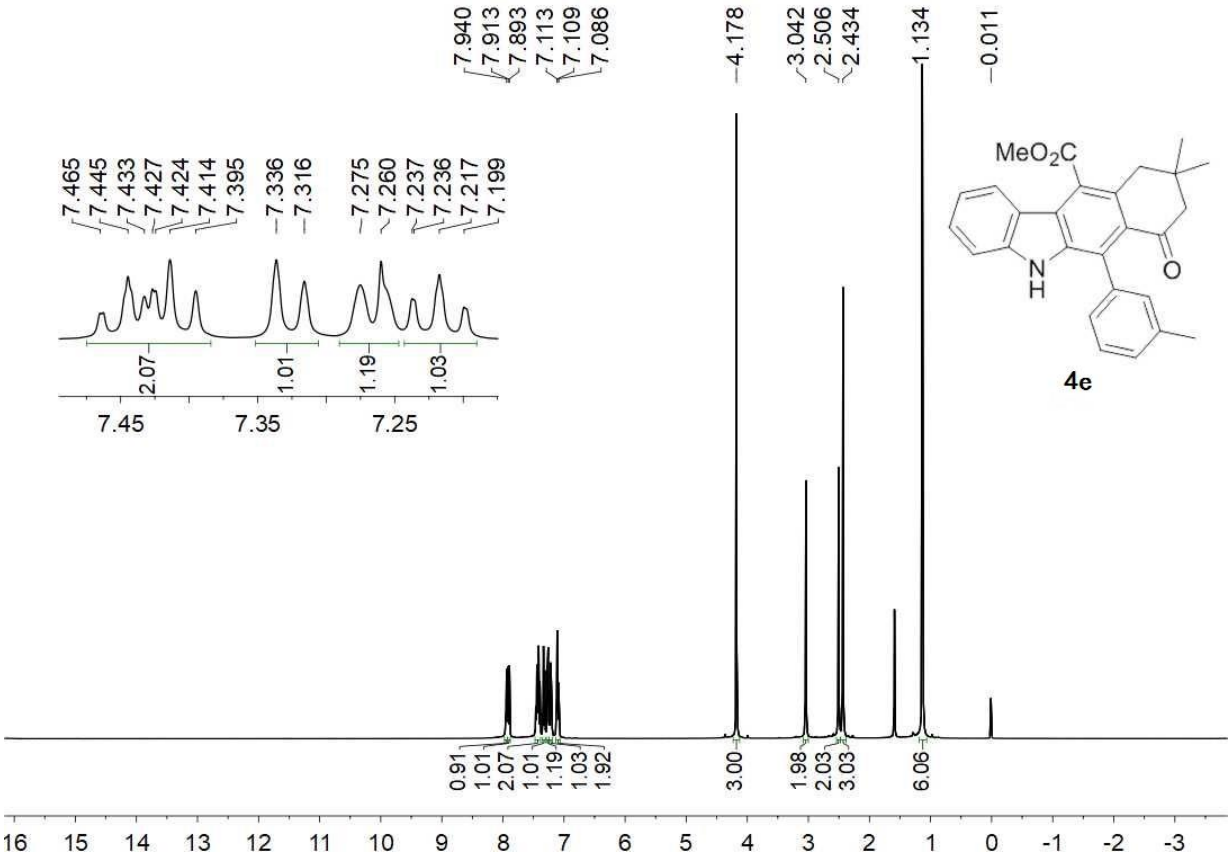
^{1}H NMR spectrum of the compound **4d** (400 MHz, $CDCl_3$)



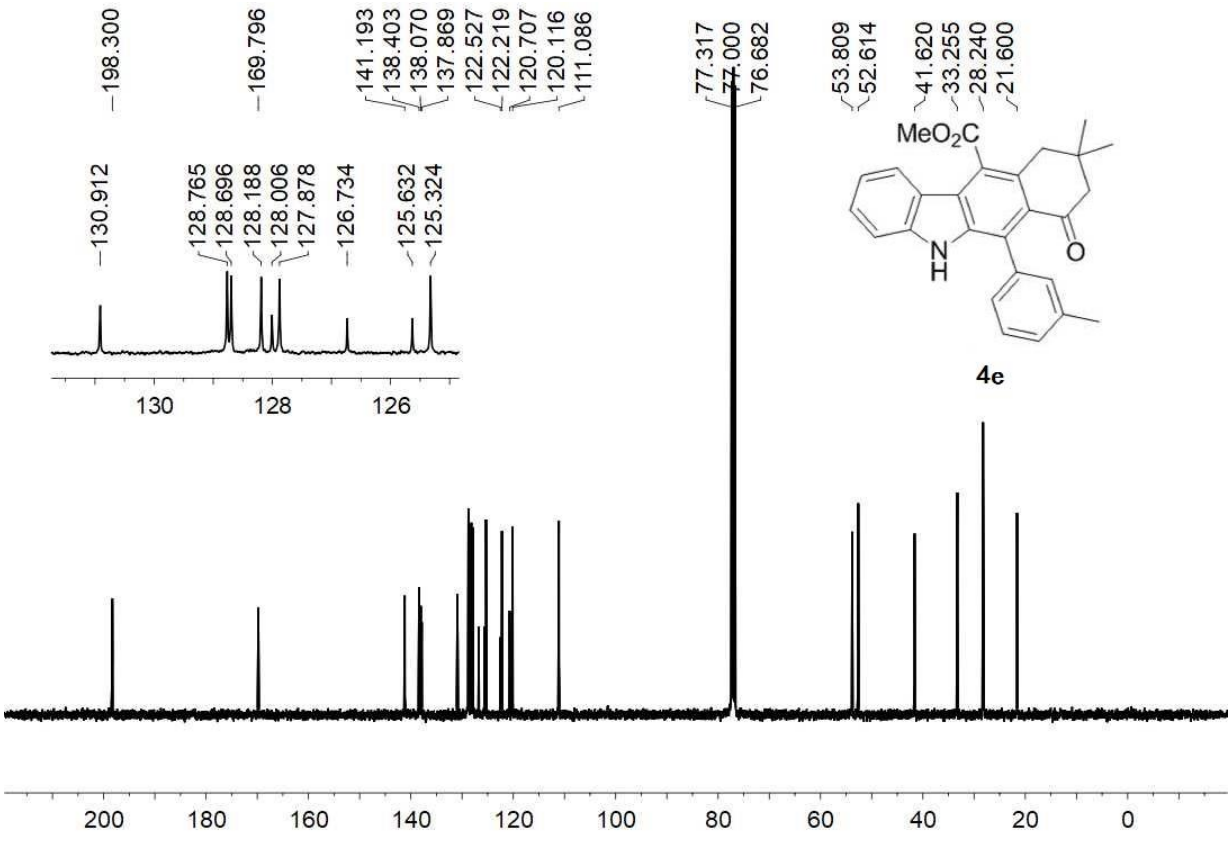
^{13}C NMR spectrum of the compound **4d** (100 MHz, $CDCl_3$)



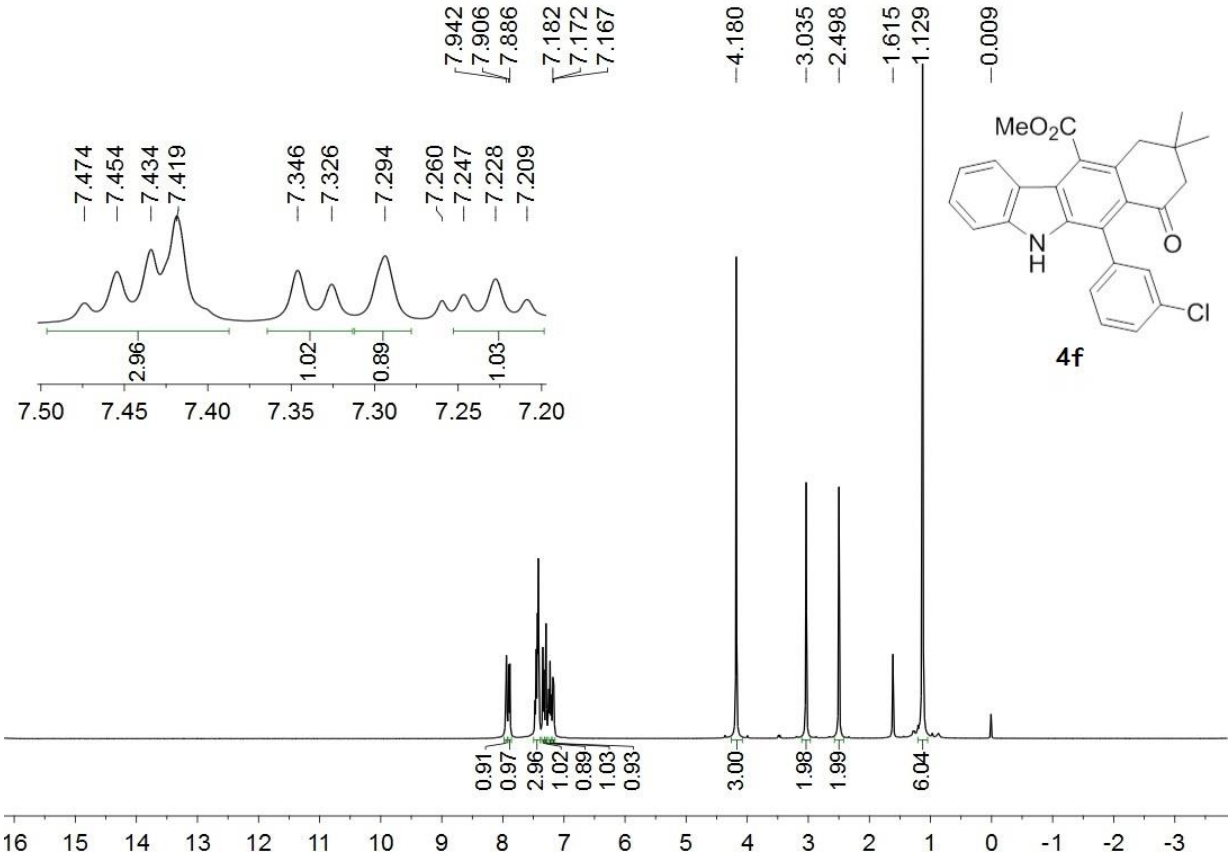
^{1}H NMR spectrum of the compound **4e** (400 MHz, $CDCl_3$)



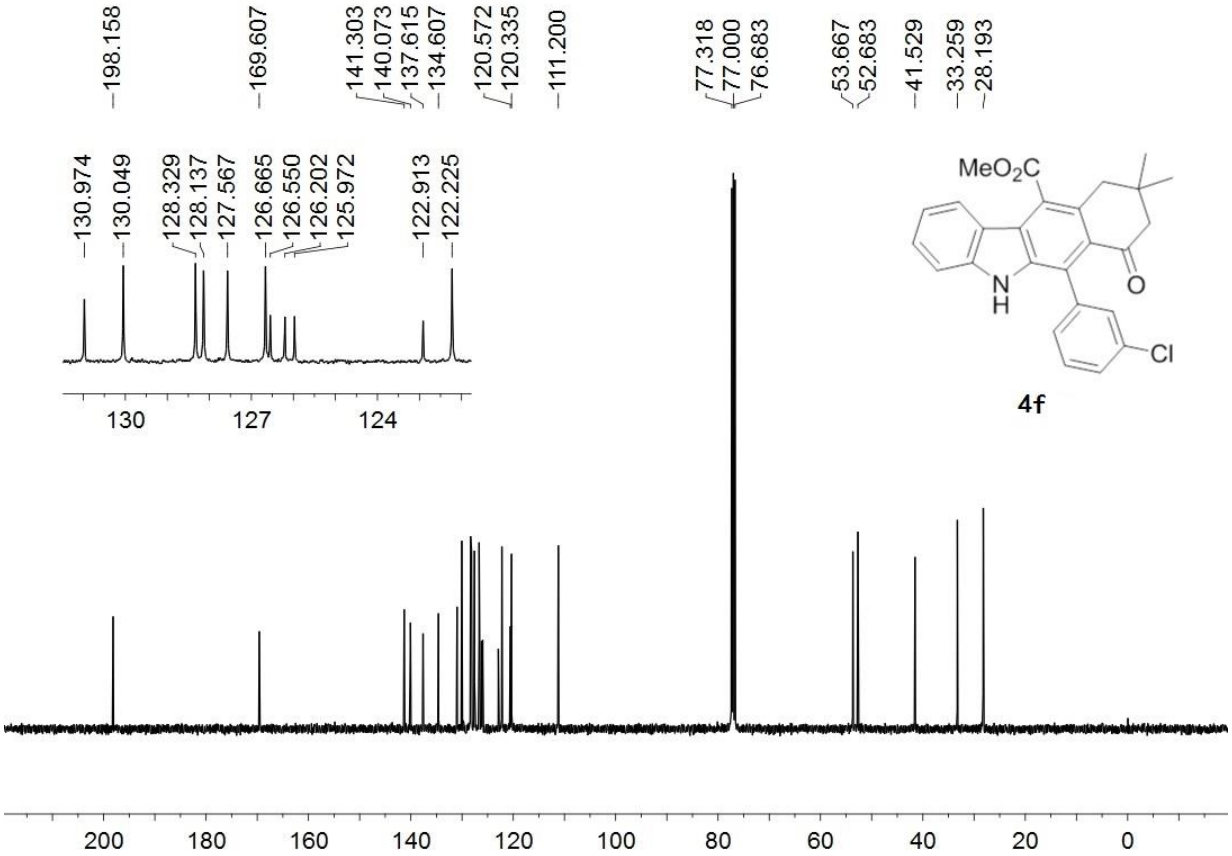
^{13}C NMR spectrum of the compound **4e** (100 MHz, $CDCl_3$)



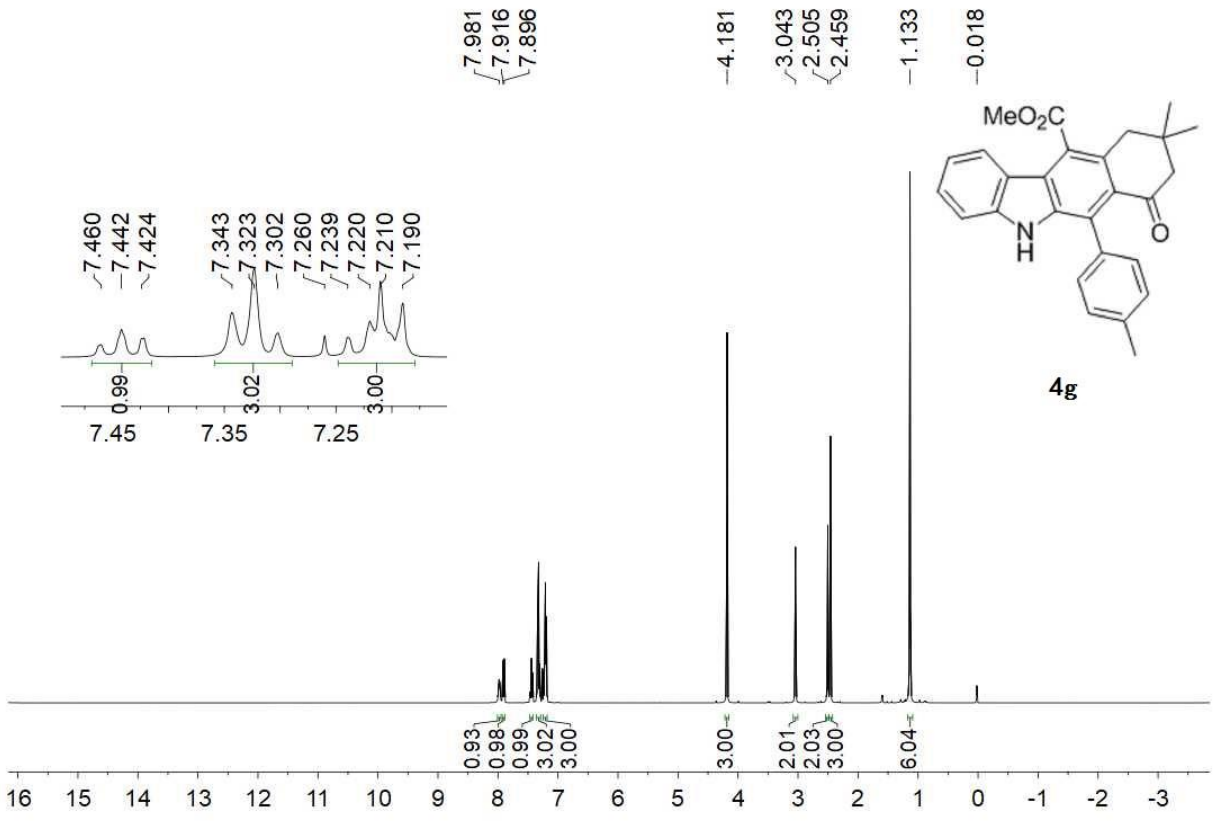
^{1}H NMR spectrum of the compound **4f** (400 MHz, $CDCl_3$)



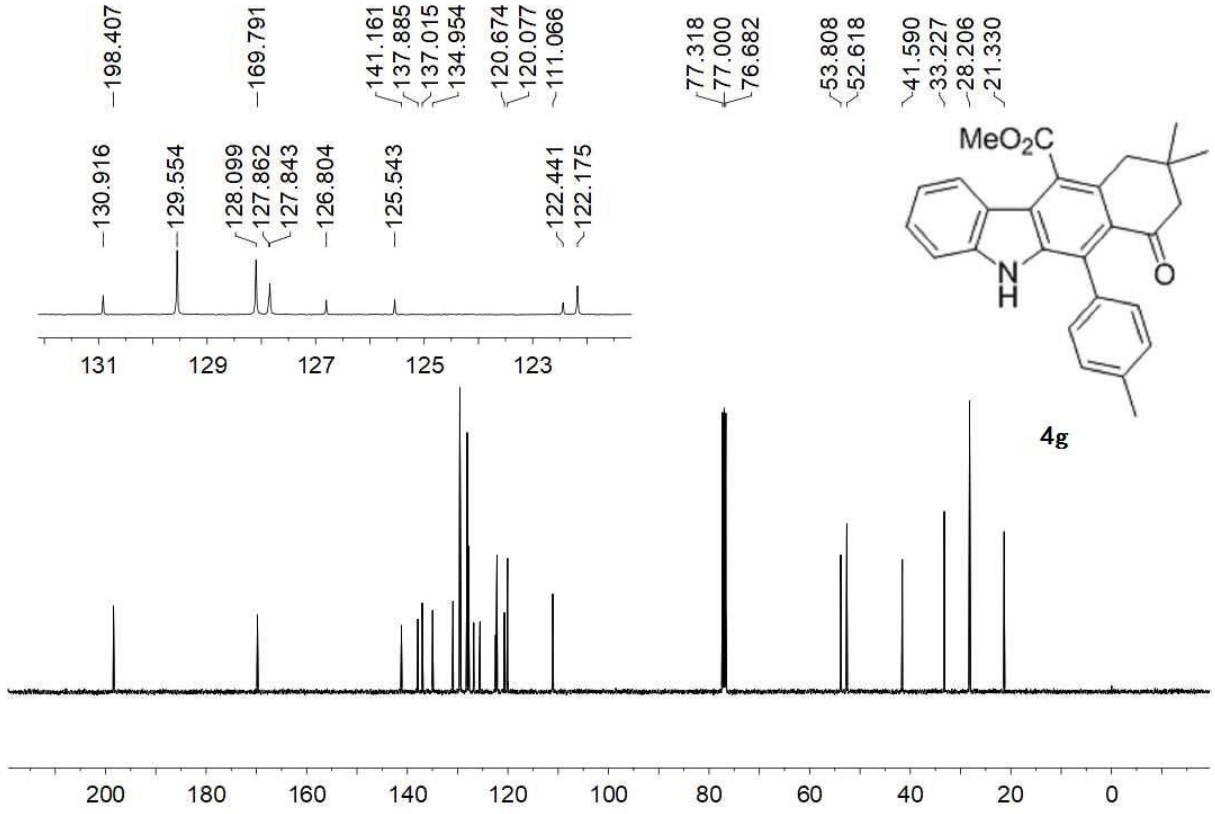
^{13}C NMR spectrum of the compound **4f** (100 MHz, $CDCl_3$)



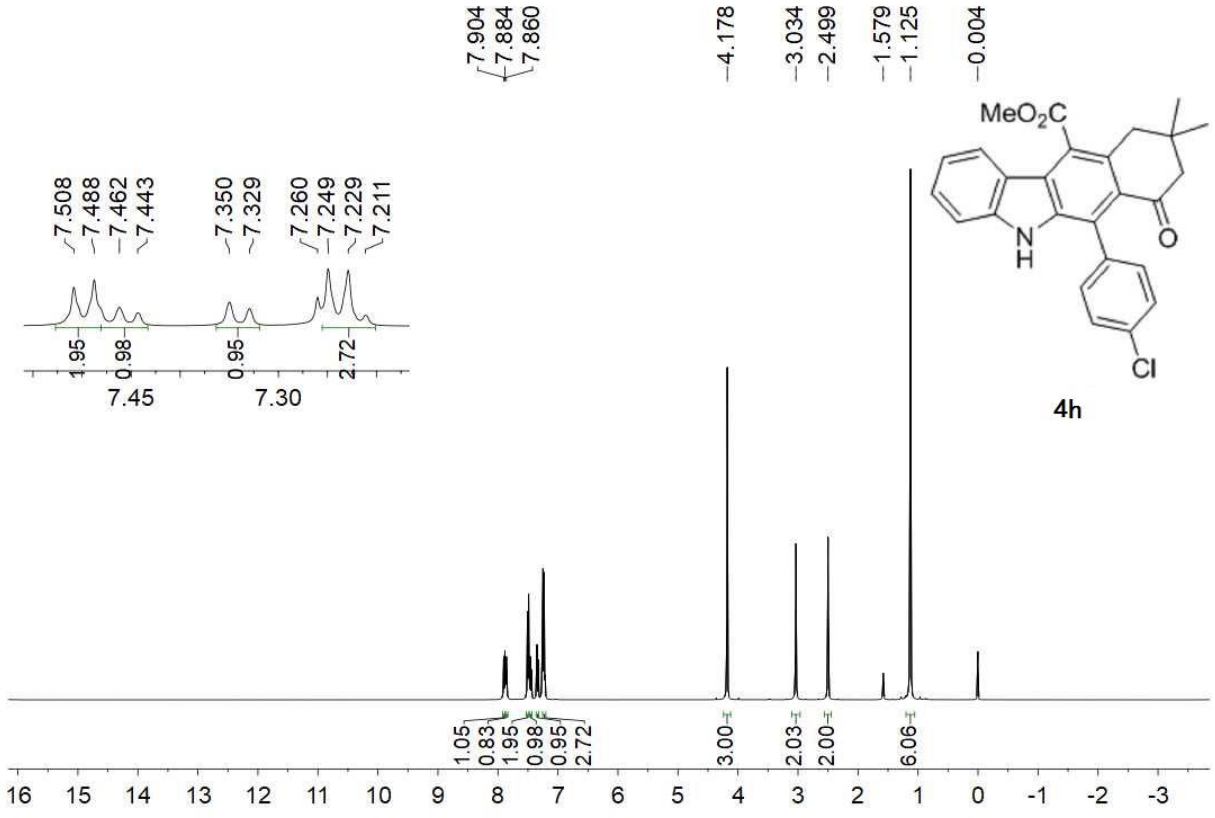
^{1}H NMR spectrum of the compound **4g** (400 MHz, $CDCl_3$)



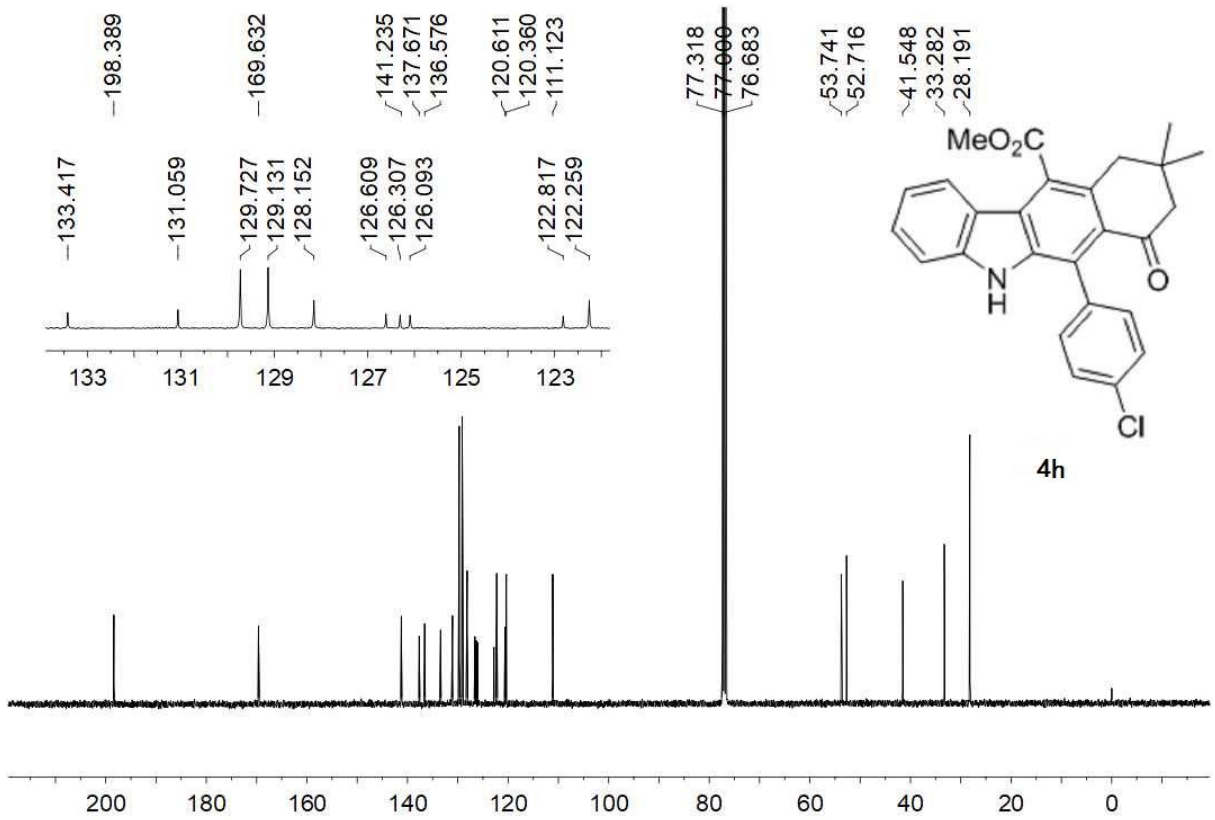
^{13}C NMR spectrum of the compound **4g** (100 MHz, $CDCl_3$)



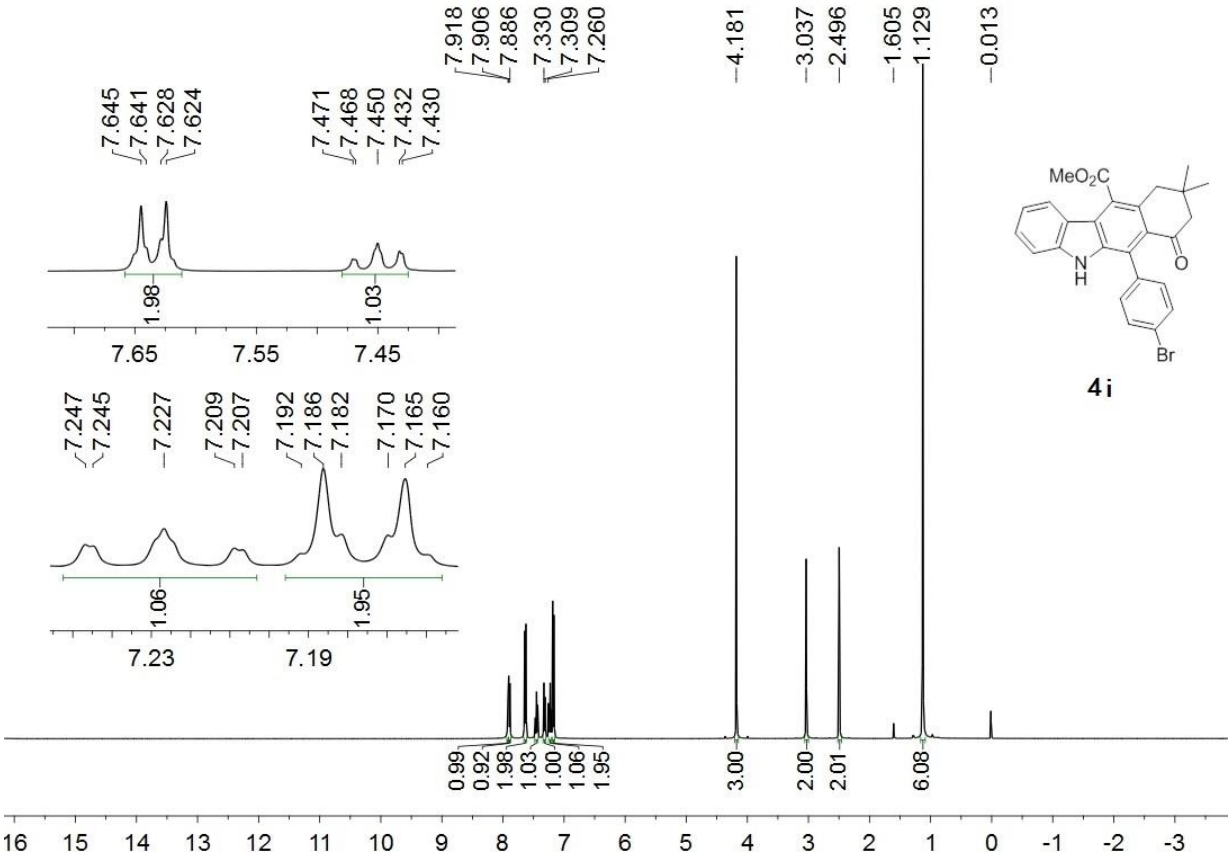
^{1}H NMR spectrum of the compound **4h** (400 MHz, $CDCl_3$)



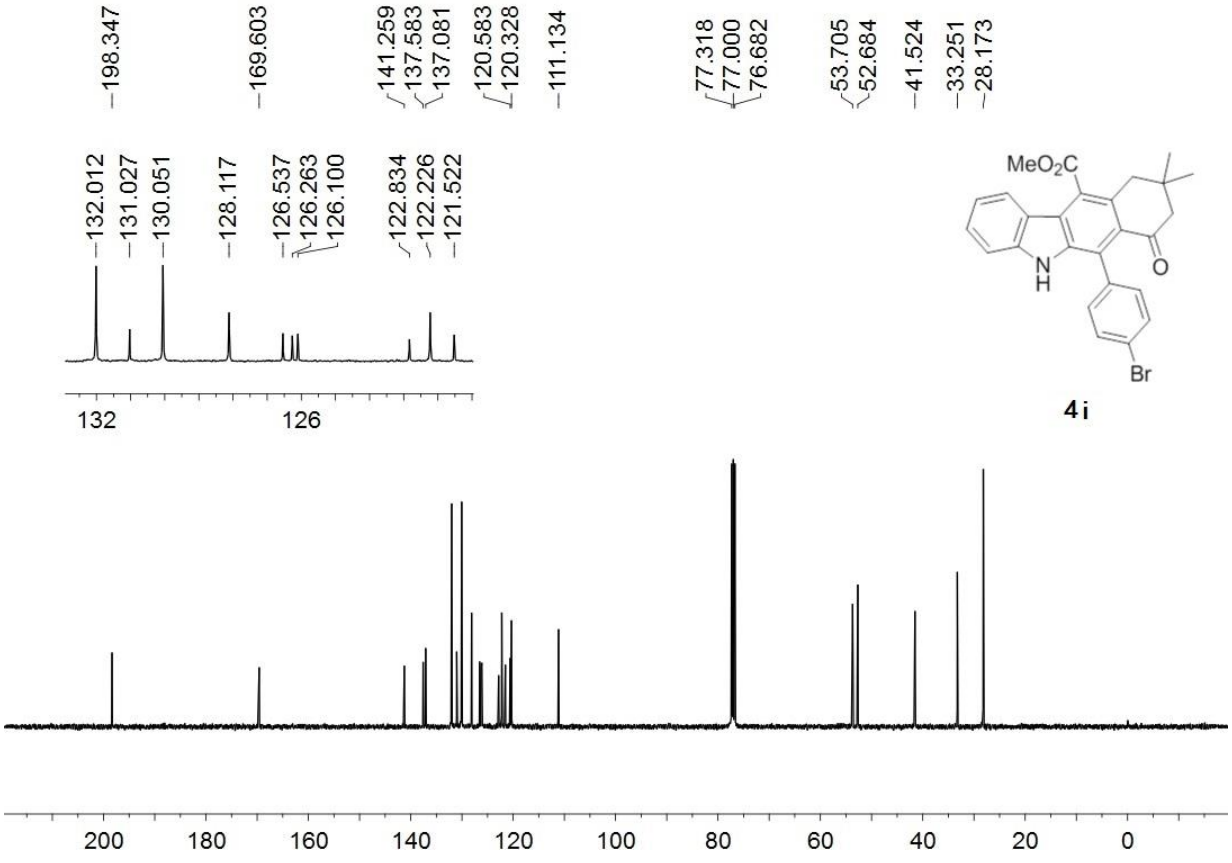
^{13}C NMR spectrum of the compound **4h** (100 MHz, $CDCl_3$)



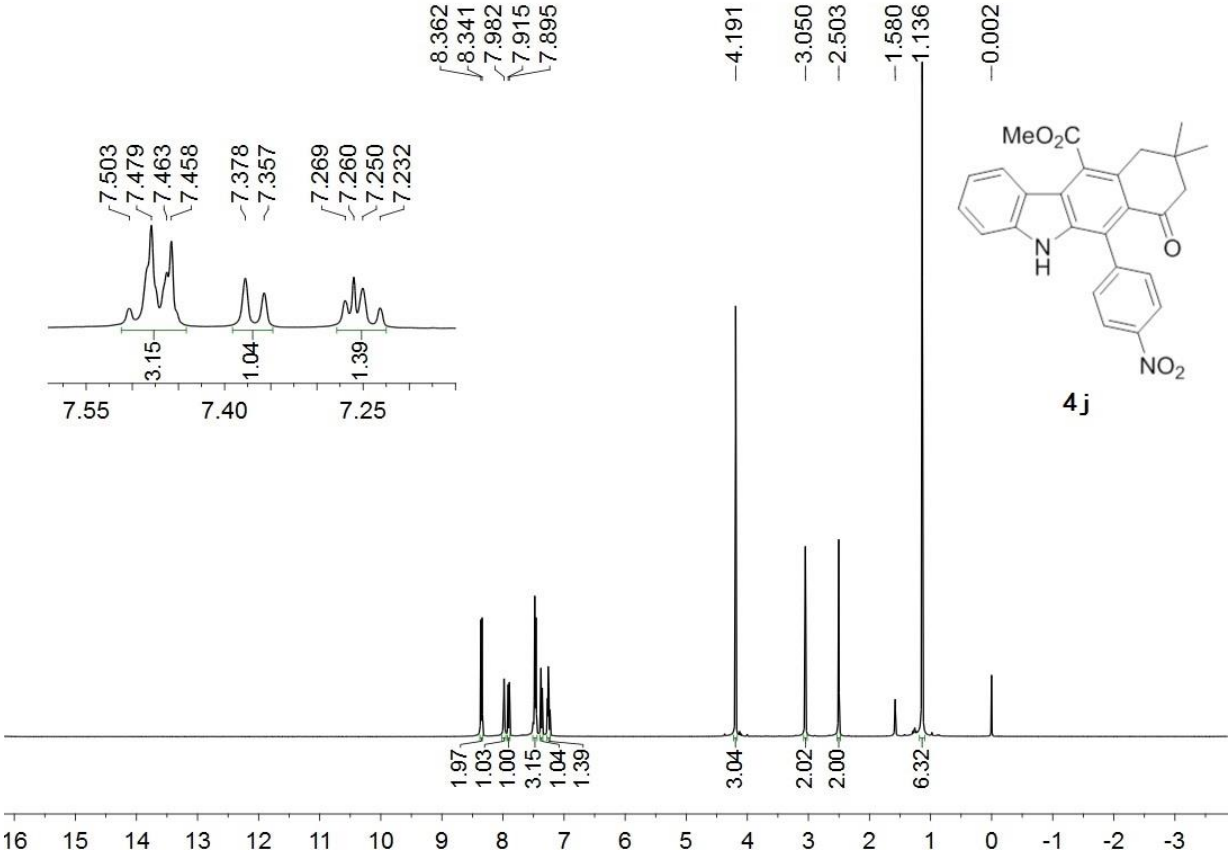
^{1}H NMR spectrum of the compound **4i** (400 MHz, $CDCl_3$)



