Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information:

One-Pot C–C/C–O Bonds Formation: Synthesis of Spirocyclic Lactones

Pedireddi Niharika and Gedu Satyanarayana*

Department of Chemistry, Indian Institute of Technology, Hyderabad

Kandi – 502 285, Sangareddy, Telangana, INDIA

Phone: (040) 2301 6033; Fax: (040) 2301 6003 /32

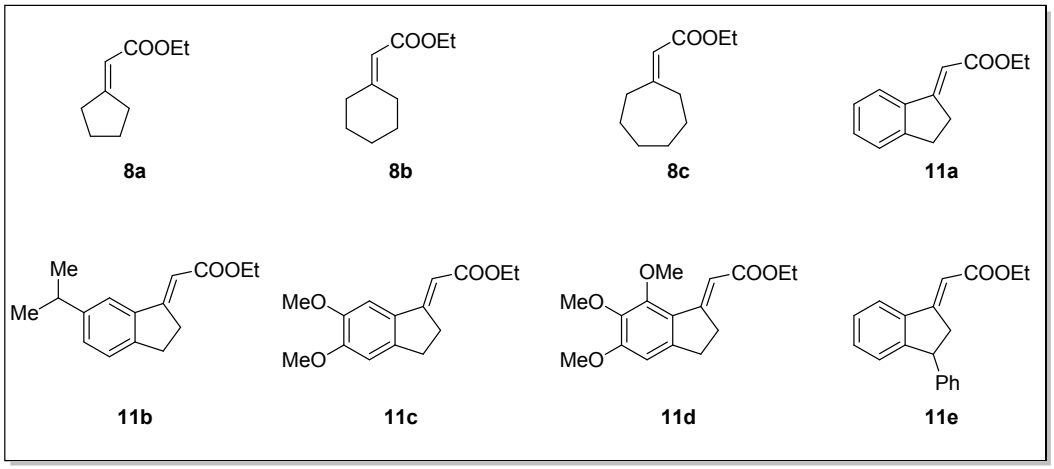
E-mail: gvsatya@iith.ac.in

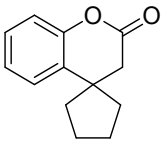
Experimental Section

General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (J in Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H =0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in $CDCl_3$; chemical shifts (δ in ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of triplet)]. In the ^{13}C NMR, the nature of carbons (C, CH, CH_2 and CH_3) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^{1}H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui =quintet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by ^{1}H, ^{13}C CPD and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF using multimode source. All small scale dry reactions were carried out using standard syringe-septum technique. Regarding Horner-Wadsworth-Emmons reaction, TEPA from Avra Synthesis with a purity of 98%, NaH from Sigma-Aldrich (60% immersion in mineral oil), and benzaldehydes/acetophenones from Sisco Research Laboratories having 97-98% purity were used. Solvent THF was dried over sodium metal. Similarly, for cyclization reaction anhydrous $FeCl_3$ from Merck Chemicals and phenols from Sisco Research Laboratories were used. DCE was dried over calcium hydride and used. Reactions were monitored by TLC on silica gel using a mixture of petroleum ether and ethyl acetate as eluents. Reactions were generally run under an argon or nitrogen atmosphere. Solvents were distilled prior use; petroleum ether with a boiling range of 60 to 80 °C was used. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

General Procedure (GP) for Cyclization: To an oven dried schlenk tube under nitrogen atmosphere, α,β-unsaturated ester **8** or **11** (77–146 mg, 0.5 mmol), phenol **9** (141–216 mg, 1.5 mmol) and anhydrous $FeCl_3$ (243 mg, 1.5 mmol) were added followed by benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous $NaHCO_3$ and extracted in ethyl acetate (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in *vacuo*. Purification of the residue on silica gel column chromatography using petroleum ether/ethyl acetate as eluent furnished novel spirolactones **10** & **12** (45–87%) as viscous liquid/solid.

The required α,β-unsaturated esters **8a**, **8b**, **8c**, **11a**, **11b**, **11c**, **11d** and **11e** were prepared and known in the literature.[1]

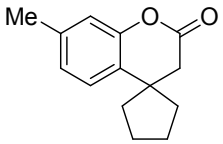




10aa

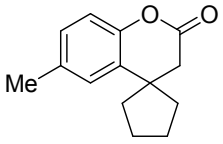
Spiro[chromene-4,1'-cyclopentan]-2(3*H*)-one (10aa): GP was carried out on the ester **8a** (77 mg, 0.5 mmol), phenol **9a** (141.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**8a**)=0.83, R_f(**10aa**)=0.66, (petroleum ether/ethyl acetate 98:2, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2 as eluent) furnished the lactone **10aa** (51 mg, 51%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3054, 1767, 1422, 1264, 895, 731 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.30–7.20 (m, 2H, ArH), 7.14 (ddd, 1H, *J*=7.8, 7.8 and 1.5 Hz, ArH), 7.07 (dd, 1H, *J*=7.8 and 1.5 Hz, ArH), 2.69 (s, 2H, CH_2CO), 2.05–1.90 (m, 2H, 2 × CH_aH_b), 1.86 (d, 1H, *J*=10.3 Hz, CH_aH_b), 1.85 (d, 1H, *J*=6.8 Hz, CH_aH_b), 1.83 (d, 1H, *J*=7.3 Hz, CH_aH_b), 1.82 (d, 1H, *J*=10.3 Hz, CH_aH_b), 1.77–1.62 (m, 2H, 2 × CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=168.4 (s, O–C=O), 150.9 (s, ArC), 131.5 (s, ArC), 128.0 (d, ArCH), 124.5 (2 × d, 2C, 2 × ArCH), 117.1 (d, ArCH), 43.8 (s, C_q), 41.3 (t, CH_2CO), 37.8 (t, 2C, 2 × CH_2), 24.5 (t, 2C, 2 × CH_2) ppm. HR-MS (ESI^+) m/z calculated for $[C_{13}H_{14}NaO_2]^+$=$[M+Na]^+$: 225.0886; found 225.0886.

[1] R. J. Comito, F. G. Finelli and D. W. C. MacMillan, *J. Am. Chem. Soc.*, **2013**, *135*, 9358.



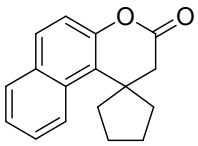
10ac

7-Methylspiro[chromene-4,1'-cyclopentan]-2(3*H*)-one (10ac): GP was carried out on the ester **8a** (77 mg, 0.5 mmol), phenol **9c** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**8a**)=0.83, R_f(**10ac**)=0.70, (petroleum ether/ethyl acetate 98:2, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2 as eluent) furnished the lactone **10ac** (73.2 mg, 68%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2954, 1766, 1505, 1415, 1256, 1219, 1166, 966, 815, 776 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.11 (d, 1H, J=7.8 Hz, ArH), 6.93 (dd, 1H, J=7.8 and 1.0 Hz, ArH), 6.86 (d, 1H, J=1.0 Hz, ArH), 2.65 (s, 2H, CH_2CO), 2.32 (s, 3H, $ArCH_3$), 2.05–1.86 (m, 2H, 2 × C$H_a$$H_b$), 1.83 (d, 1H, J=10.8 Hz, CH_aH_b), 1.82 (d, 1H, J=7.3 Hz, C$H_a$$H_b$), 1.80 (d, 1H, J=6.8 Hz, CH_aH_b), 1.79 (d, 1H, J=10.8 Hz, CH_aH_b), 1.75–1.60 (m, 2H, 2 × CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=168.7 (s, O–C=O), 150.7 (s, ArC), 138.2 (s, ArC), 128.4 (s, ArC), 125.2 (d, ArCH), 124.3 (d, ArCH), 117.5 (d, ArCH), 43.5 (s, C_q), 41.4 (t, CH_2CO), 37.8 (t, 2C, 2 × CH_2), 24.4 (t, 2C, 2 × CH_2), 20.9 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{14}H_{17}O_2]^+$=$[M+H]^+$: 217.1223; found 217.1215.



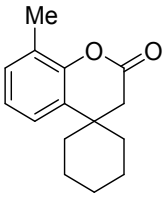
10ad

6-Methylspiro[chromene-4,1'-cyclopentan]-2(3*H*)-one (10ad): GP was carried out on the ester **8a** (77 mg, 0.5 mmol), phenol **9d** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**8a**)=0.83, R_f(**10ad**)=0.70, (petroleum ether/ethyl acetate 98:2, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2 as eluent) furnished the lactone **10ad** (77.0 mg, 71%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2954, 1767, 1492, 1416, 1271, 1207, 1153, 822 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.07–6.97 (m, 2H, ArH), 6.93 (d, 1H, J=8.8 Hz, ArH), 2.65 (s, 2H, CH_2CO), 2.33 (s, 3H, $ArCH_3$), 2.00–1.87 (m, 2H, 2 × C$H_a$$H_b$), 1.84 (d, 1H, J=10.3 Hz, CH_aH_b), 1.83 (d, 1H, J=6.8 Hz, C$H_a$$H_b$), 1.81 (d, 1H, J=7.3 Hz, CH_aH_b), 1.80 (d, 1H, J=10.3 Hz, CH_aH_b), 1.75–1.60 (m, 2H, 2 × CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=168.6 (s, O–C=O), 148.8 (s, ArC), 134.0 (s, ArC), 131.1 (s, ArC), 128.4 (d, ArCH), 124.9 (d, ArCH), 116.8 (d, ArCH), 43.7 (s, C_q), 41.4 (t, CH_2CO), 37.8 (t, 2C, 2 × CH_2), 24.5 (t, 2C, 2 × CH_2), 21.0 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{14}H_{17}O_2]^+$=$[M+H]^+$: 217.1223; found 217.1218.



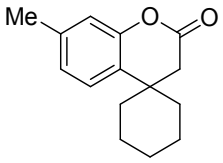
10af

Spiro[benzo[*f*]chromene-1,1'-cyclopentan]-3(2*H*)-one (10af): GP was carried out on the ester **8a** (77 mg, 0.5 mmol), phenol **9f** (216.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**8a**)=0.83, R_f(**10af**)=0.68, (petroleum ether/ethyl acetate 97:3, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2 as eluent) furnished the lactone **10af** (69 mg, 64%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 1766, 1511, 1466, 1257, 1119, 1046, 823 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.98 (d, 1H, *J*=8.8 Hz, ArH), 7.84 (d, 1H, *J*=8.3 Hz, ArH), 7.72 (d, 1H, *J*=8.8 Hz, ArH), 7.50 (dd, 1H, *J*=8.8 and 8.3 Hz, ArH), 7.43 (dd, 1H, *J*=8.8 and 8.3 Hz, ArH), 7.19 (d, 1H, *J*=8.8 Hz, ArH), 2.78 (s, 2H, CH_2CO), 2.58–2.45 (m, 2H, CH_2), 2.20–1.90 (m, 4H, 2 × CH_2), 1.85–1.70 (m, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=167.5 (s, O–C=O), 149.3 (s, ArC), 131.8 (s, ArC), 130.3 (s, ArC), 129.4 (2 × d, 2C, 2 × ArCH), 126.0 (d, ArCH), 124.4 (d, ArCH), 124.0 (d, ArCH), 123.3 (s, ArC), 117.7 (d, ArCH), 44.8 (s, C_q), 43.9 (t, *C*H_2CO), 39.1 (t, 2C, 2 × CH_2), 26.6 (t, 2C, 2 × CH_2) ppm. HR-MS (ESI^+) m/z calculated for $[C_{17}H_{16}NaO_2]^+$=$[M+Na]^+$: 275.1043; found 275.1039.



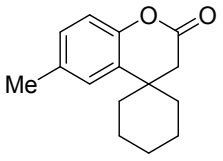
10bb

8-Methylspiro[chromene-4,1'-cyclohexan]-2(3*H*)-one (10bb): GP was carried out on the ester **8b** (84 mg, 0.5 mmol), phenol **9b** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**8b**)=0.85, R_f(**10bb**)=0.72, (petroleum ether/ethyl acetate 98:2, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2 as eluent) furnished the lactone **10bb** (71 mg, 62%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2927, 1770, 1460, 1263, 1186, 1155, 919, 749 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.18 (dd, 1H, *J*=7.8 and 1.0 Hz, ArH), 7.10 (dd, 1H, *J*=7.3 and 1.0 Hz, ArH), 7.04 (dd, 1H, *J*=7.8 and 7.3 Hz, ArH), 2.77 (s, 2H, CH_2CO), 2.30 (s, 3H, $ArCH_3$), 1.83–1.47 (m, 8H, 4 × CH_2), 1.35–1.22 (m, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=168.5 (s, O–C=O), 149.2 (s, ArC), 132.4 (s, ArC), 129.6 (d, ArCH), 126.4 (s, ArC), 124.2 (d, ArCH), 121.5 (d, ArCH), 37.2 (t, *C*H_2CO), 36.2 (s, C_q), 35.0 (t, 2C, 2 × CH_2), 25.6 (t, CH_2), 21.5 (t, 2C, 2 × CH_2), 16.0 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{15}H_{19}O_2]^+$=$[M+H]^+$: 231.1380; found 231.1373.



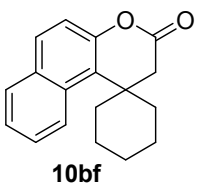
10bc

7-Methylspiro[chromene-4,1'-cyclohexan]-2(3*H*)-one (10bc): GP was carried out on the ester **8b** (84 mg, 0.5 mmol), phenol **9c** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**8b**)=0.85, R_f(**10bc**)=0.72, (petroleum ether/ethyl acetate 98:2, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2 as eluent) furnished the lactone **10bc** (77 mg, 67%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2923, 1767, 1505, 1454, 1416, 1242, 1191, 1155, 953, 815 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.26 (d, 1H, *J*=7.8 Hz, ArH), 6.99 (dd, 1H, *J*=7.8 and 1.0 Hz, ArH), 6.90 (d, 1H, *J*=1.0 Hz, ArH), 2.80 (s, 2H, CH_2CO), 2.36 (s, 3H, $ArCH_3$), 1.87–1.45 (m, 9H, 4 × CH_2 and CH_{2a}), 1.40–1.25 (m, 1H, CH_{2b}) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=168.6 (s, O–C=O), 150.8 (s, ArC), 138.3 (s, ArC), 129.6 (s, ArC), 125.4 (d, ArCH), 123.9 (d, ArCH), 117.6 (d, ArCH), 37.5 (t, *C*H_2CO), 35.9 (s, C_q), 35.1 (t, 2C, 2 × CH_2), 25.6 (t, CH_2), 21.5 (t, 2C, 2 × CH_2), 20.9 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{15}H_{18}NaO_2]^+$=$[M+Na]^+$: 253.1199; found 253.1194.



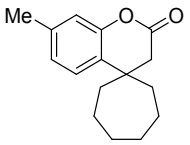
10bd

6-Methylspiro[chromene-4,1'-cyclohexan]-2(3*H*)-one (10bd): GP was carried out on the ester **8b** (84 mg, 0.5 mmol), phenol **9d** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**8b**)=0.85, R_f(**10bd**)=0.72, (petroleum ether/ethyl acetate 98:2, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2 as eluent) furnished the lactone **10bd** (63 mg, 55%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2923, 1765, 1491, 1454, 1256, 1187, 1156, 914, 811 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.14 (d, 1H, *J*=1.5 Hz, ArH), 7.03 (dd, 1H, *J*=8.3 and 1.5 Hz, ArH), 6.93 (d, 1H, *J*=8.3 Hz, ArH), 2.76 (s, 2H, CH_2CO), 2.33 (s, 3H, $ArCH_3$), 1.85–1.45 (m, 8H, 4 × CH_2), 1.35–1.15 (m, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=168.6 (s, O–C=O), 148.9 (s, ArC), 134.2 (s, ArC), 132.2 (s, ArC), 128.4 (d, ArCH), 124.5 (d, ArCH), 116.9 (d, ArCH), 37.3 (t, *C*H_2CO), 36.1 (s, C_q), 35.0 (t, 2C, 2 × CH_2), 25.6 (t, CH_2), 21.5 (t, 2C, 2 × CH_2), 21.0 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{15}H_{18}NaO_2]^+$=$[M+Na]^+$: 253.1199; found 253.1190.



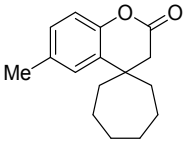
10bf

Spiro[benzo[*f*]chromene-1,1'-cyclohexan]-3(2*H*)-one (10bf): GP was carried out on the ester **8b** (84 mg, 0.5 mmol), phenol **9f** (216.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**8b**)=0.85, R_f(**10bf**)=0.66, (petroleum ether/ethyl acetate 97:3, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2 as eluent) furnished the lactone **10bf** (68.3 mg, 51%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2923, 1765, 1599, 1511, 1456, 1259, 1200, 1161, 1000, 813, 746 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=8.42 (d, 1H, *J*=8.8 Hz, ArH), 7.83 (dd, 1H, *J*=8.3 and 1.5 Hz, ArH), 7.73 (d, 1H, *J*=8.8 Hz, ArH), 7.50 (ddd, 1H, *J*=8.8, 8.3 and 1.5 Hz, ArH), 7.42 (dd, 1H, *J*=8.8 and 8.8 Hz, ArH), 7.18 (d, 1H, *J*=8.8 Hz, ArH), 2.98 (s, 2H, CH_2CO), 2.85–2.65 (m, 2H, CH_2), 1.97–1.32 (m, 8H, 4 × CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=167.9 (s, O–C=O), 149.3 (s, ArC), 132.1 (s, ArC), 130.9 (s, ArC), 129.8 (d, ArCH), 129.5 (d, ArCH), 125.5 (d, ArCH), 125.1 (s, ArC), 124.3 (d, ArCH), 123.4 (s, ArC), 117.9 (d, ArCH), 39.2 (s, C_q), 38.9 (t, *C*H_2CO), 34.1 (t, 2C, 2 × CH_2), 25.3 (t, CH_2), 21.5 (t, 2C, 2 × CH_2) ppm. HR-MS (ESI^+) m/z calculated for $[C_{18}H_{19}O_2]^+$=$[M+H]^+$: 267.1380; found 267.1373.