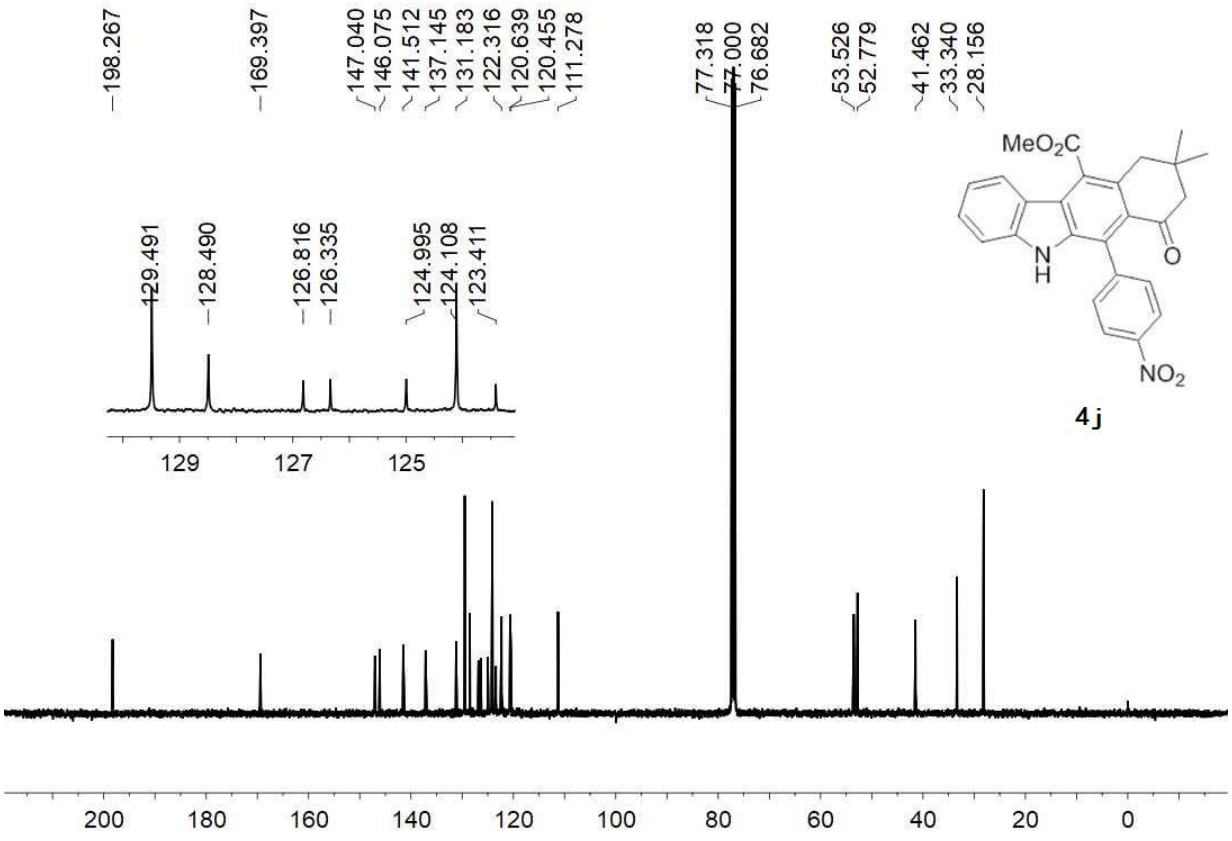
^{13}C NMR spectrum of the compound **4i** (100 MHz, $CDCl_3$)



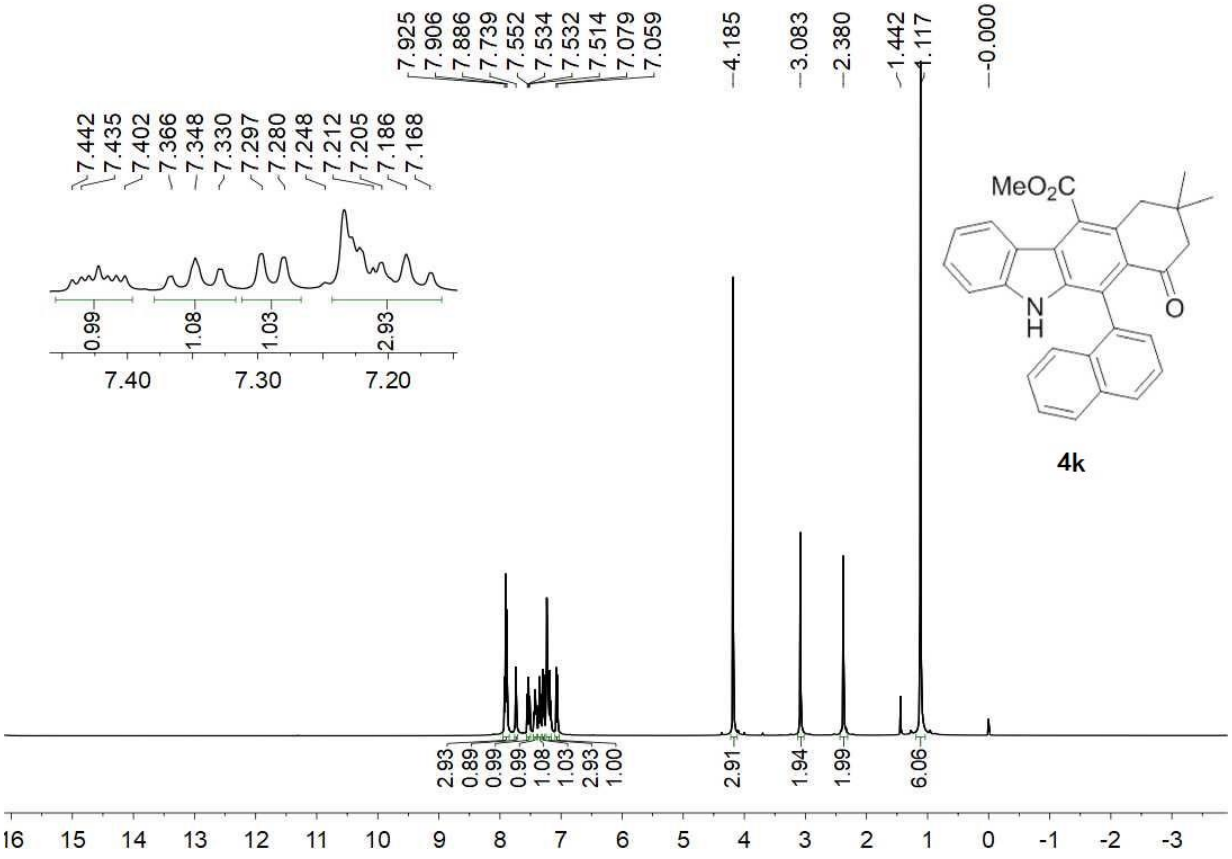
^{1}H NMR spectrum of the compound **4j** (400 MHz, $CDCl_3$)



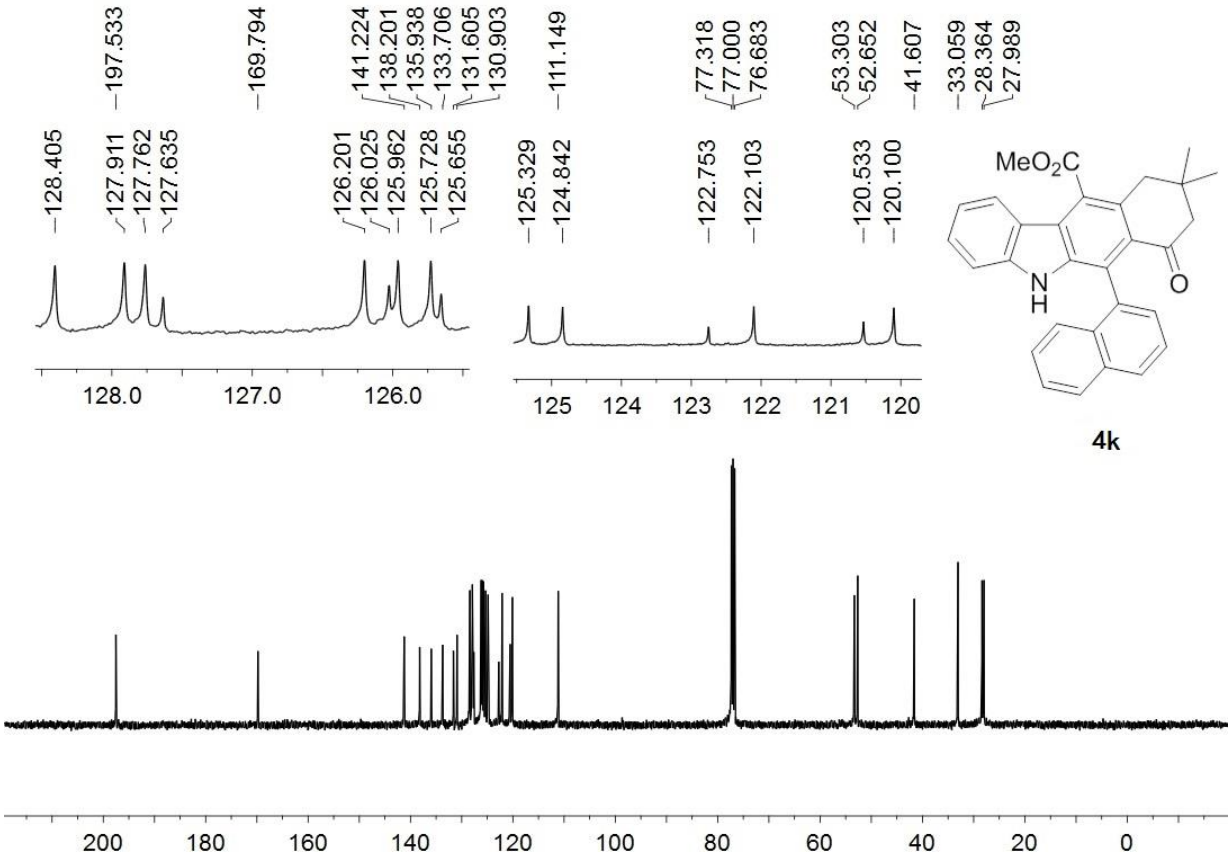
^{13}C NMR spectrum of the compound **4j** (100 MHz, $CDCl_3$)



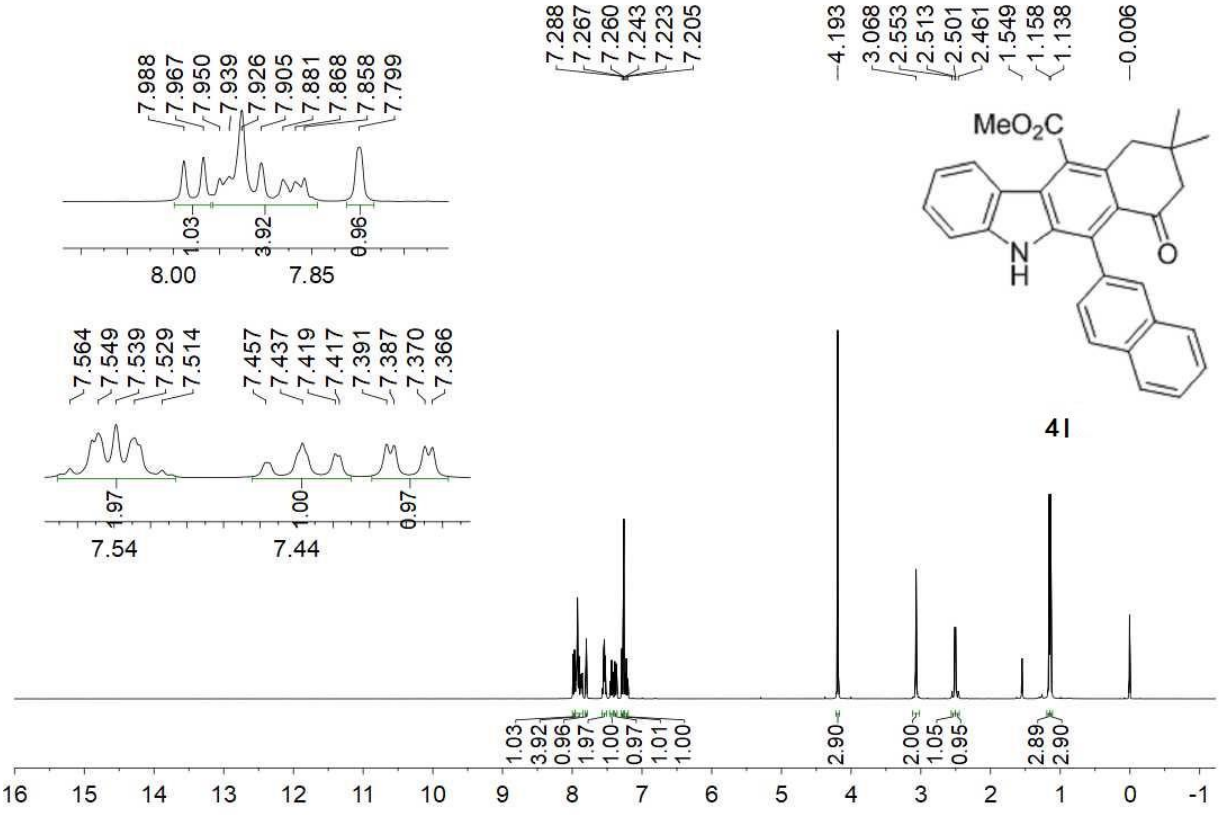
^{1}H NMR spectrum of the compound **4k** (400 MHz, $CDCl_3$)



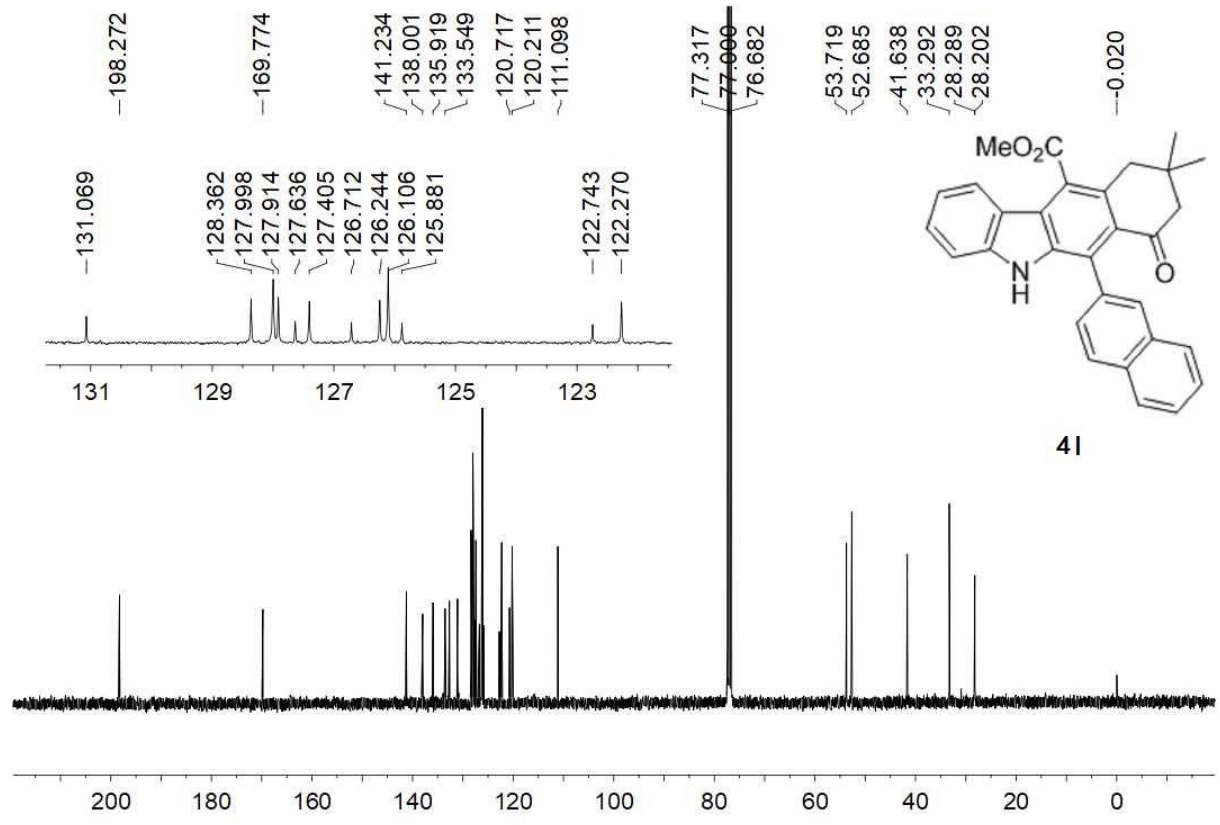
^{13}C NMR spectrum of the compound **4k** (100 MHz, $CDCl_3$)



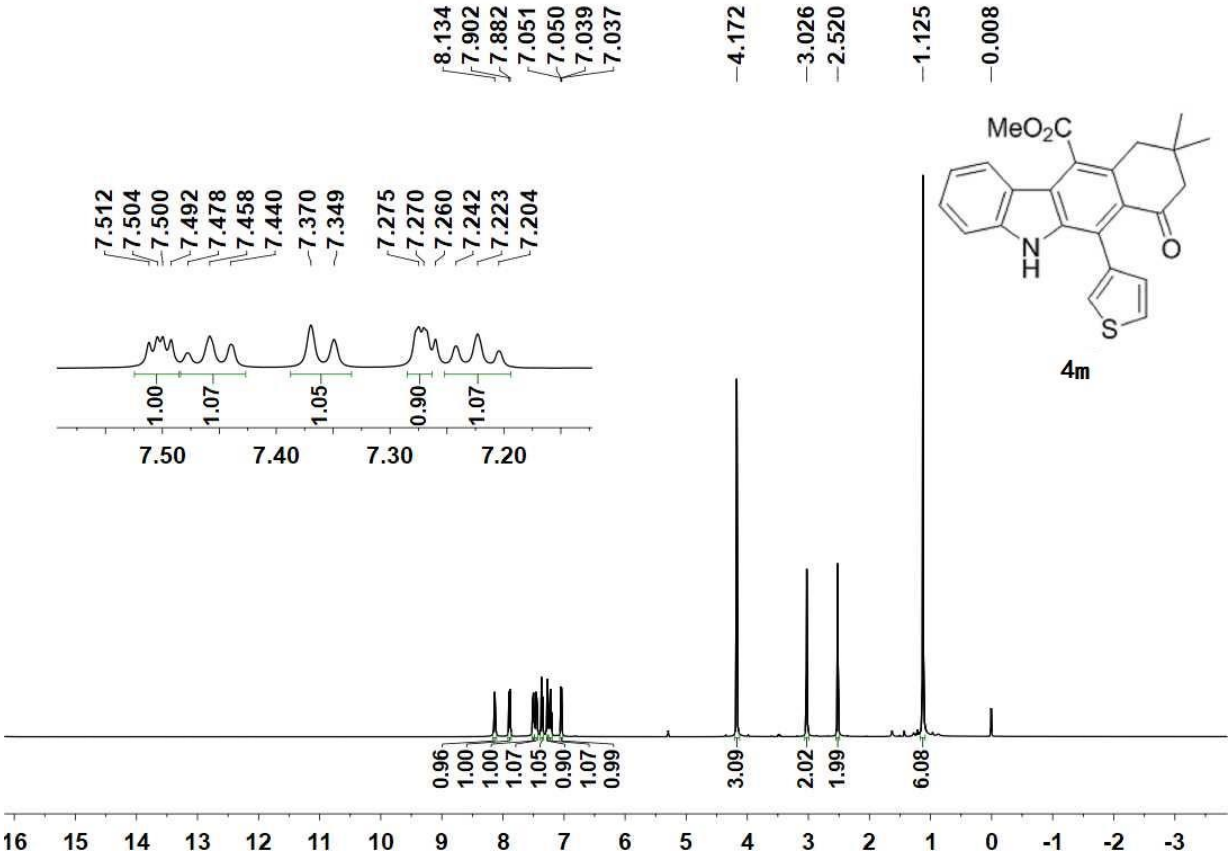
^{1}H NMR spectrum of the compound **4l** (400 MHz, $CDCl_3$)



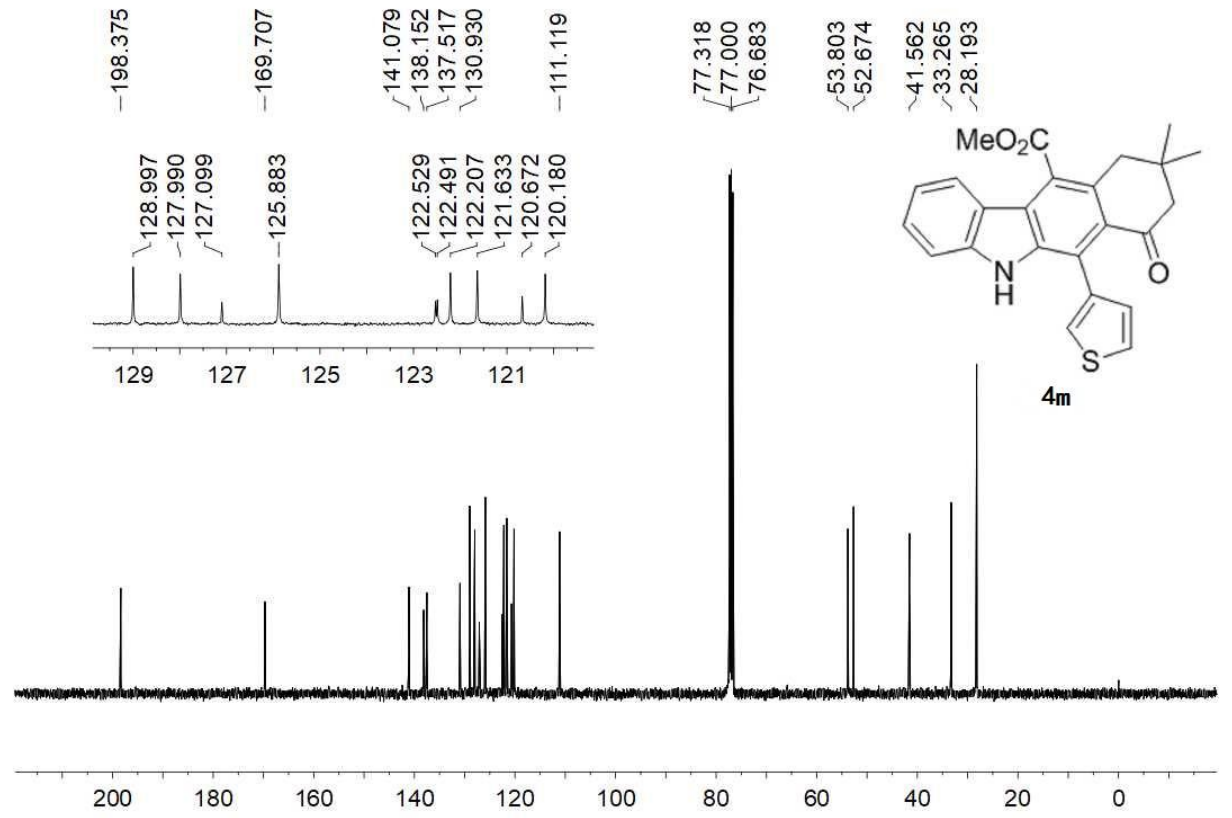
^{13}C NMR spectrum of the compound **4l** (100 MHz, $CDCl_3$)



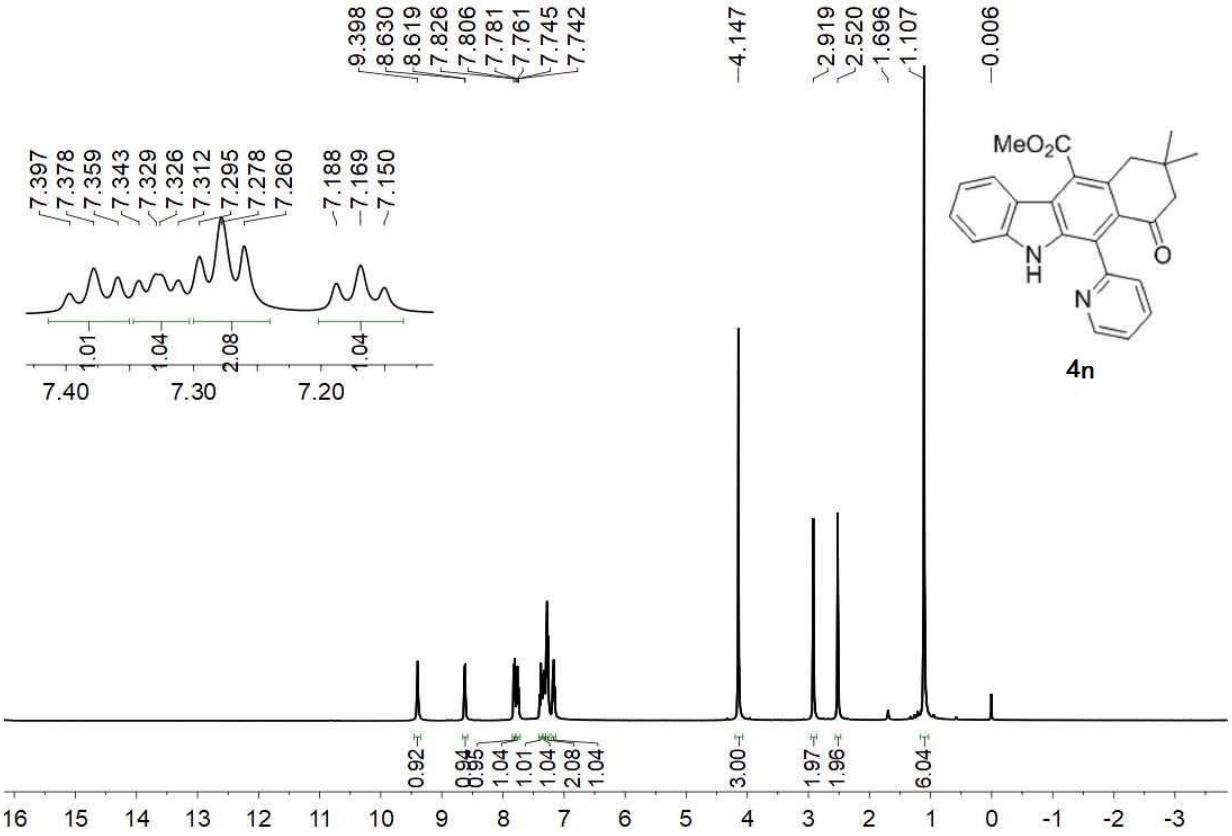
^{1}H NMR spectrum of the compound **4m** (400 MHz, $CDCl_3$)



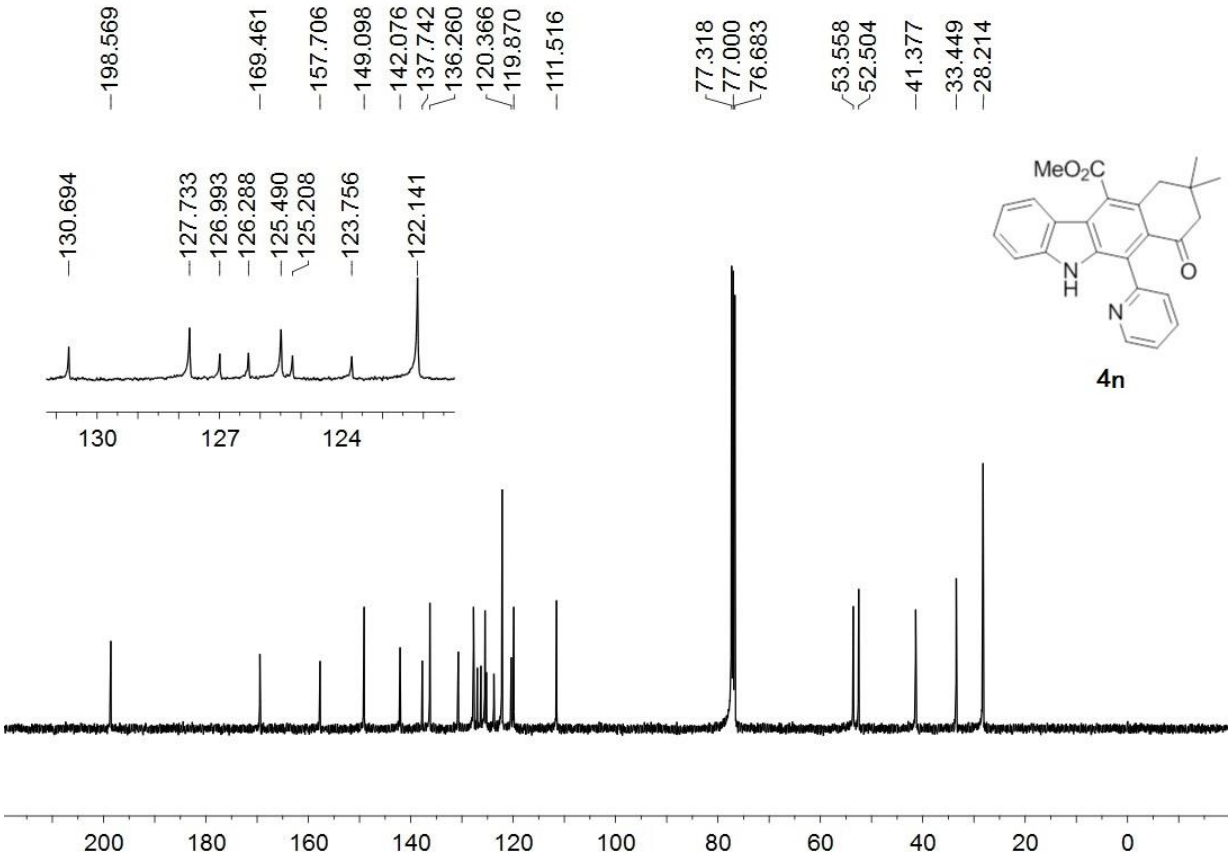
^{13}C NMR spectrum of the compound **4m** (100 MHz, $CDCl_3$)



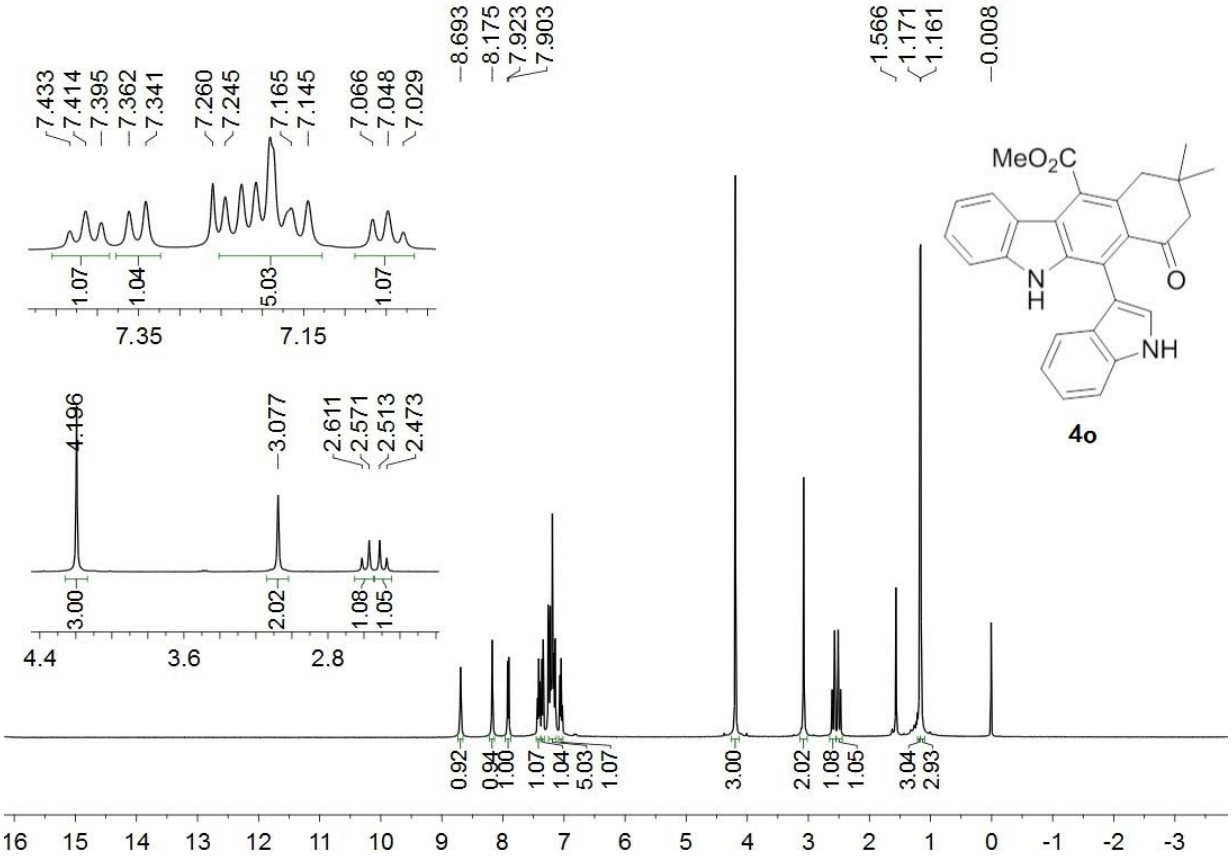
^{1}H NMR spectrum of the compound **4n** (400 MHz, $CDCl_3$)



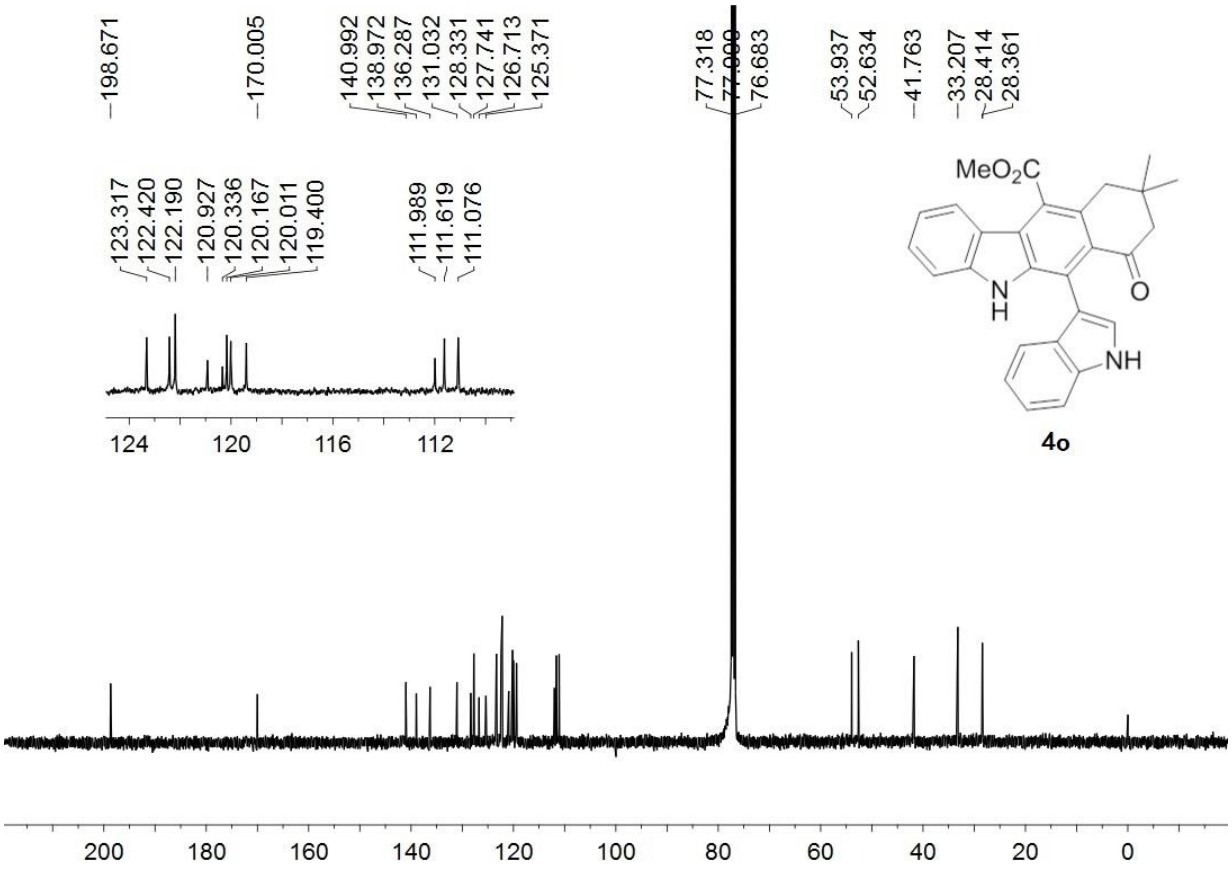
^{13}C NMR spectrum of the compound **4n** (100 MHz, $CDCl_3$)



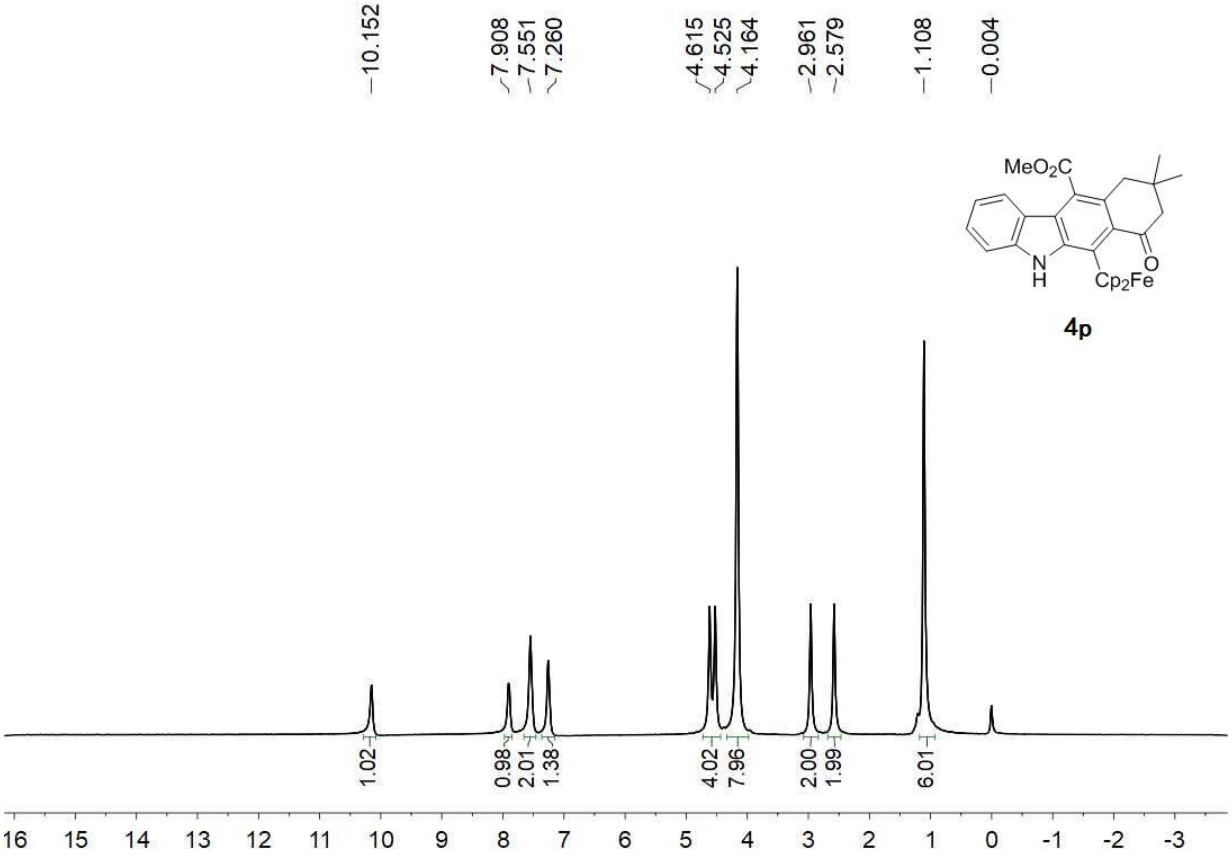
^{1}H NMR spectrum of the compound **4o** (400 MHz, $CDCl_3$)