10cc

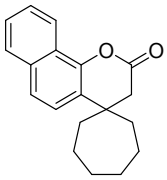
7-Methylspiro[chromene-4,1'-cycloheptan]-2(3*H*)-one (10cc): GP was carried out on the ester **8c** (91 mg, 0.5 mmol), phenol **9c** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**8c**)=0.83, R_f(**10cc**)=0.72, (petroleum ether/ethyl acetate 98:2, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2 as eluent) furnished the lactone **10cc** (89.1 mg, 73%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2920, 1766, 1504, 1460, 1415, 1211, 1168, 1134, 968, 814 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.25 (d, 1H, *J*=7.8 Hz, ArH), 6.93 (dd, 1H, *J*=7.8 and 1.0 Hz, ArH), 6.84 (d, 1H, *J*=1.0 Hz, ArH), 2.63 (s, 2H, CH_2CO), 2.31 (s, 3H, $ArCH_3$), 2.00–1.85 (m, 2H, CH_2), 1.75–1.45 (m, 10H, 5 × CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=168.6 (s, O–C=O), 150.3 (s, ArC), 138.0 (s, ArC), 130.4 (s, ArC), 125.3 (d, ArCH), 124.4 (d, ArCH), 117.6 (d, ArCH), 41.5 (t, *C*H_2CO), 38.8 (s, C_q), 38.5 (t, 2C, 2 × CH_2), 30.3 (t, 2C, 2 × CH_2), 23.2 (t, 2C, 2 × CH_2), 20.8 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{16}H_{21}O_2]^+$=$[M+H]^+$: 245.1536; found 245.1525.



10cd

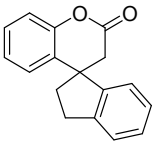
6-Methylspiro[chromene-4,1'-cycloheptan]-2(3*H*)-one (10cd): GP was carried out on the ester **8c** (91 mg, 0.5 mmol), phenol **9d** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol)

and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**8c**)=0.83, R_f(**10ac**)=0.72, (petroleum ether/ethyl acetate 98:2, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2 as eluent) furnished the lactone **10cd** (82.9 mg, 68%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2919, 1765, 1490, 1461, 1203, 1167, 818 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.15 (d, 1H, *J*=1.5 Hz, ArH), 7.01 (dd, 1H, *J*=7.8 and 1.5 Hz, ArH), 6.91 (d, 1H, *J*=7.8 Hz, ArH), 2.63 (s, 2H, CH_2CO), 2.33 (s, 3H, $ArCH_3$), 2.02–1.85 (m, 2H, CH_2), 1.80–1.50 (m, 10H, 5 × CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=168.7 (s, O–C=O), 148.4 (s, ArC), 134.1 (s, ArC), 133.2 (s, ArC), 128.3 (d, ArCH), 125.1 (d, ArCH), 116.9 (d, ArCH), 41.4 (t, *C*H_2CO), 39.1 (s, C_q), 38.5 (t, 2C, 2 × CH_2), 30.4 (t, 2C, 2 × CH_2), 23.3 (t, 2C, 2 × CH_2), 21.0 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{16}H_{21}O_2]^+$=$[M+H]^+$: 245.1536; found 245.1524.



10ce

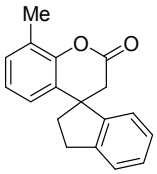
Spiro[benzo[*h*]chromene-4,1'-cycloheptan]-2(3*H*)-one (10ce): GP was carried out on the ester **8c** (91 mg, 0.5 mmol), phenol **9e** (216.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**8c**)=0.83, R_f(**10aa**)=0.68, (petroleum ether/ethyl acetate 98:2, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2 as eluent) furnished the lactone **10ce** (105 mg, 75%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 1770, 1506, 1457, 1257, 1220, 1167, 1095, 815 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=8.25 (d, 1H, *J*=7.8 Hz, ArH), 7.80 (d, 1H, *J*=8.8 Hz, ArH), 7.64 (d, 1H, *J*=8.3 Hz, ArH), 7.57–7.47 (m, 3H, ArH), 2.78 (s, 2H, CH_2CO), 2.12–1.97 (m, 2H, CH_2), 1.84–1.52 (m, 10H, 5 × CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=168.5 (s, O–C=O), 145.1 (s, ArC), 133.1 (s, ArC), 128.2 (s, ArC), 127.3 (d, ArCH), 126.5 (d, ArCH), 126.4 (d, ArCH), 124.3 (d, ArCH), 123.7 (s, ArC), 122.0 (d, ArCH), 121.5 (d, ArCH), 41.3 (t, *C*H_2CO), 39.3 (s, C_q), 38.7 (t, 2C, 2 × CH_2), 30.5 (t, 2C, 2 × CH_2), 23.6 (t, 2C, 2 × CH_2) ppm. HR-MS (ESI^+) m/z calculated for $[C_{19}H_{20}NaO_2]^+$=$[M+Na]^+$: 303.1356; found 303.1351.



12aa

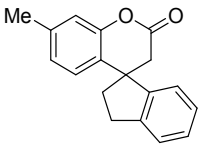
2',3'-Dihydrospiro[chromene-4,1'-inden]-2(3*H*)-one (12aa): GP was carried out on the ester **11a** (101 mg, 0.5 mmol), phenol **9a** (141.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**11a**)=0.80, R_f(**12aa**)=0.55, (petroleum ether/ethyl acetate 95:5, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3 as eluent) furnished the lactone **12aa** (77.5 mg, 62%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2923, 1767, 1505, 1457, 1253, 1153, 1016, 815 cm^{-1}. ^1H NMR ($CDCl_3$, 400

MHz): δ=7.45–7.22 (m, 4H, ArH), 7.13 (dd, 1H, *J*=8.3 and 1.0 Hz, ArH), 7.10 (d, 1H, *J*=7.3 Hz, ArH), 7.03 (ddd, 1H, *J*=8.8, 8.8 and 1.0 Hz, ArH), 6.74 (dd, 1H, *J*=7.8 and 1.5 Hz, ArH), 3.10–2.95 (m, 3H, CH_2 and $CH_{2a}CO$), 2.69 (d, 1H, *J*=15.6 Hz, $CH_{2b}CO$), 2.40–2.15 (m, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=167.7 (s, O–C=O), 151.1 (s, ArC), 144.7 (s, ArC), 144.0 (s, ArC), 130.2 (s, ArC), 128.5 (d, ArCH), 128.1 (d, ArCH), 127.3 (d, ArCH), 126.2 (d, ArCH), 125.0 (d, ArCH), 124.6 (d, ArCH), 123.6 (d, ArCH), 117.1 (d, ArCH), 49.6 (s, C_q), 41.0 (t, *C*H_2CO), 39.7 (t, CH_2), 29.9 (t, CH_2) ppm. HR-MS (ESI^+) m/z calculated for $[C_{17}H_{14}NaO_2]^+$=$[M+Na]^+$: 273.0886; found 273.0882.



12ab

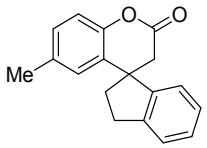
8-Methyl-2',3'-dihydrospiro[chromene-4,1'-inden]-2(3*H*)-one (12ab): GP was carried out on the ester **11a** (101 mg, 0.5 mmol), phenol **9b** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**11a**)=0.80, R_f(**12aa**)=0.65, (petroleum ether/ethyl acetate 95:5, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3 as eluent) furnished the lactone **12ab** (88.4 mg, 67%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2948, 1768, 1591, 1461, 1265, 1243, 1189, 1146, 921, 762 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.26 (d, 1H, *J*=7.3 Hz, ArH), 7.25–7.12 (m, 2H, ArH), 7.02 (dd, 2H, *J*=8.3 and 7.3 Hz, ArH), 6.83 (dd, 1H, *J*=7.8 and 7.3 Hz, ArH), 6.47 (d, 1H, *J*=7.8 Hz, ArH), 3.00–2.85 (m, 3H, CH_2 and $CH_{2a}CO$), 2.76 (d, 1H, *J*=15.6 Hz, $CH_{2b}CO$), 2.29 (s, 3H, $ArCH_3$), 2.26–2.05 (m, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=167.8 (s, O–C=O), 149.3 (s, ArC), 144.9 (s, ArC), 144.0 (s, ArC), 130.1 (d, ArCH), 130.0 (s, ArC), 128.0 (d, ArCH), 127.2 (d, ArCH), 126.4 (s, ArC), 125.0 (d, ArCH), 124.0 (d, ArCH), 123.7 (d, ArCH), 123.6 (d, ArCH), 49.7 (s, C_q), 40.9 (t, *C*H_2CO), 39.6 (t, CH_2), 29.9 (t, CH_2), 15.9 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{18}H_{16}NaO_2]^+$=$[M+Na]^+$: 287.1042; found 287.1043.



12ac

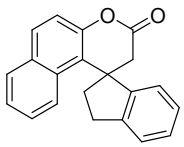
7-Methyl-2',3'-dihydrospiro[chromene-4,1'-inden]-2(3*H*)-one (12ac): GP was carried out on the ester **11a** (101 mg, 0.5 mmol), phenol **9c** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**11a**)=0.80, R_f(**12ac**)=0.66, (petroleum ether/ethyl acetate 95:5, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3 as eluent) furnished the lactone **12ac** (92.4 mg, 70%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2945, 1766, 1577, 1454, 1253, 1210, 1163, 1115, 816, 760 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.37–7.20 (m, 3H, ArH), 7.08 (d, 1H, *J*=7.3 Hz, ArH), 6.94 (s, 1H, ArH), 6.83 (dd, 1H, *J*=7.8 and 1.0 Hz, ArH), 6.63 (d, 1H, *J*=7.8 Hz, ArH), 3.07–2.92 (m, 3H,

CH_2 and $CH_{2a}CO$), 2.84 (d, 1H, *J*=15.6 Hz, $CH_{2b}CO$), 2.33 (s, 3H, $ArCH_3$), 2.32–2.12 (m, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=167.9 (s, O–C=O), 150.9 (s, ArC), 144.9 (s, ArC), 144.0 (s, ArC), 138.8 (s, ArC), 128.0 (d, ArCH), 127.2 (d, ArCH), 127.1 (s, ArC), 125.9 (d, ArCH), 125.3 (d, ArCH), 125.0 (d, ArCH), 123.5 (d, ArCH), 117.5 (d, ArCH), 49.3 (s, C_q), 41.1 (t, *C*H_2CO), 39.7 (t, CH_2), 29.9 (t, CH_2), 21.0 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{18}H_{16}NaO_2]^+$=$[M+Na]^+$: 287.1042; found 287.1043.



12ad

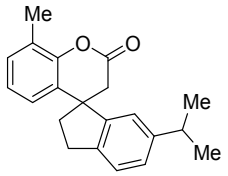
6-Methyl-2',3'-dihydrospiro[chromene-4,1'-inden]-2(3*H*)-one (12ad): GP was carried out on the ester **11a** (101 mg, 0.5 mmol), phenol **9d** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**11a**)=0.80, R_f(**12ad**)=0.65, (petroleum ether/ethyl acetate 95:5, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3 as eluent) furnished the lactone **12ad** (162.6 mg, 77%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2925, 1765, 1491, 1456, 1265, 1204, 1157, 1041, 922, 821, 761 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.42–7.21 (m, 3H, ArH), 7.15–6.95 (m, 3H, ArH), 6.55 (d, 1H, *J*=1.0 Hz, ArH), 3.15–2.91 (m, 3H, CH_2 and $CH_{2a}CO$), 2.83 (d, 1H, *J*=15.6 Hz, $CH_{2b}CO$), 2.40–2.10 (m, 2H, CH_2), 2.21 (s, 3H, $ArCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=167.8 (s, O–C=O), 149.0 (s, ArC), 144.8 (s, ArC), 143.9 (s, ArC), 134.3 (s, ArC), 129.8 (s, ArC), 129.0 (d, ArCH), 128.0 (d, ArCH), 127.2 (d, ArCH), 126.3 (d, ArCH), 125.0 (d, ArCH), 123.6 (d, ArCH), 116.7 (d, ArCH), 49.6 (s, C_q), 41.1 (t, *C*H_2CO), 39.6 (t, CH_2), 29.9 (t, CH_2), 20.8 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{18}H_{16}NaO_2]^+$=$[M+Na]^+$: 287.1042; found 287.1047.



12af

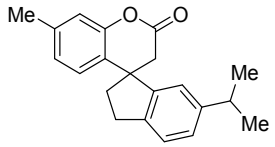
2',3'-Dihydrospiro[benzo[*f*]chromene-1,1'-inden]-3(2*H*)-one (12af): GP was carried out on the ester **11a** (101 mg, 0.5 mmol), phenol **9f** (216.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**11a**)=0.80, R_f(**12af**)=0.66, (petroleum ether/ethyl acetate 98:2, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3 as eluent) furnished the lactone **12af** (100.5 mg, 67%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2925, 1761, 1599, 1514, 1460, 1248, 1213, 1169, 1044, 948, 731 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.82 (d, 1H, *J*=8.8 Hz, ArH), 7.81 (d, 1H, *J*=7.8 Hz, ArH), 7.40 (d, 1H, *J*=7.8 Hz, ArH), 7.35–7.26 (m, 3H, ArH), 7.13 (dd, 1H, *J*=7.8 and 7.3 Hz, ArH), 7.10–7.02 (m, 2H, ArH), 6.80 (d, 1H, *J*=7.8 Hz, ArH), 3.30–3.15 (m, 2H, CH_2), 2.93 (d, 1H, *J*=15.6 Hz, $CH_{2a}CO$), 2.84 (dd, 1H, *J*=15.6 and 1.5 Hz, $CH_{2b}CO$), 2.57–2.35 (m, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=166.9 (s, O–C=O), 150.4 (s, ArC), 148.3 (s, ArC), 141.4 (s, ArC), 132.0 (s, ArC), 130.3 (d, 2C, 2 × ArCH), 130.1 (s, ArC), 129.0 (d, ArCH), 127.8 (d,

ArCH), 127.5 (d, ArCH), 125.7 (d, ArCH), 125.5 (d, ArCH), 124.5 (d, ArCH), 123.9 (d, ArCH), 120.9 (s, ArC), 117.7 (d, ArCH), 50.9 (s, C_q), 42.2 (t, *C*H_2CO), 36.8 (t, CH_2), 29.9 (t, CH_2) ppm. HR-MS (ESI^+) m/z calculated for $[C_{21}H_{16}NaO_2]^+$=$[M+Na]^+$: 323.1043; found 323.1042.



12bb

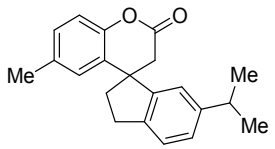
6'-Isopropyl-8-methyl-2',3'-dihydrospiro[chromene-4,1'-inden]-2(3*H*)-one (12bb): GP was carried out on the ester **11b** (122 mg, 0.5 mmol), phenol **9b** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**11b**)=0.85, R_f(**12bb**)=0.67, (petroleum ether/ethyl acetate 97:3, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3 as eluent) furnished the lactone **12bb** (128.5 mg, 84%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2957, 1768, 1461, 1264, 1188, 1146, 922, 829 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.26 (d, 1H, *J*=7.3 Hz, ArH), 7.18 (d, 1H, *J*=7.8 Hz, ArH), 7.11 (d, 1H, *J*=7.3 Hz, ArH), 6.95 (s, 1H, ArH), 6.92 (dd, 1H, *J*=7.8 and 7.3 Hz, ArH), 6.56 (d, 1H, *J*=7.3 Hz, ArH), 3.03 (d, 1H, *J*=15.6 Hz, $CH_{2a}CO$), 2.98–2.84 [m, 3H, CH_2 and C*H*$(CH_3)_2$], 2.85 (d, 1H, *J*=15.6 Hz, $CH_{2b}CO$), 2.37 (s, 3H, $ArCH_3$), 2.34–2.12 (m, 2H, CH_2), 1.22 [d, 6H, *J*=6.8 Hz, CH(C*H*$_3)_2$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=167.9 (s, O–C=O), 149.3 (s, ArC), 148.2 (s, ArC), 144.9 (s, ArC), 141.5 (s, ArC), 130.2 (s, ArC), 130.0 (d, ArCH), 126.4 (s, ArC), 126.2 (d, ArCH), 124.7 (d, ArCH), 124.0 (d, ArCH), 123.7 (d, ArCH), 121.5 (d, ArCH), 49.7 (s, C_q), 40.9 (t, *C*H_2CO), 39.9 (t, CH_2), 34.0 [d, *C*H$(CH_3)_2$], 29.4 (t, CH_2), 24.1 [q, 2C, CH(*C*$H_3)_2$], 15.9 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{21}H_{22}NaO_2]^+$=$[M+Na]^+$: 329.1512; found 329.1512.



12bc

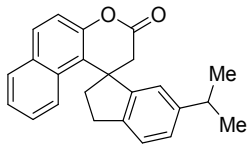
6'-Isopropyl-7-methyl-2',3'-dihydrospiro[chromene-4,1'-inden]-2(3*H*)-one (12bc): GP was carried out on the ester **11b** (162 mg, 0.5 mmol), phenol **9c** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**11b**)=0.85, R_f(**12bc**)=0.66, (petroleum ether/ethyl acetate 97:3, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3 as eluent) furnished the lactone **12bc** (125.5 mg, 82%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2958, 1766, 1491, 1456, 1253, 1213, 1163, 1036, 817 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.26 (d, 1H, *J*=7.8 Hz, ArH), 7.18 (d, 1H, *J*=7.8 Hz, ArH), 6.95 (2 × s, 2H, 2 × ArH), 6.85 (d, 1H, *J*=7.8 Hz, ArH), 6.65 (d, 1H, *J*=7.8 Hz, ArH), 3.00 (d, 1H, *J*=15.6 Hz, $CH_{2a}CO$), 2.99–2.85 [m, 3H, CH_2 and C*H*$(CH_3)_2$], 2.85 (d, 1H, *J*=15.6 Hz, $CH_{2b}CO$), 2.34 (s, 3H, $ArCH_3$), 2.30–2.12 (m, 2H, CH_2), 1.23 [d, 6H, *J*=6.8 Hz, CH(C*H*$_3)_2$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=167.9 (s, O–C=O), 150.9 (s, ArC), 148.2 (s, ArC), 144.9

(s, ArC), 141.3 (s, ArC), 138.6 (s, ArC), 127.2 (s, ArC), 126.2 (d, ArCH), 125.9 (d, ArCH), 125.3 (d, ArCH), 124.7 (d, ArCH), 121.3 (d, ArCH), 117.4 (d, ArCH), 49.2 (s, C_q), 41.0 (t, CH_2CO), 40.0 (t, CH_2), 34.0 [d, $CH(CH_3)_2$], 29.4 (t, CH_2), 24.1 [q, 2C, $CH(CH_3)_2$], 20.9 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{21}H_{22}NaO_2]^+$=$[M+Na]^+$: 329.1512; found 329.1509.