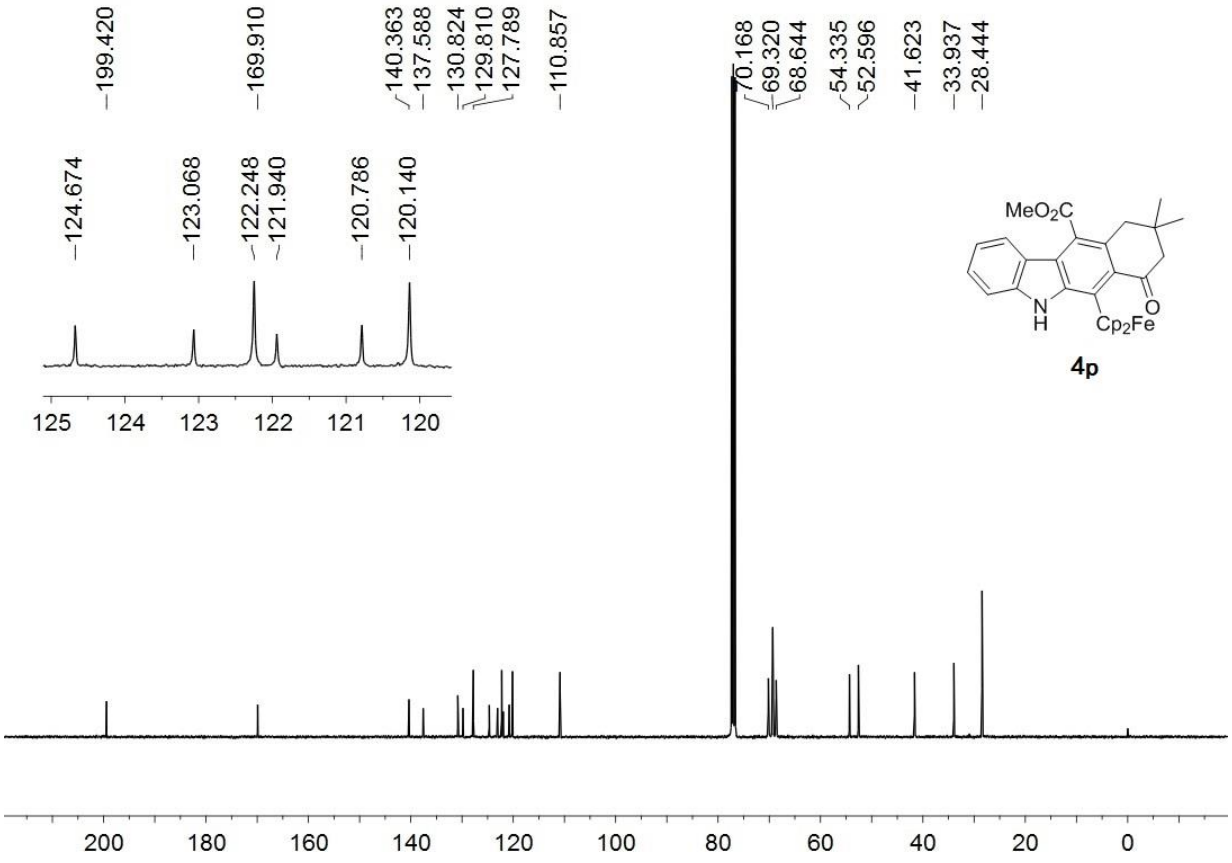
^{13}C NMR spectrum of the compound **4o** (100 MHz, $CDCl_3$)



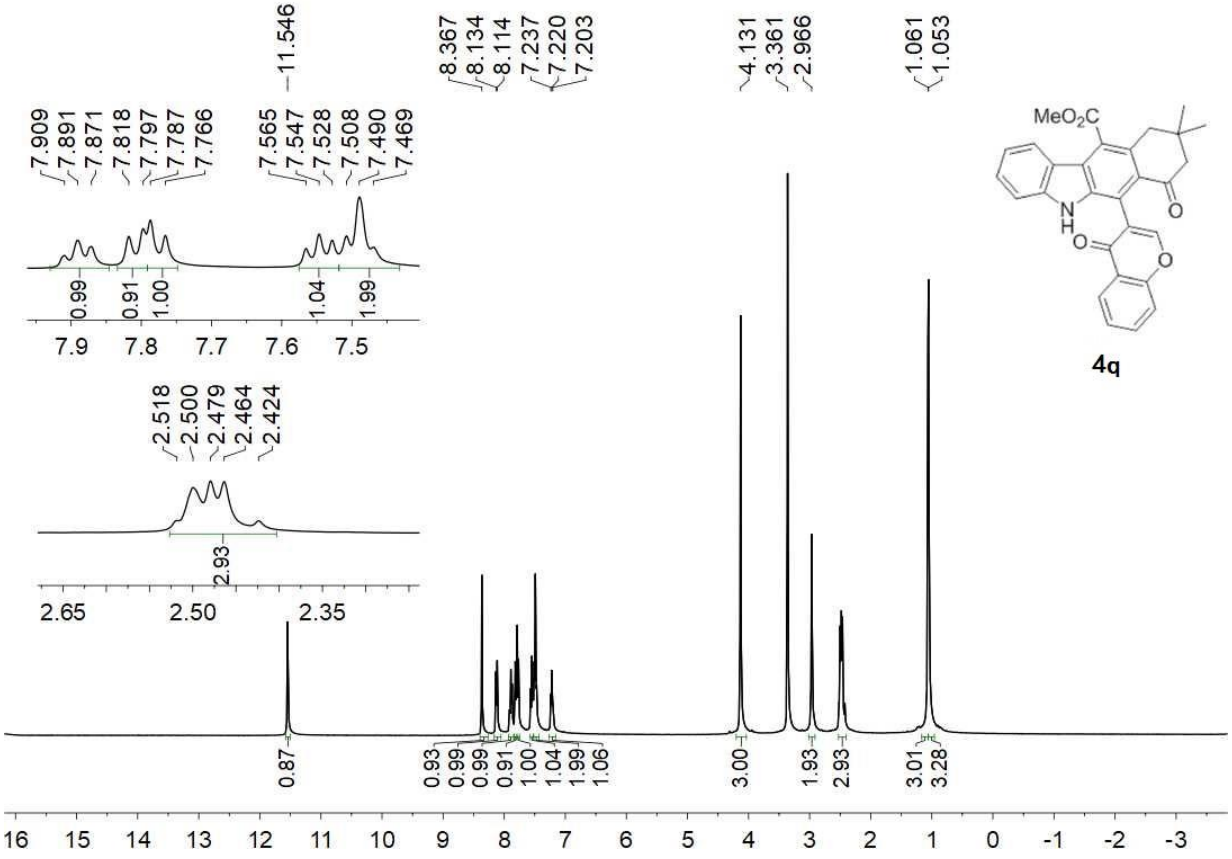
^{1}H NMR spectrum of the compound **4p** (400 MHz, $CDCl_3$)



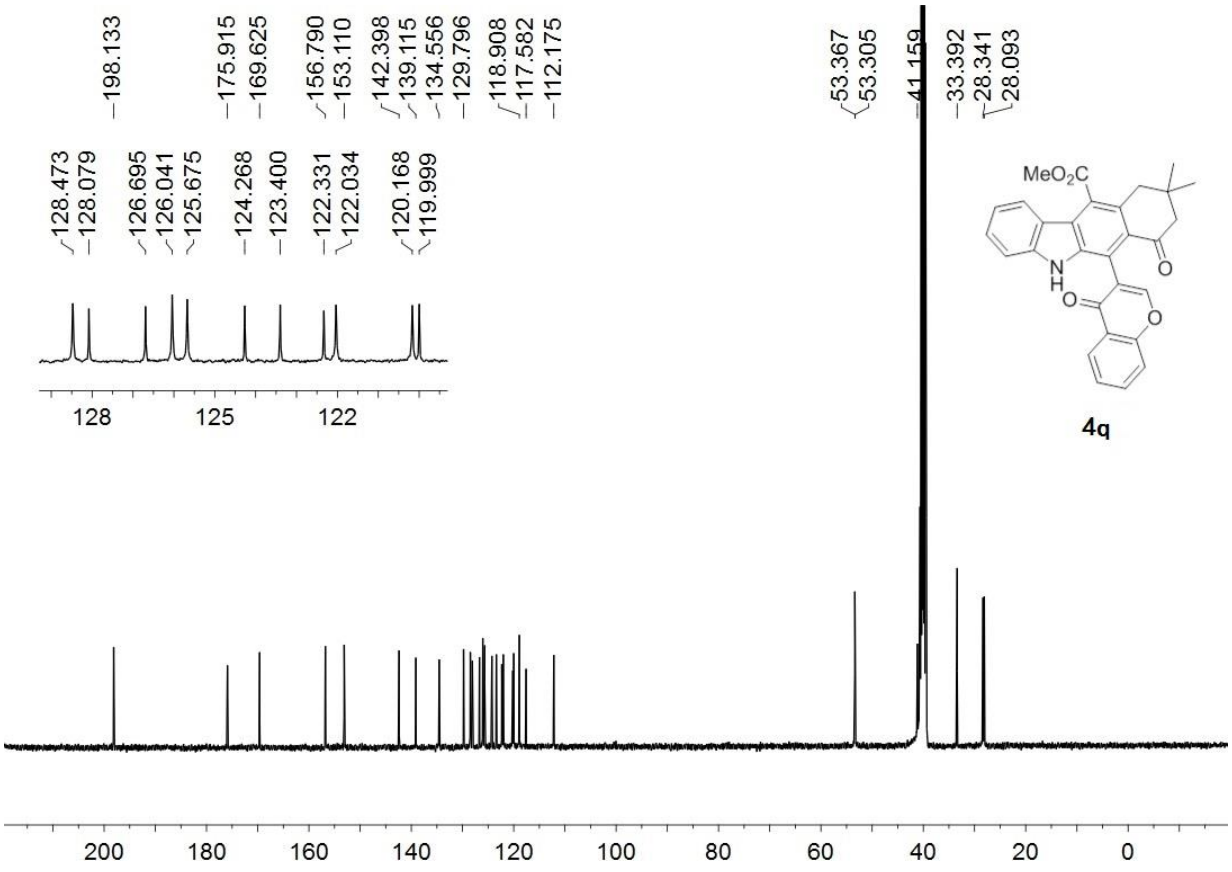
^{13}C NMR spectrum of the compound **4p** (100 MHz, $CDCl_3$)



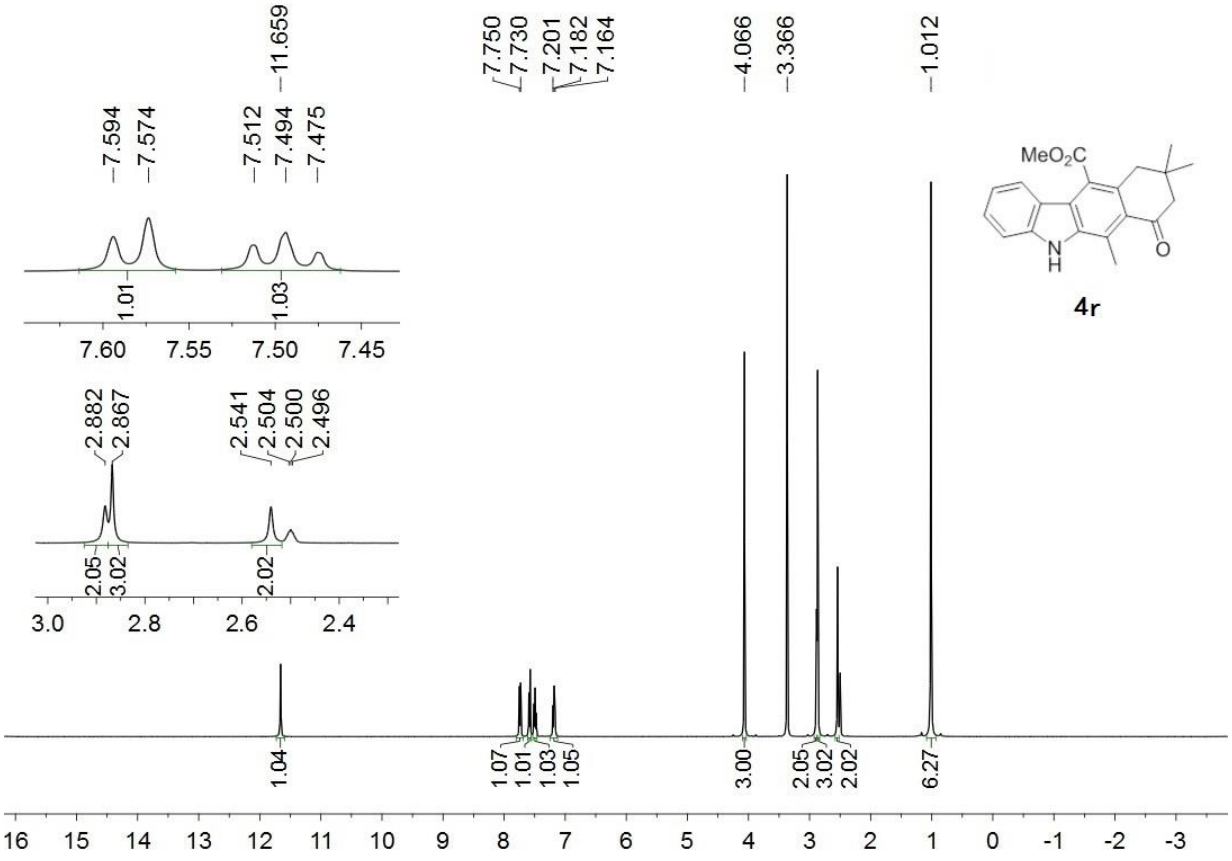
[1]H NMR spectrum of the compound **4q** (400 MHz, DMSO-d_6)



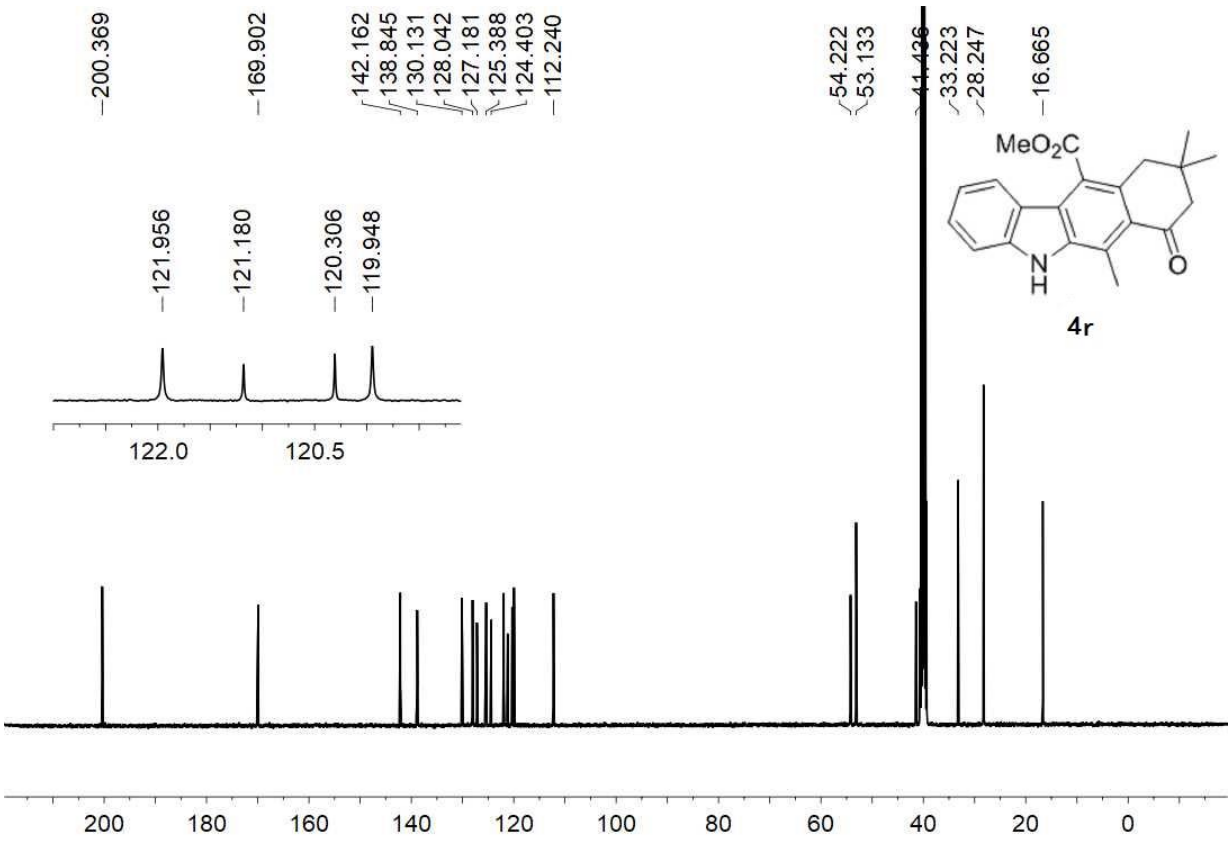
[13]C NMR spectrum of the compound **4q** (100 MHz, DMSO-d_6)



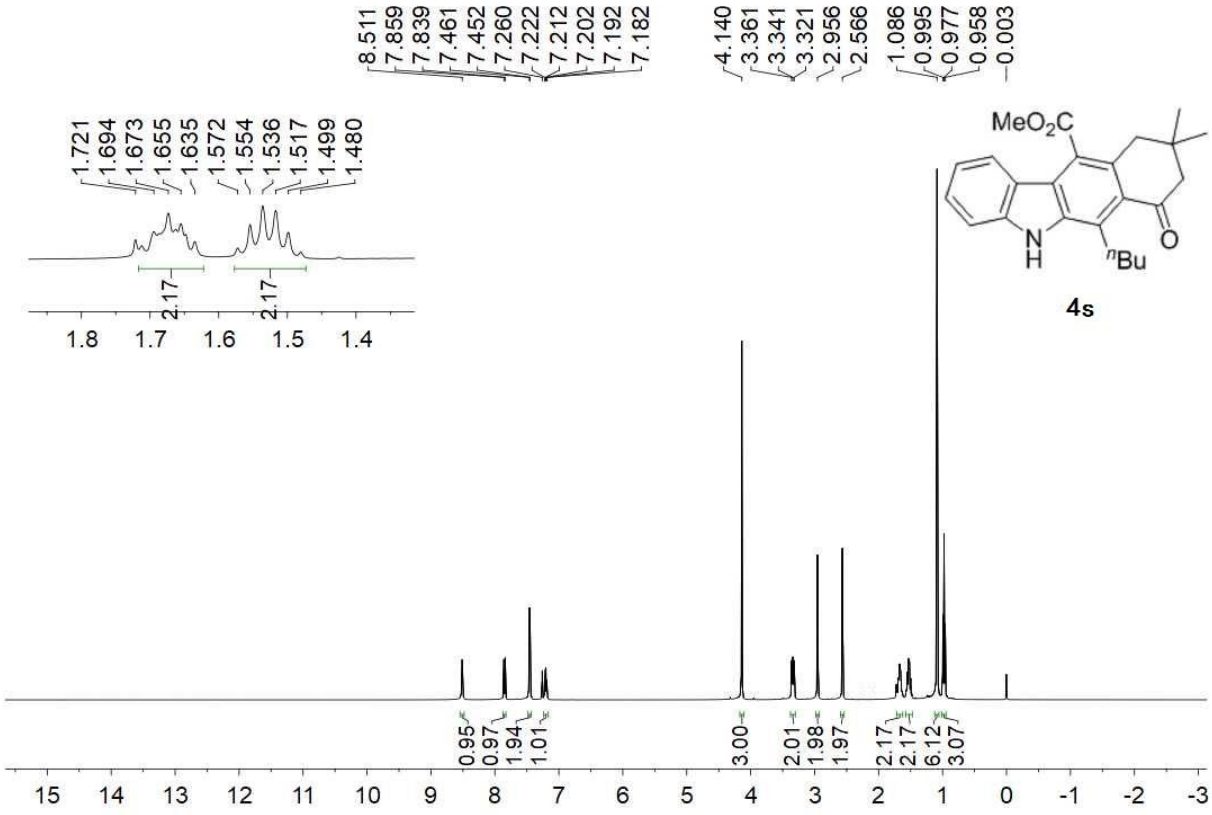
^{1}H NMR spectrum of the compound **4r** (400 MHz, DMSO-d_6)



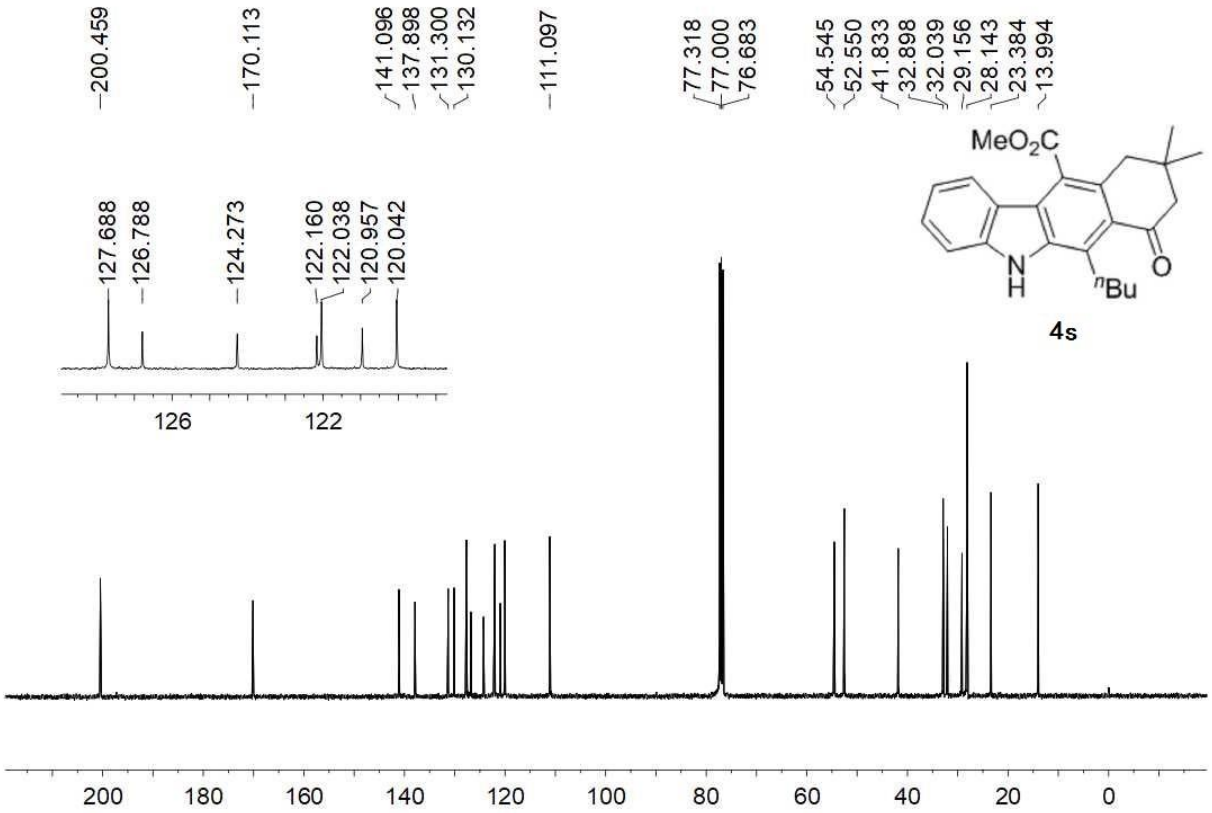
^{13}C NMR spectrum of the compound **4r** (100 MHz, DMSO-d_6)



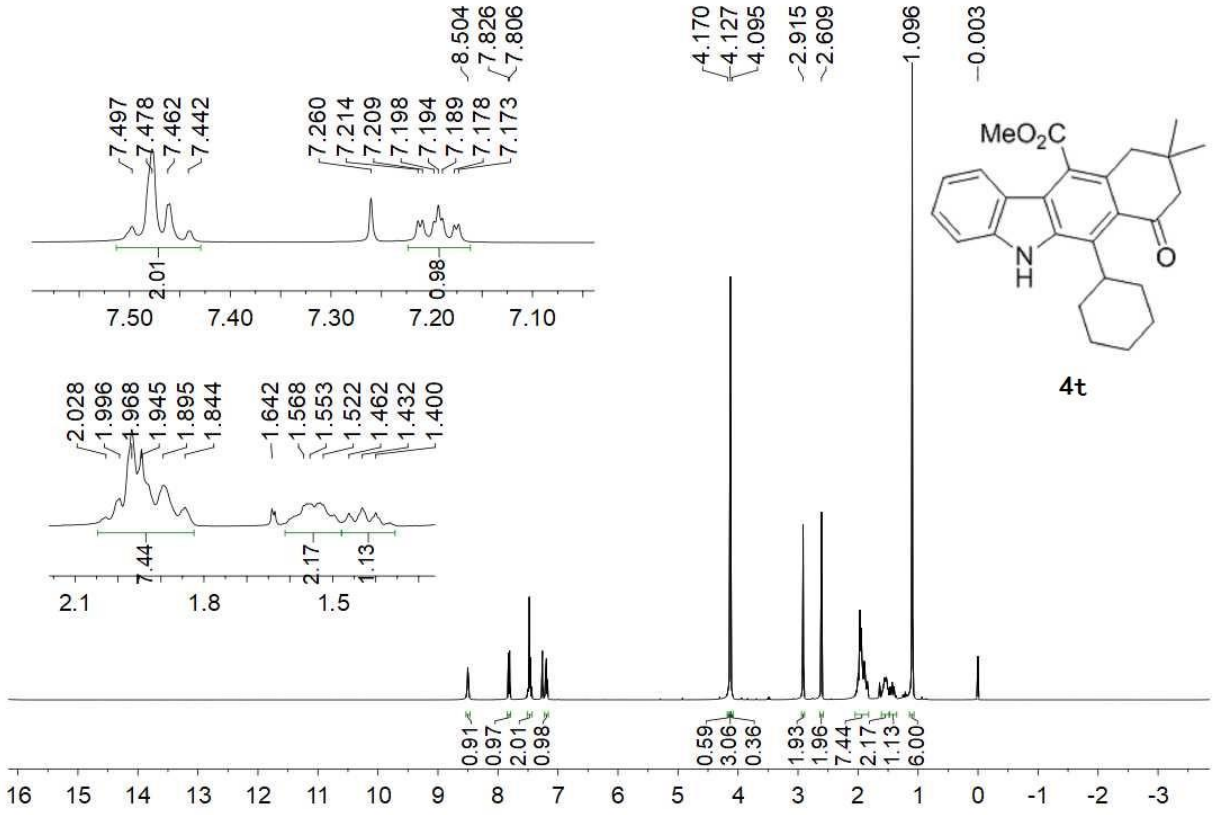
^{1}H NMR spectrum of the compound **4s** (400 MHz, $CDCl_3$)



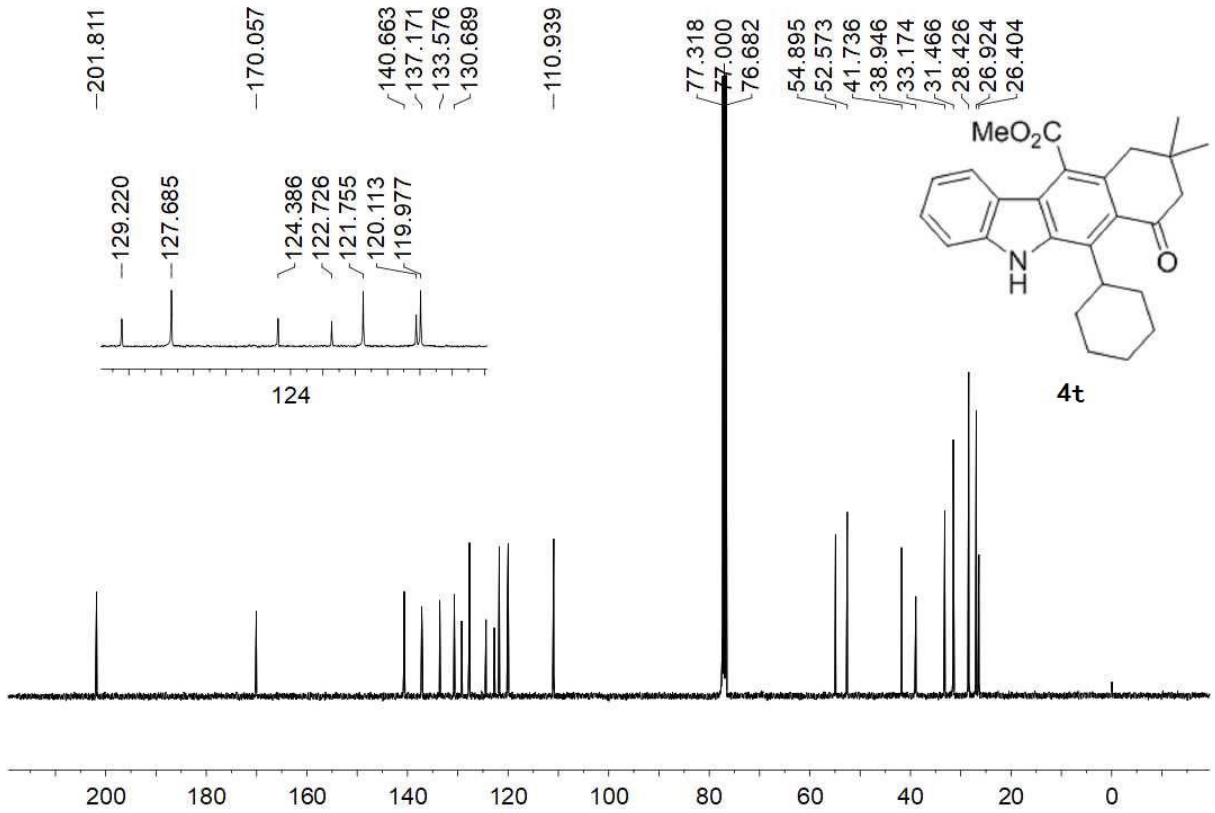
^{13}C NMR spectrum of the compound **4s** (100 MHz, $CDCl_3$)



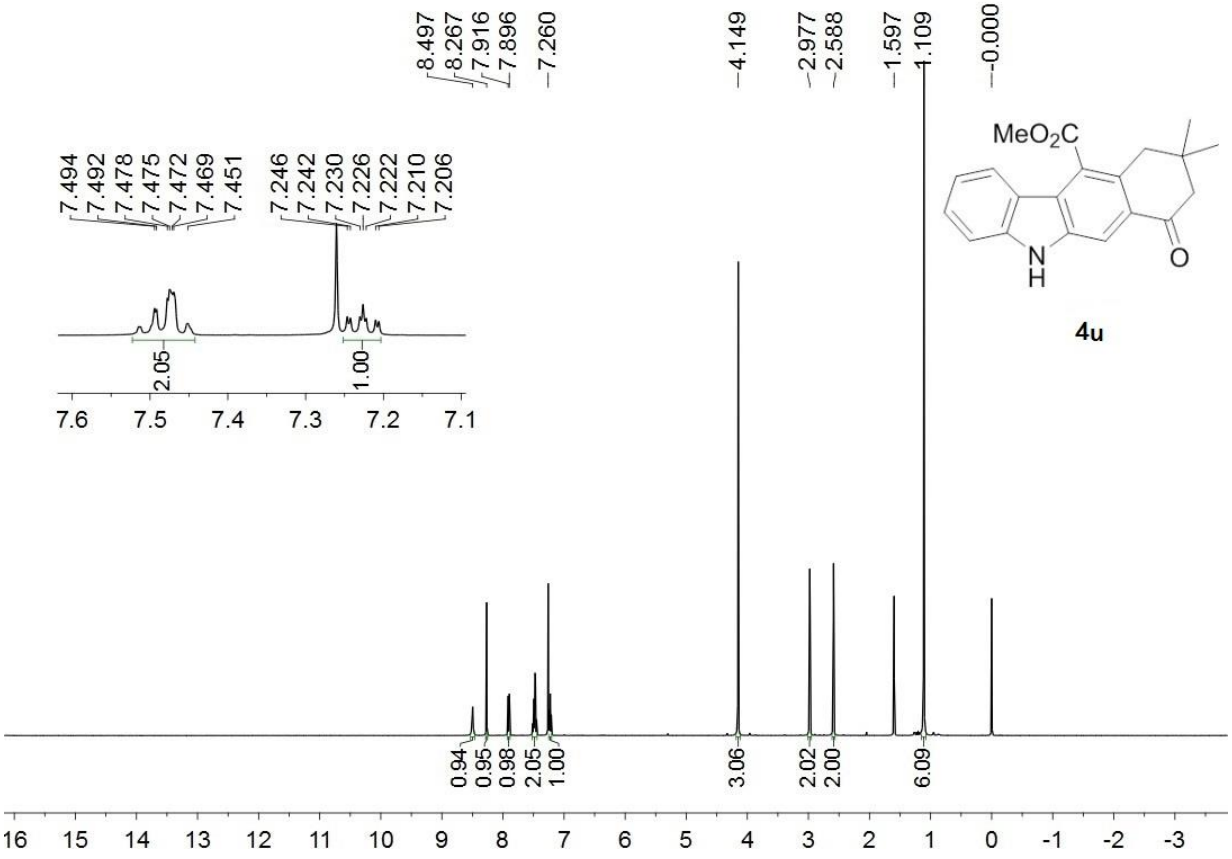
^{1}H NMR spectrum of the compound **4t** (400 MHz, $CDCl_3$)



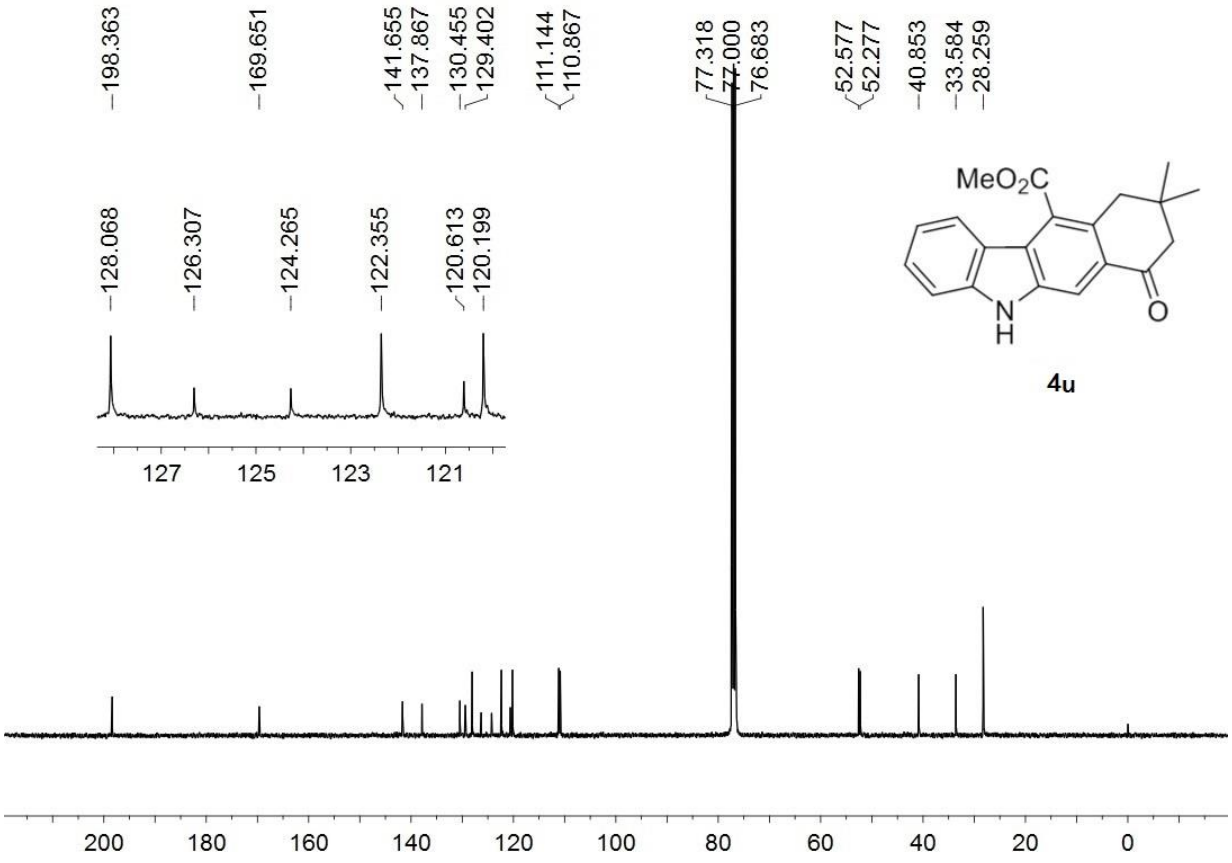
^{13}C NMR spectrum of the compound **4t** (100 MHz, $CDCl_3$)