12bd

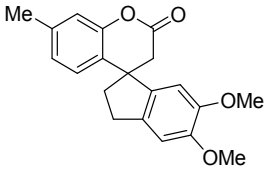
6'-Isopropyl-6-methyl-2',3'-dihydrospiro[chromene-4,1'-inden]-2(3*H*)-one (12bd): GP was carried out on the ester **11b** (122 mg, 0.5 mmol), phenol **9d** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**11b**)=0.83, R_f(**12bd**)=0.66, (petroleum ether/ethyl acetate 97:3, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2 as eluent) furnished the lactone **12bd** (133.1 mg, 87%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2958, 1768, 1491, 1266, 1206, 1160, 923, 823 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.26 (d, 1H, *J*=7.8 Hz, ArH), 7.18 (dd, 1H, *J*=7.8 and 1.5 Hz, ArH), 7.05 (d, 1H, *J*=8.3 Hz, ArH), 7.01 (d, 1H, *J*=8.3 Hz, ArH), 6.95 (s, 1H, ArH), 6.57 (d, 1H, *J*=1.5 Hz, ArH), 2.98 (d, 1H, *J*=15.6 Hz, $CH_{2a}CO$), 2.98–2.75 [m, 3H, CH_2 and $CH(CH_3)_2$], 2.83 (d, 1H, *J*=15.6 Hz, $CH_{2b}CO$), 2.40–2.10 (m, 2H, CH_2), 2.21 (s, 3H, $ArCH_3$), 1.22 [d, 6H, *J*=6.8 Hz, $CH(CH_3)_2$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=167.9 (s, O–C=O), 149.0 (s, ArC), 148.2 (s, ArC), 144.9 (s, ArC), 141.4 (s, ArC), 134.2 (s, ArC), 129.9 (s, ArC), 128.9 (d, ArCH), 126.4 (d, ArCH), 126.2 (d, ArCH), 124.7 (d, ArCH), 121.5 (d, ArCH), 116.8 (d, ArCH), 49.6 (s, C_q), 41.1 (t, CH_2CO), 39.9 (t, CH_2), 34.0 [d, $CH(CH_3)_2$], 29.5 (t, CH_2), 24.2 [q, $CH(CH_3)_{2a}$], 24.1 [q, $CH(CH_3)_{2b}$], 20.8 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{21}H_{22}NaO_2]^+$=$[M+Na]^+$: 329.1512; found 329.1512.



12bf

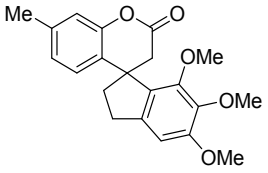
6'-Isopropyl-2',3'-dihydrospiro[benzo[*f*]chromene-1,1'-inden]-3(2*H*)-one (12bf): GP was carried out on the ester **11b** (122 mg, 0.5 mmol), phenol **9f** (216.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**11b**)=0.80, R_f(**12bf**)=0.61, (petroleum ether/ethyl acetate 97:3, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3 as eluent) furnished the lactone **12bf** (112.9 mg, 66%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2957, 1773, 1513, 1460, 1248, 1212, 1166, 988, 814, 746 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.82 (d, 1H, *J*=8.8 Hz, ArH), 7.80 (d, 1H, *J*=8.8 Hz, ArH), 7.35–7.26 (m, 3H, ArH), 7.16 (d, 1H, *J*=1.5 Hz, ArH), 7.07–7.00 (m, 2H, ArH), 6.63 (d, 1H, *J*=1.5 Hz, ArH), 3.25–3.05 (m, 2H, CH_2), 2.94 (d, 1H, *J*=15.6 Hz, $CH_{2a}CO$), 2.85

(dd, 1H, *J*=15.6 and 1.5 Hz, $CH_{2b}CO$), 2.72 [sept, 1H, *J*=6.8 Hz, $CH(CH_3)_2$], 2.52–2.32 (m, 2H, CH_2), 1.04 [d, 6H, *J*=6.8 Hz, $CH(CH_3)_2$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=167.1 (s, O–C=O), 150.3 (s, ArC), 148.6 (s, ArC), 148.2 (s, ArC), 138.8 (s, ArC), 132.0 (s, ArC), 130.2 (d, ArCH), 130.0 (s, ArC), 128.8 (d, ArCH), 125.9 (2 × d, 2C, 2 × ArCH), 125.5 (d, ArCH), 125.1 (d, ArCH), 124.5 (d, ArCH), 122.0 (d, ArCH), 121.2 (s, ArC), 117.6 (d, ArCH), 50.8 (s, C_q), 42.0 (t, CH_2CO), 37.2 (t, CH_2), 33.9 [d, $CH(CH_3)_2$], 29.5 (t, CH_2), 24.1 [q, $CH(CH_3)_{2a}$], 23.8 [q, $CH(CH_3)_{2b}$] ppm. HR-MS (ESI^+) m/z calculated for $[C_{24}H_{22}NaO_2]^+$=$[M+Na]^+$: 365.1512; found 365.1508.



12cc

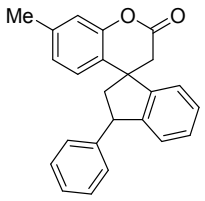
5',6'-Dimethoxy-7-methyl-2',3'-dihydrospiro[chromene-4,1'-inden]-2(3*H*)-one (12cc): GP was carried out on the ester **11c** (131 mg, 0.5 mmol), phenol **9c** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**11c**)=0.80, R_f(**12cc**)=0.55, (petroleum ether/ethyl acetate 90:10, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 93:7 as eluent) furnished the lactone **12cc** (116.6 mg, 72%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2935, 1765, 1502, 1454, 1257, 1166, 1037, 823 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=6.92 (s, 1H, ArH), 6.84 (d, 1H, *J*=7.8 Hz, ArH), 6.83 (s, 1H, ArH), 6.64 (d, 1H, *J*=7.8 Hz, ArH), 6.55 (s, 1H, ArH), 3.89 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 2.95 (d, 1H, *J*=15.6 Hz, $CH_{2a}CO$), 2.94–2.86 (m, 2H, CH_2), 2.81 (d, 1H, *J*=15.6 Hz, $CH_{2b}CO$), 2.32 (s, 3H, $ArCH_3$), 2.32–2.10 (m, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=167.9 (s, O–C=O), 150.8 (s, ArC), 149.3 (s, ArC), 148.7 (s, ArC), 138.8 (s, ArC), 136.1 (s, ArC), 135.7 (s, ArC), 127.3 (s, ArC), 125.9 (d, ArCH), 125.3 (d, ArCH), 117.5 (d, ArCH), 107.6 (d, ArCH), 106.1 (d, ArCH), 55.9 (2 × q, 2C, 2 × OCH_3), 49.5 (s, C_q), 41.2 (t, CH_2CO), 40.1 (t, CH_2), 29.8 (t, CH_2), 20.9 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{20}H_{20}NaO_4]^+$=$[M+Na]^+$: 347.1253; found 347.1254.



12dc

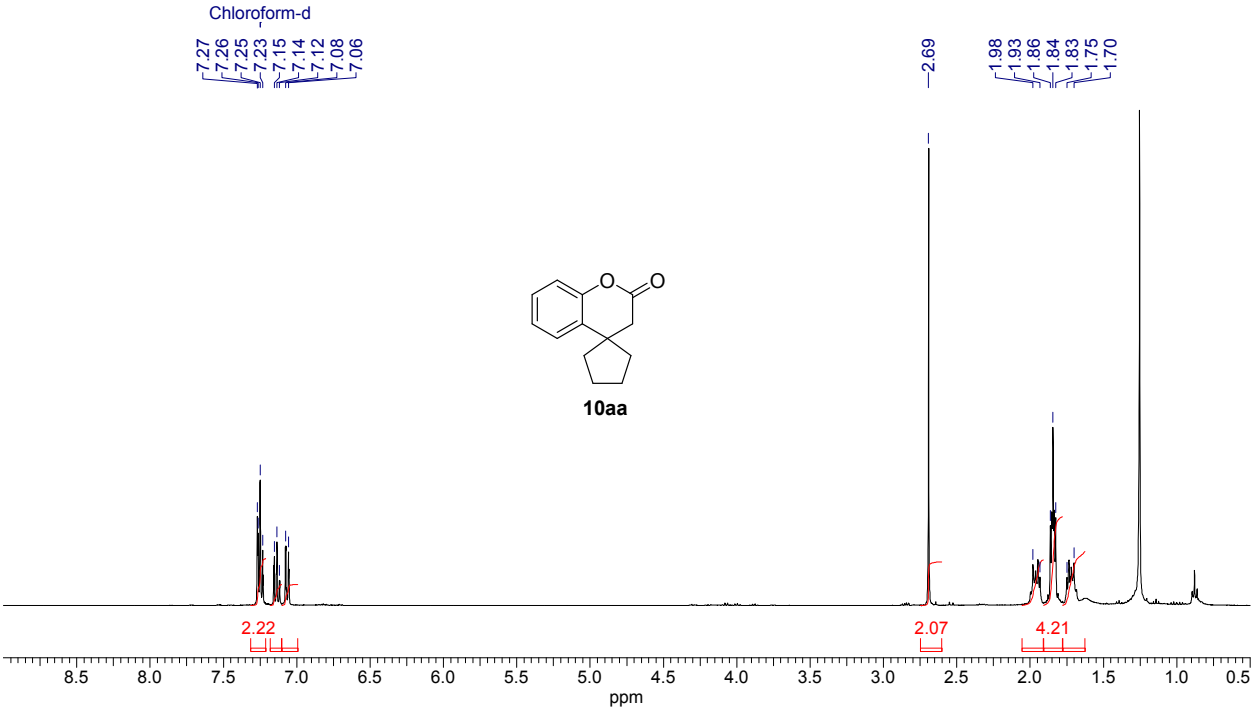
5',6',7'-Trimethoxy-7-methyl-2',3'-dihydrospiro[chromene-4,1'-inden]-2(3*H*)-one (12dc): GP was carried out on the ester **11d** (146 mg, 0.5 mmol), phenol **9c** (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**11d**)=0.81, R_f(**12dc**)=0.58, (petroleum ether/ethyl acetate 90:10, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 93:7 as eluent) furnished the lactone **12dc** (136.3 mg, 77%) as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2937, 1767, 1583, 1464, 1413,

1338, 1226, 1165, 1115, 1062, 820 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=6.90 (s, 1H, ArH), 6.79 (d, 1H, *J*=7.8 Hz, ArH), 6.60 (s, 1H, ArH), 6.55 (d, 1H, *J*=7.8 Hz, ArH), 3.87 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.57 (d, 1H, *J*=15.6 Hz, $CH_{2b}CO$), 2.97–2.85 (m, 2H, CH_2), 2.80 (d, 1H, *J*=15.6 Hz, $CH_{2b}CO$), 2.31 (s, 3H, $ArCH_3$), 2.29–2.12 (m, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=168.5 (s, O–C=O), 154.6 (s, ArC), 150.4 (s, ArC), 150.2 (s, ArC), 140.8 (s, ArC), 139.7 (s, ArC), 138.5 (s, ArC), 128.3 (s, ArC), 127.3 (s, ArC), 125.4 (d, ArCH), 125.0 (d, ArCH), 117.5 (d, ArCH), 103.1 (d, ArCH), 60.8 (q, OCH_3), 60.2 (q, OCH_3), 56.1 (q, OCH_3), 49.4 (s, C_q), 41.0 (t, CH_2CO), 40.7 (t, CH_2), 30.8 (t, CH_2), 21.0 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{21}H_{22}NaO_5]^+$=$[M+Na]^+$: 377.1359; found 377.1353.

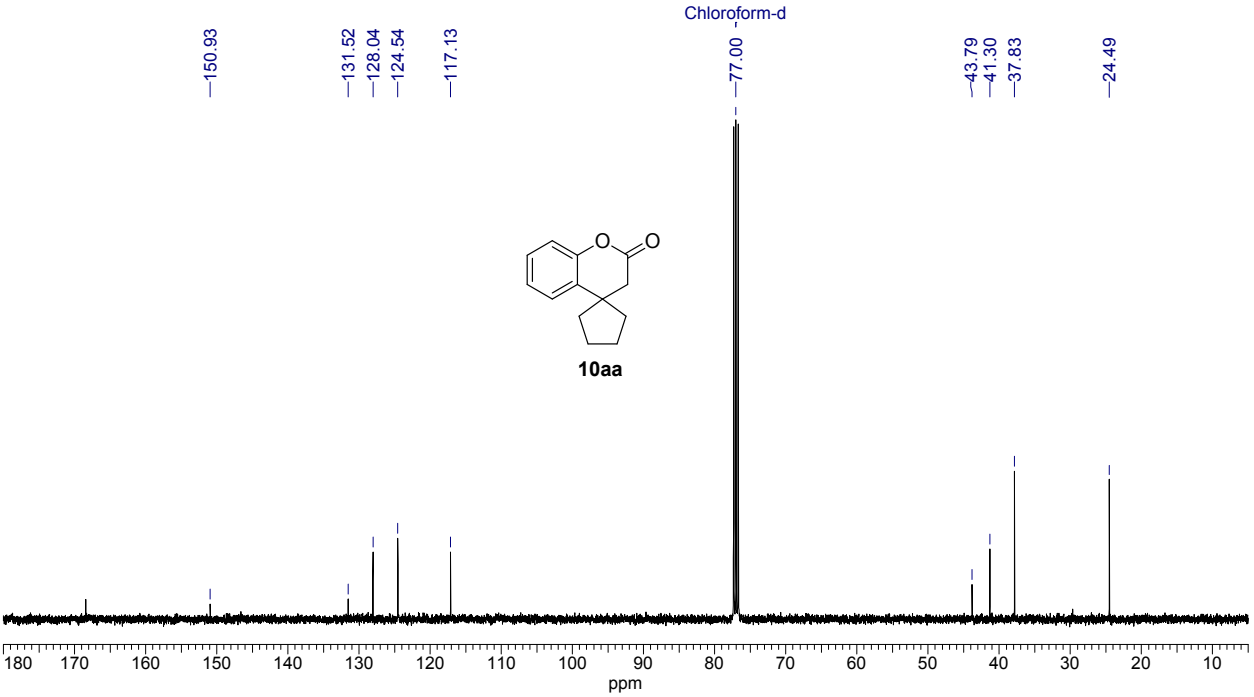


12ec

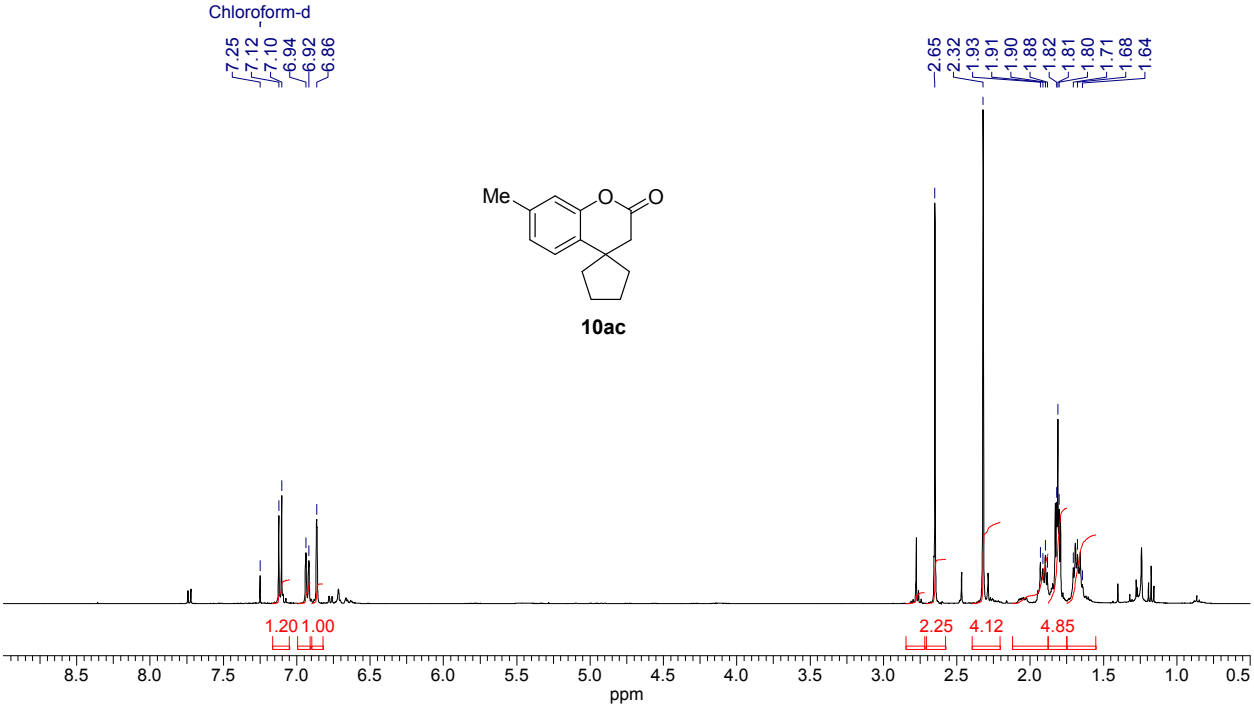
7-Methyl-3'-phenyl-2',3'-dihydrospiro[chromene-4,1'-inden]-2(3*H*)-one (12ec): GP was carried out on the ester **11e** (139 mg, 0.5 mmol), phenol **9a**c (162.0 mg, 1.5 mmol), anhydrous $FeCl_3$ (243 mg, 1.5 mmol) and benzene (1.5 mL). The resulting reaction mixture was stirred at rt for 12 h. [TLC control R_f(**11e**)=0.8, R_f(**12ec**)=0.66, (petroleum ether/ethyl acetate 95:5, UV detection)]. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3 as eluent) furnished the lactone **12ec** (76.5 mg, 45%) as white solid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 1772, 1500, 1453, 1223, 1166, 1025, 820, 756 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.37–7.26 (m, 4H, ArH), 7.25 (t, 1H, *J*=7.3 Hz, ArH), 7.20–7.12 (m, 3H, ArH), 7.04 (d, 1H, *J*=8.3 Hz, ArH), 6.96 (s, 1H, ArH), 6.80 (d, 1H, *J*=7.8 Hz, ArH), 6.36 (d, 1H, *J*=7.8 Hz, ArH), 4.37 (dd, 1H, *J*=10.3 and 7.3 Hz, C*H*CH_2), 3.29 (d, 1H, *J*=15.6 Hz, $CH_{2a}CO$), 2.92 (d, 1H, *J*=15.6 Hz, $CH_{2b}CO$), 2.66 (dd, 1H, *J*=12.7 and 7.3 Hz, CHCH_{2a}), 2.33 (s, 3H, $ArCH_3$), 2.27 (dd, 1H, *J*=12.7 and 10.3 Hz, CHCH_{2b}) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=168.0 (s, O–C=O), 150.5 (s, ArC), 147.4 (s, ArC), 144.5 (s, ArC), 143.1 (s, ArC), 139.0 (s, ArC), 128.7 (d, 2C, 2 × ArCH), 128.5 (d, ArCH), 128.3 (d, 2C, 2 × ArCH), 127.9 (d, ArCH), 127.3 (s, ArC), 126.9 (d, ArCH), 125.6 (d, ArCH), 125.4 (d, ArCH), 125.2 (d, ArCH), 123.1 (d, ArCH), 117.7 (d, ArCH), 50.9 (t, CH_2), 48.6 (t, *C*HCH_2), 48.1 (s, C_q), 41.6 (t, CH_2), 21.0 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z calculated for $[C_{24}H_{20}NaO_2]^+$=$[M+Na]^+$: 363.1356; found 363.1358.