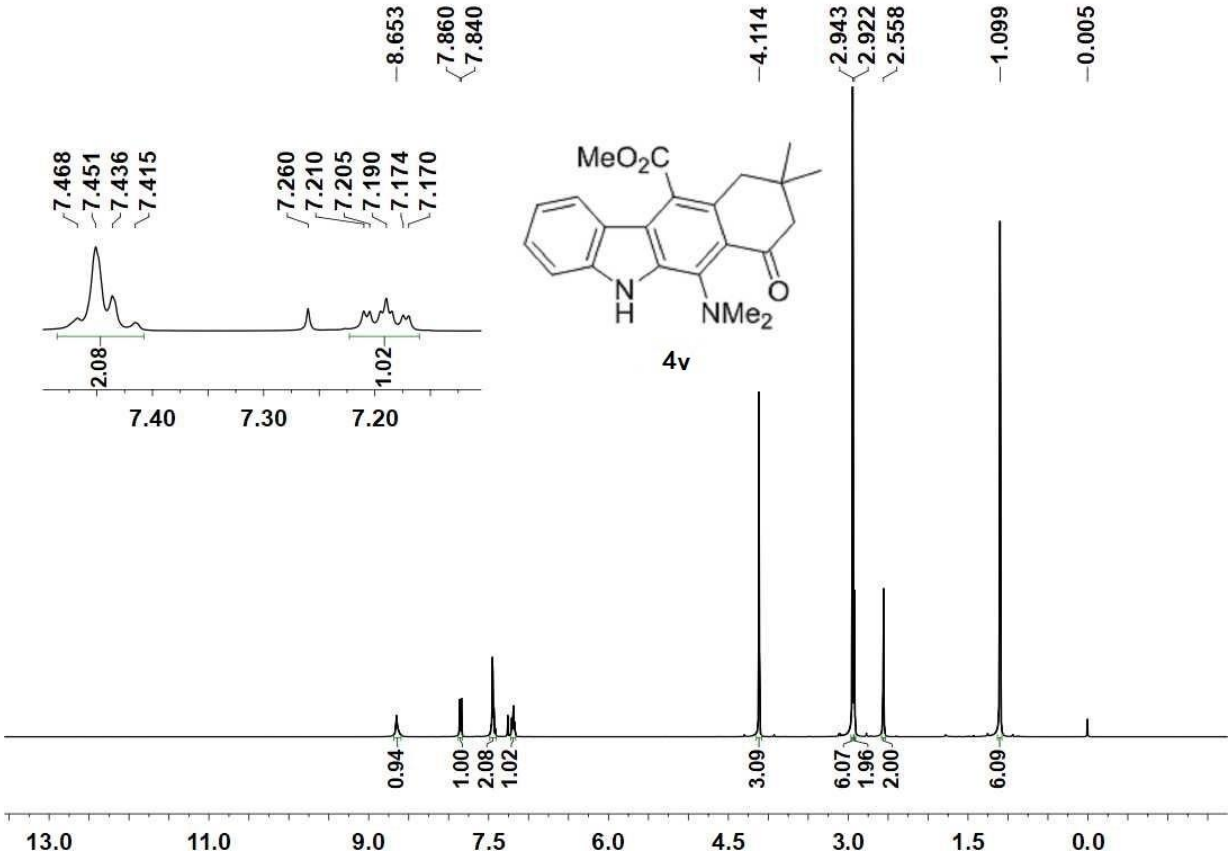
^{1}H NMR spectrum of the compound **4u** (400 MHz, $CDCl_3$)



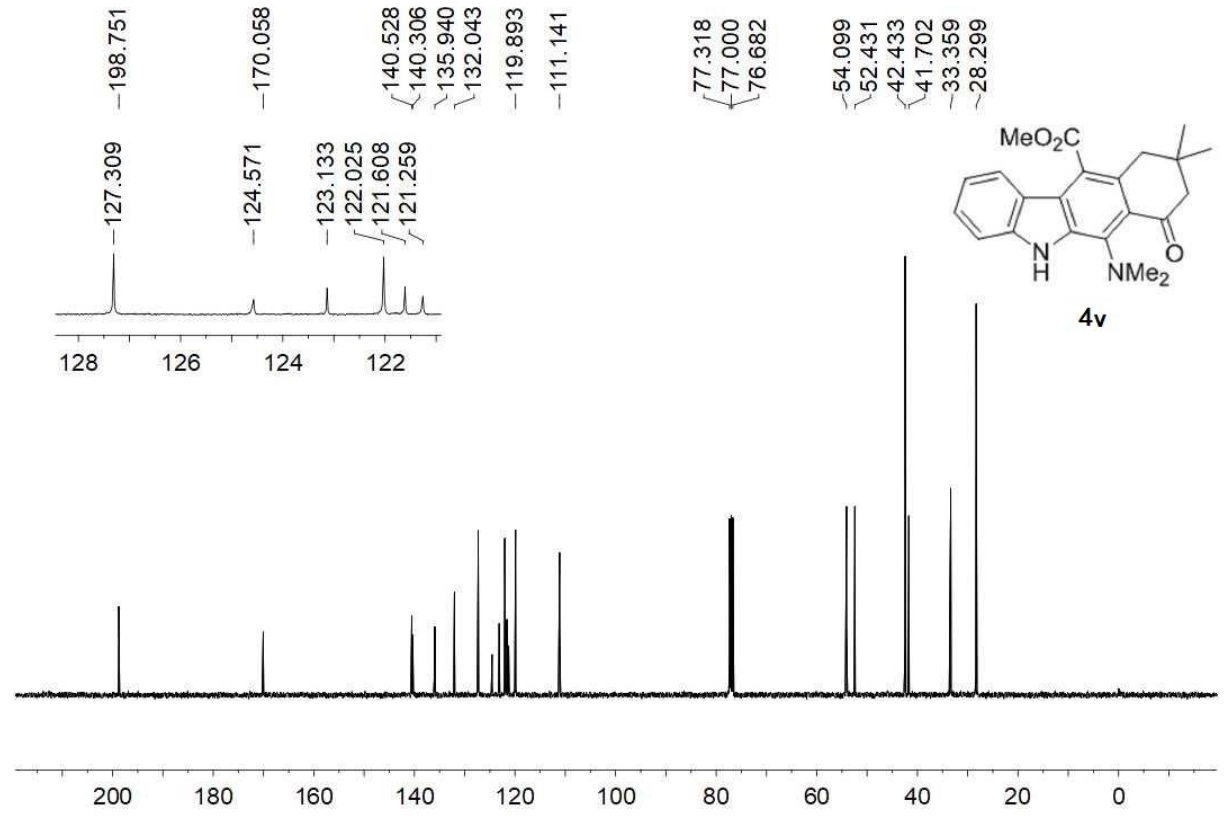
^{13}C NMR spectrum of the compound **4u** (100 MHz, $CDCl_3$)



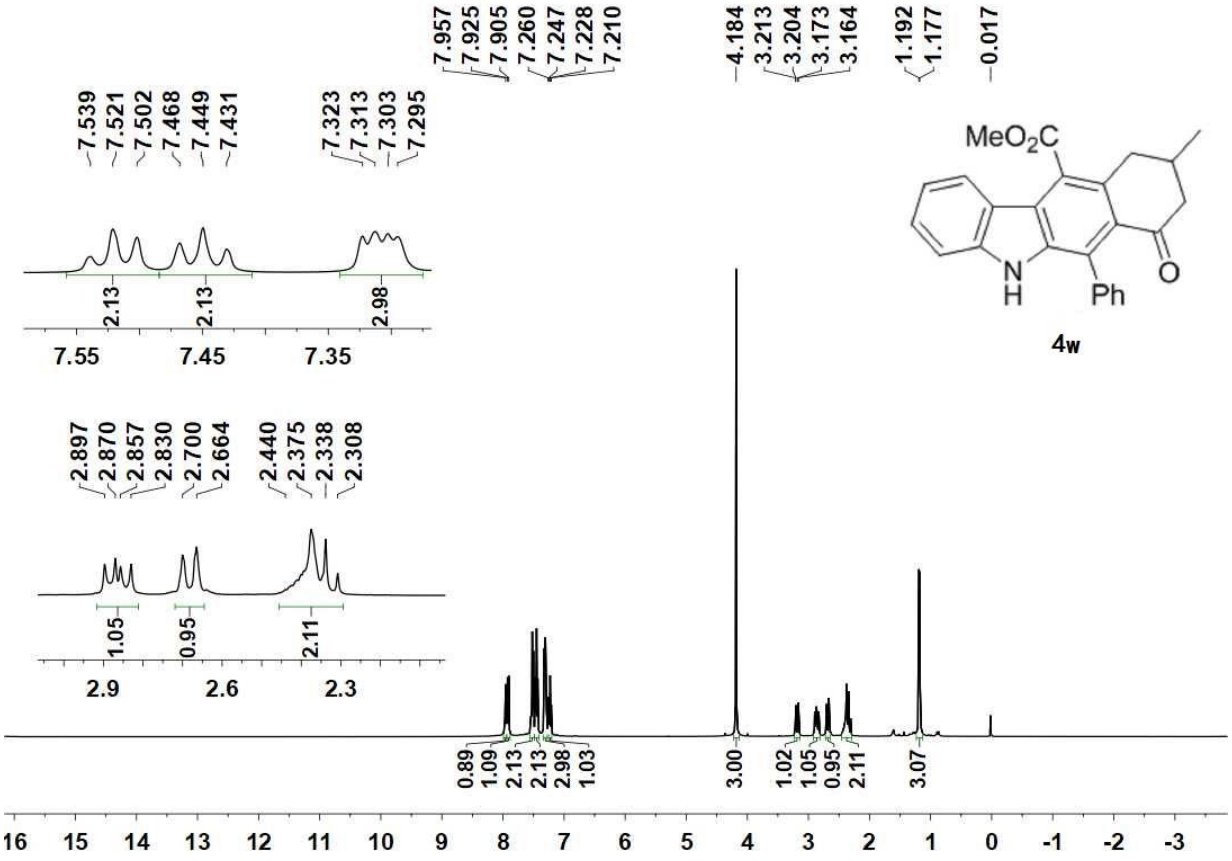
^{1}H NMR spectrum of the compound **4v** (400 MHz, $CDCl_3$)



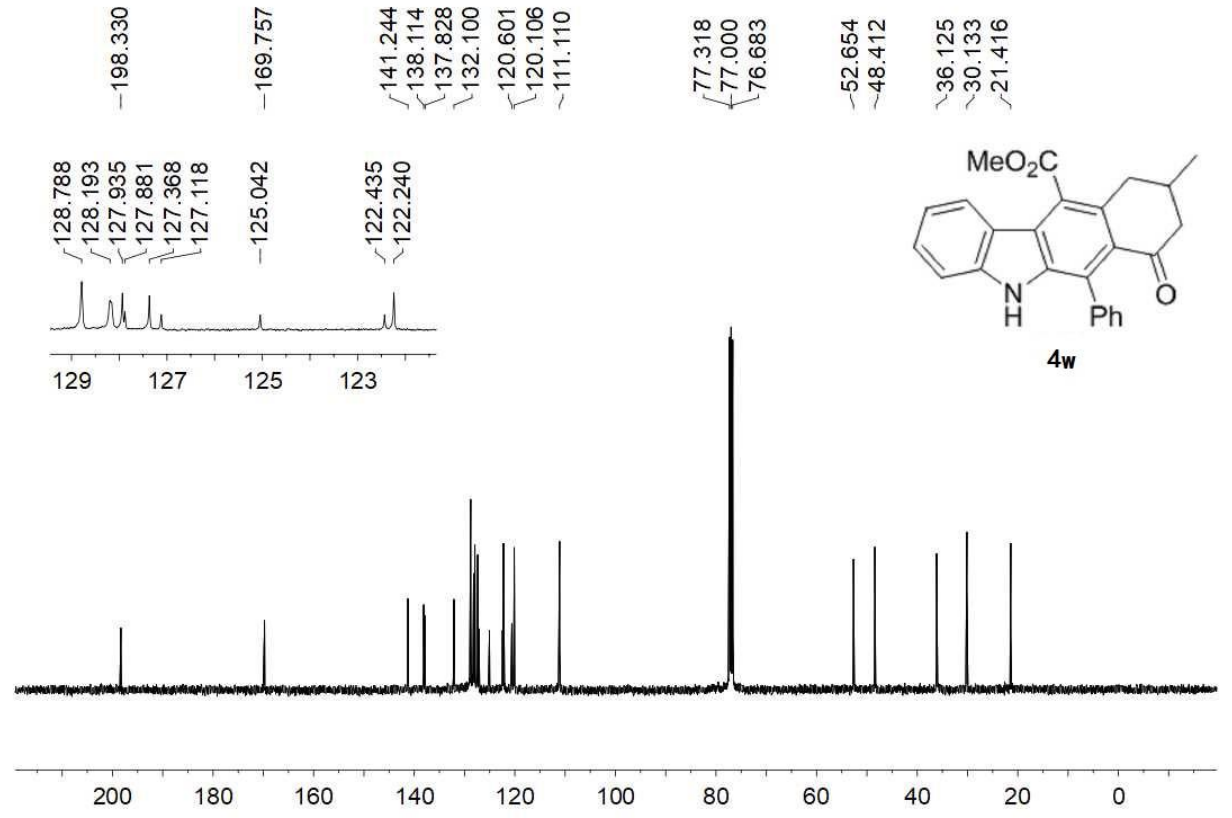
^{13}C NMR spectrum of the compound **4v** (100 MHz, $CDCl_3$)



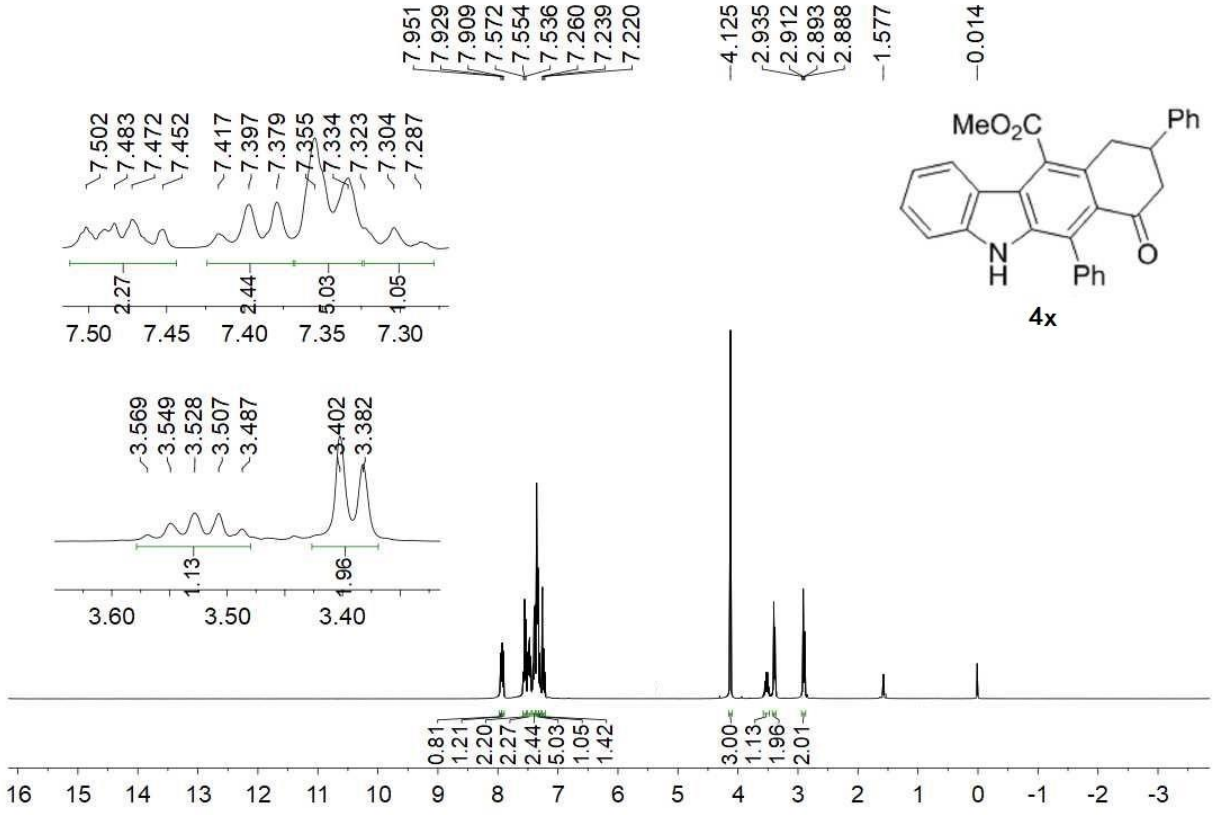
^{1}H NMR spectrum of the compound **4w** (400 MHz, $CDCl_3$)



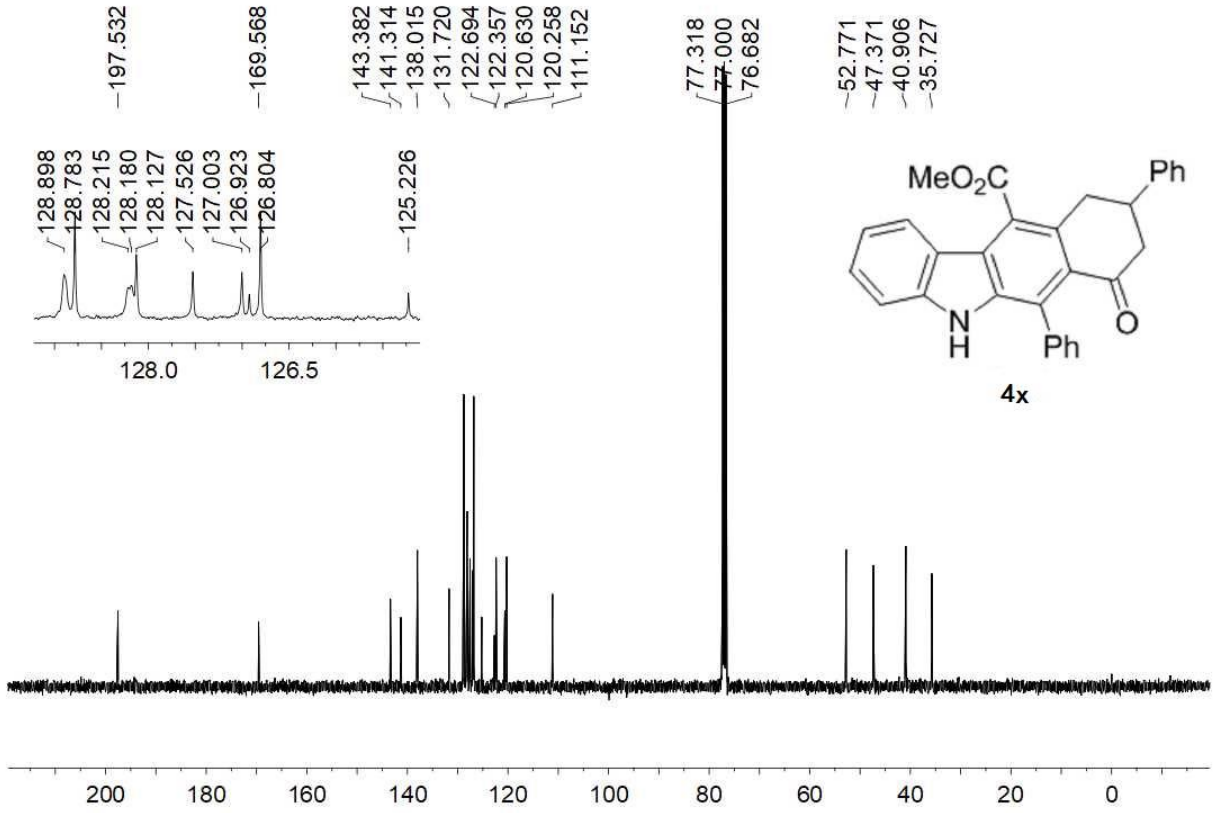
^{13}C NMR spectrum of the compound **4w** (100 MHz, $CDCl_3$)



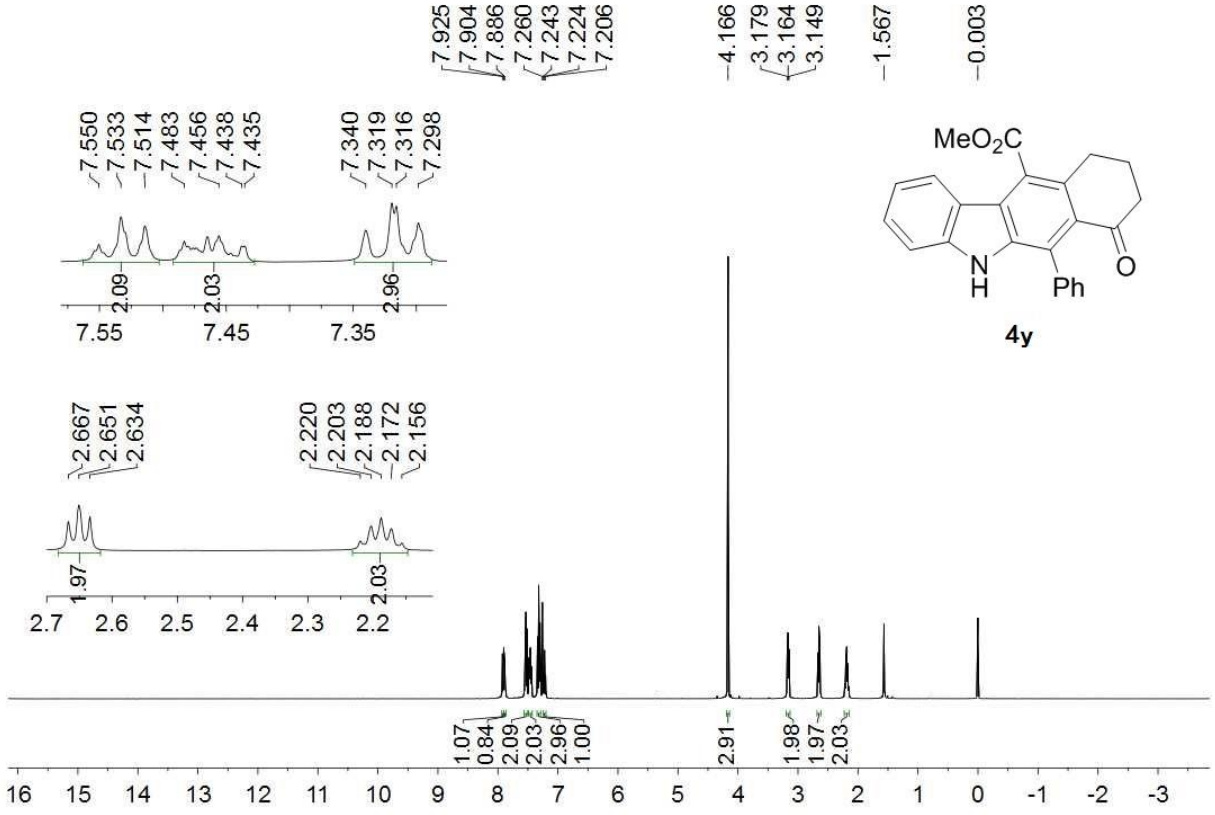
^{1}H NMR spectrum of the compound **4x** (400 MHz, $CDCl_3$)



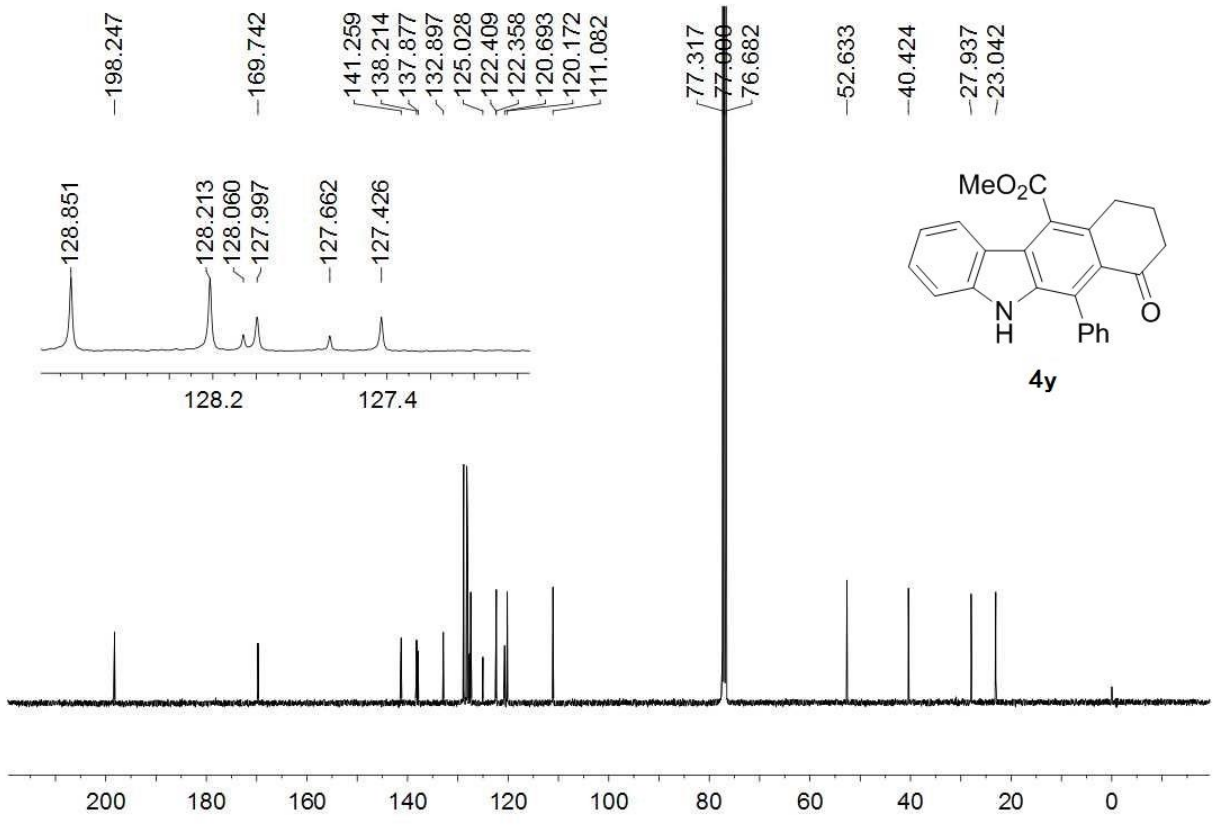
^{13}C NMR spectrum of the compound **4x** (100 MHz, $CDCl_3$)



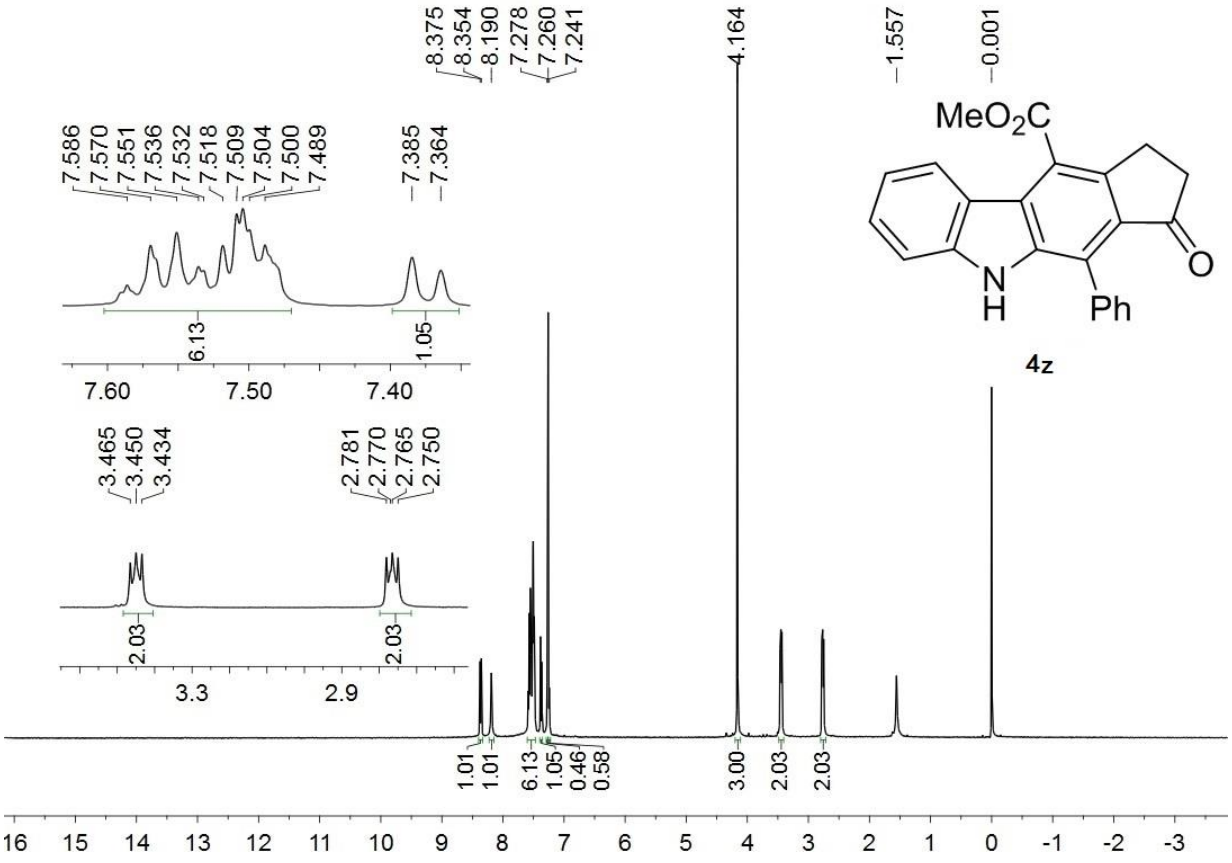
^{1}H NMR spectrum of the compound **4y** (400 MHz, $CDCl_3$)



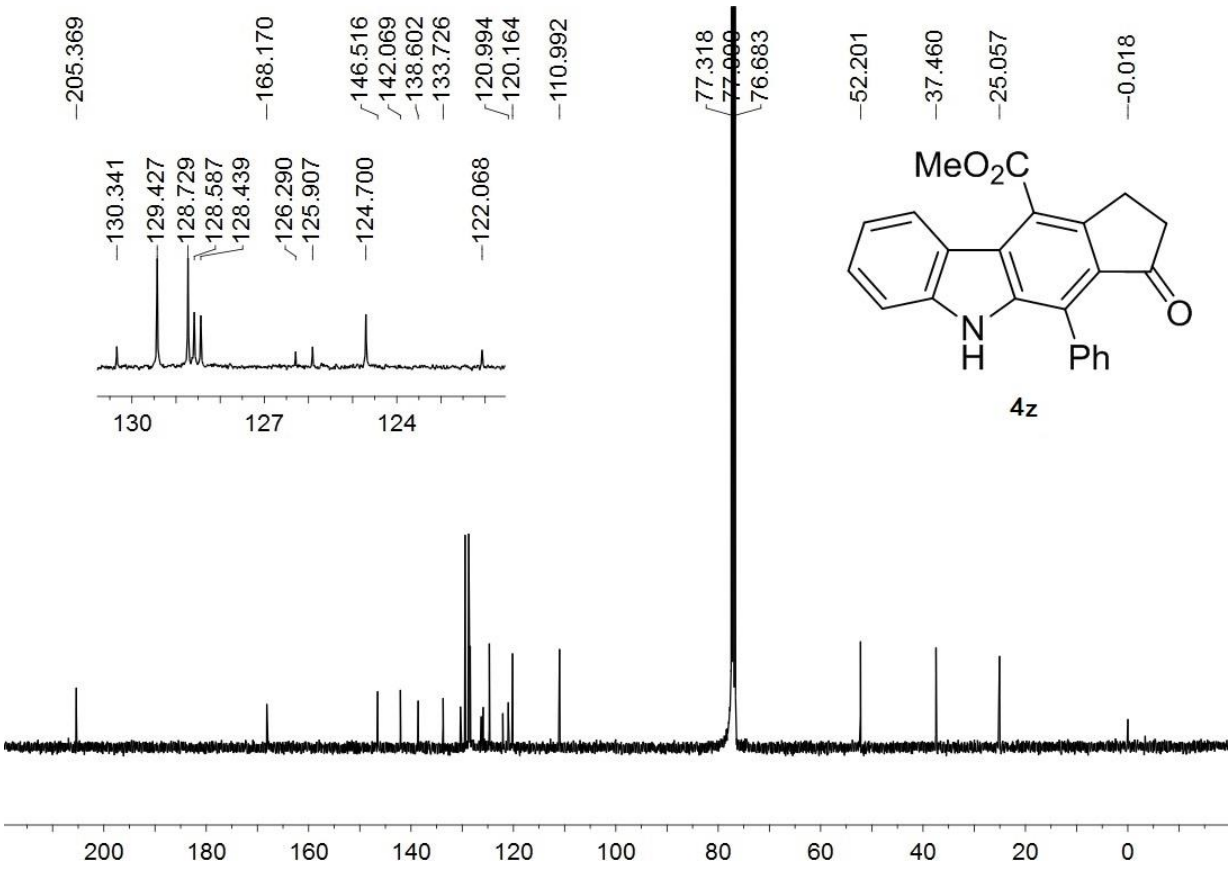
^{13}C NMR spectrum of the compound **4y** (100 MHz, $CDCl_3$)



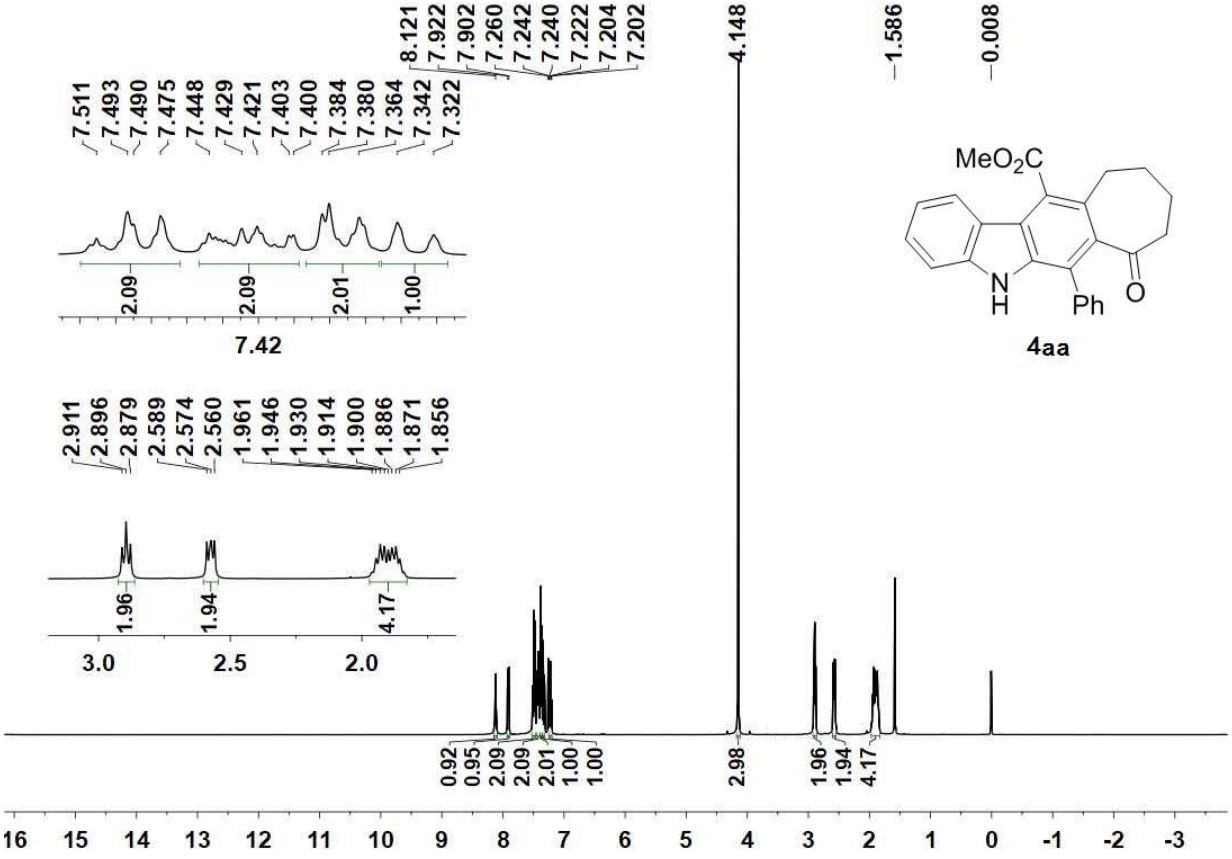
^{1}H NMR spectrum of the compound **4z** (400 MHz, $CDCl_3$)