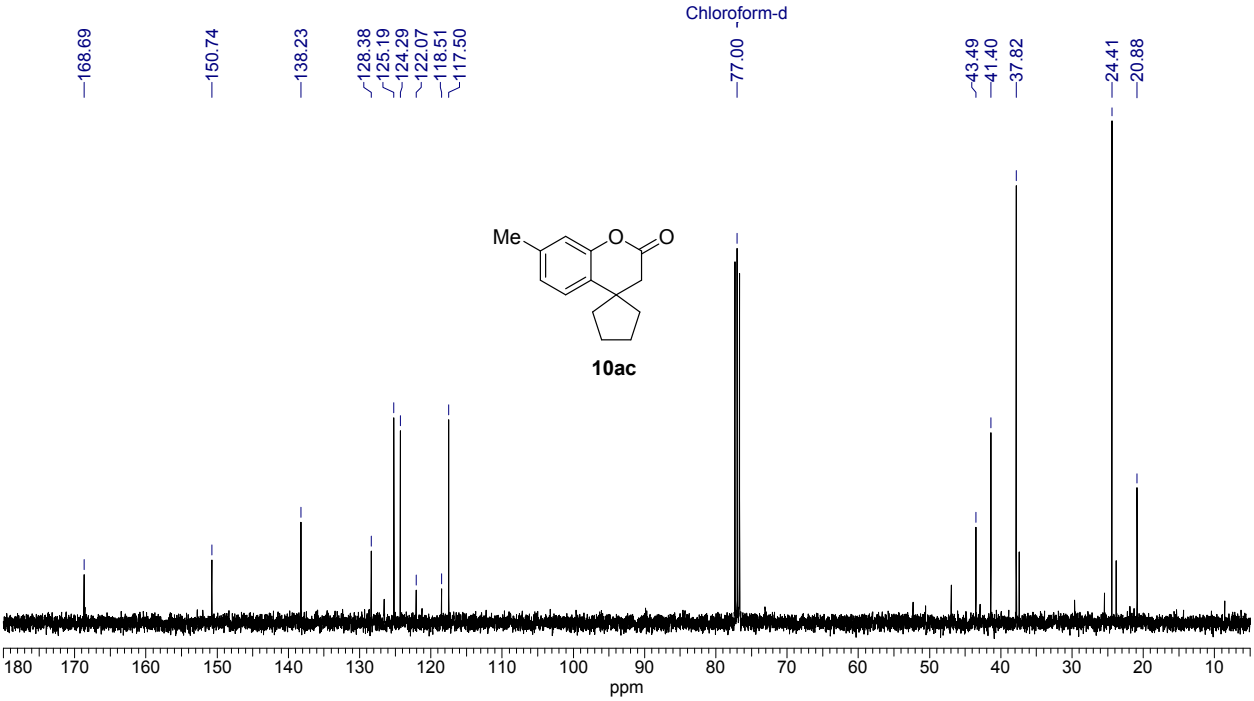
^{1}H NMR (400 MHz) spectrum of **10aa** in $CDCl_3$



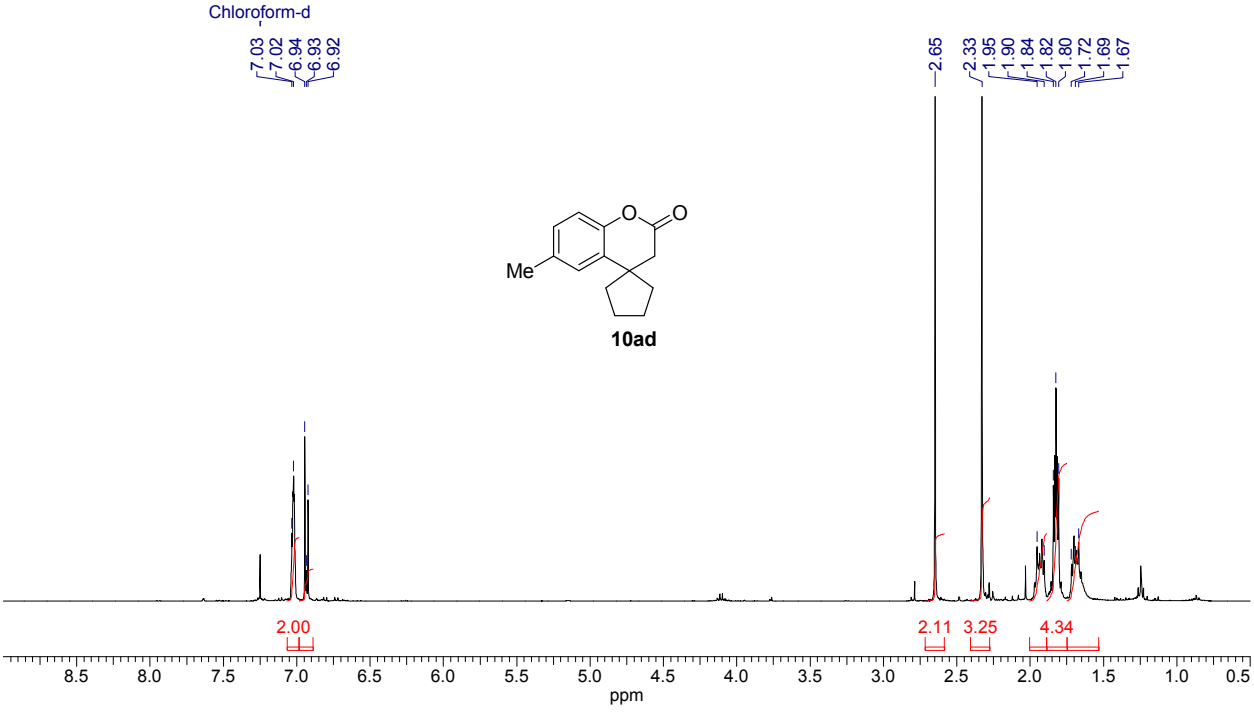
^{13}C NMR (100 MHz) spectrum of **10aa** in $CDCl_3$



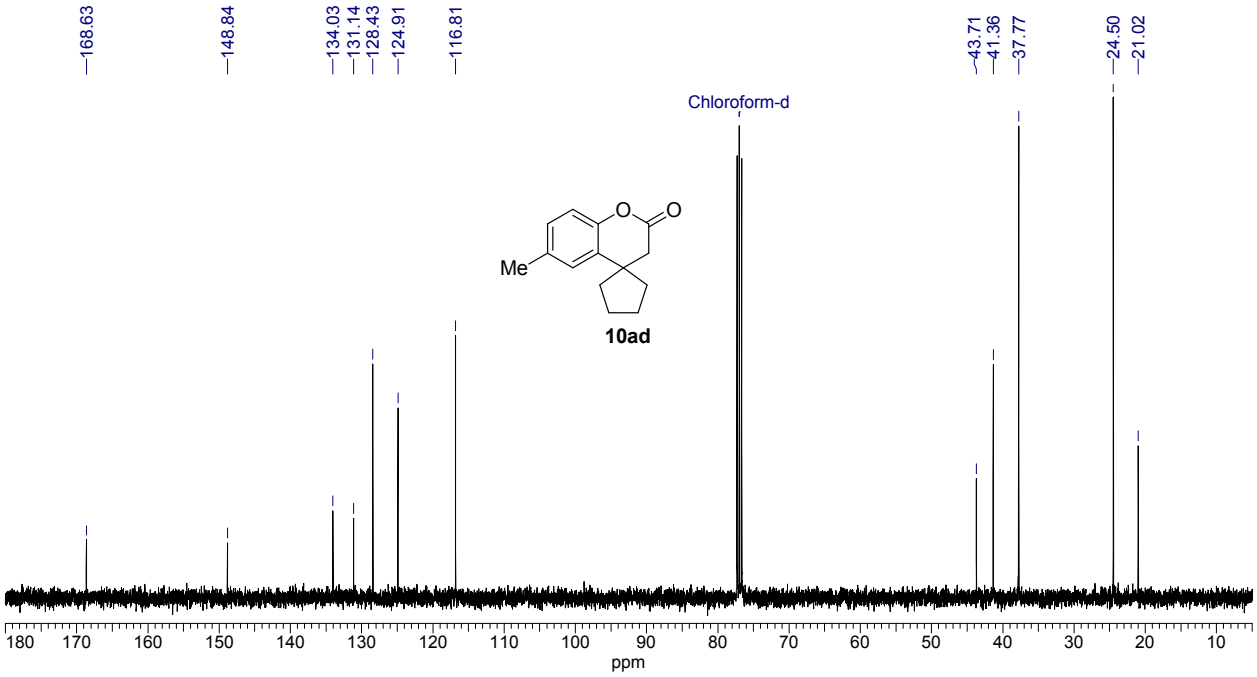
^{1}H NMR (400 MHz) spectrum of **10ac** in $CDCl_3$



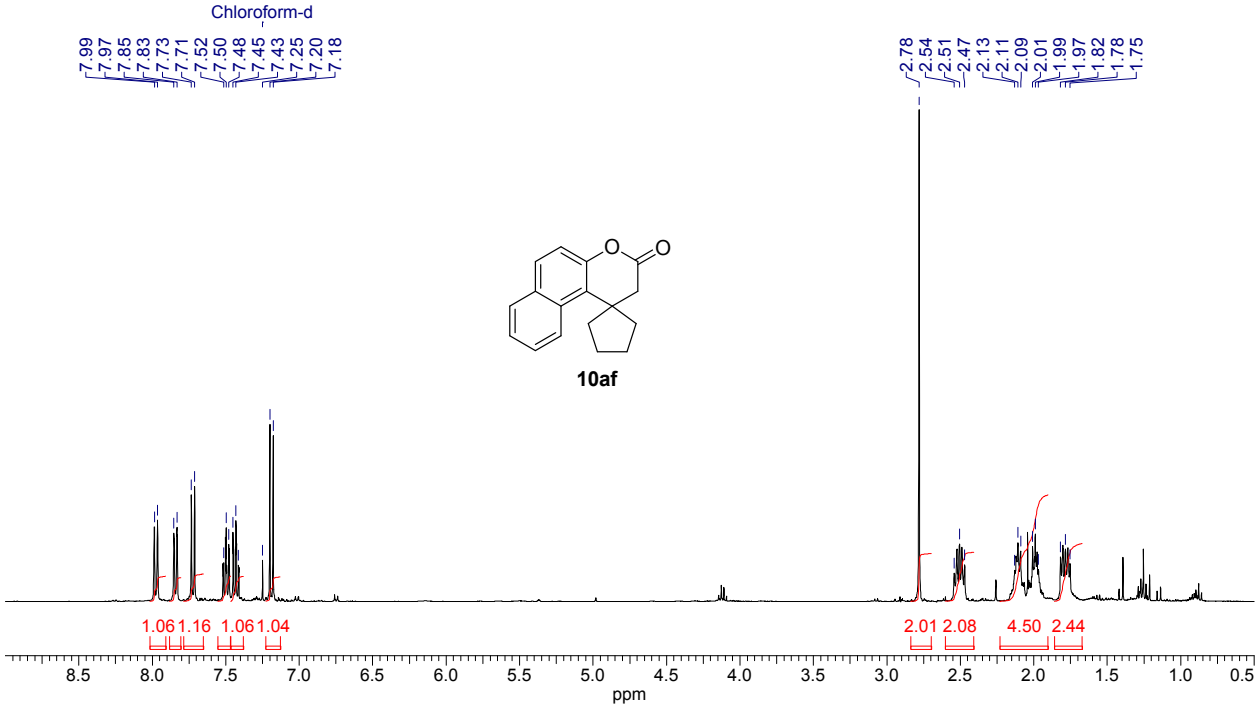
^{13}C NMR (100 MHz) spectrum of **10ac** in $CDCl_3$



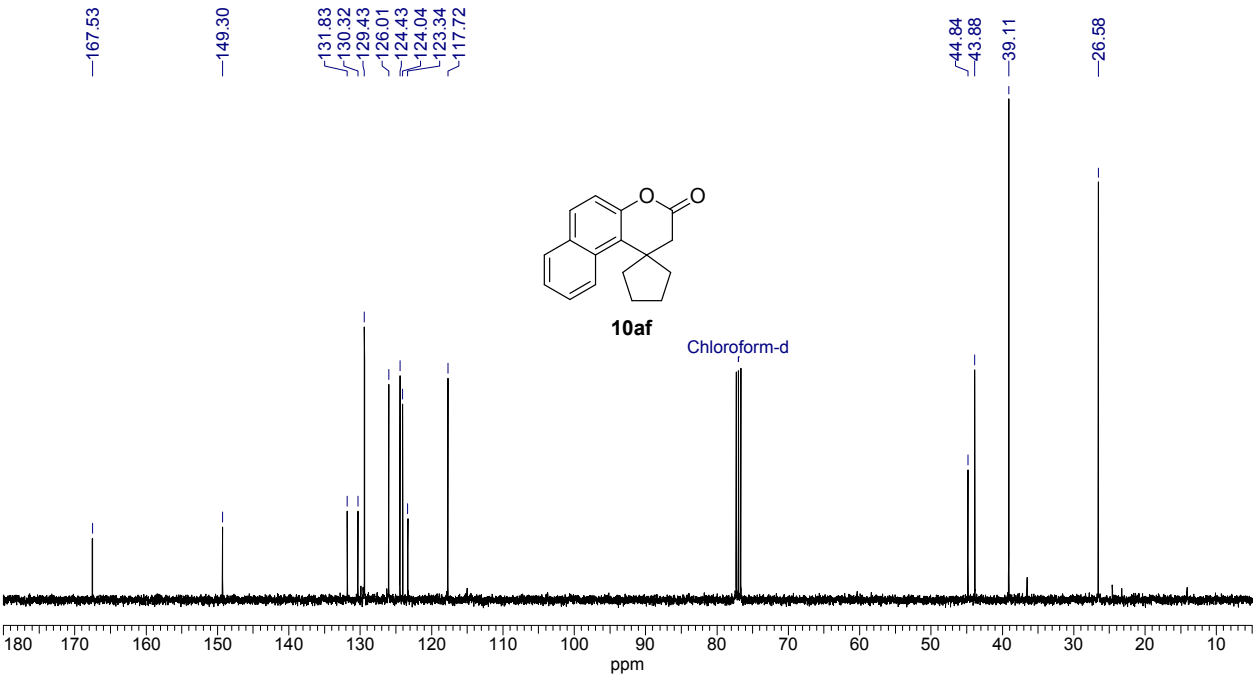
^{1}H NMR (400 MHz) spectrum of **10ad** in $CDCl_3$



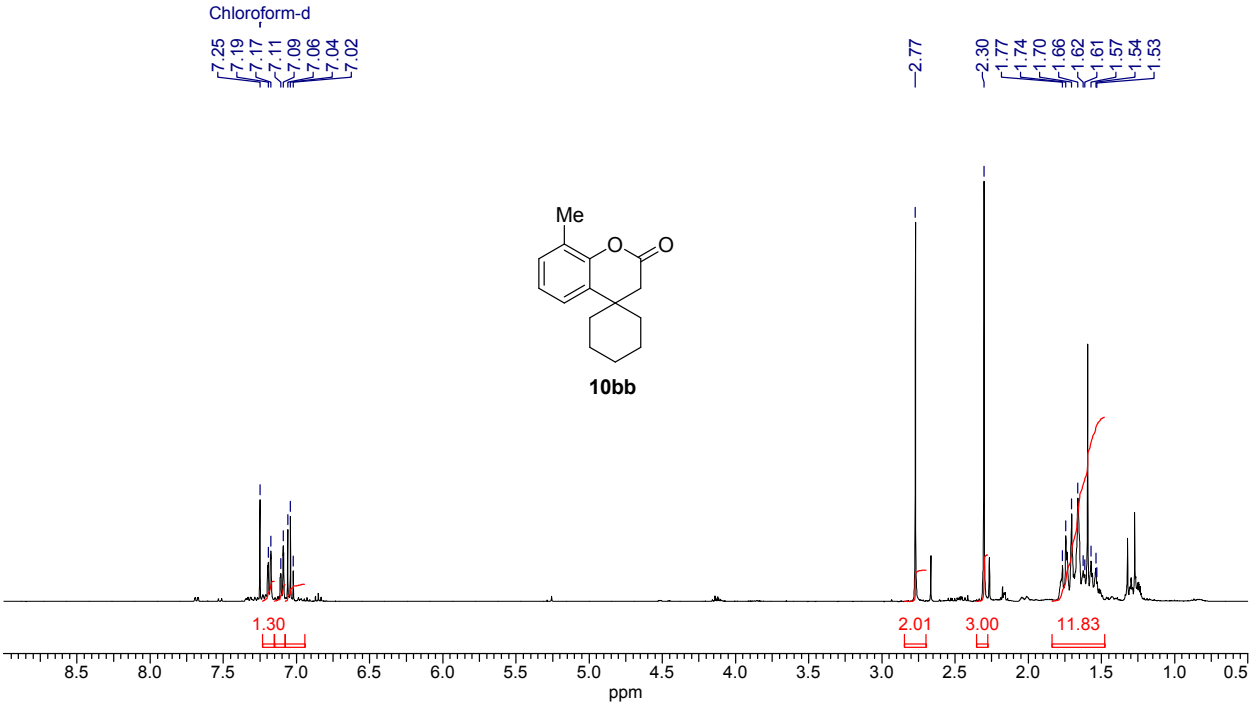
^{13}C NMR (100 MHz) spectrum of **10ad** in $CDCl_3$



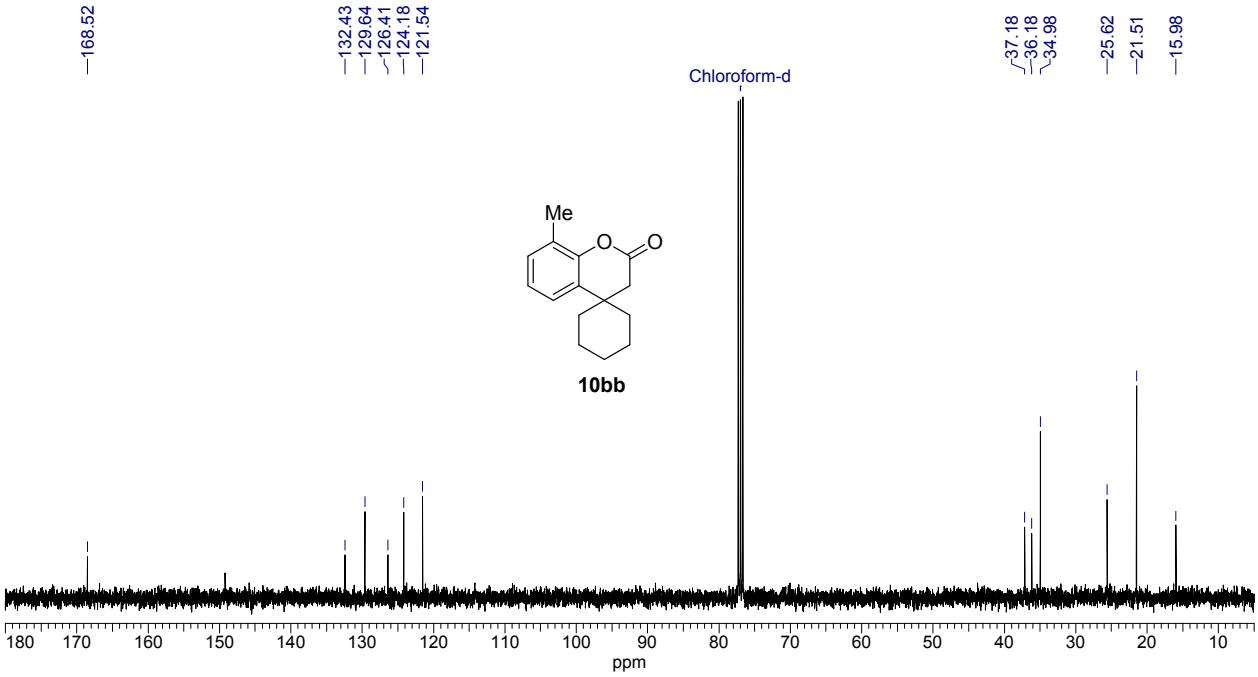
^{1}H NMR (400 MHz) spectrum of **10af** in $CDCl_3$



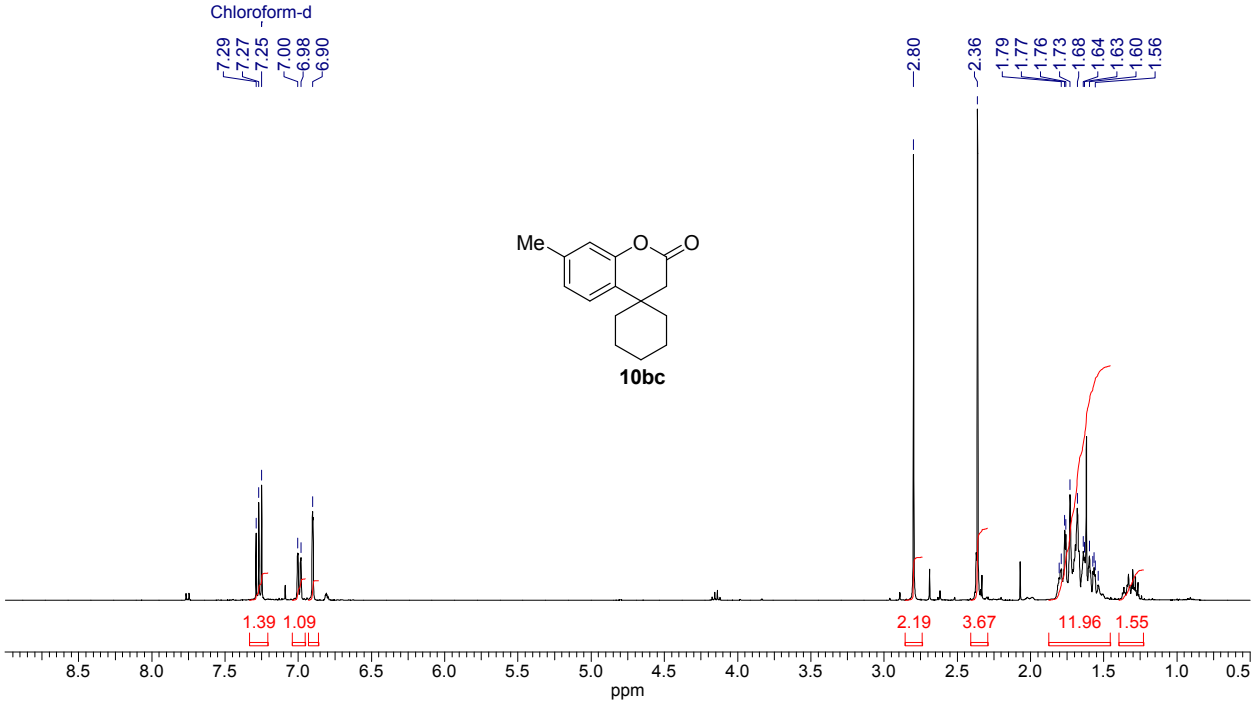
^{13}C NMR (100 MHz) spectrum of **10af** in $CDCl_3$



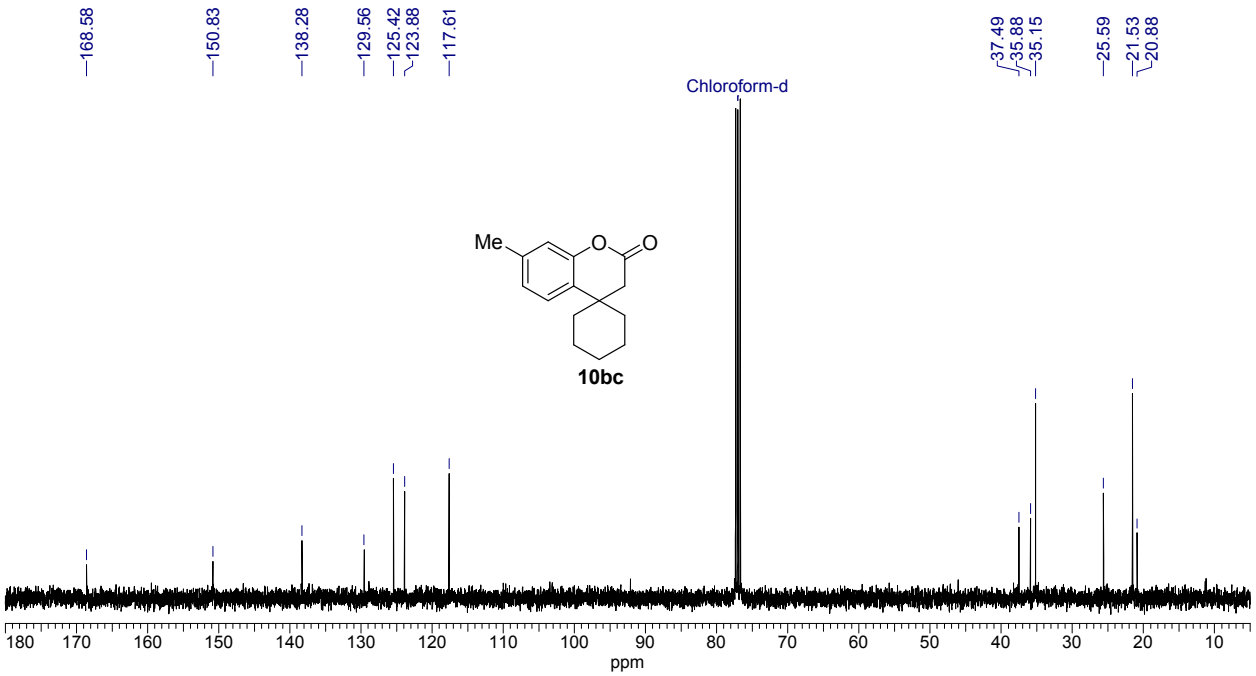
^{1}H NMR (400 MHz) spectrum of **10bb** in $CDCl_3$



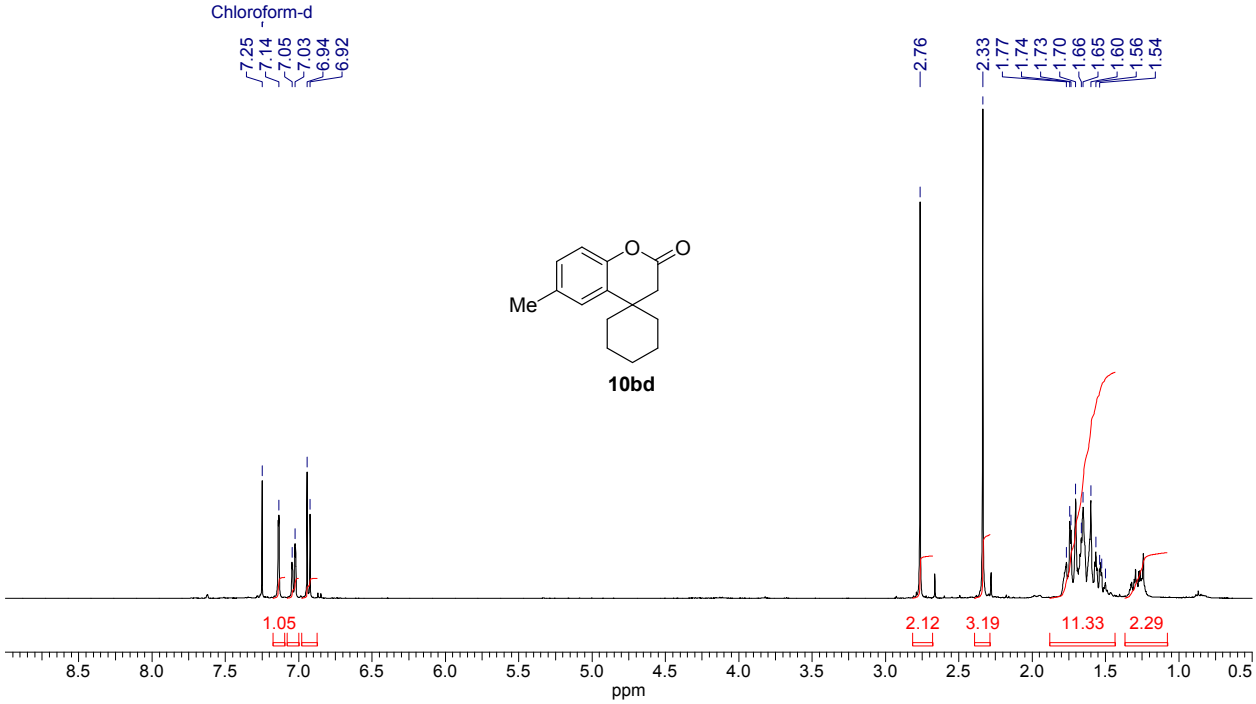
^{13}C NMR (100 MHz) spectrum of **10bb** in $CDCl_3$



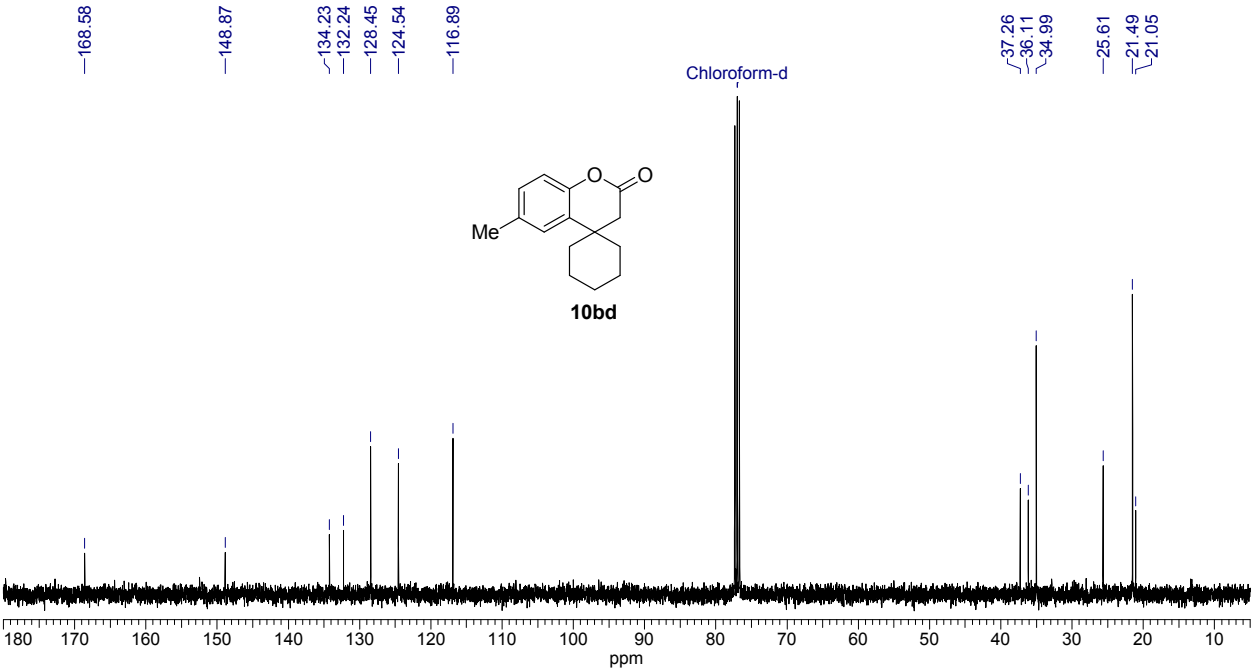
^{1}H NMR (400 MHz) spectrum of **10bc** in $CDCl_3$



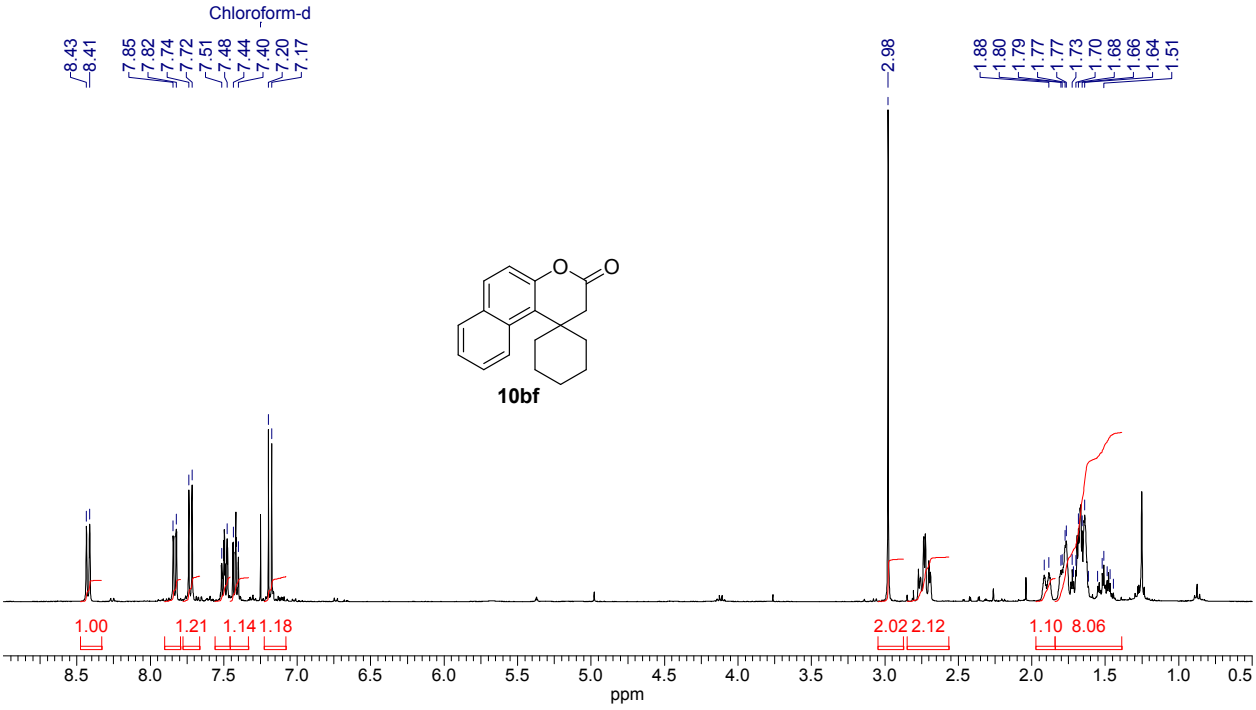
^{13}C NMR (100 MHz) spectrum of **10bc** in $CDCl_3$