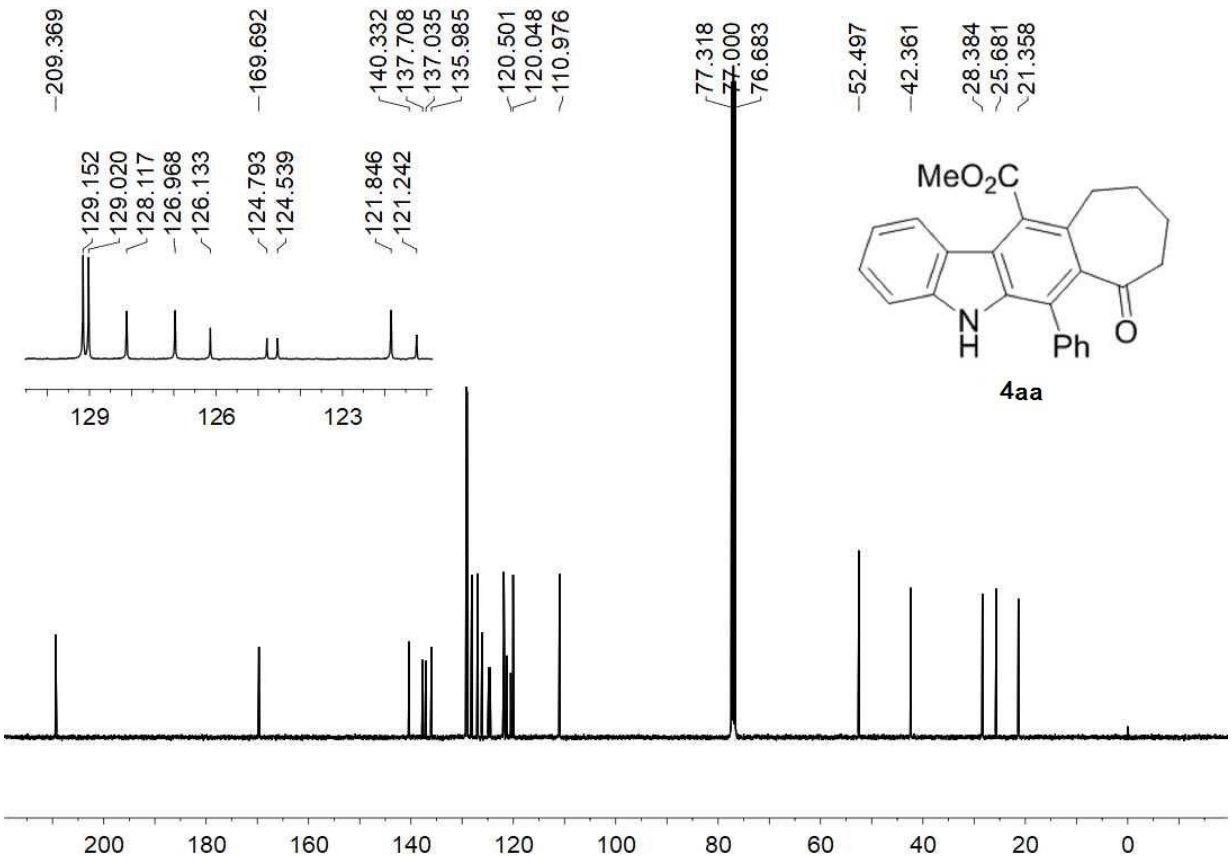
^{13}C NMR spectrum of the compound **4z** (100 MHz, $CDCl_3$)



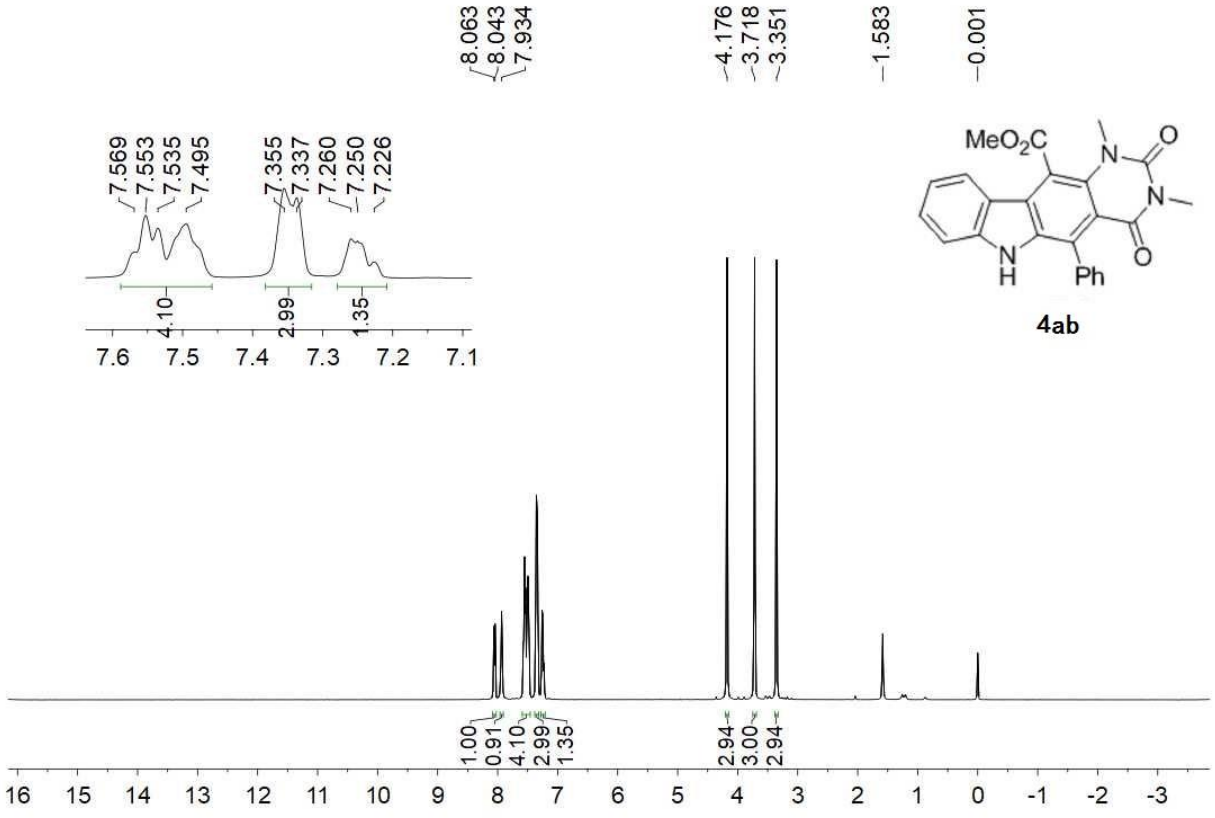
^{1}H NMR spectrum of the compound **4aa** (400 MHz, $CDCl_3$)



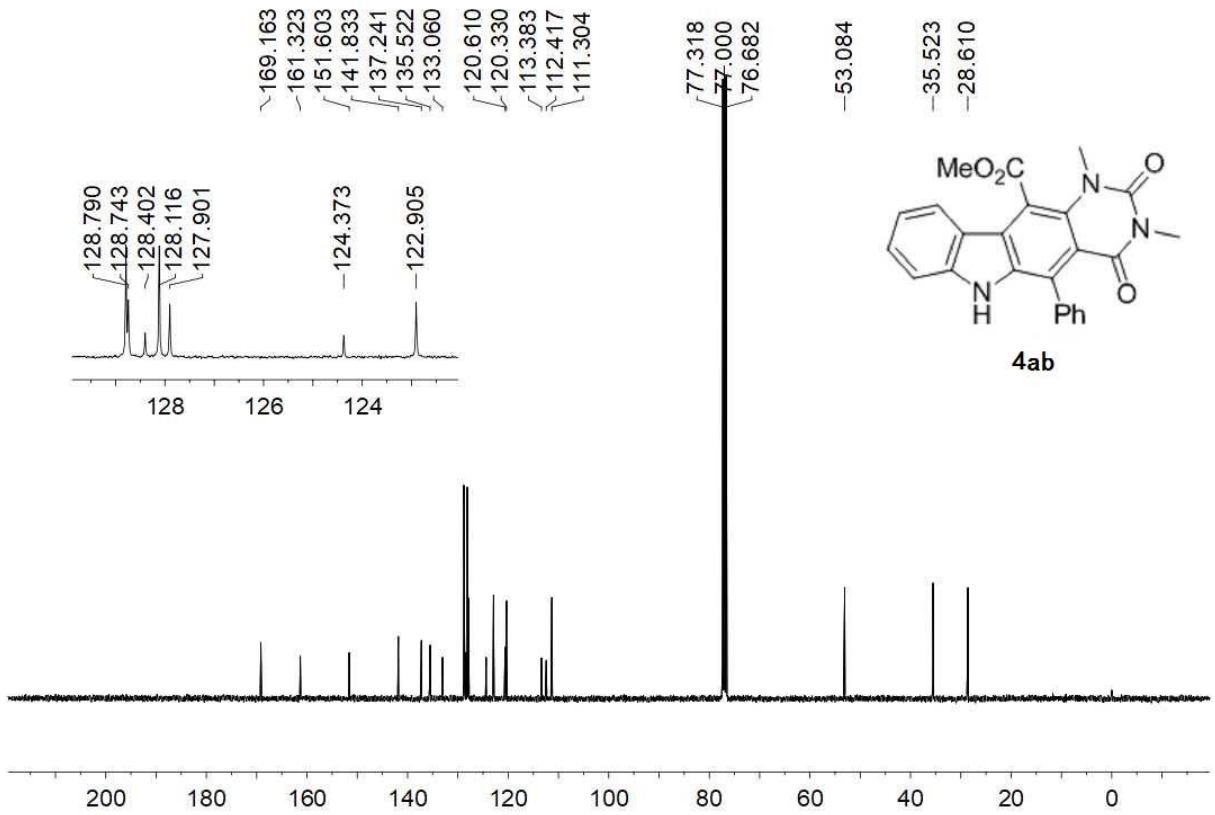
^{13}C NMR spectrum of the compound **4aa** (100 MHz, $CDCl_3$)



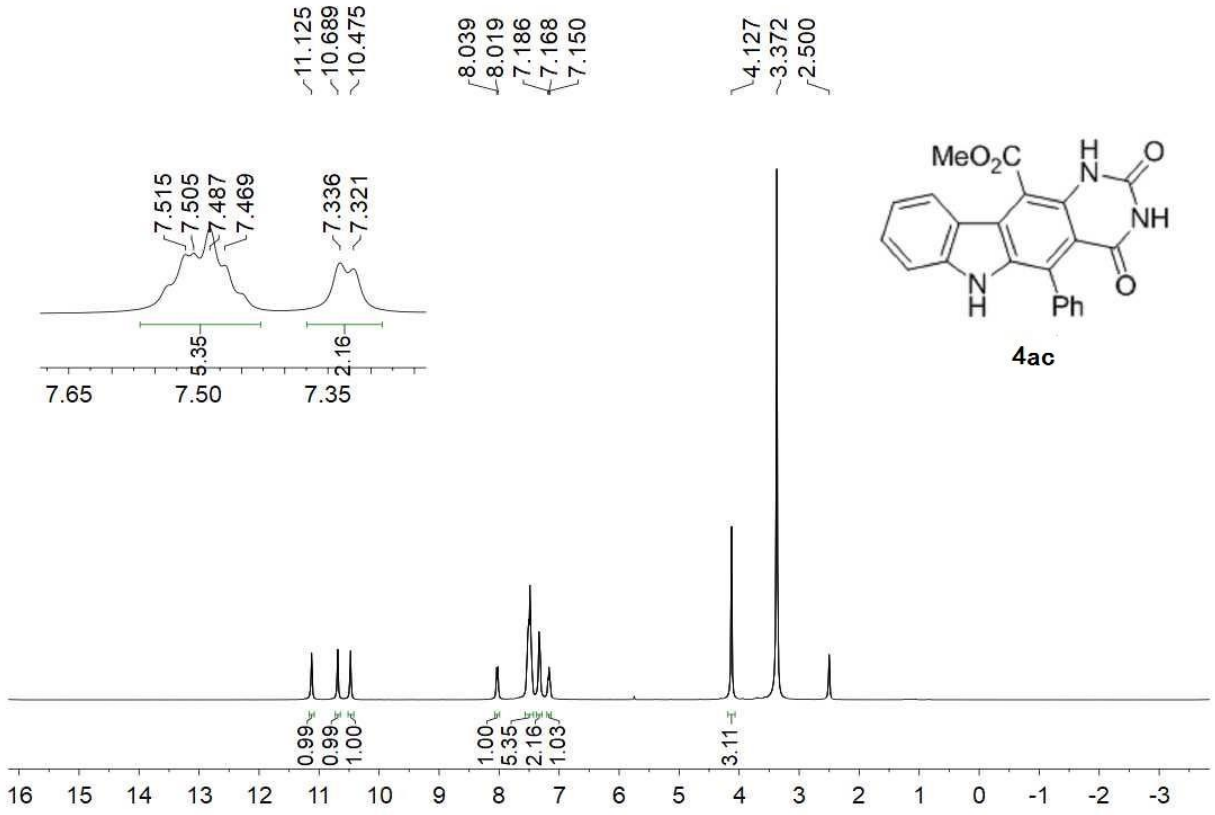
^{1}H NMR spectrum of the compound **4ab** (400 MHz, $CDCl_3$)



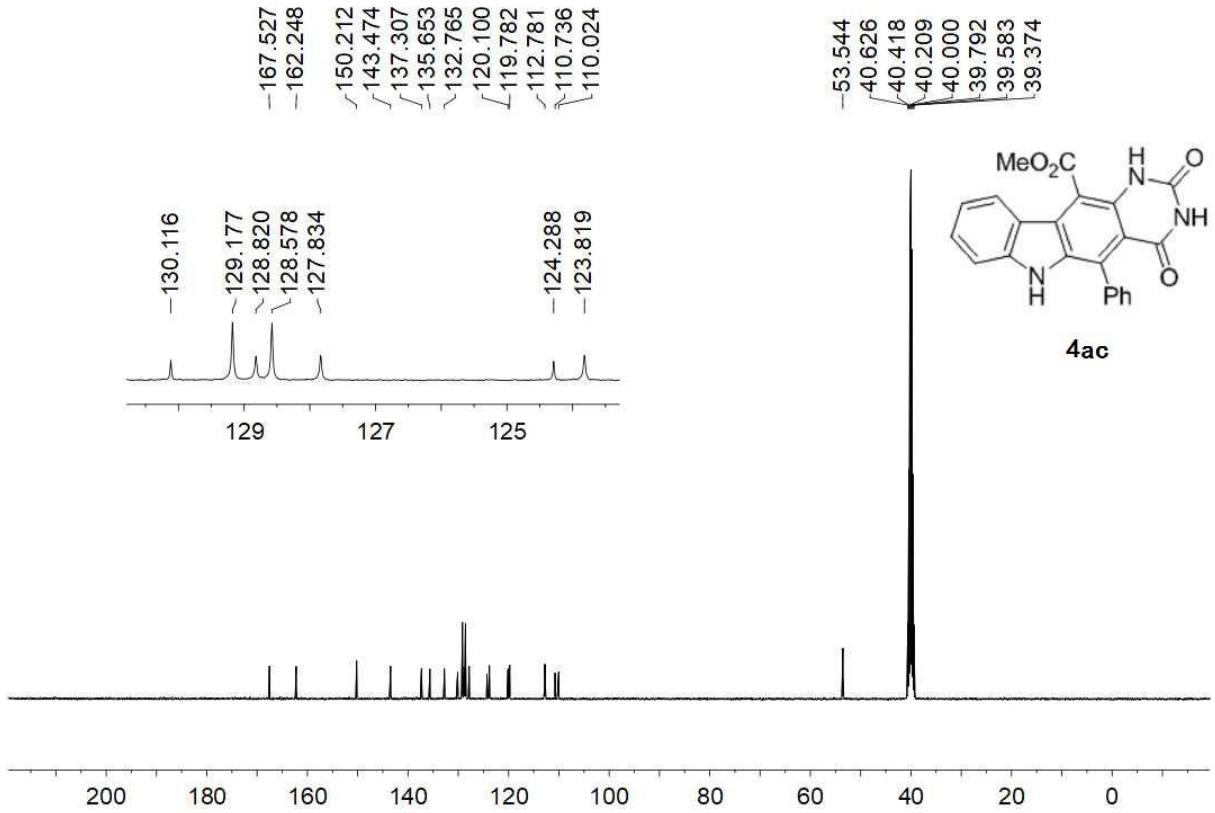
^{13}C NMR spectrum of the compound **4ab** (100 MHz, $CDCl_3$)



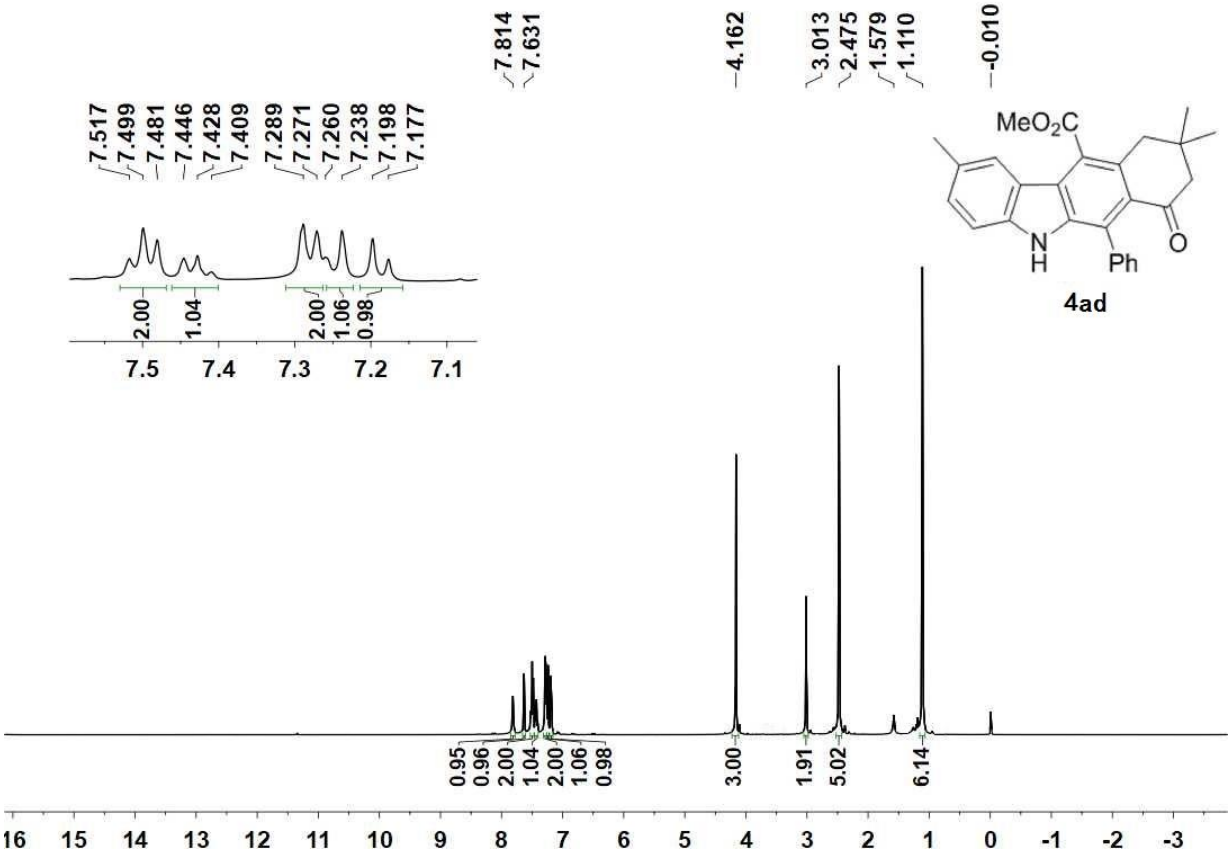
^{1}H NMR spectrum of the compound **4ac** (400 MHz, DMSO-d_6)



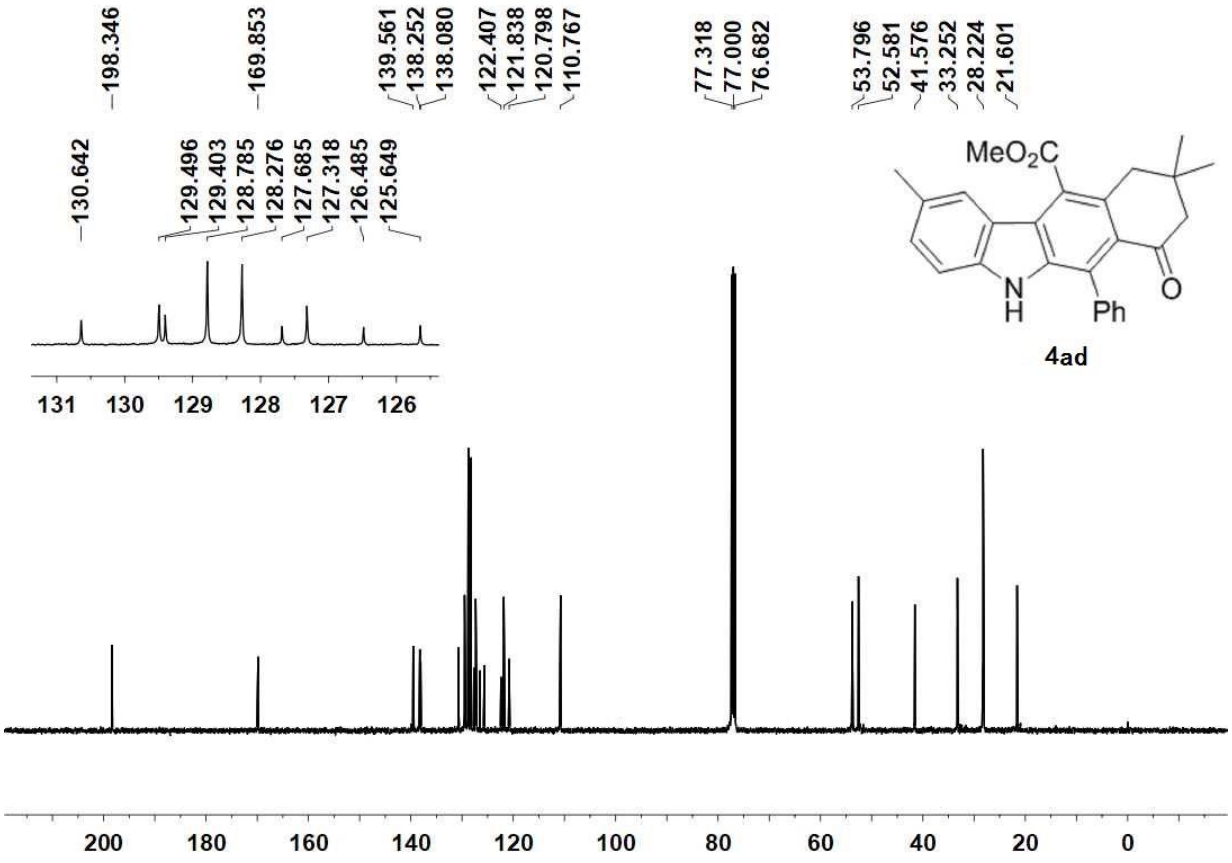
^{13}C NMR spectrum of the compound **4ac** (100 MHz, DMSO-d_6)



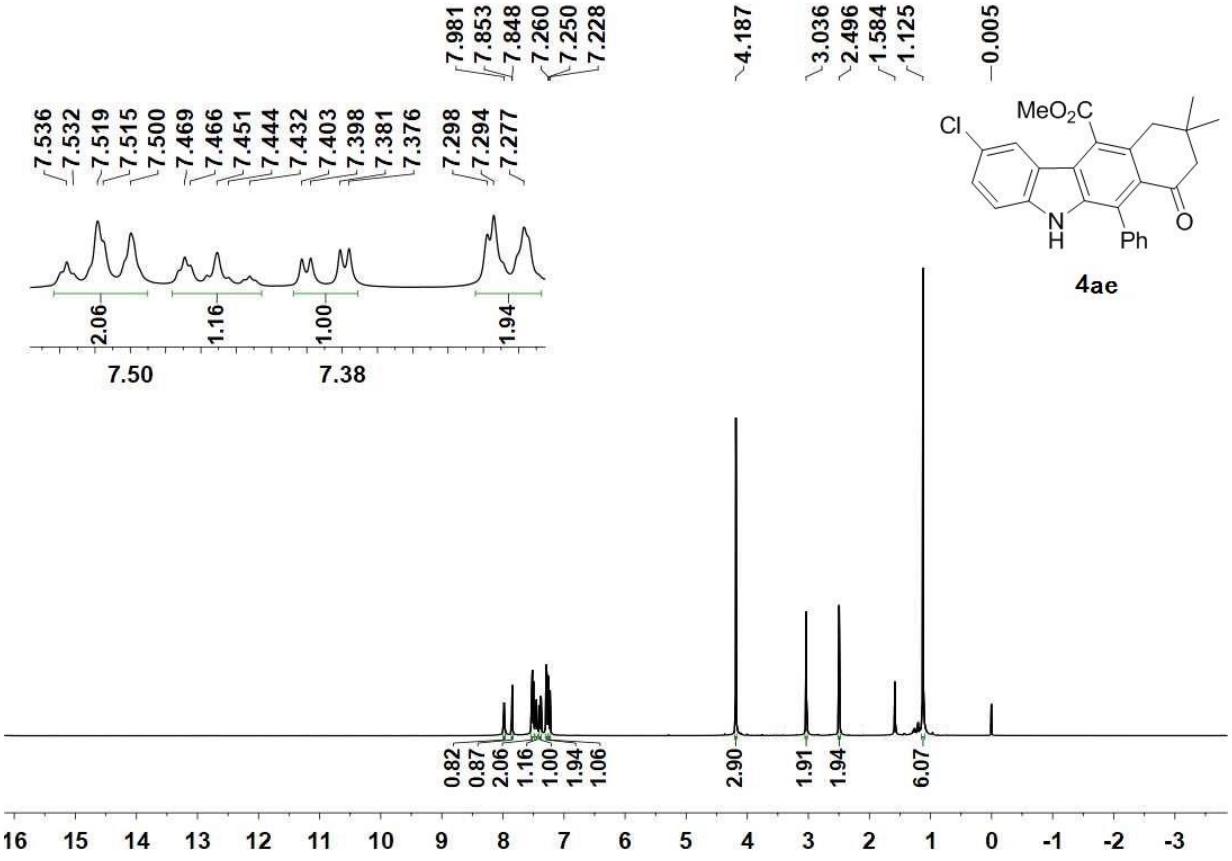
^{1}H NMR spectrum of the compound **4ad** (400 MHz, $CDCl_3$)



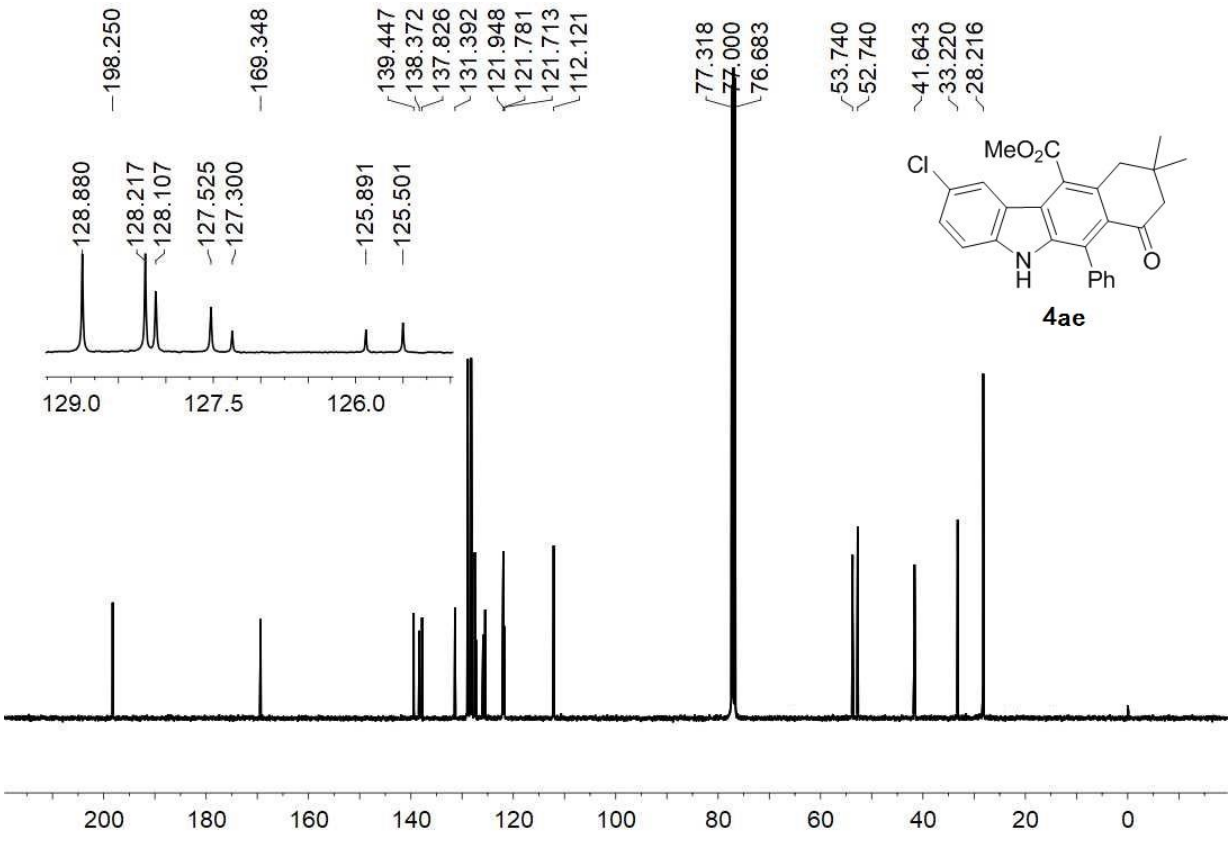
^{13}C NMR spectrum of the compound **4ad** (100 MHz, $CDCl_3$)



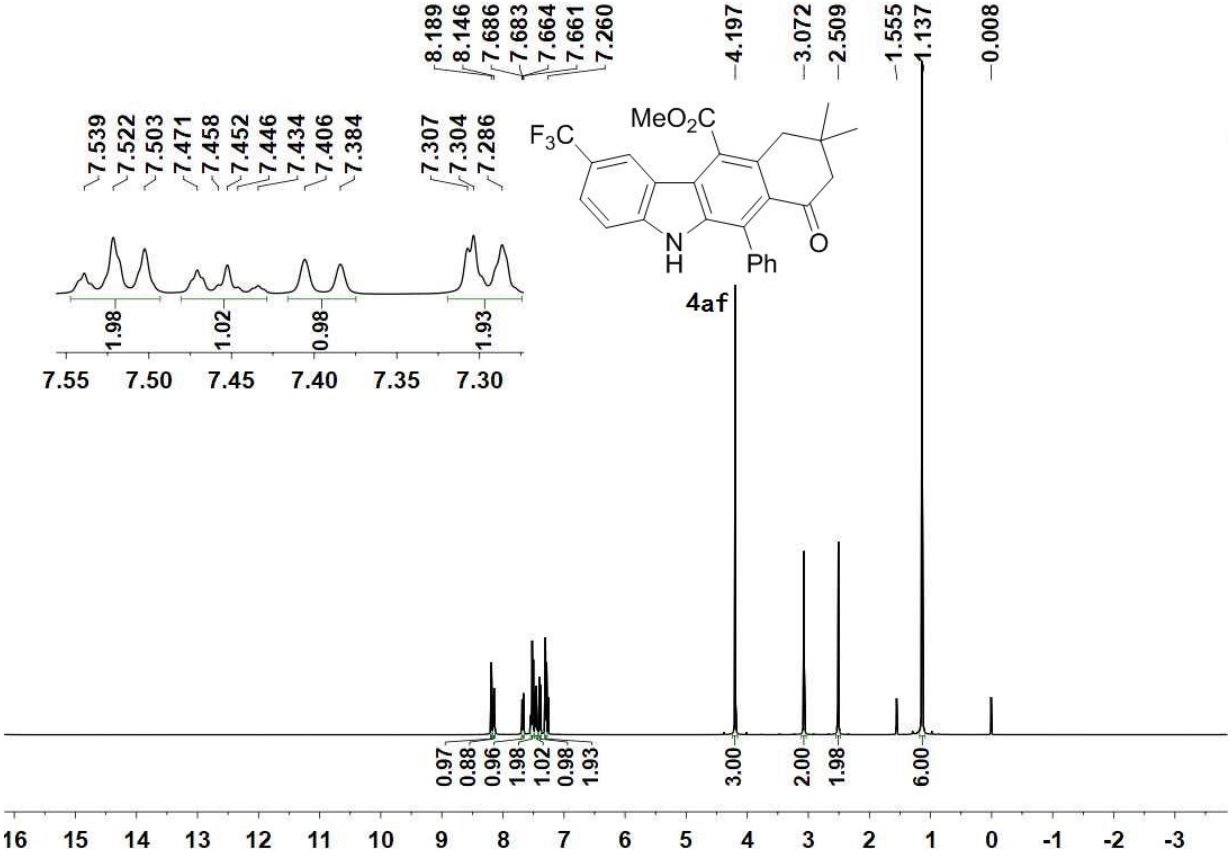
^{1}H NMR spectrum of the compound **4ae** (400 MHz, $CDCl_3$)



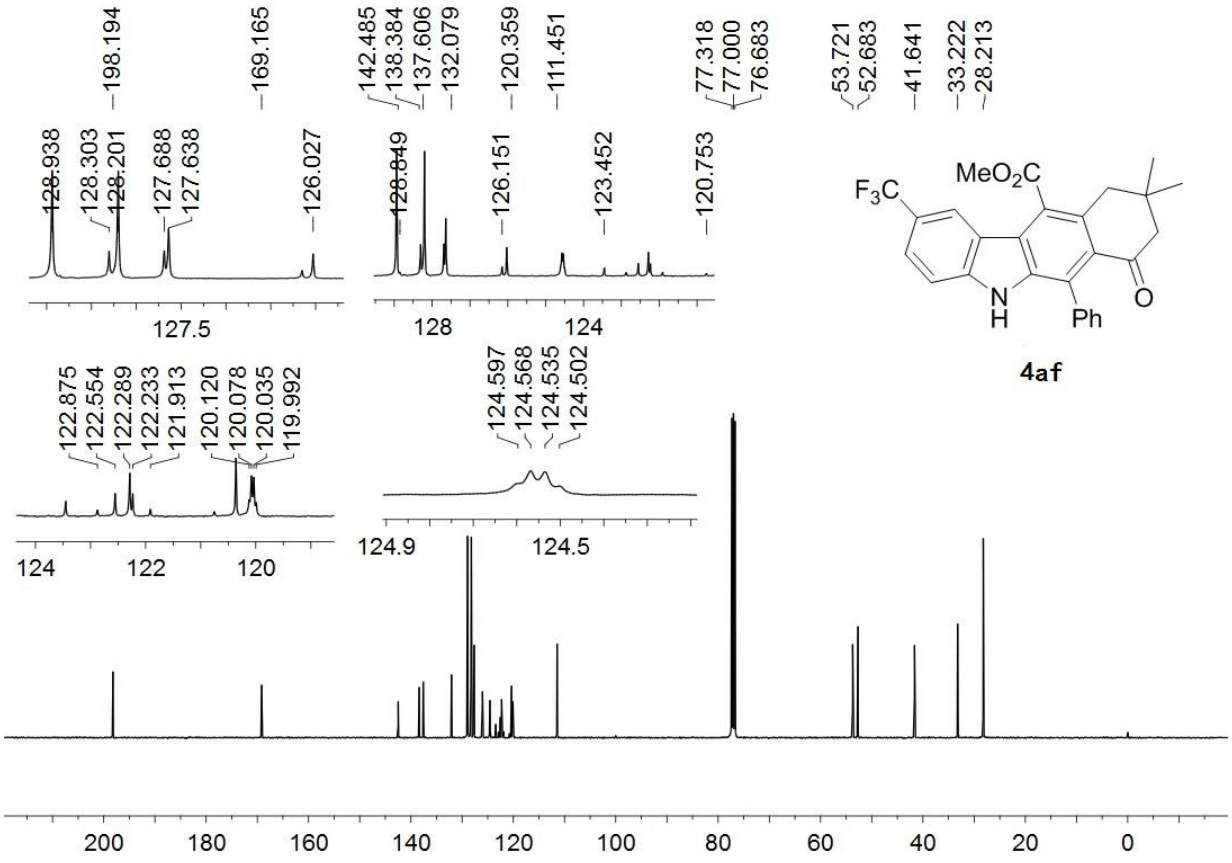
^{13}C NMR spectrum of the compound **4ae** (100 MHz, $CDCl_3$)



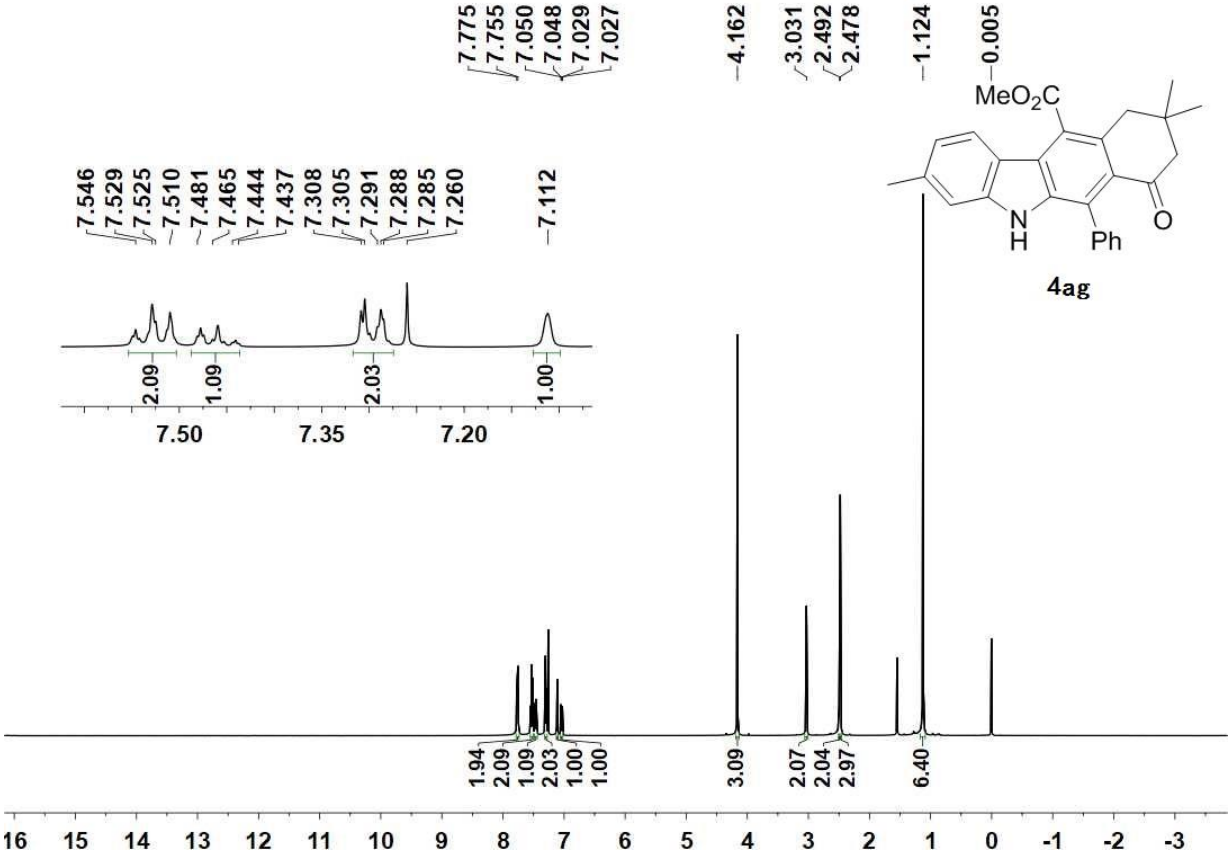
^{1}H NMR spectrum of the compound **4af** (400 MHz, $CDCl_3$)



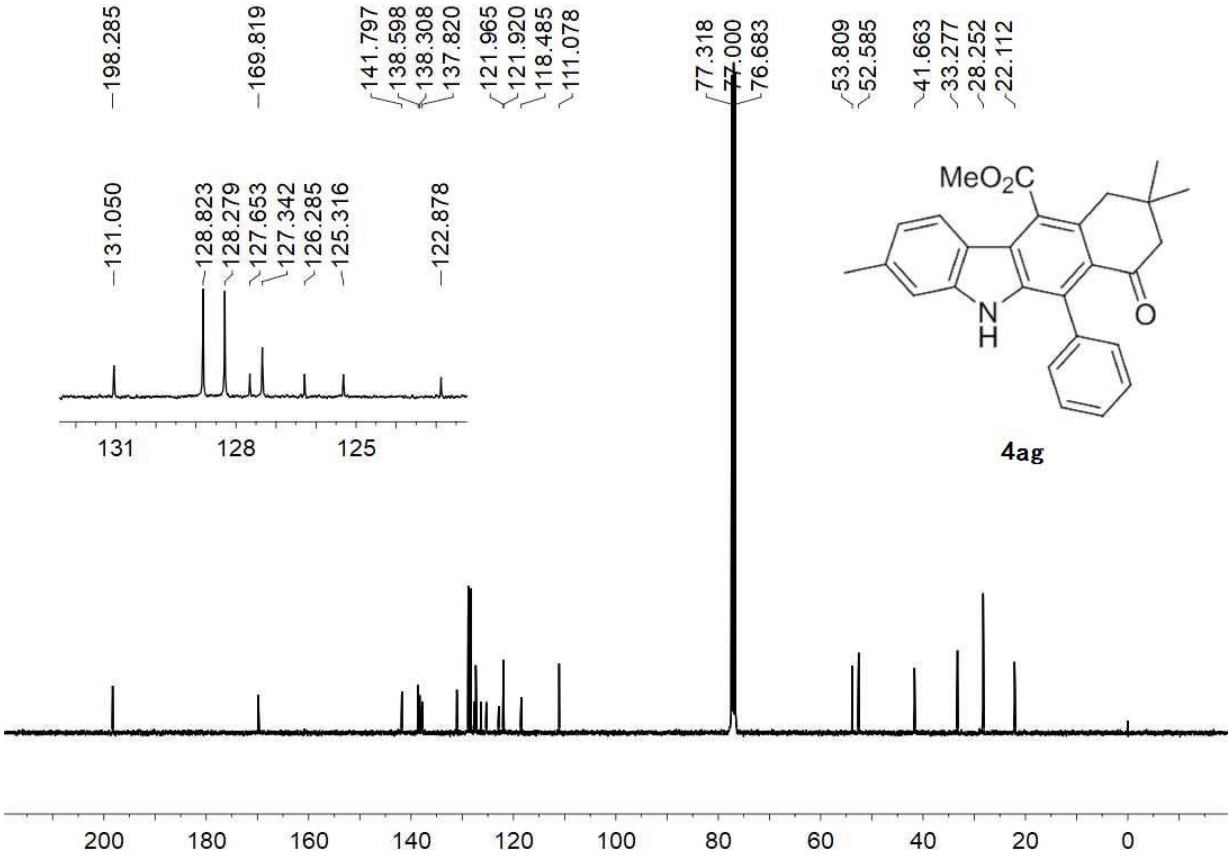
^{13}C NMR spectrum of the compound **4af** (100 MHz, $CDCl_3$)



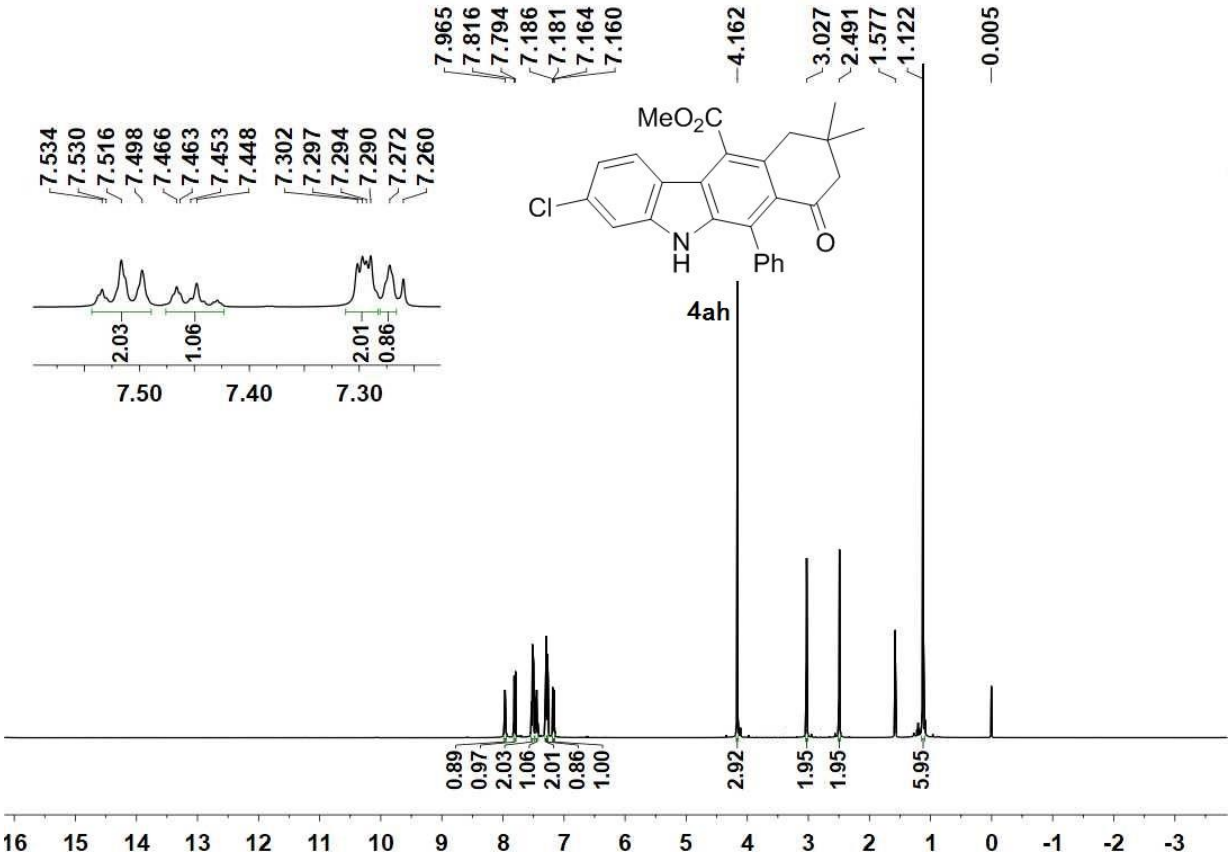
^{1}H NMR spectrum of the compound **4ag** (400 MHz, $CDCl_3$)



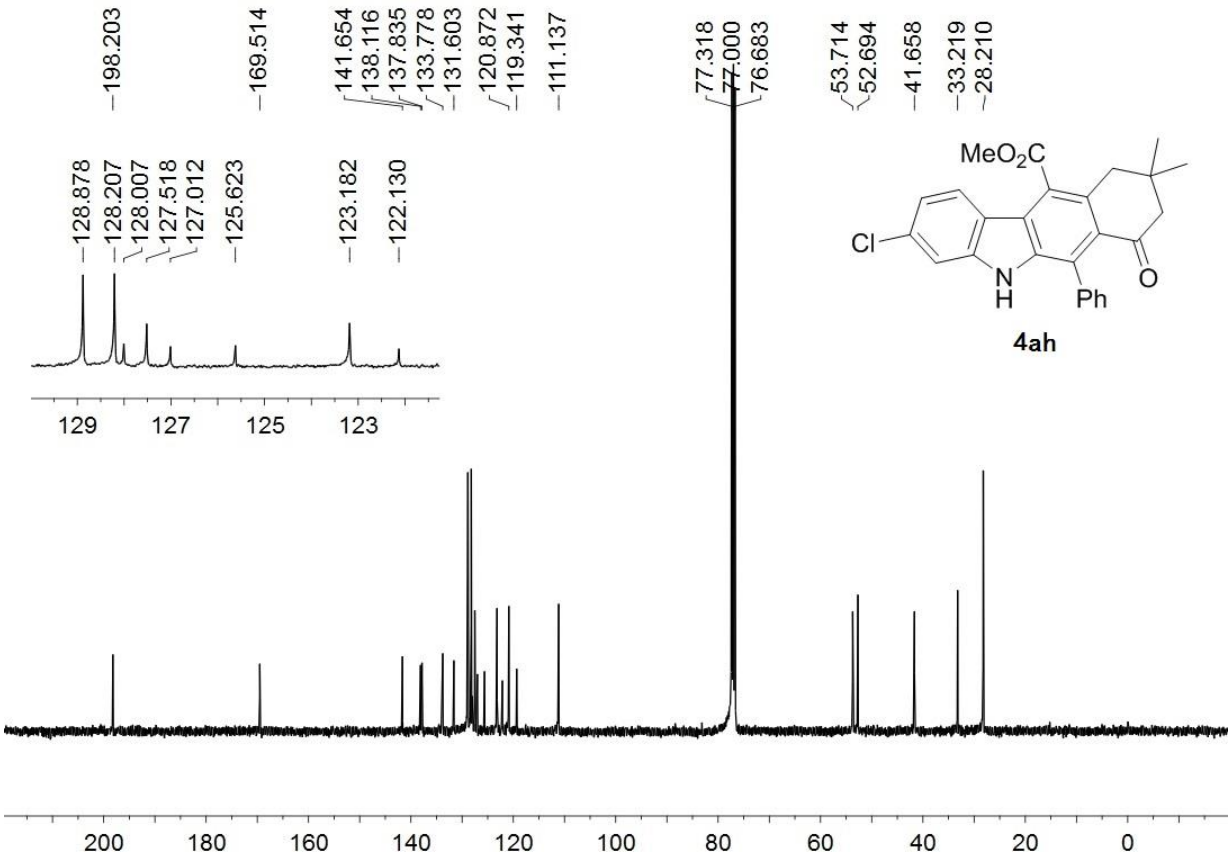
^{13}C NMR spectrum of the compound **4ag** (100 MHz, $CDCl_3$)



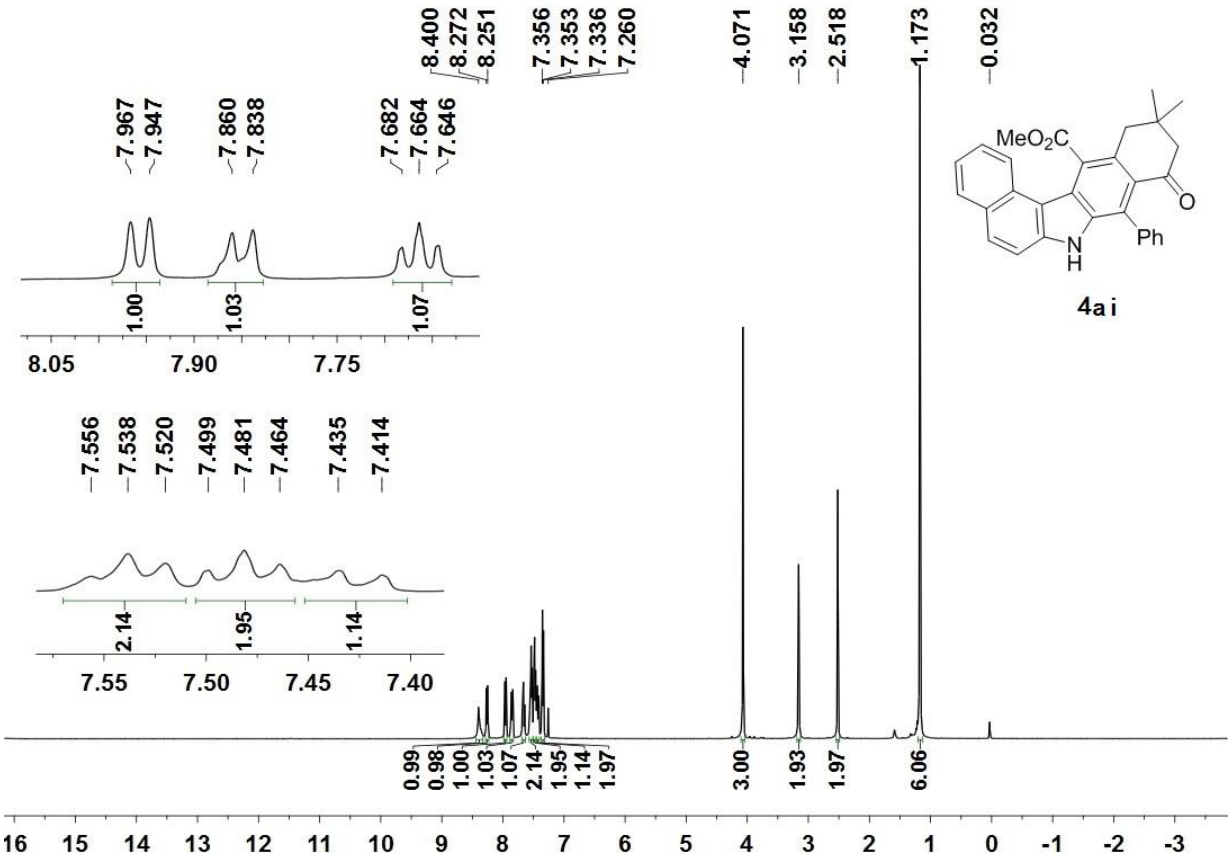
^{1}H NMR spectrum of the compound **4ah** (400 MHz, $CDCl_3$)



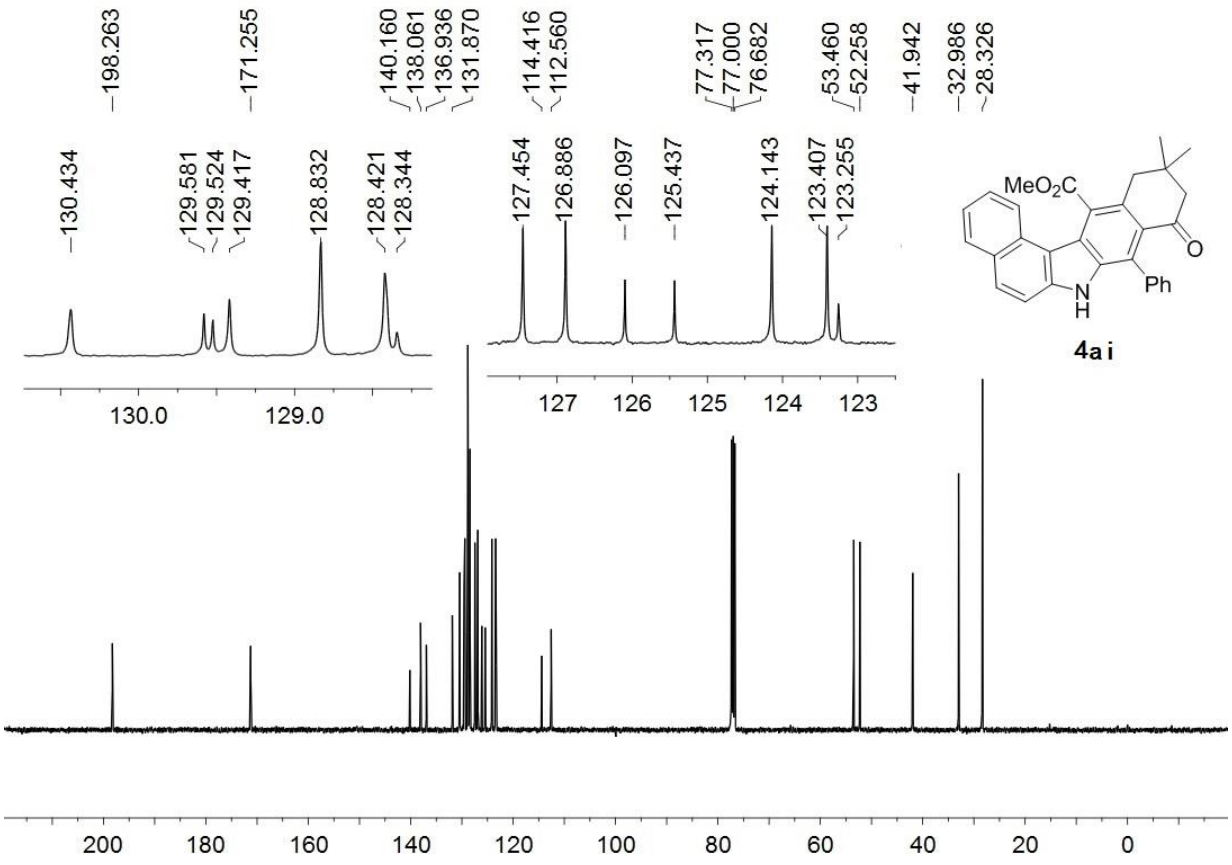
^{13}C NMR spectrum of the compound **4ah** (100 MHz, $CDCl_3$)



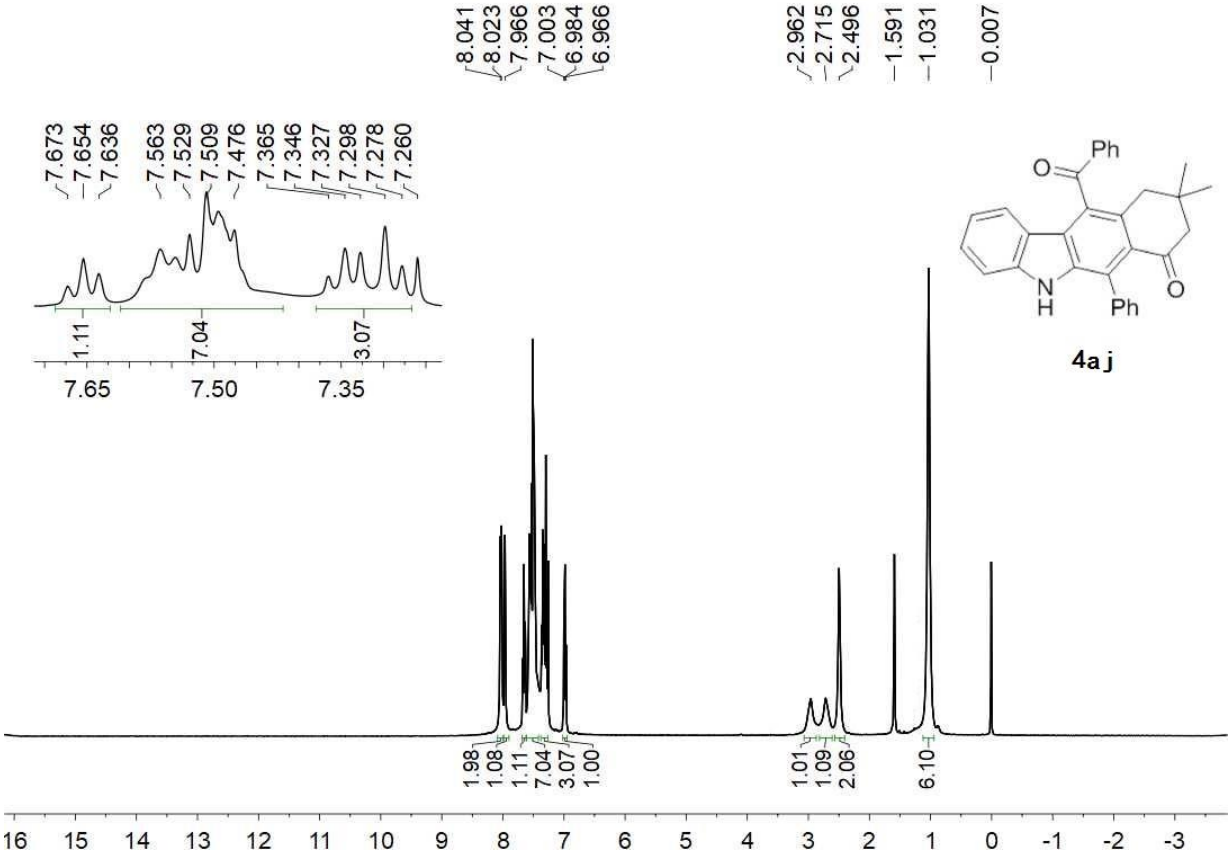
^{1}H NMR spectrum of the compound **4ai** (400 MHz, $CDCl_3$)



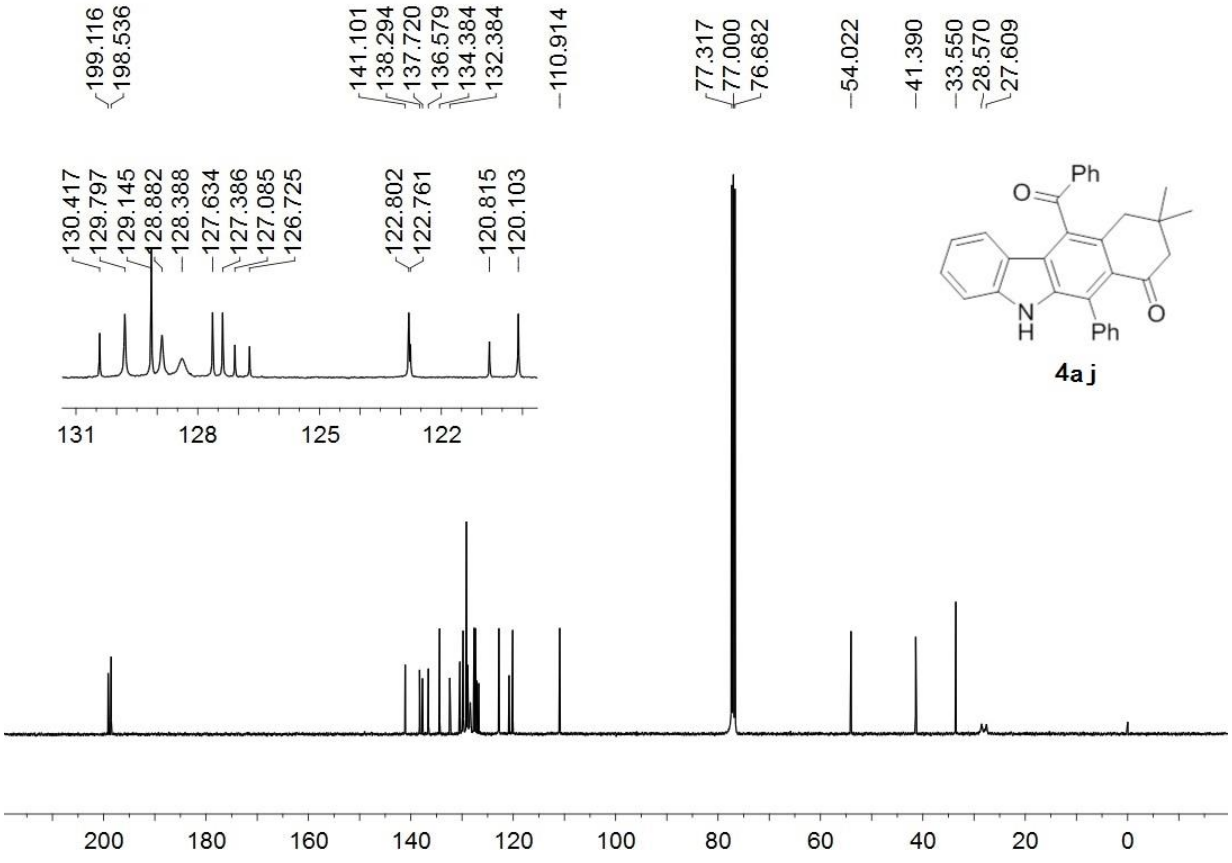
^{13}C NMR spectrum of the compound **4ai** (100 MHz, $CDCl_3$)



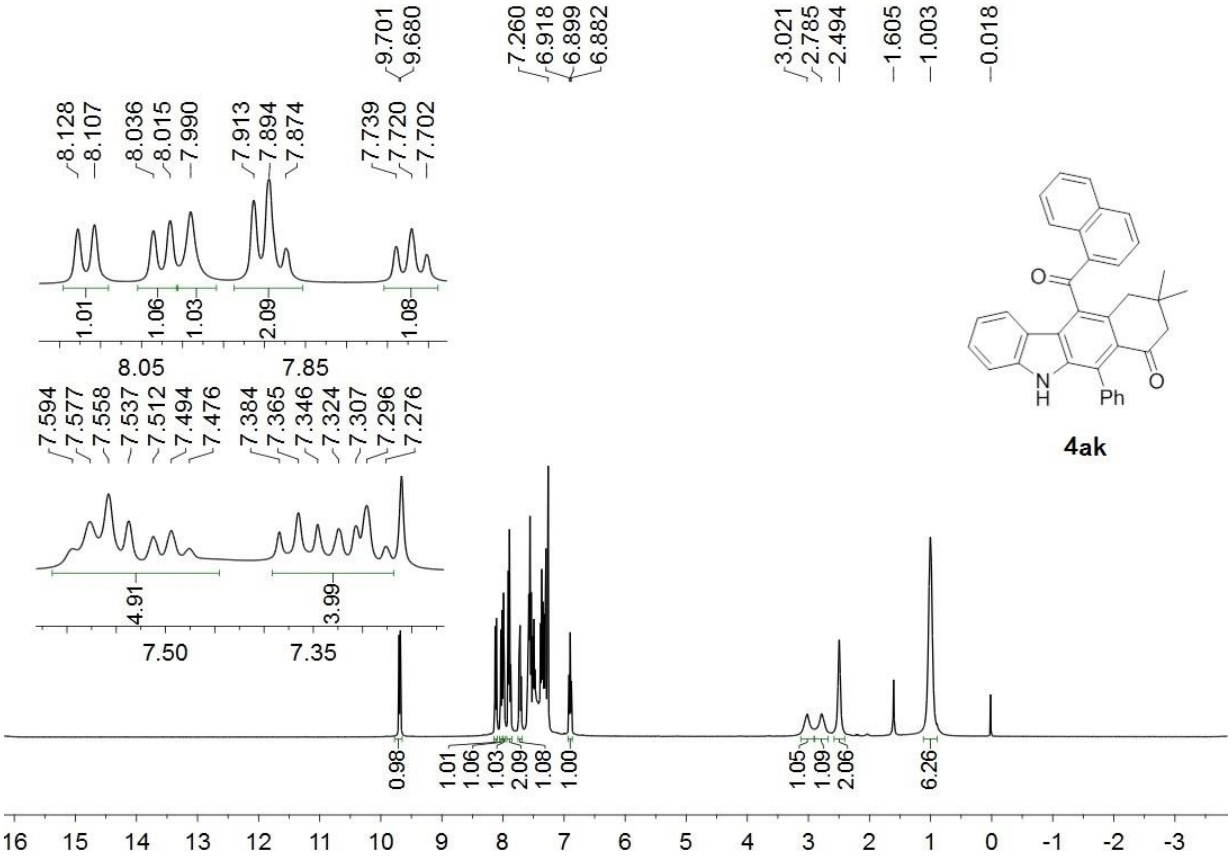
^{1}H NMR spectrum of the compound **4aj** (400 MHz, $CDCl_3$)



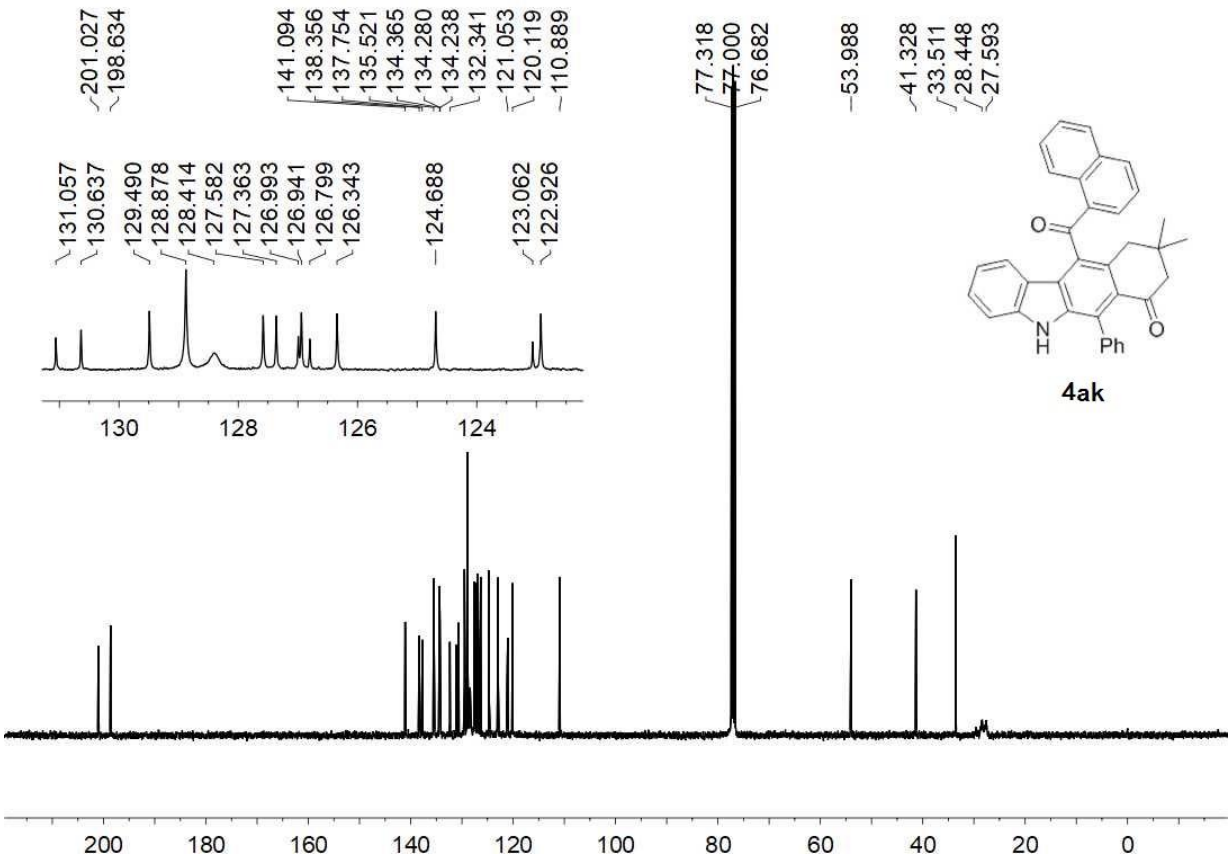
^{13}C NMR spectrum of the compound **4aj** (100 MHz, $CDCl_3$)



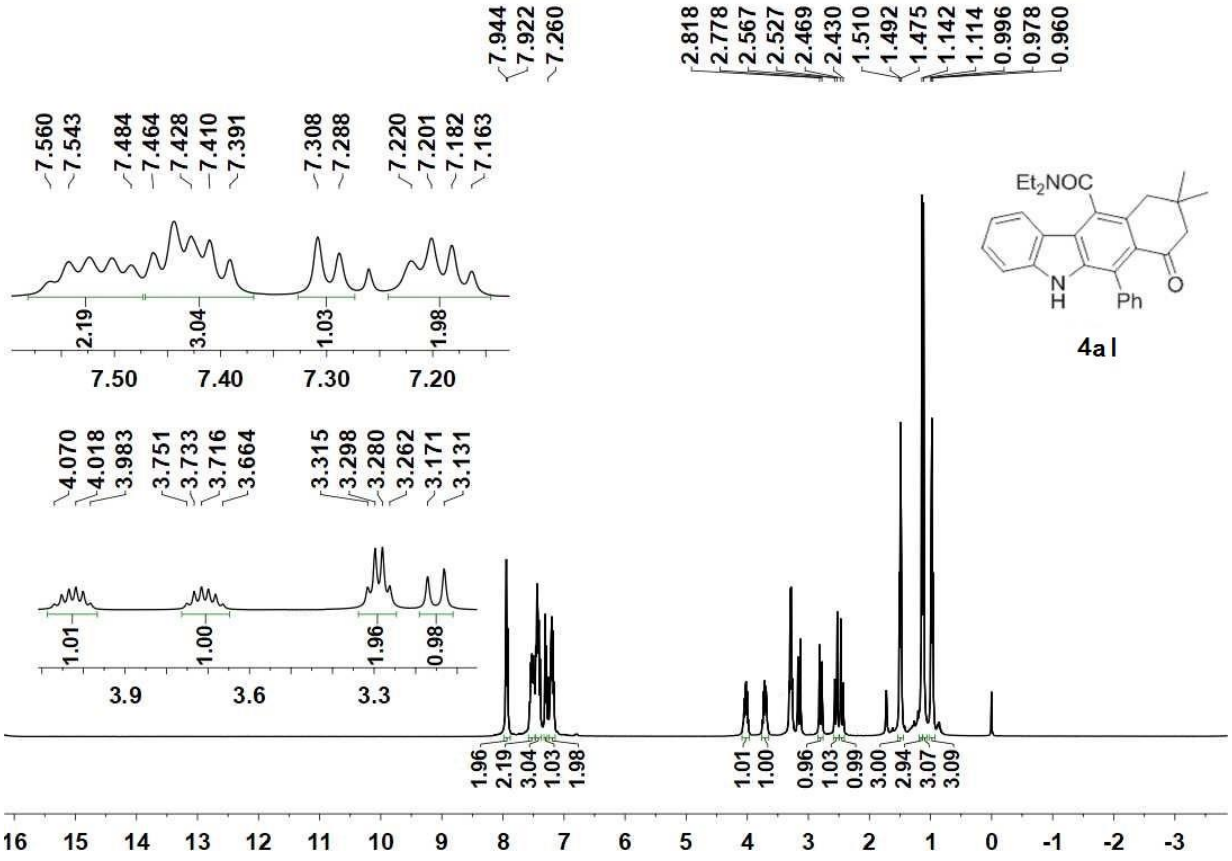
^{1}H NMR spectrum of the compound **4ak** (400 MHz, $CDCl_3$)



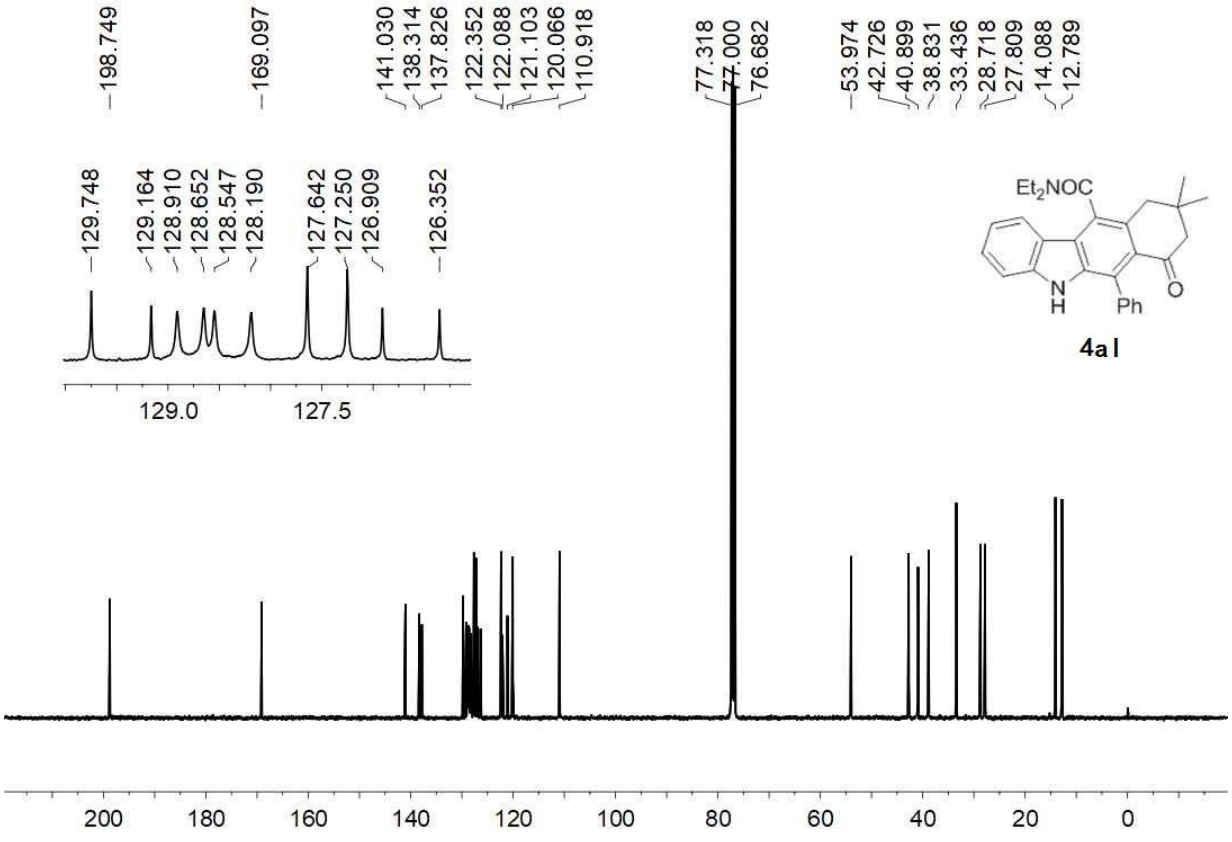
^{13}C NMR spectrum of the compound **4ak** (100 MHz, $CDCl_3$)