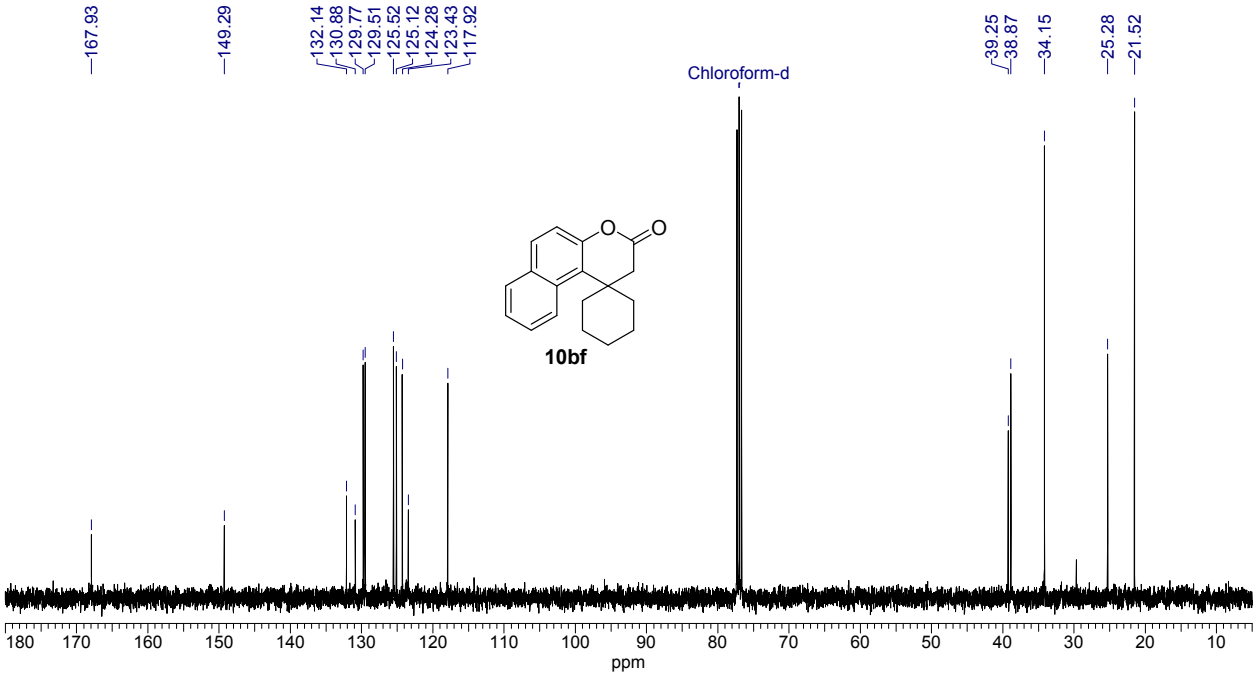
^{1}H NMR (400 MHz) spectrum of **10bd** in $CDCl_3$



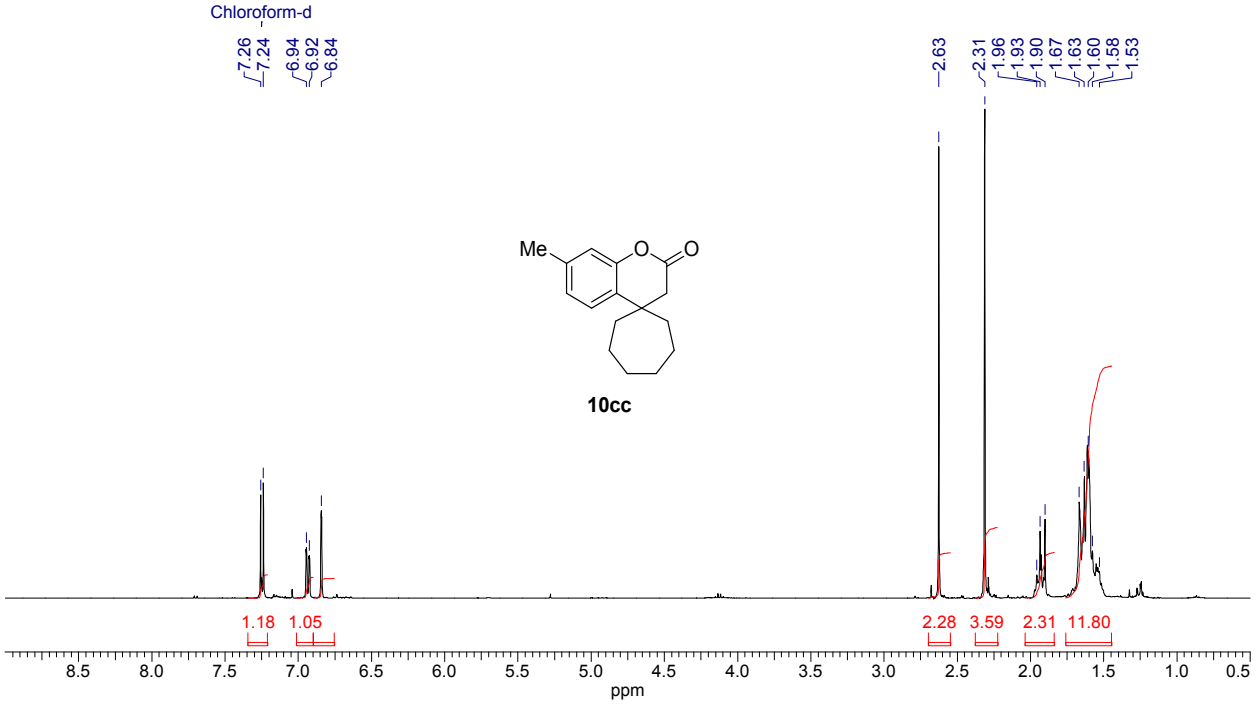
^{13}C NMR (100 MHz) spectrum of **10bd** in $CDCl_3$



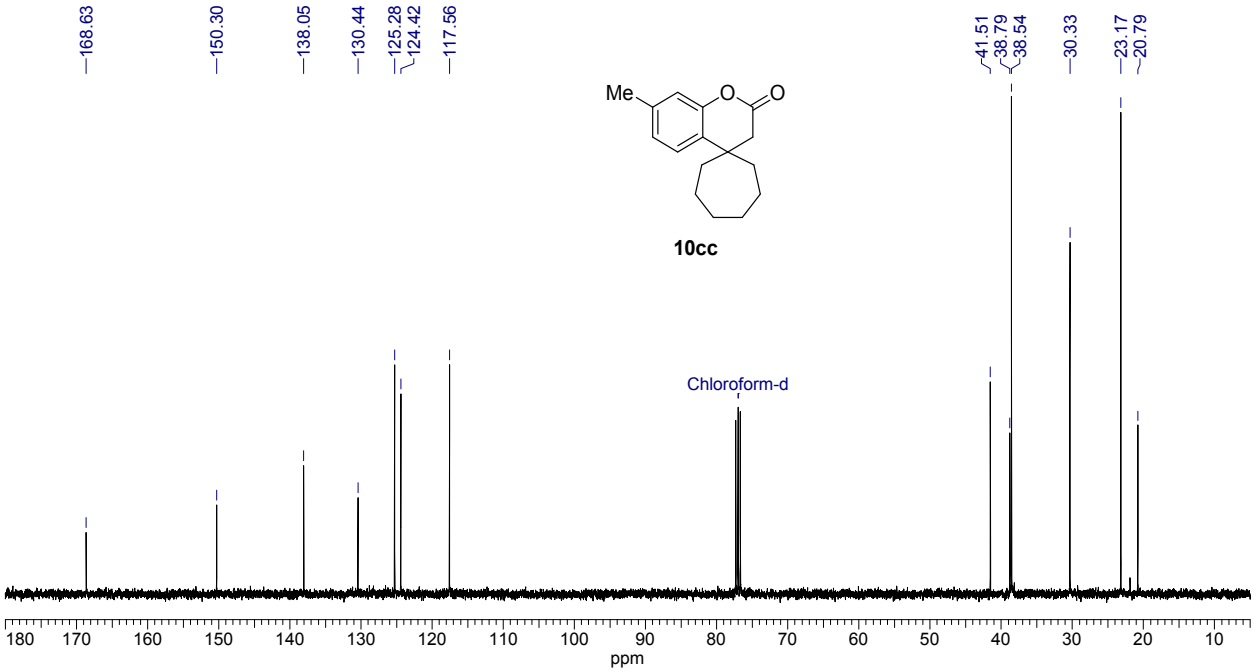
^{1}H NMR (400 MHz) spectrum of **10bf** in $CDCl_3$



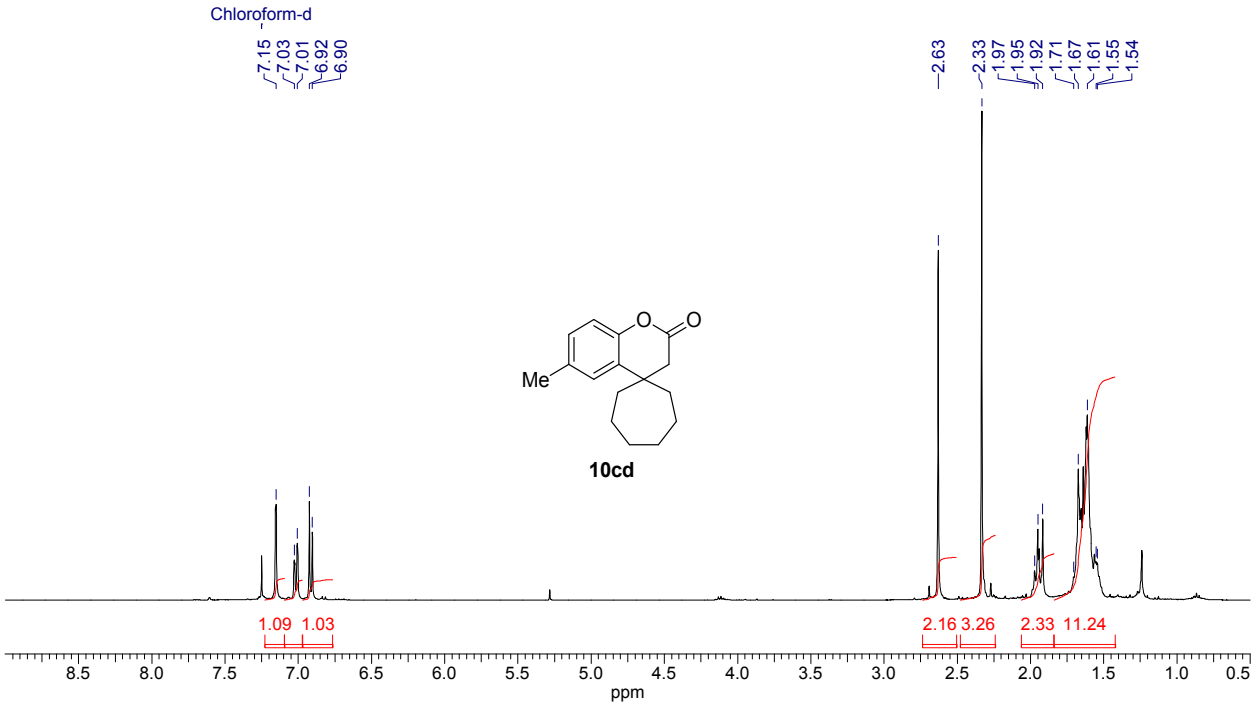
^{13}C NMR (100 MHz) spectrum of **10bf** in $CDCl_3$



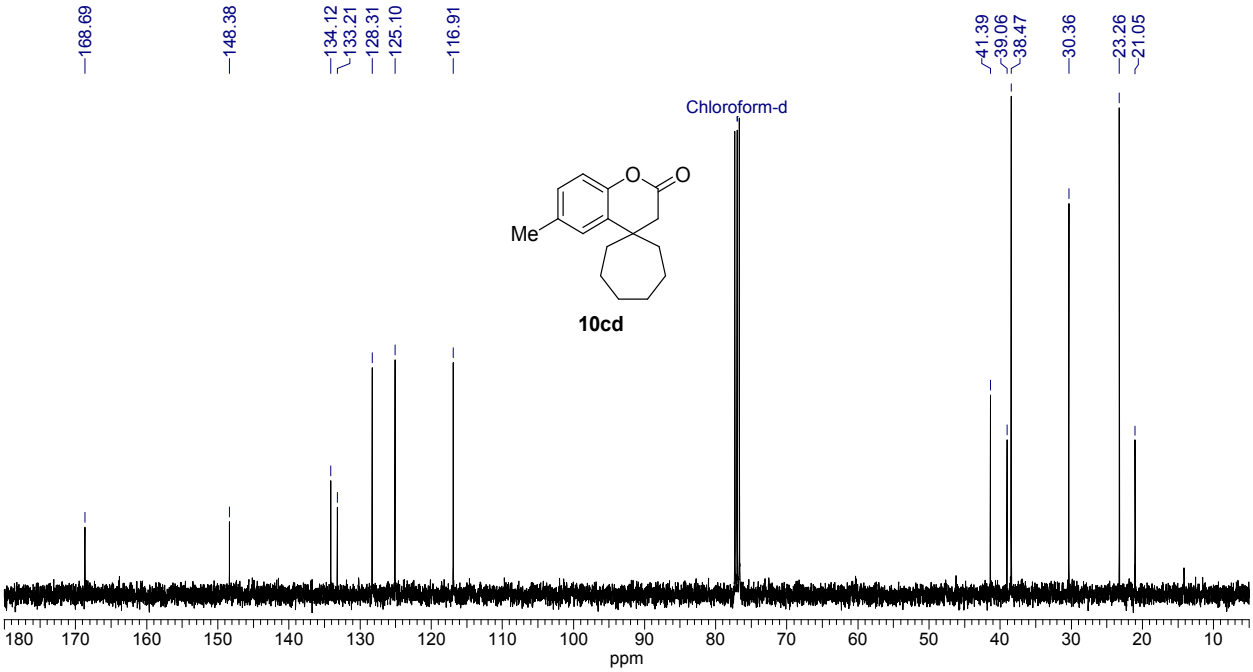
^{1}H NMR (400 MHz) spectrum of **10cc** in $CDCl_3$



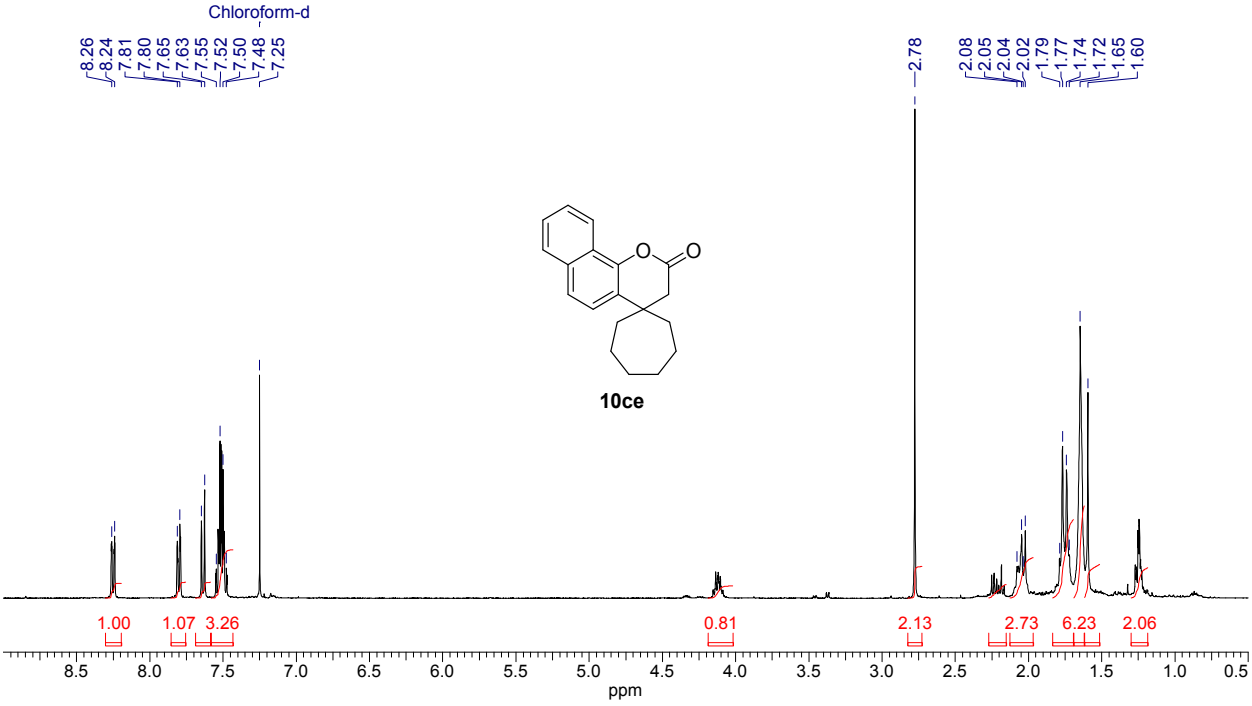
^{13}C NMR (100 MHz) spectrum of **10cc** in $CDCl_3$