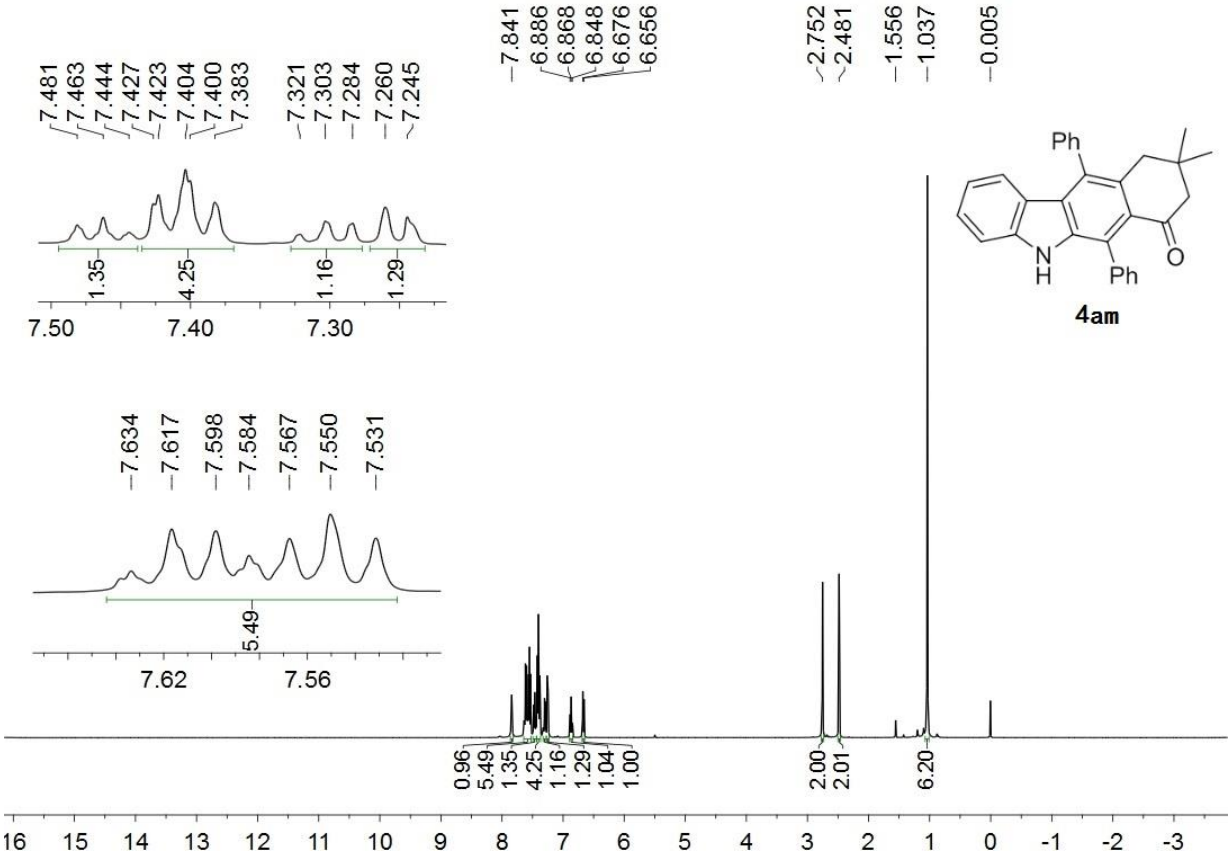
^{1}H NMR spectrum of the compound **4al** (400 MHz, $CDCl_3$)



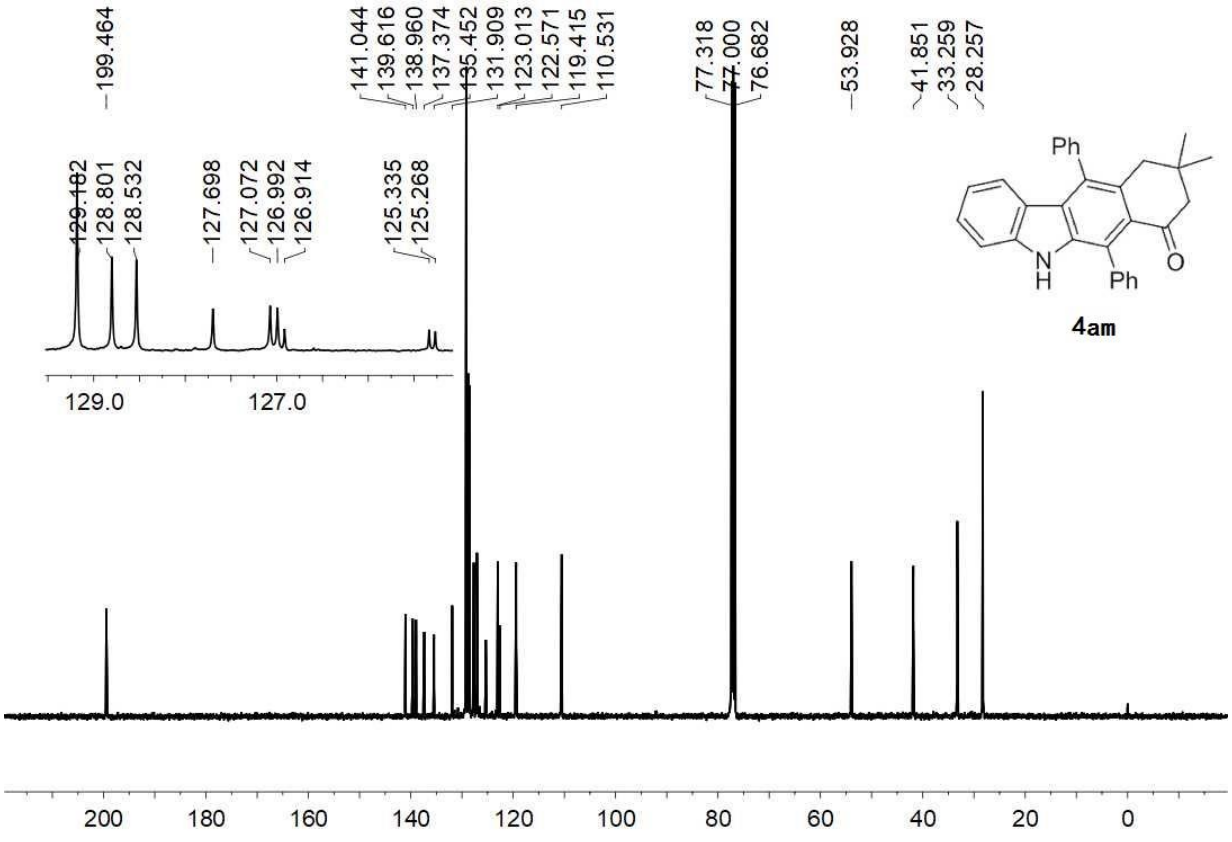
^{13}C NMR spectrum of the compound **4al** (100 MHz, $CDCl_3$)



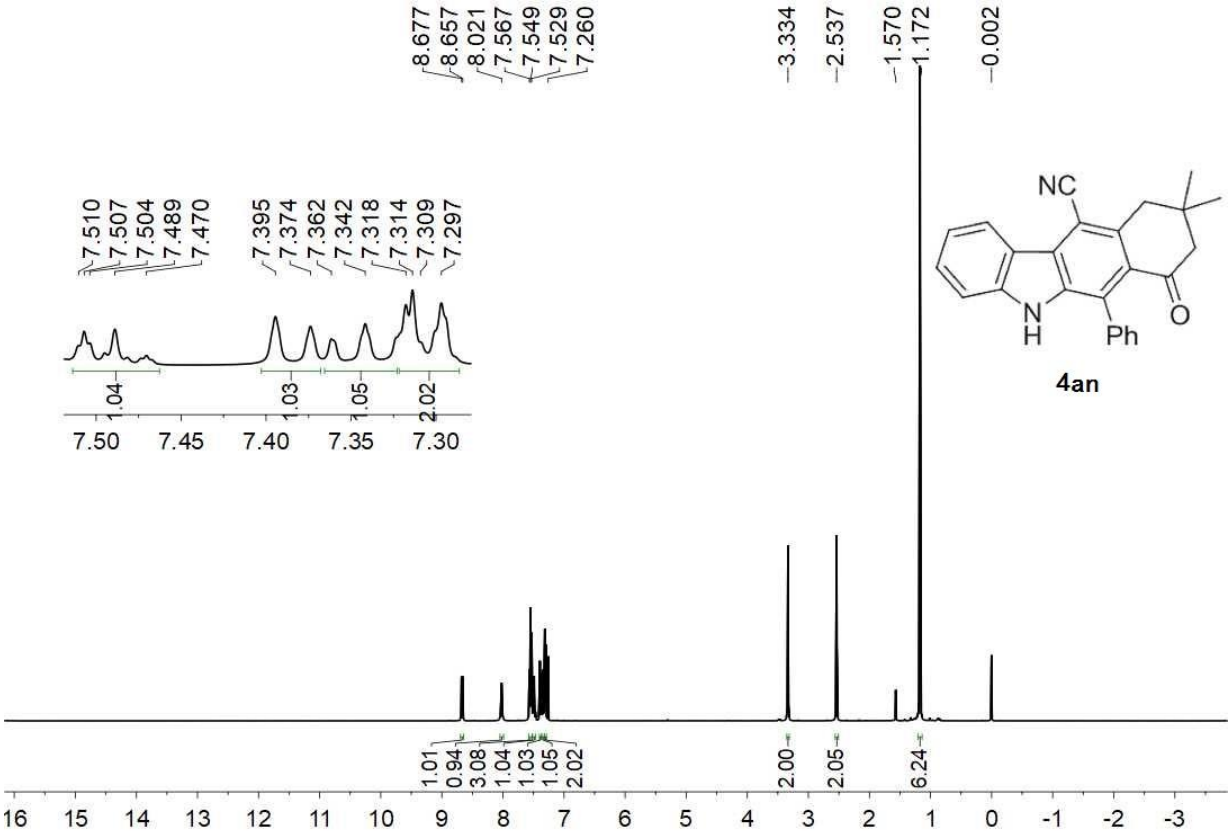
^{1}H NMR spectrum of the compound **4am** (400 MHz, $CDCl_3$)



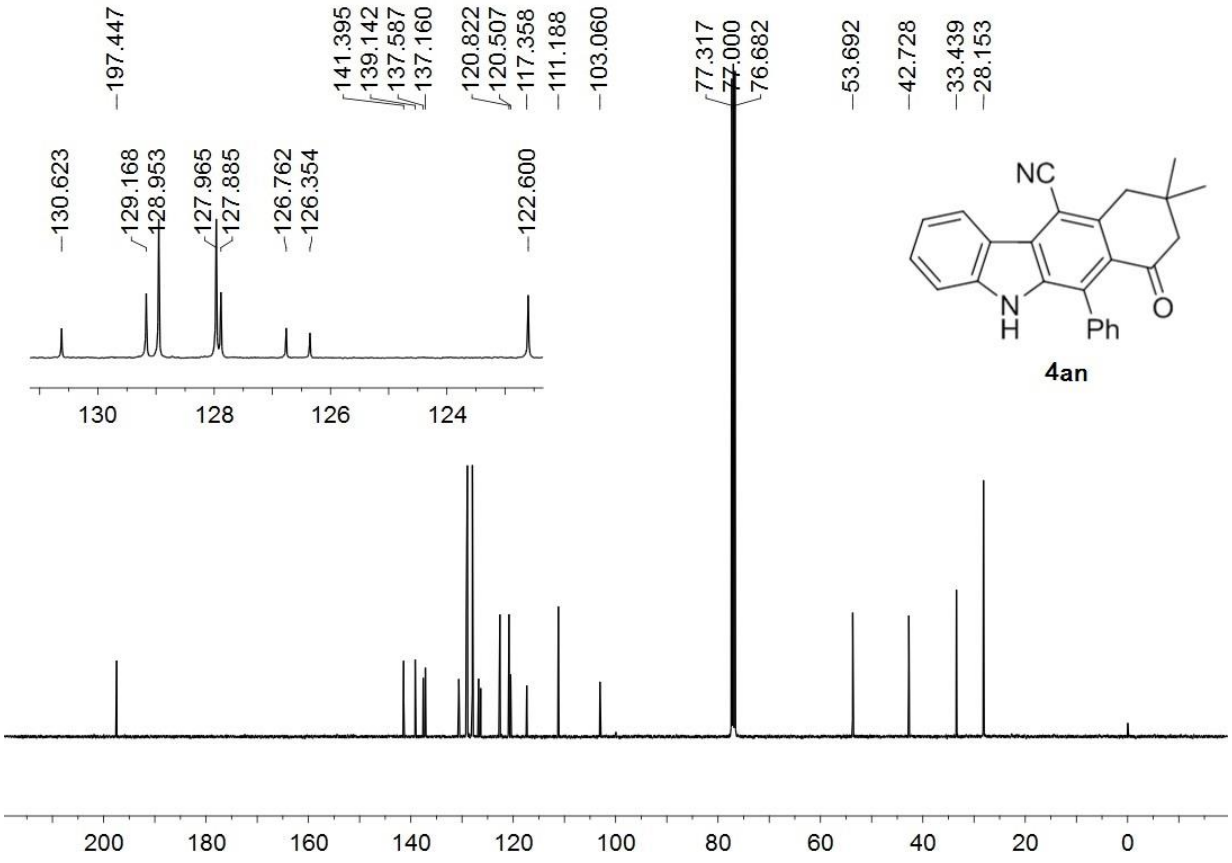
^{13}C NMR spectrum of the compound **4am** (100 MHz, $CDCl_3$)



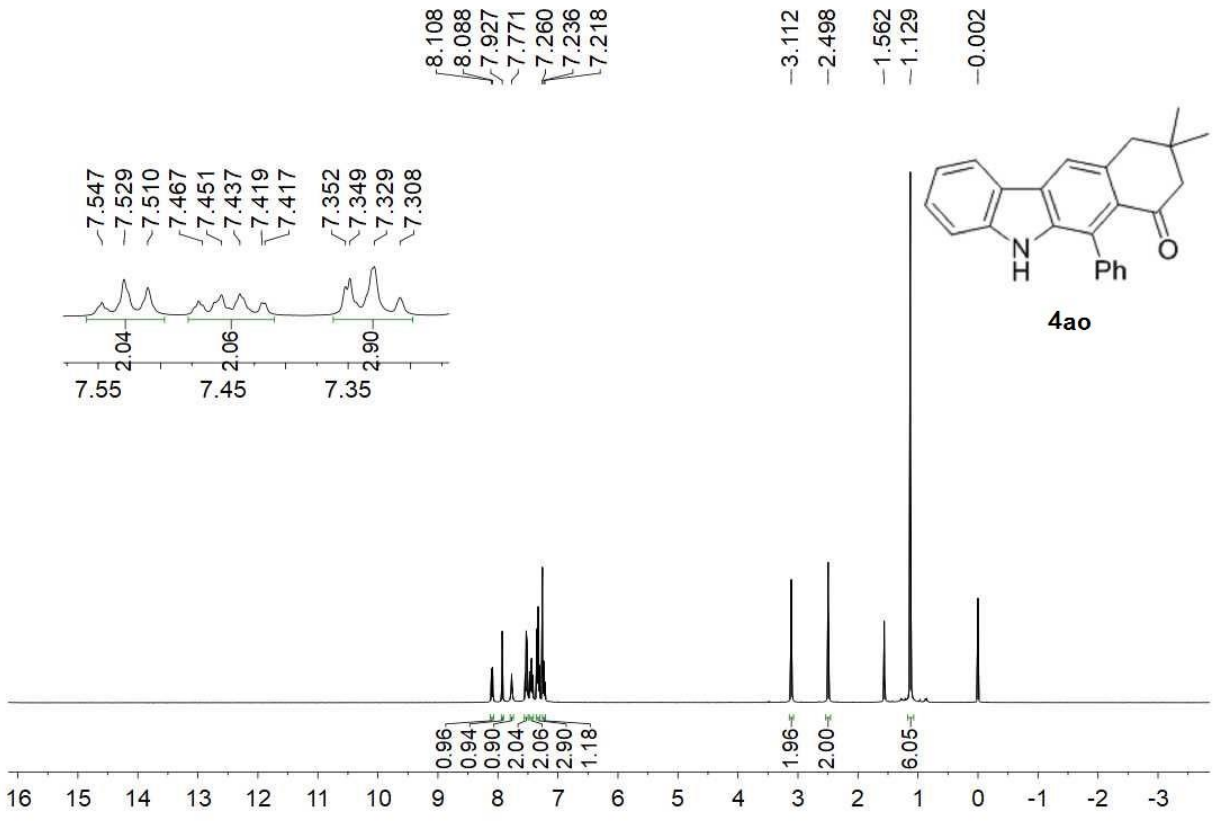
^{1}H NMR spectrum of the compound **4an** (400 MHz, $CDCl_3$)



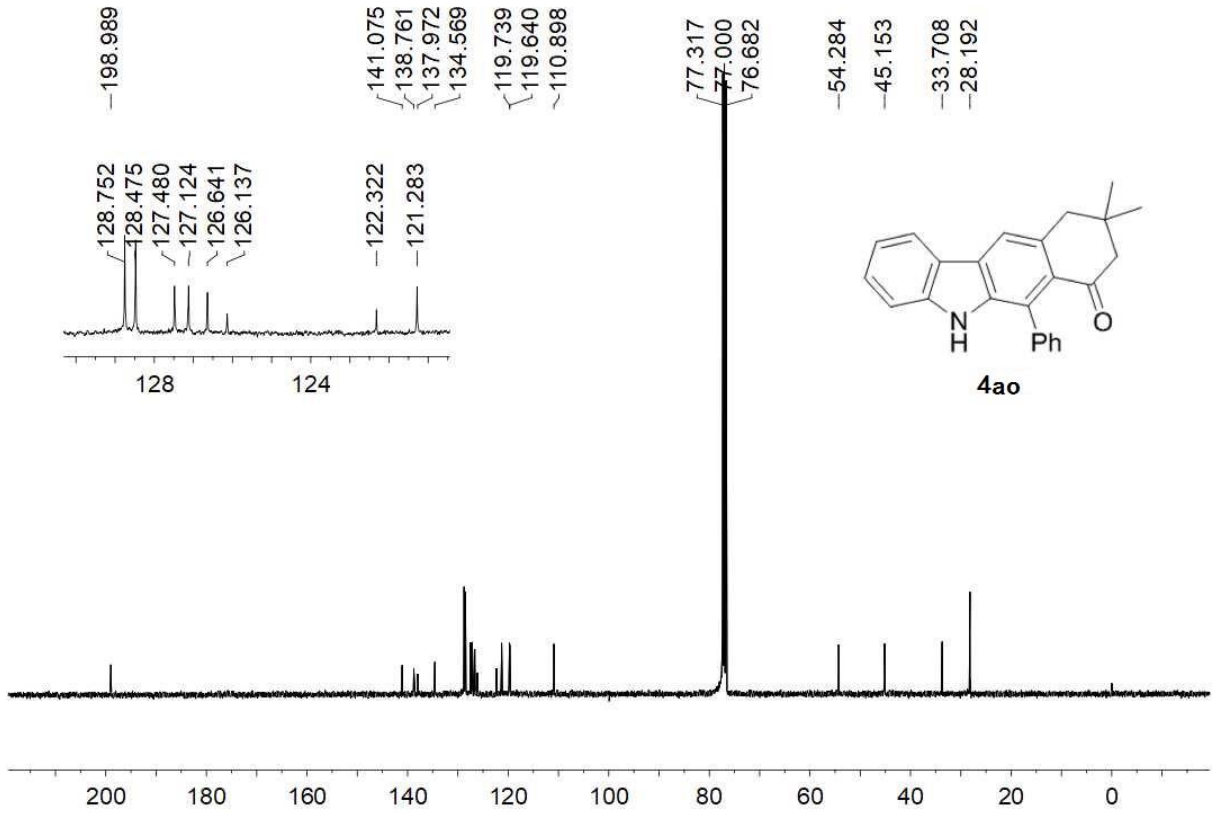
^{13}C NMR spectrum of the compound **4an** (100 MHz, $CDCl_3$)



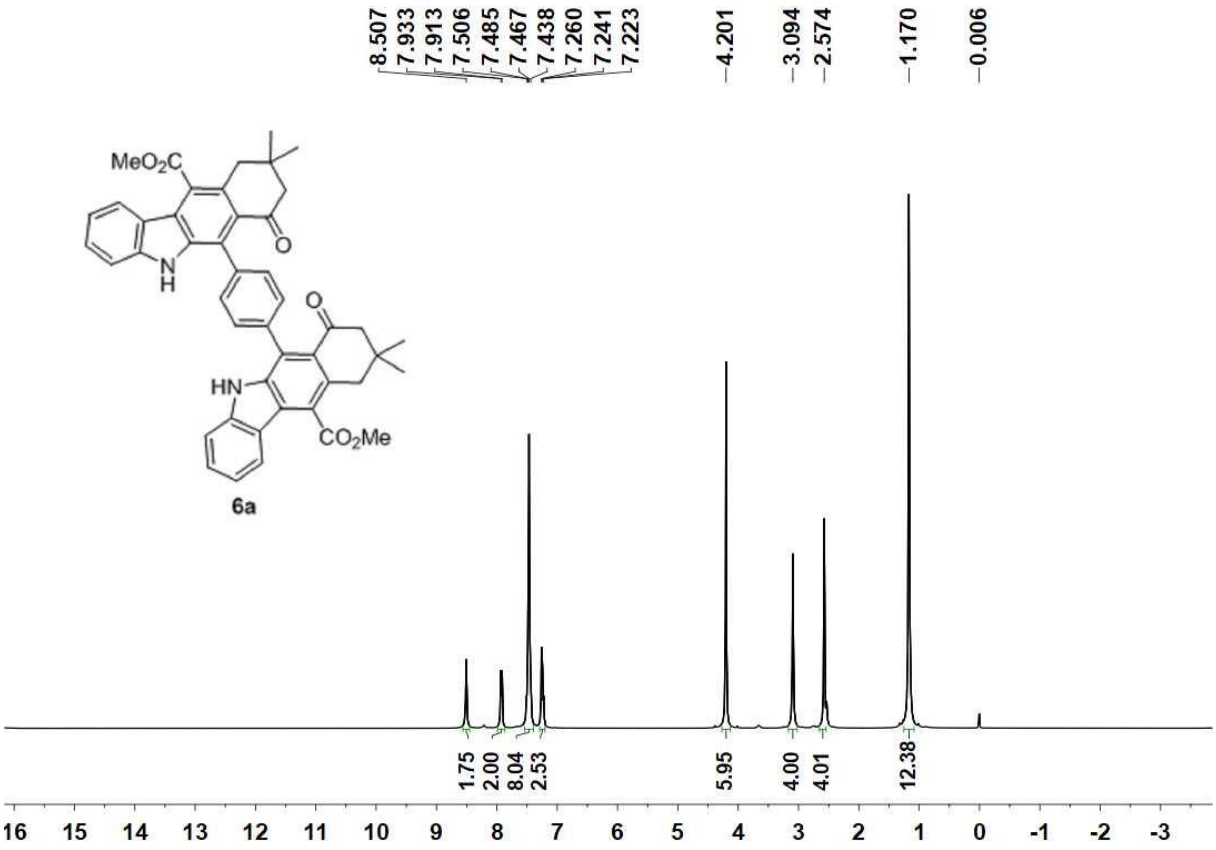
^{1}H NMR spectrum of the compound **4ao** (400 MHz, $CDCl_3$)



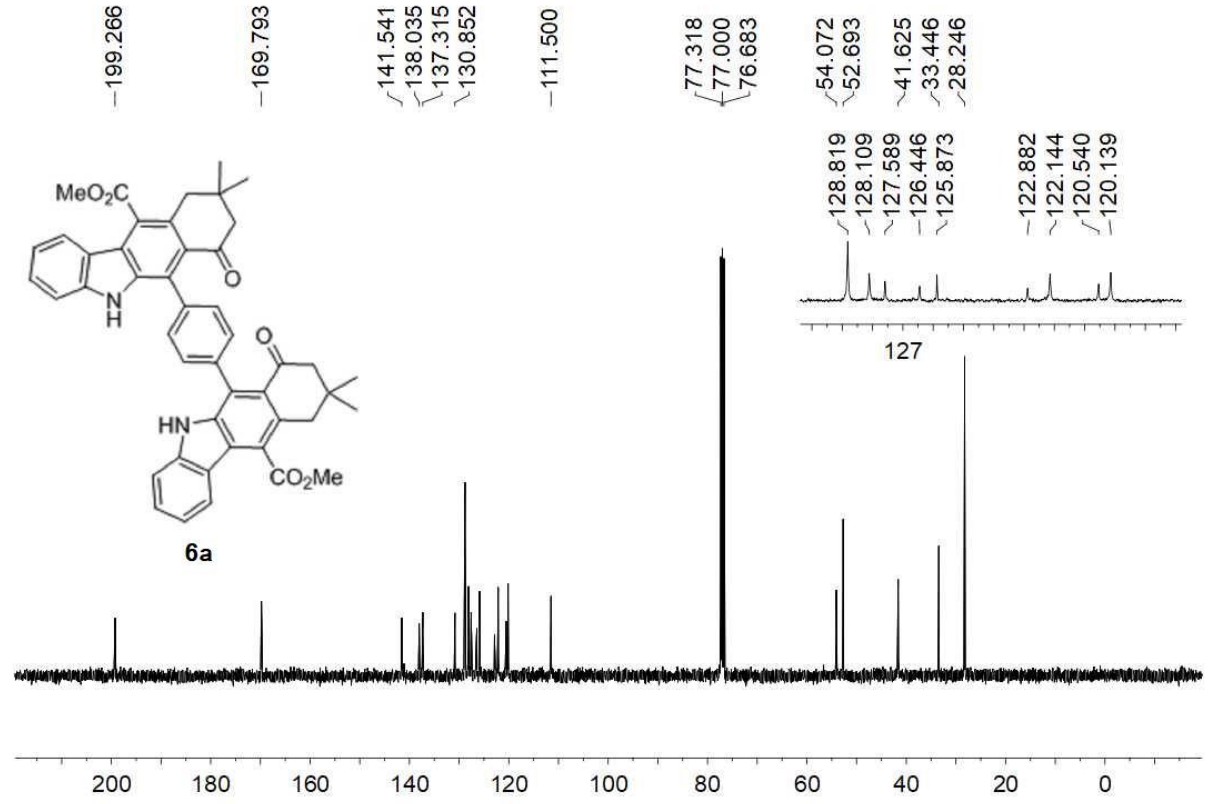
^{13}C NMR spectrum of the compound **4ao** (100 MHz, $CDCl_3$)



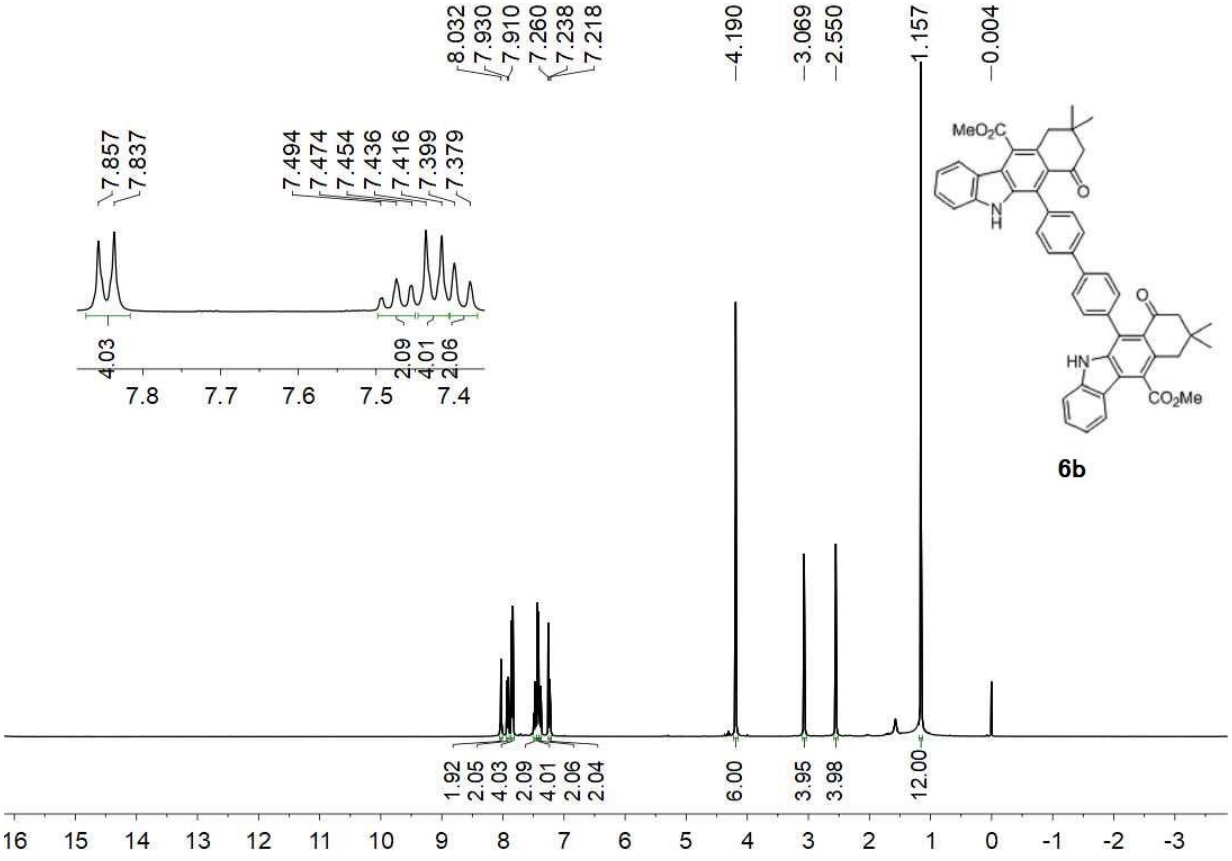
^{1}H NMR spectrum of the compound **6a** (400 MHz, $CDCl_3$)



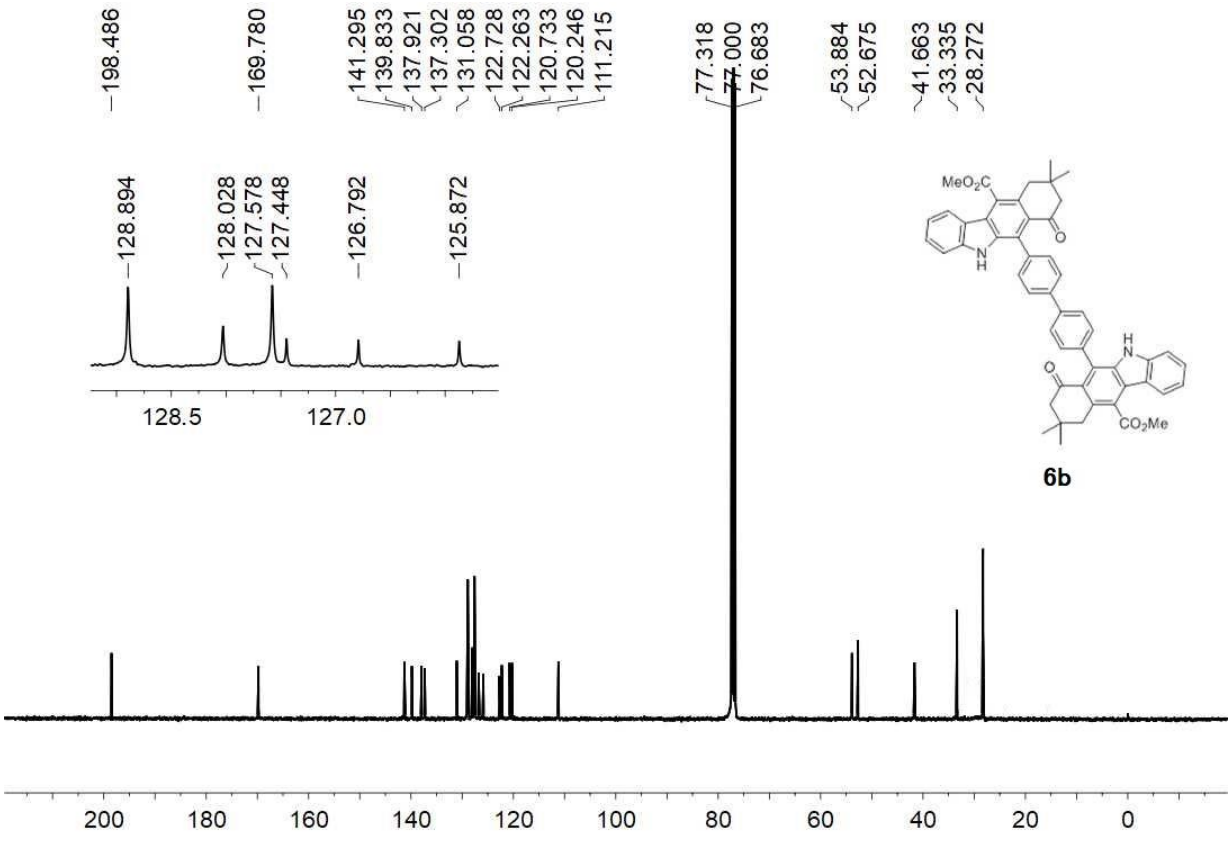
^{13}C NMR spectrum of the compound **6a** (100 MHz, $CDCl_3$)



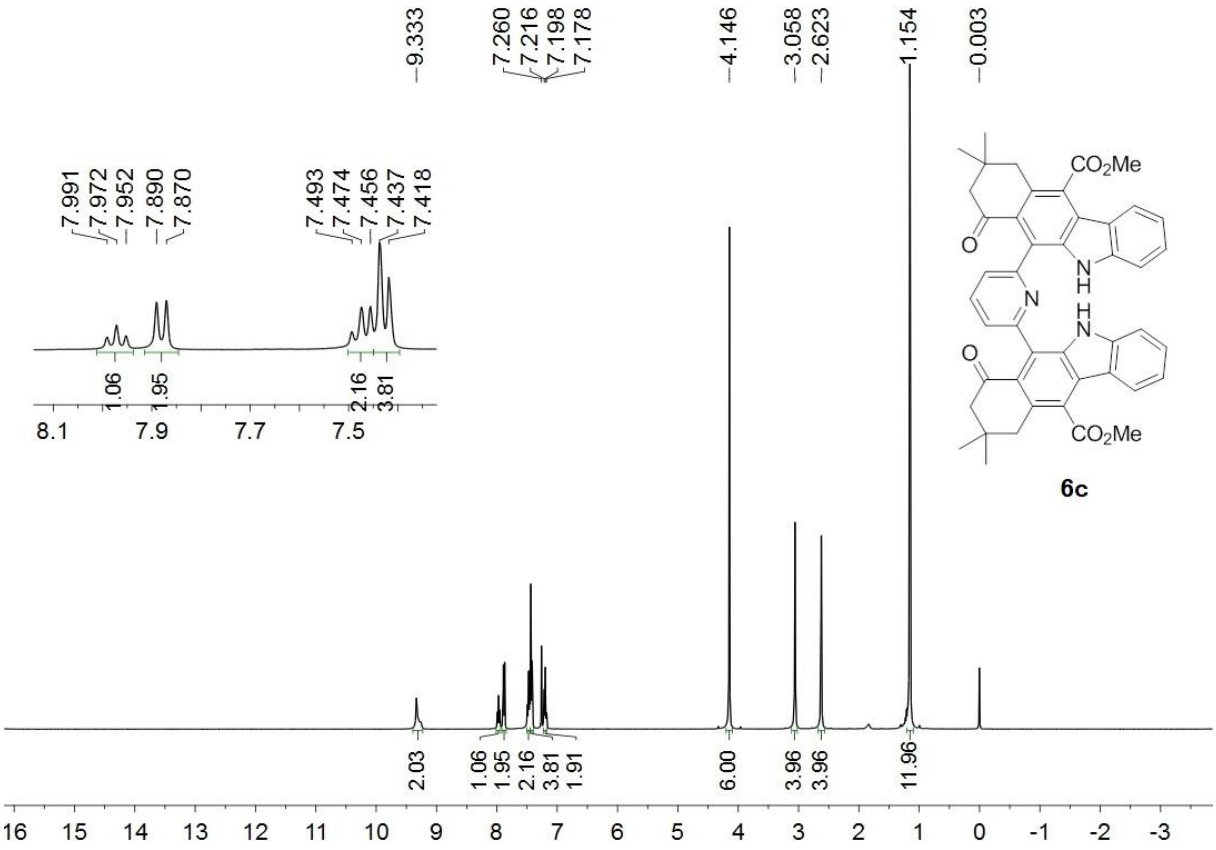
^{1}H NMR spectrum of the compound **6b** (400 MHz, $CDCl_3$)



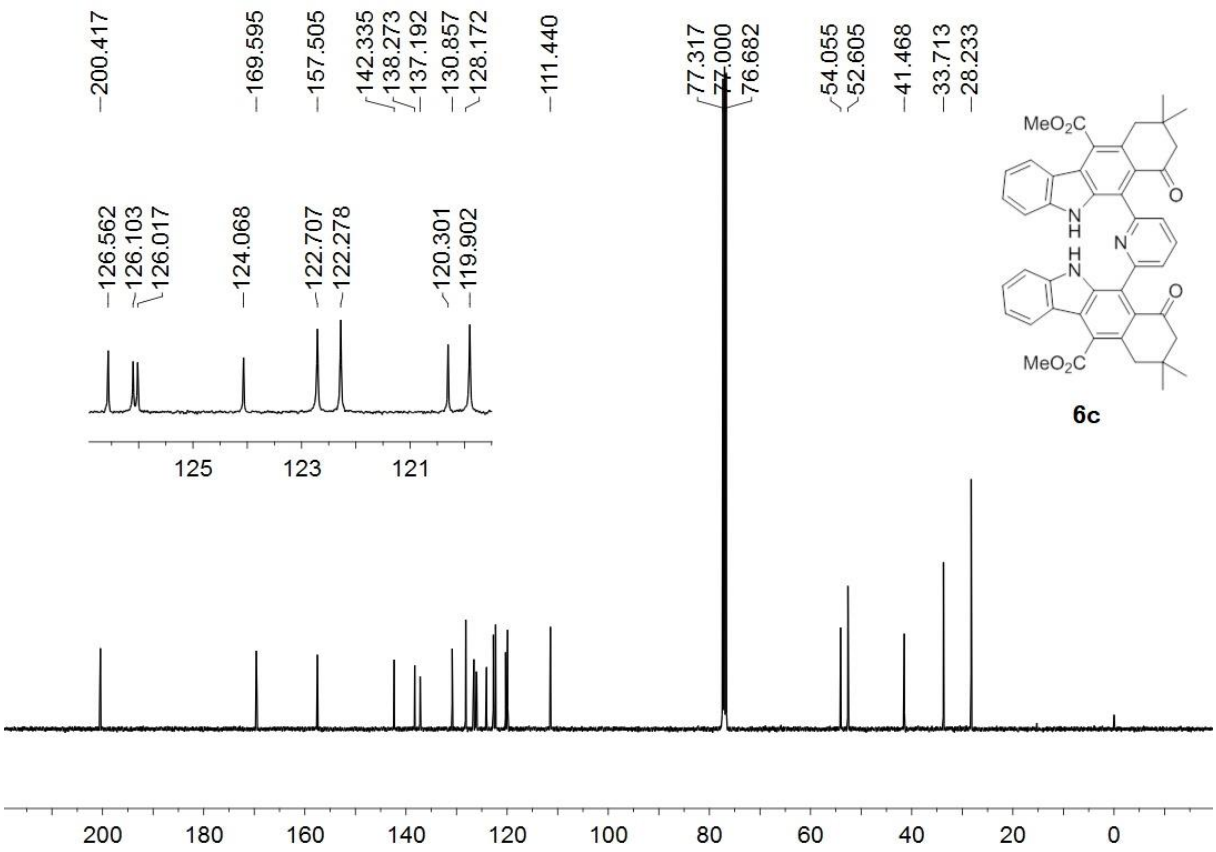
^{13}C NMR spectrum of the compound **6b** (100 MHz, $CDCl_3$)



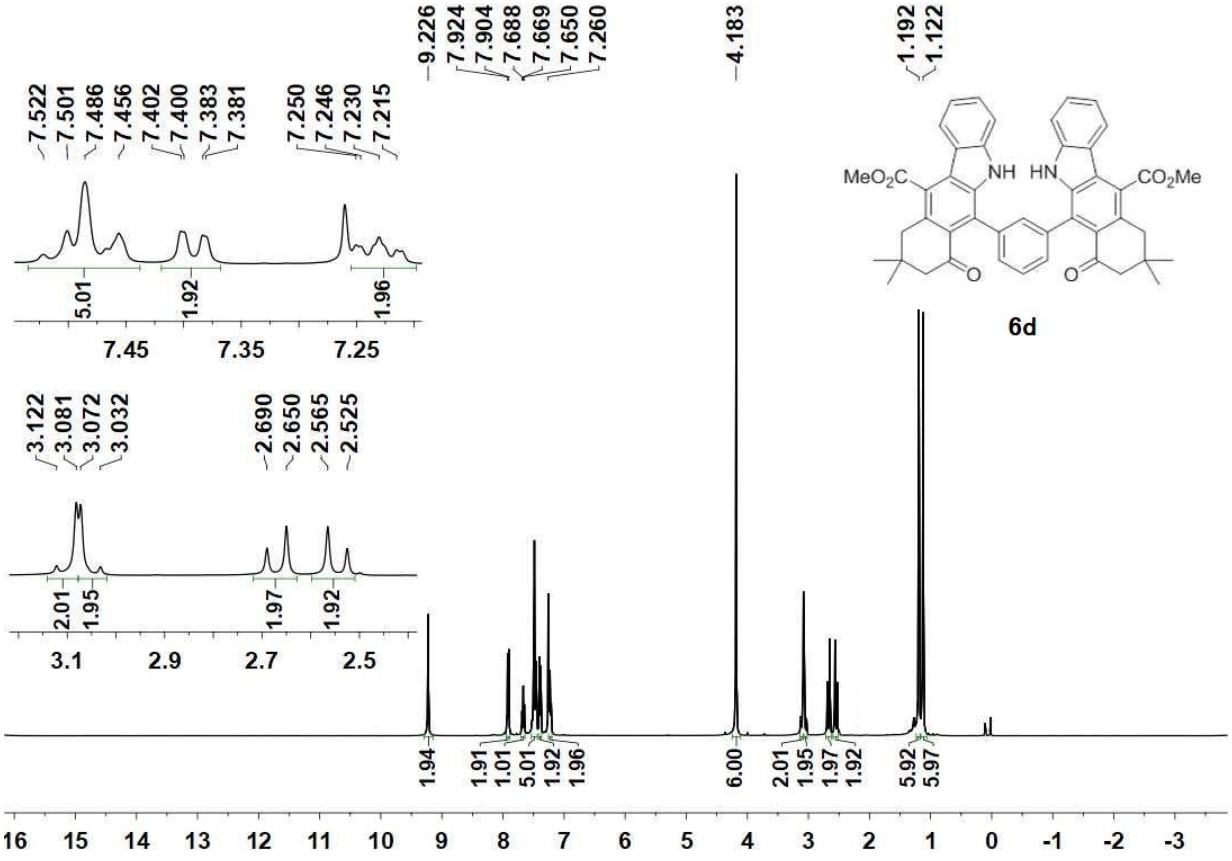
^{1}H NMR spectrum of the compound **6c** (400 MHz, $CDCl_3$)



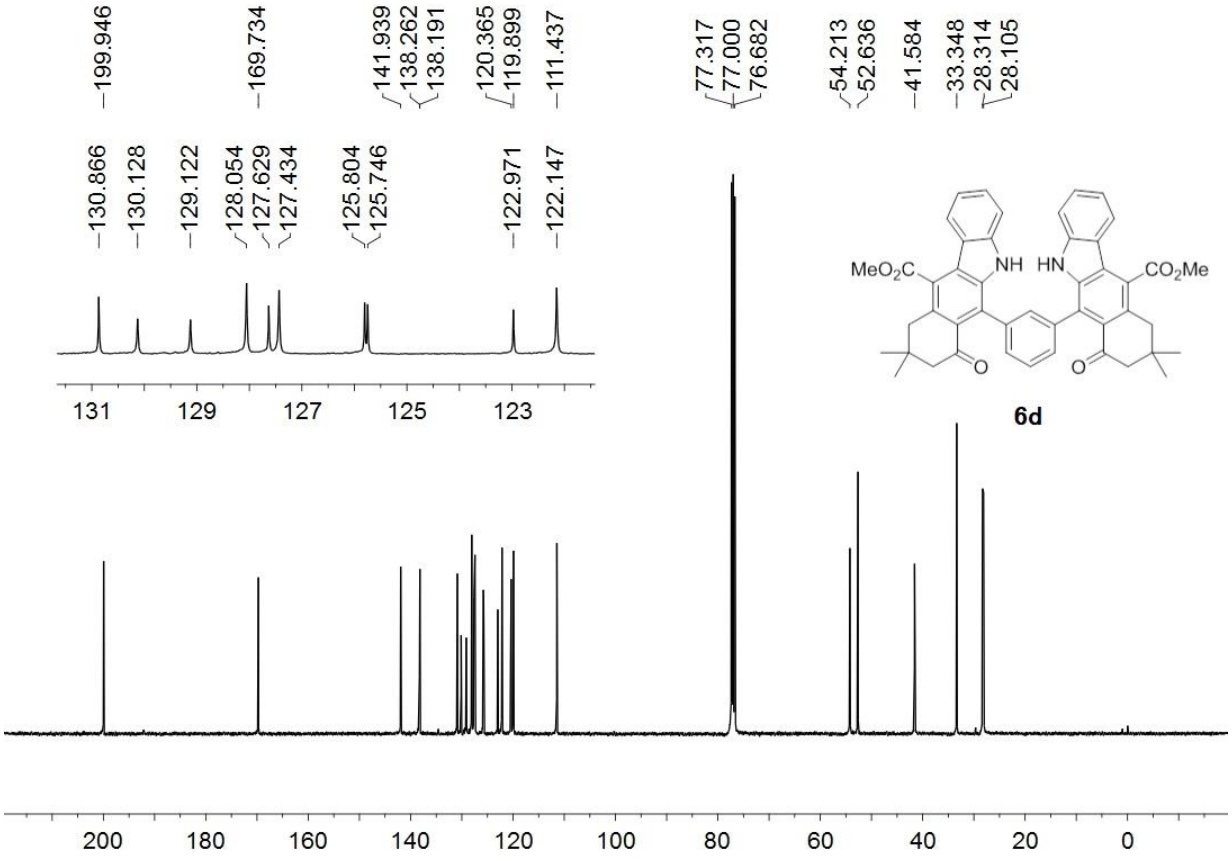
^{13}C NMR spectrum of the compound **6c** (100 MHz, $CDCl_3$)



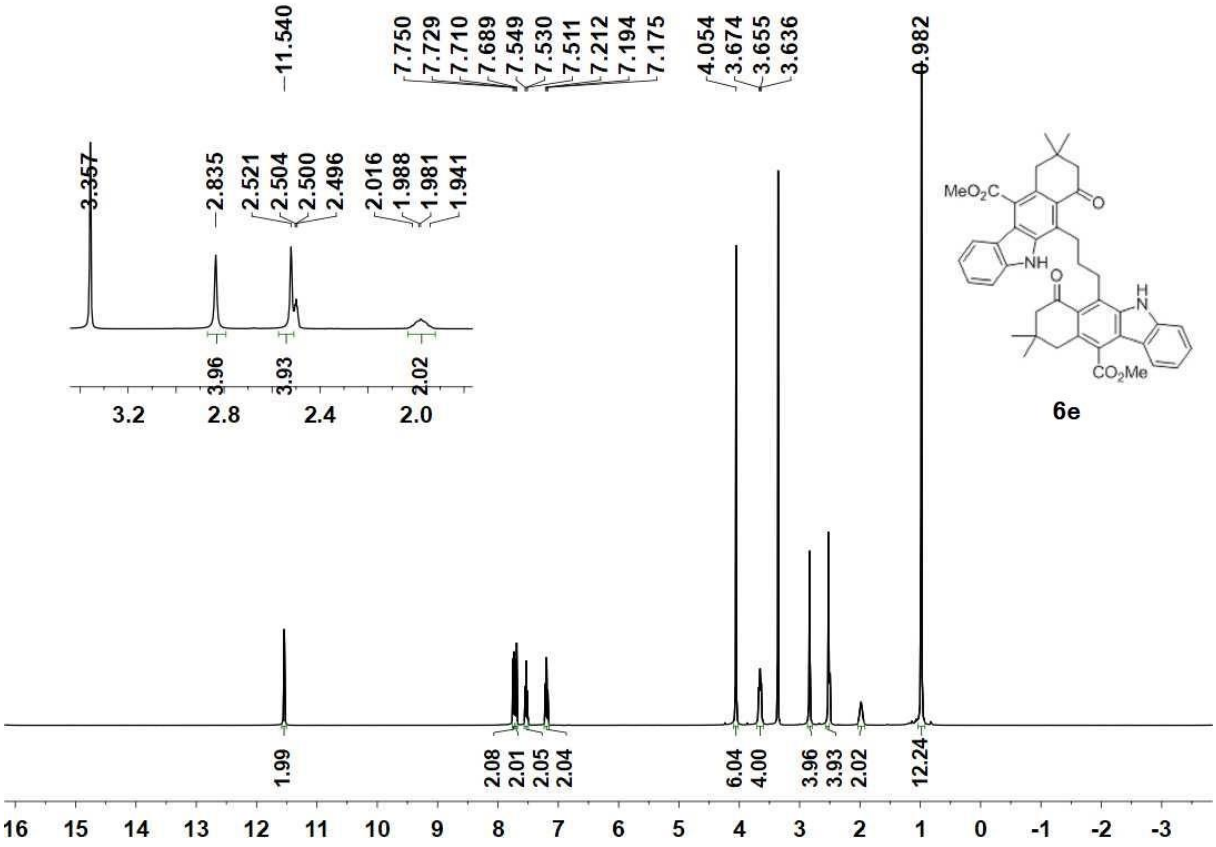
^{1}H NMR spectrum of the compound **6d** (400 MHz, $CDCl_3$)



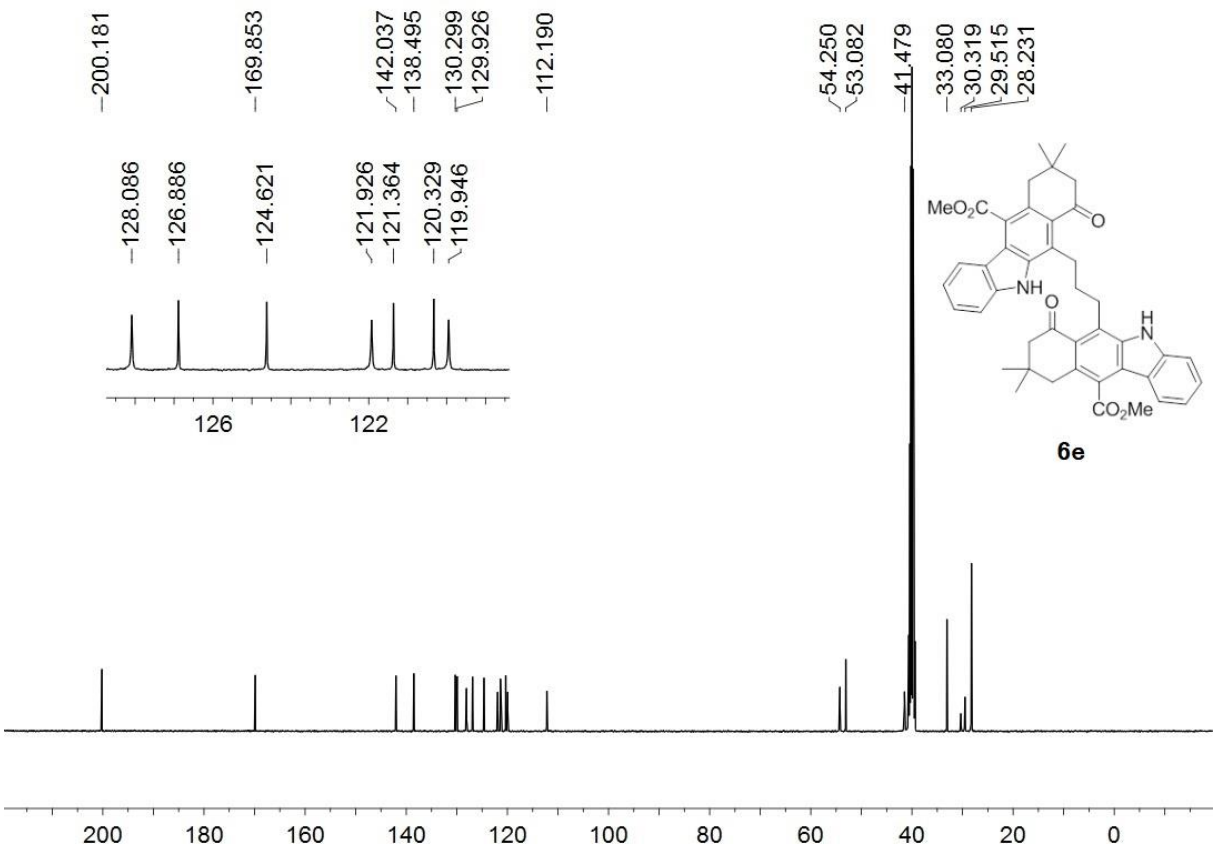
^{13}C NMR spectrum of the compound **6d** (100 MHz, $CDCl_3$)



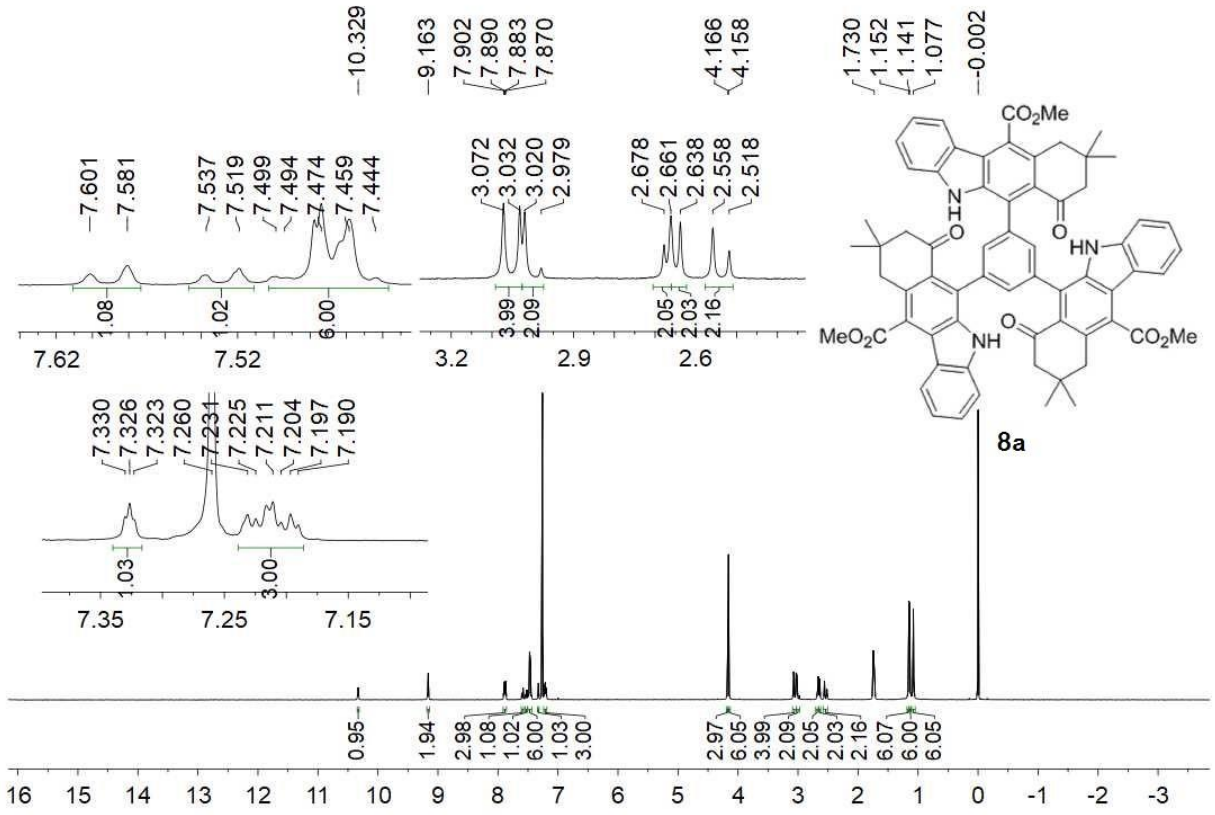
^{1}H NMR spectrum of the compound **6e** (400 MHz, DMSO-d_6)



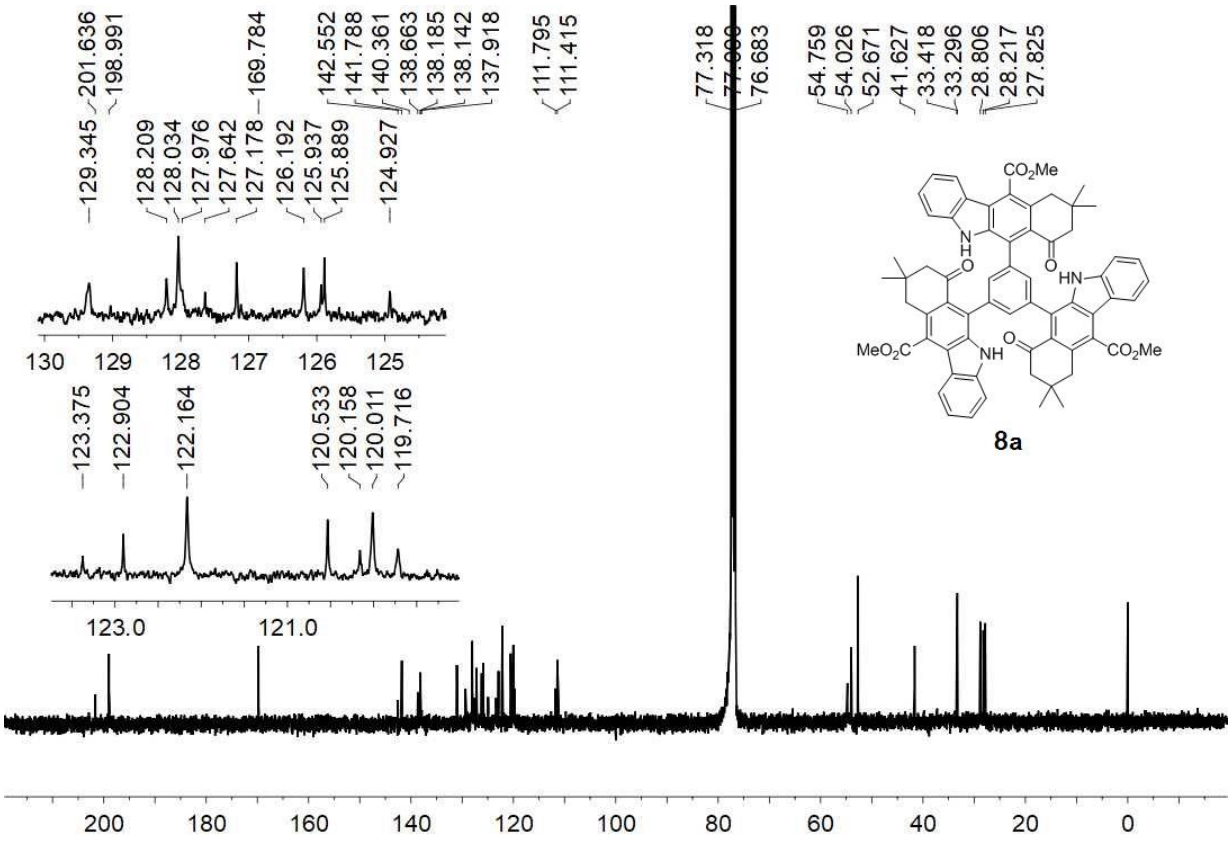
^{13}C NMR spectrum of the compound **6e** (100 MHz, DMSO-d_6)



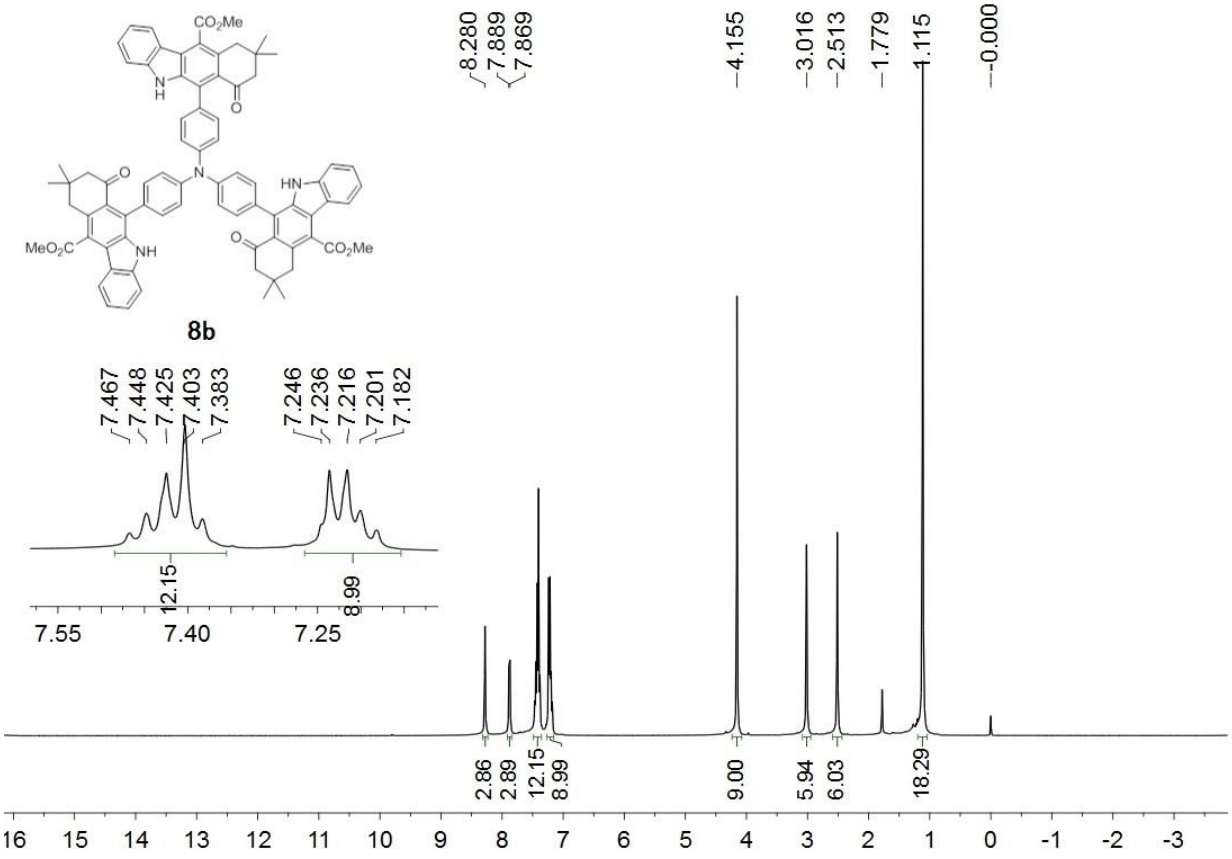
^{1}H NMR spectrum of the compound **8a** (400 MHz, $CDCl_3$)



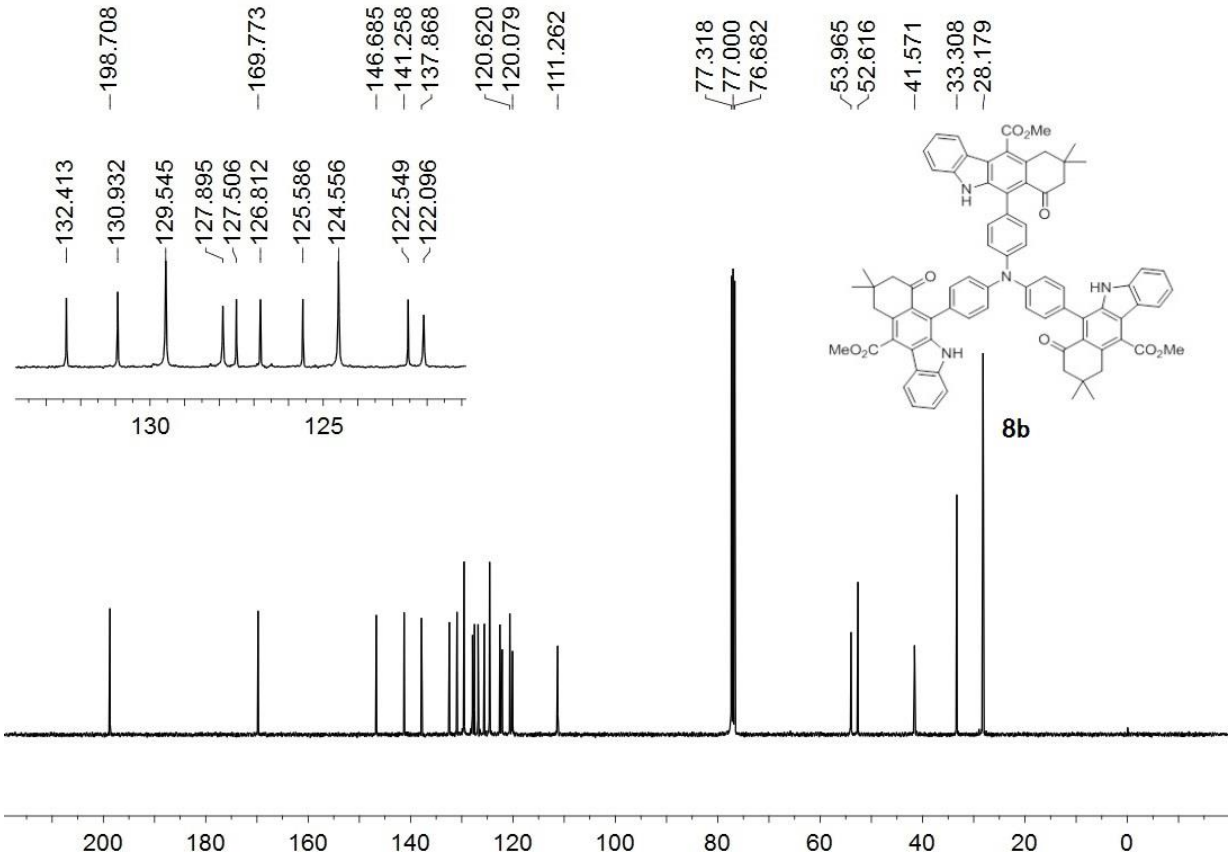
^{13}C NMR spectrum of the compound **8a** (100 MHz, $CDCl_3$)



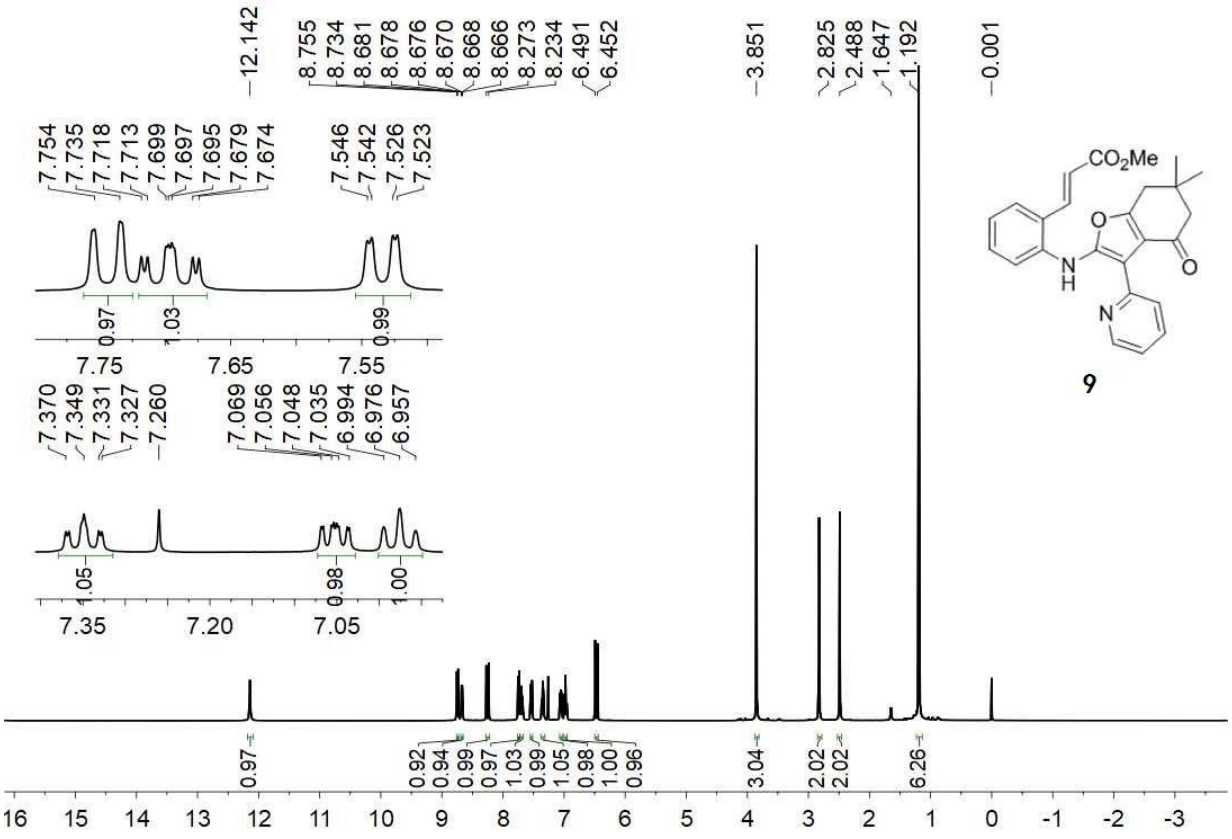
^{1}H NMR spectrum of the compound **8b** (400 MHz, $CDCl_3$)



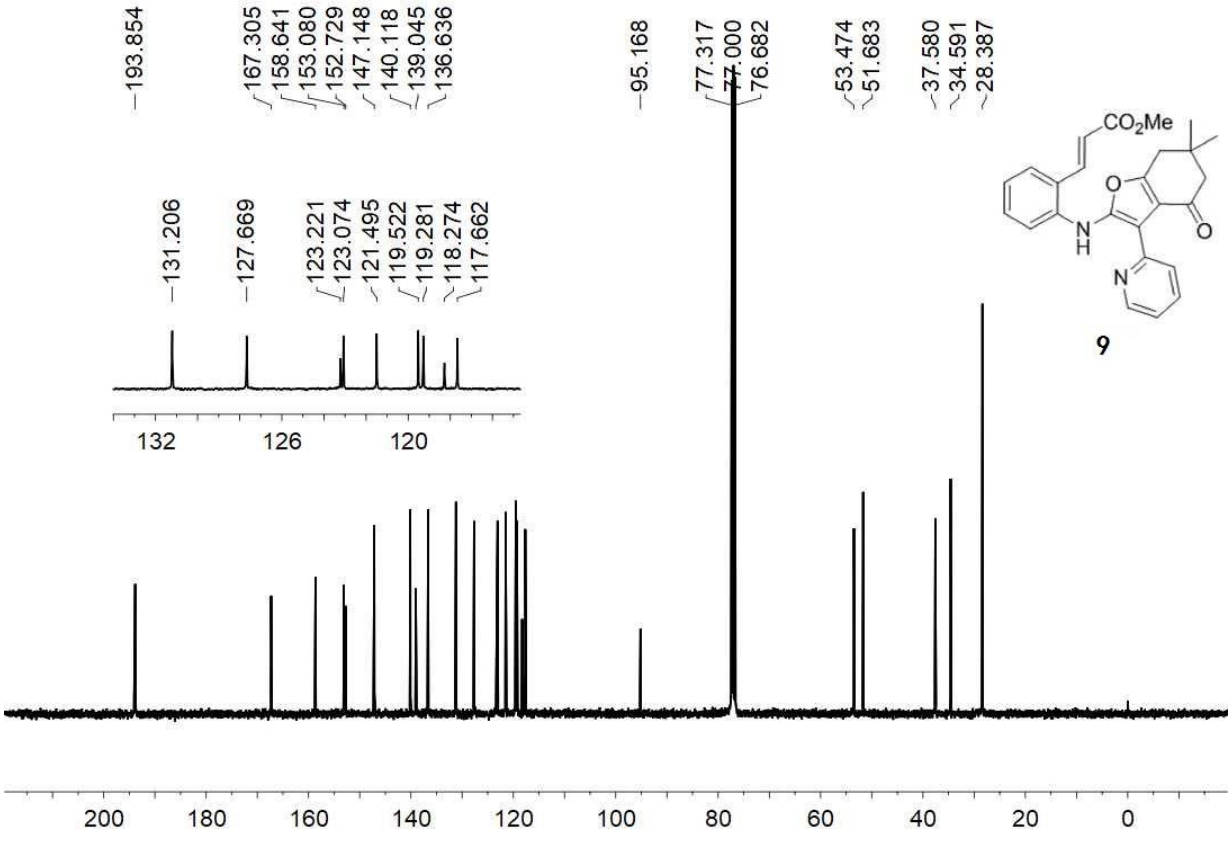
^{13}C NMR spectrum of the compound **8b** (100 MHz, $CDCl_3$)



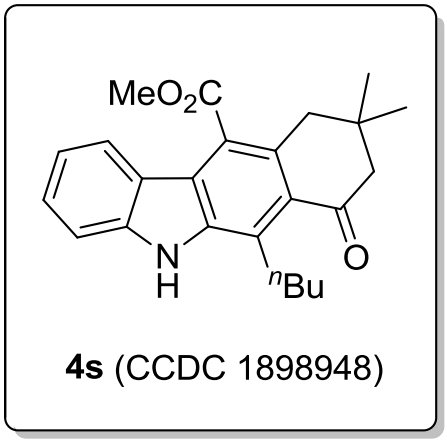
^{1}H NMR spectrum of the compound **9** (400 MHz, $CDCl_3$)

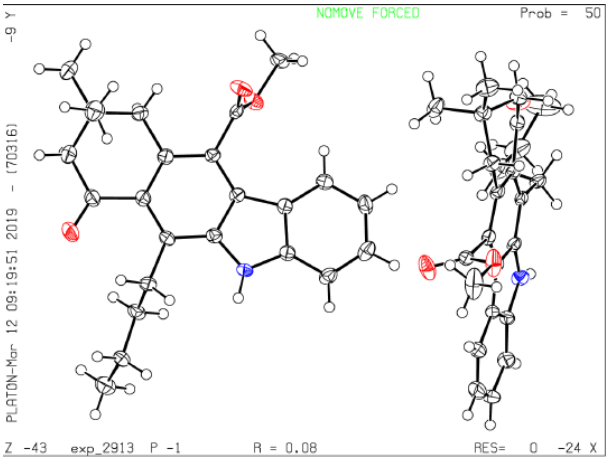


^{13}C NMR spectrum of the compound **9** (100 MHz, $CDCl_3$)



5. X-ray Crystallographic Data of compound 4s





Crystal data:

Empirical formula	$C_{25}H_{28}NO_3$
Formula weight	377.48
Temperature/K	169(20)
Crystal system	triclinic
Space group	P-1
a/Å	11.4333(7)
b/Å	12.1081(8)
c/Å	16.3377(9)
α/°	98.720(5)
β/°	99.358(5)
γ/°	109.309(6)
Volume/Å^3	2054.2(2)
Z	27
ρ_{calc}mg/mm^3	1.221
m/mm^{-1}	0.635
F(000)	808.0
Crystal size/mm^3	0.23 ×0.15 ×0.09
2Θ range for data collection	7.94 to 130.16 °
Index ranges	-13 ≤ h ≤ 12, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19
Reflections collected	12134

Independent reflections	6739[R(int) = 0.0414]
Data/restraints/parameters	6739/0/513
Goodness-of-fit on F^2	1.215
Final R indexes [I>=2σ (I)]	R_1 = 0.0762, wR_2 = 0.1983
Final R indexes [all data]	R_1 = 0.1140, wR_2 = 0.3130
Largest diff. peak/hole / e $Å^{-3}$	0.73/-0.66