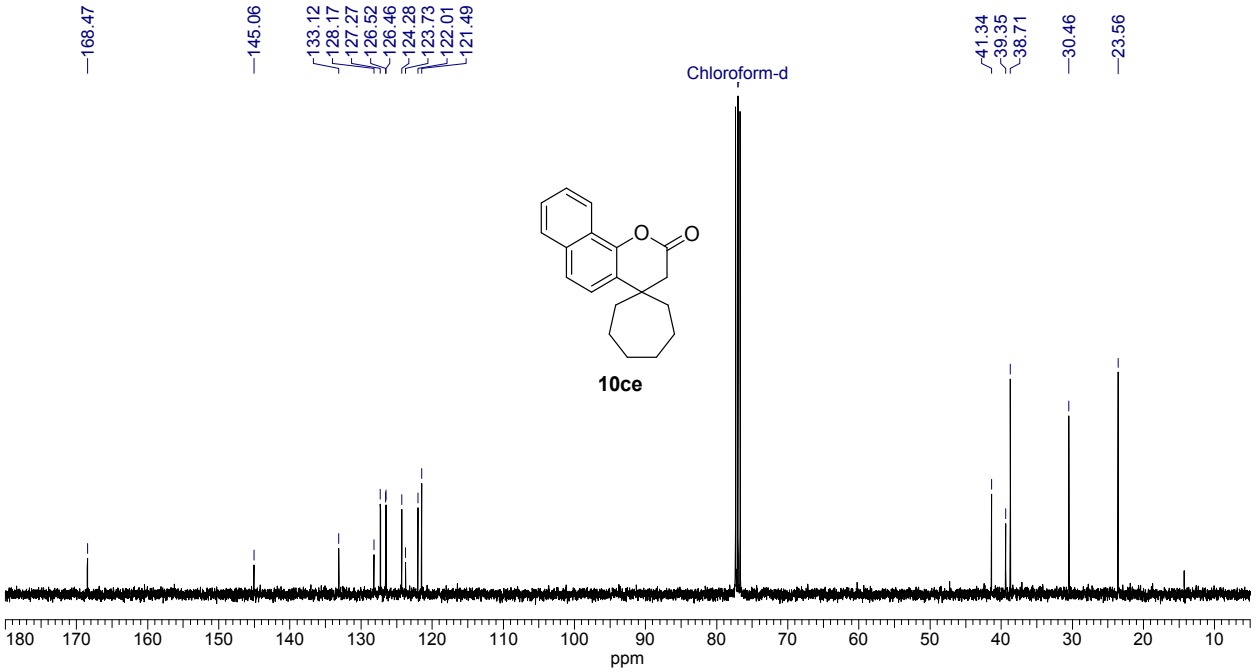
^{1}H NMR (400 MHz) spectrum of **10cd** in $CDCl_3$



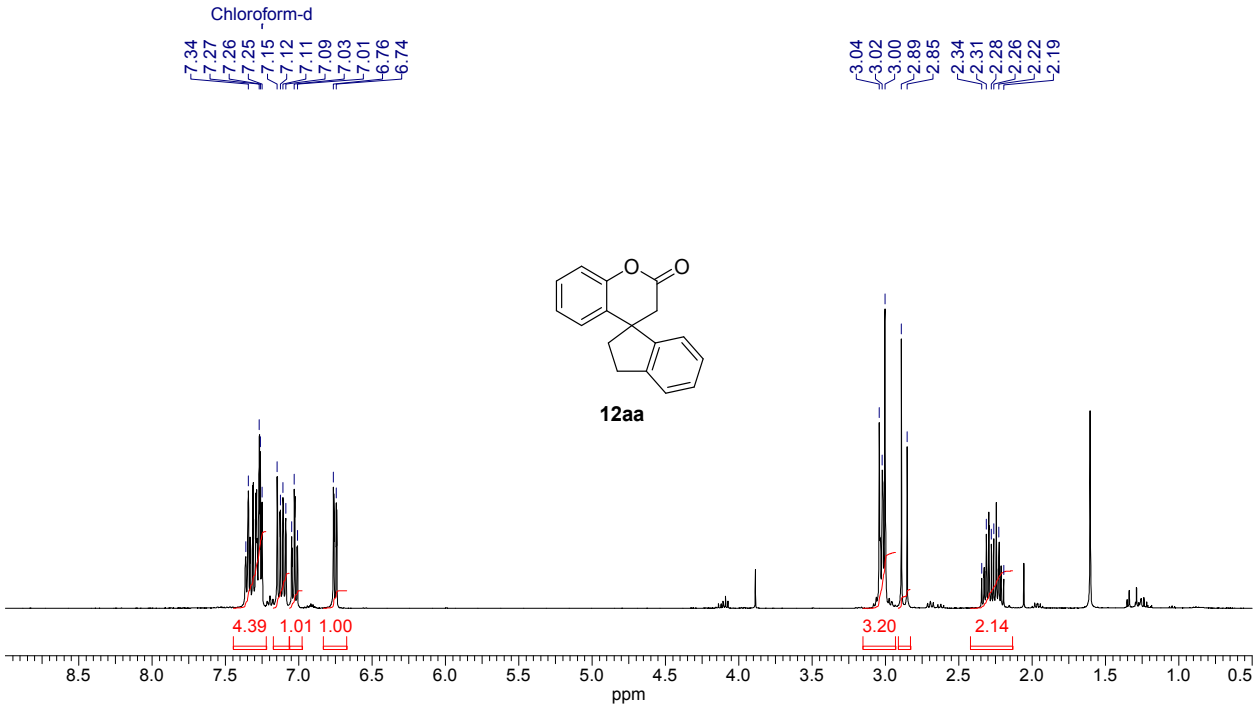
^{13}C NMR (100 MHz) spectrum of **10cd** in $CDCl_3$



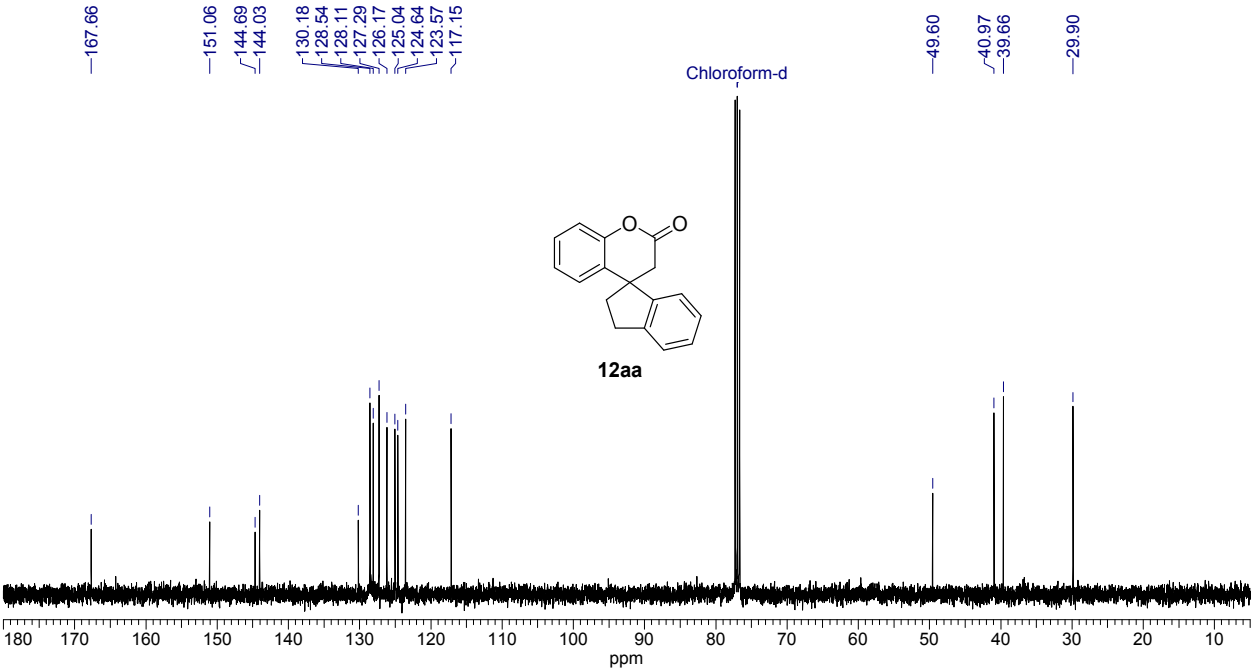
^{1}H NMR (400 MHz) spectrum of **10ce** in $CDCl_3$



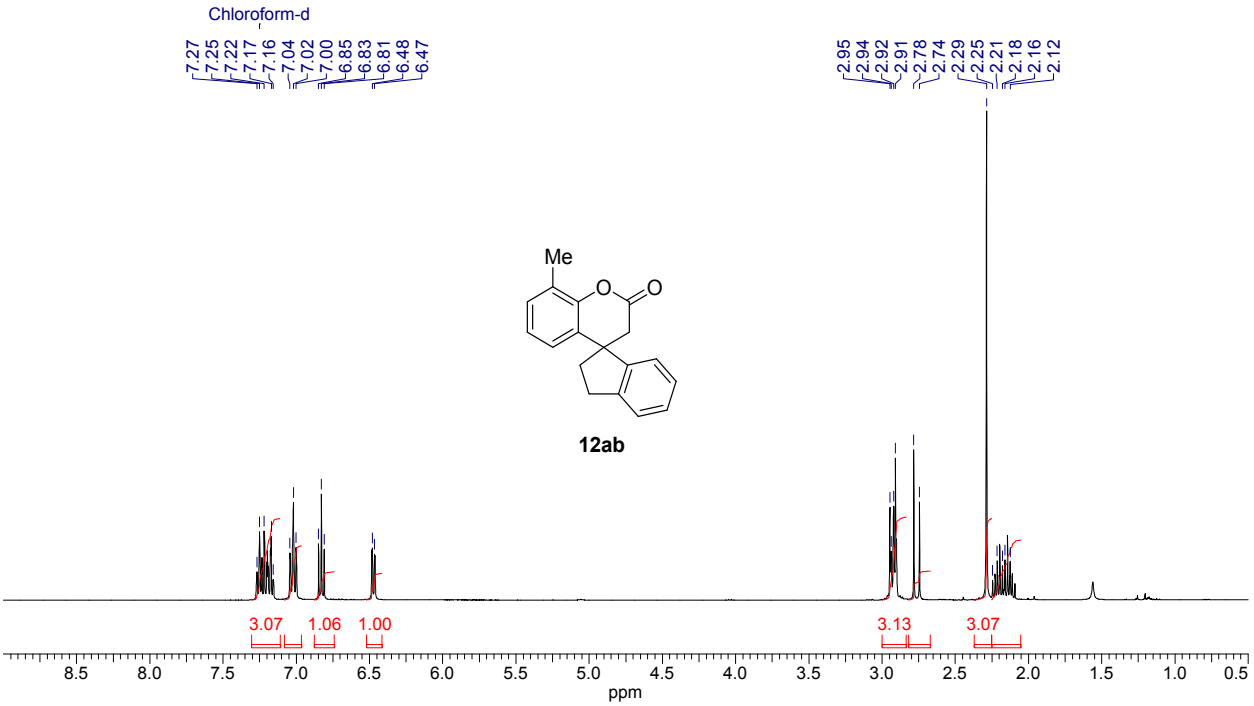
^{13}C NMR (100 MHz) spectrum of **10ce** in $CDCl_3$



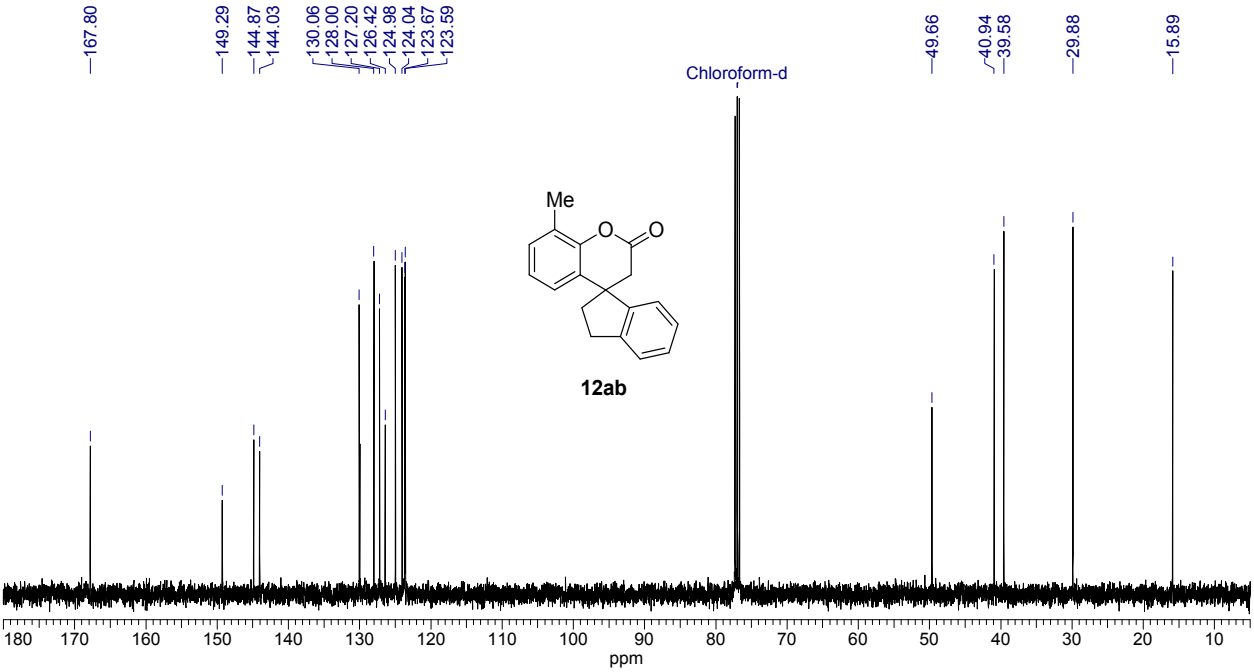
^{1}H NMR (400 MHz) spectrum of **12aa** in $CDCl_3$



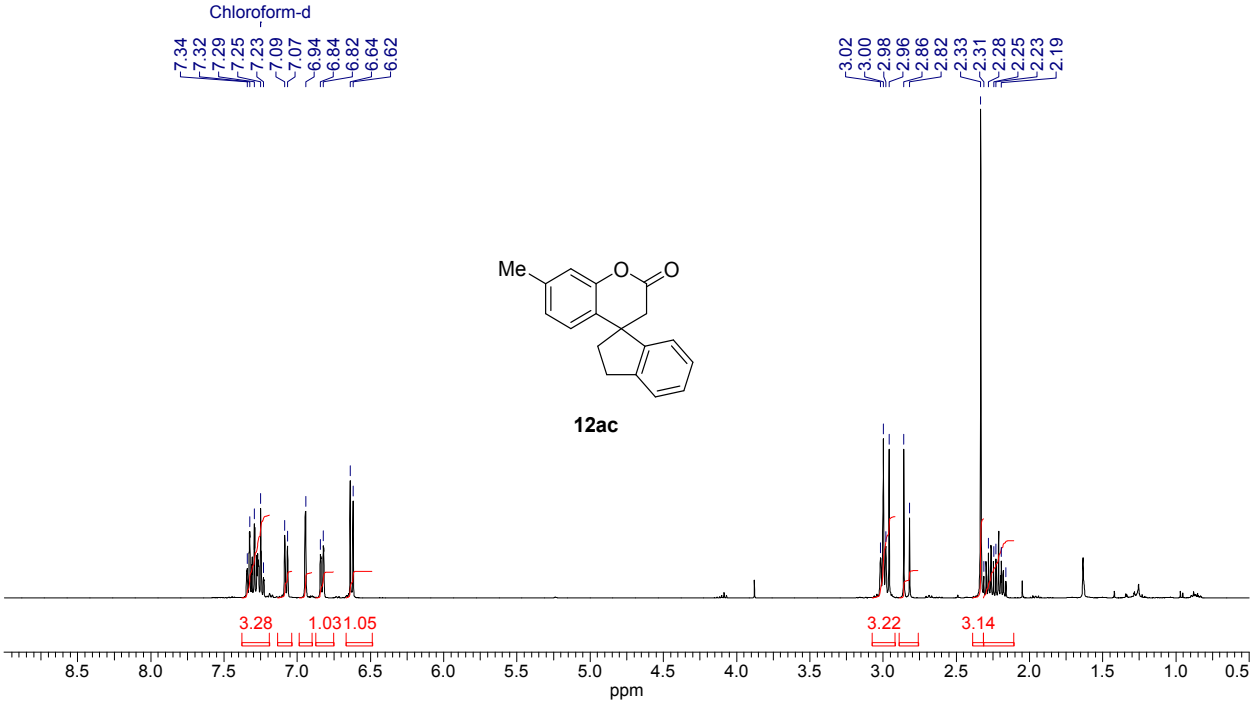
^{13}C NMR (100 MHz) spectrum of **12aa** in $CDCl_3$



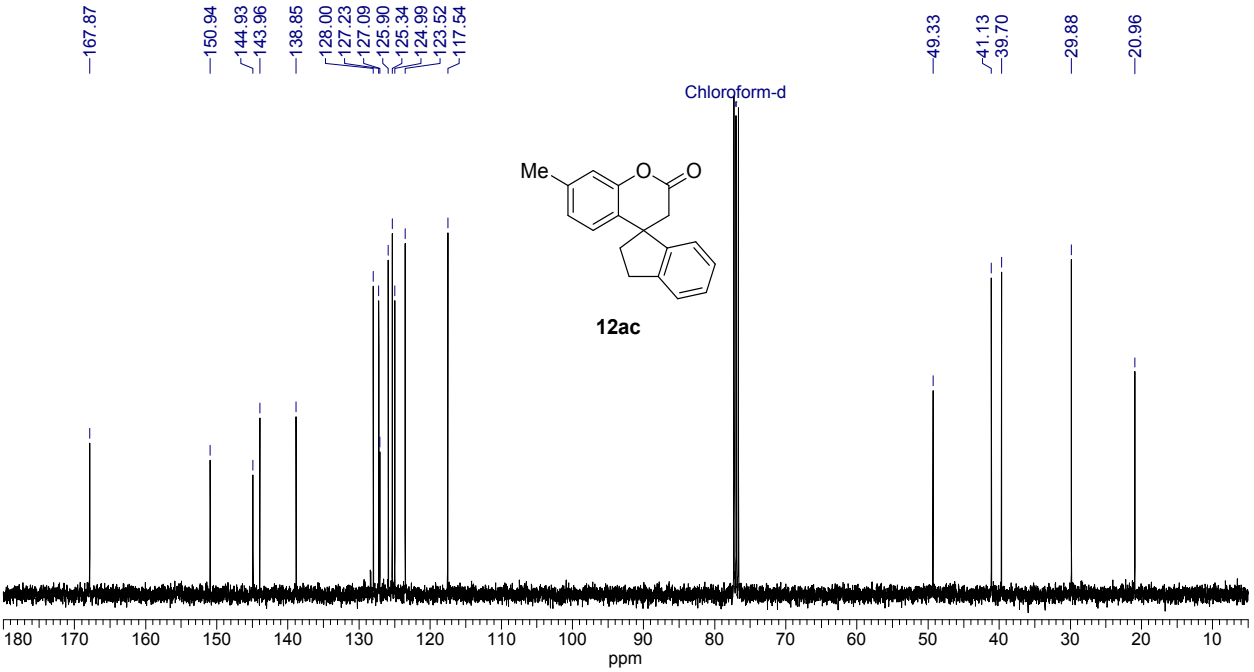
^{1}H NMR (400 MHz) spectrum of **12ab** in $CDCl_3$



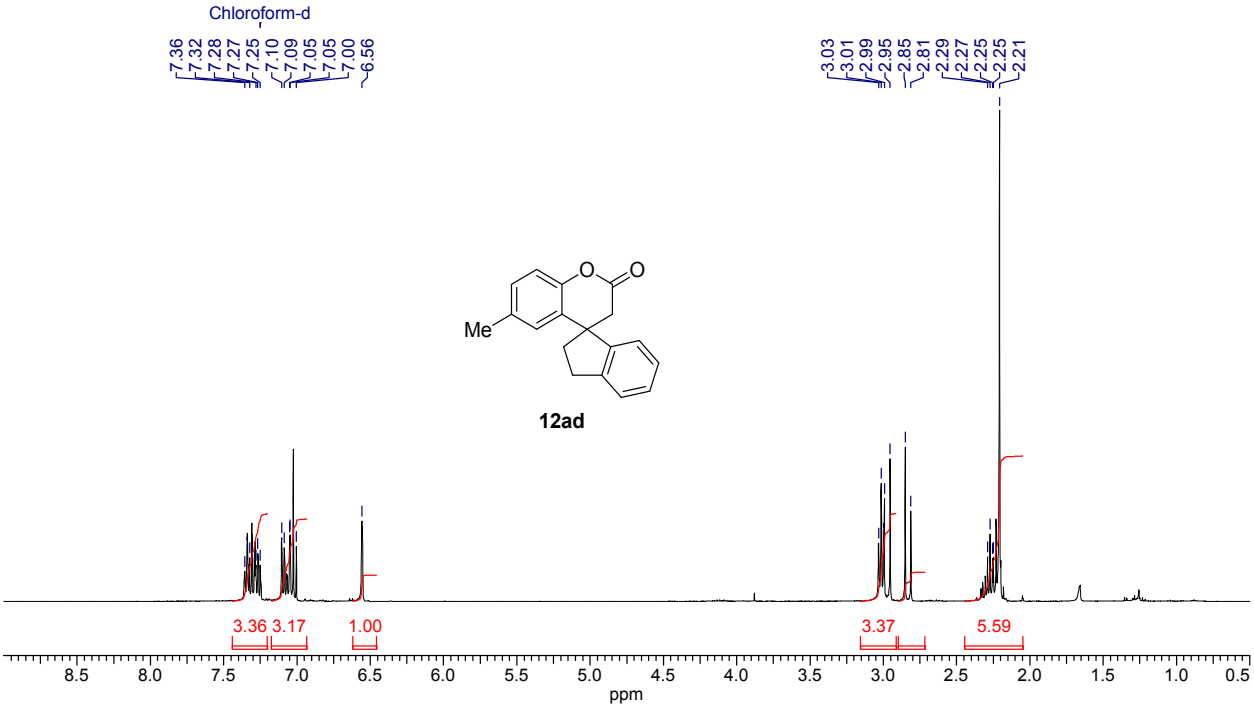
^{13}C NMR (100 MHz) spectrum of **12ab** in $CDCl_3$



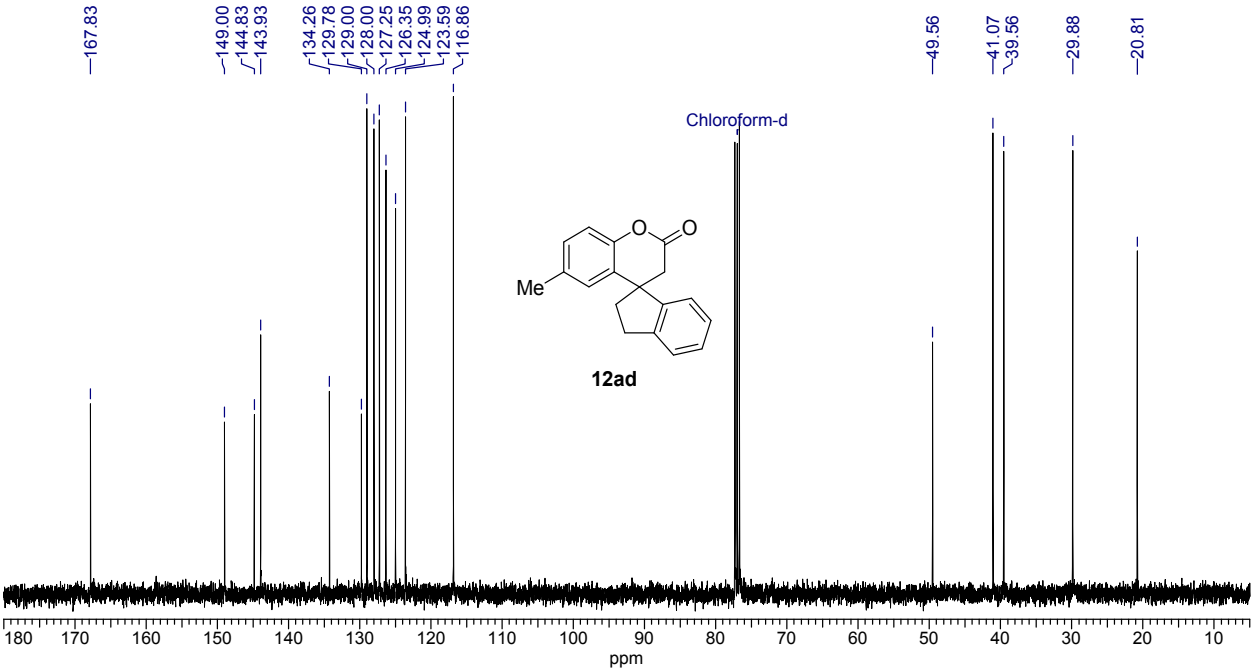
^{1}H NMR (400 MHz) spectrum of **12ac** in $CDCl_3$



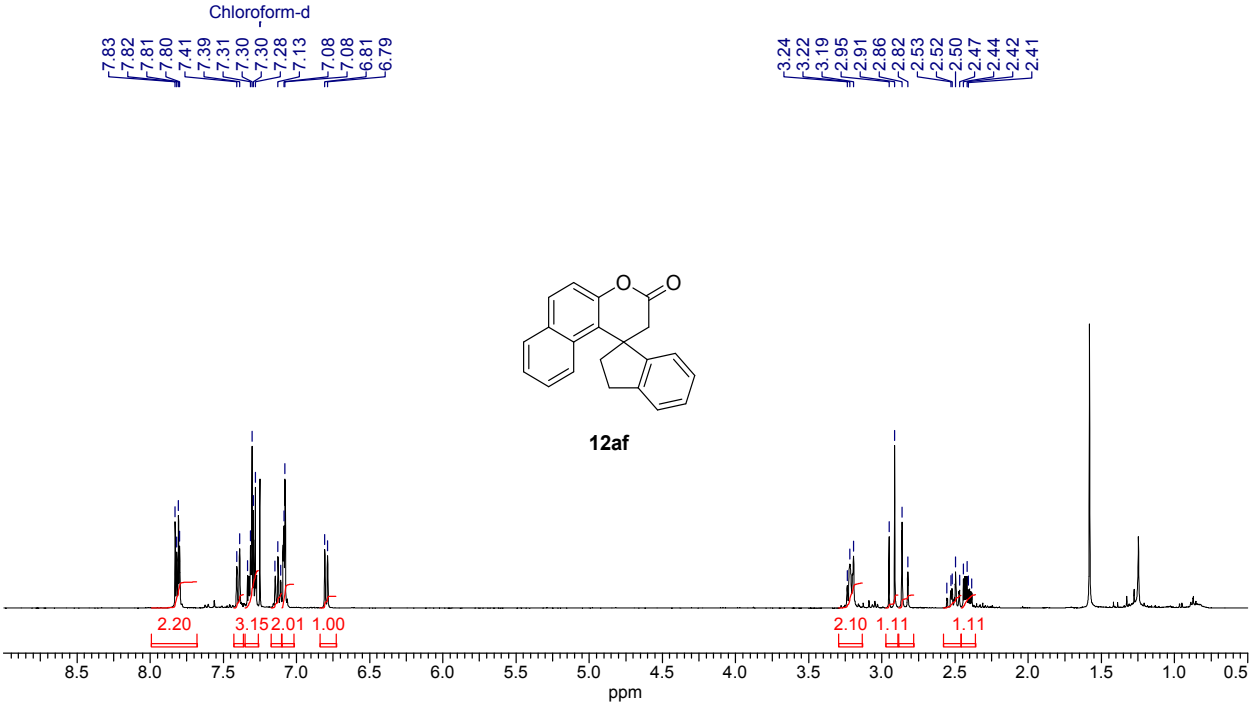
^{13}C NMR (100 MHz) spectrum of **12ac** in $CDCl_3$



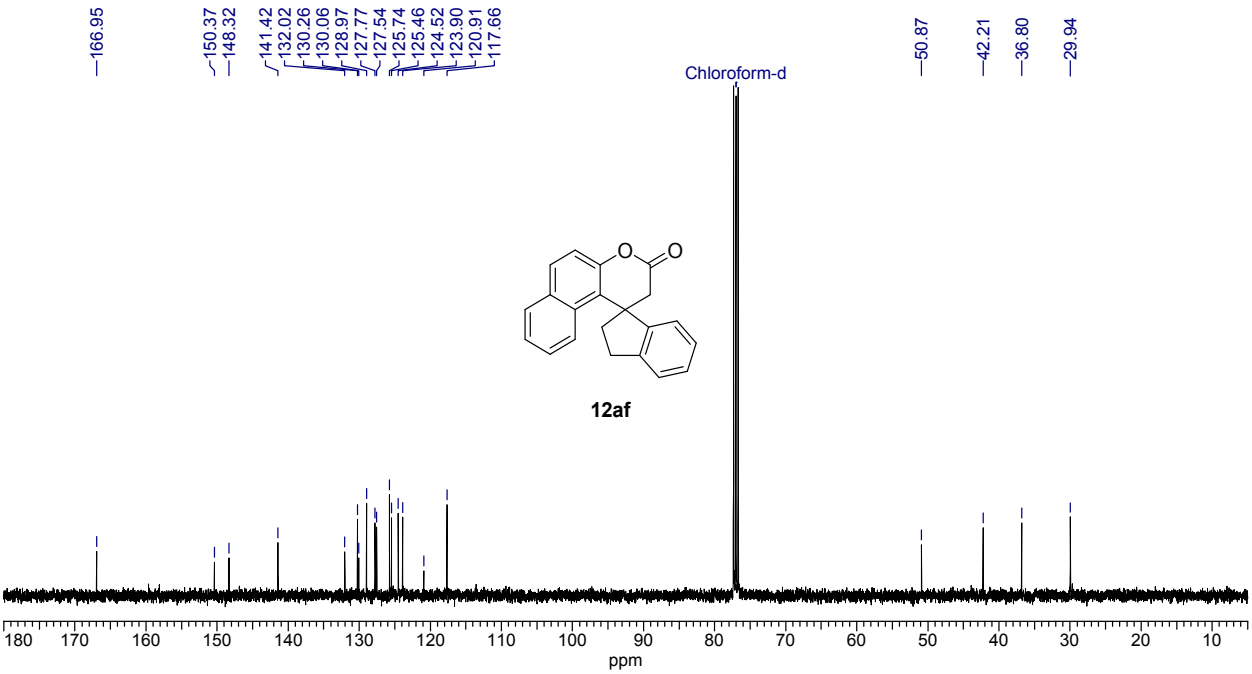
^{1}H NMR (400 MHz) spectrum of **12ad** in $CDCl_3$



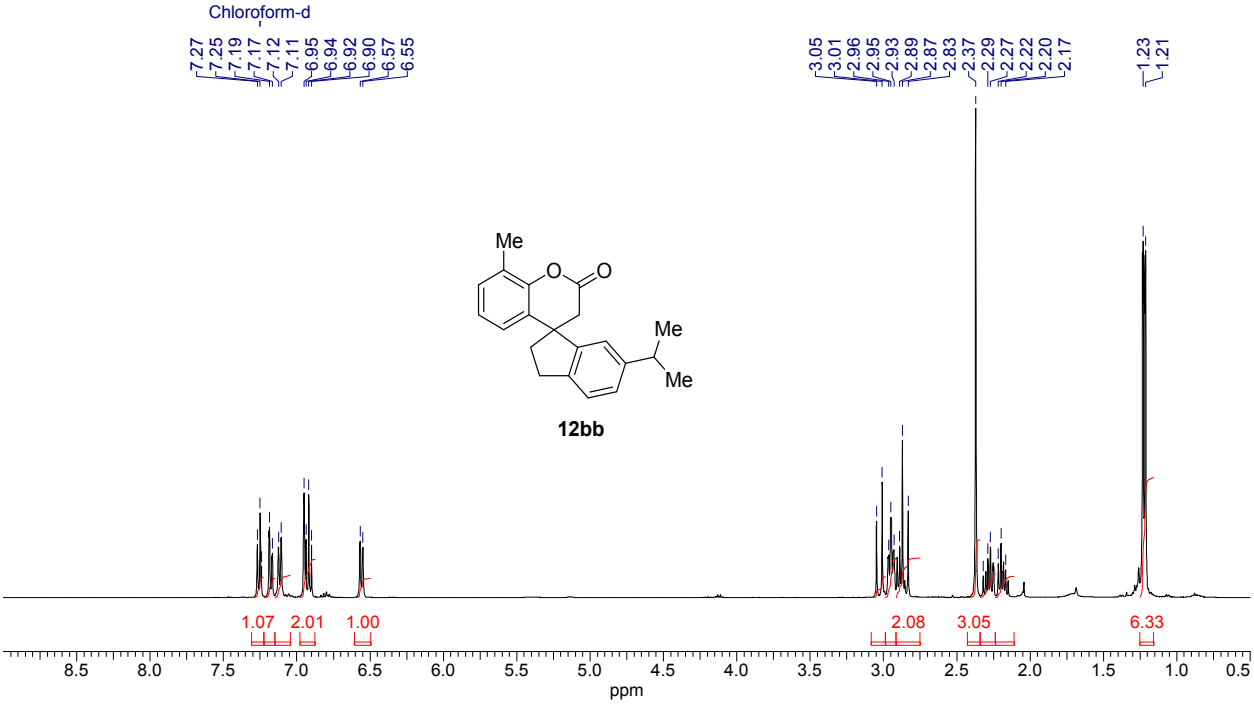
^{13}C NMR (100 MHz) spectrum of **12ad** in $CDCl_3$



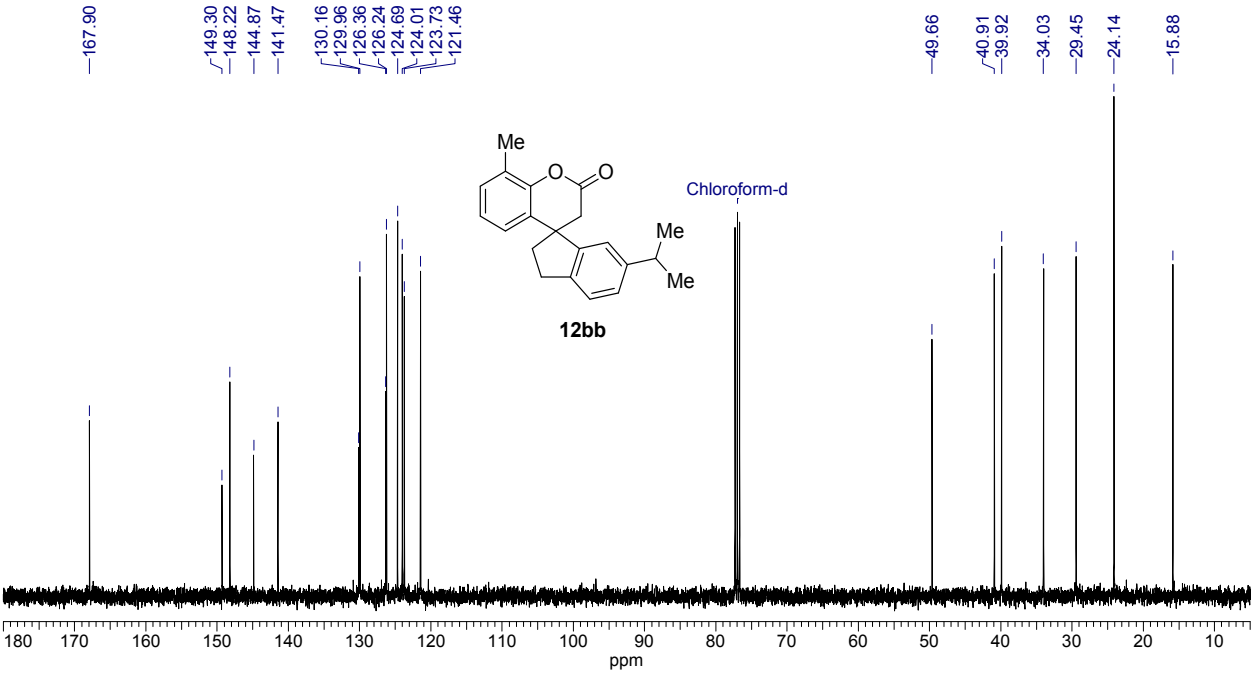
^{1}H NMR (400 MHz) spectrum of **12af** in $CDCl_3$



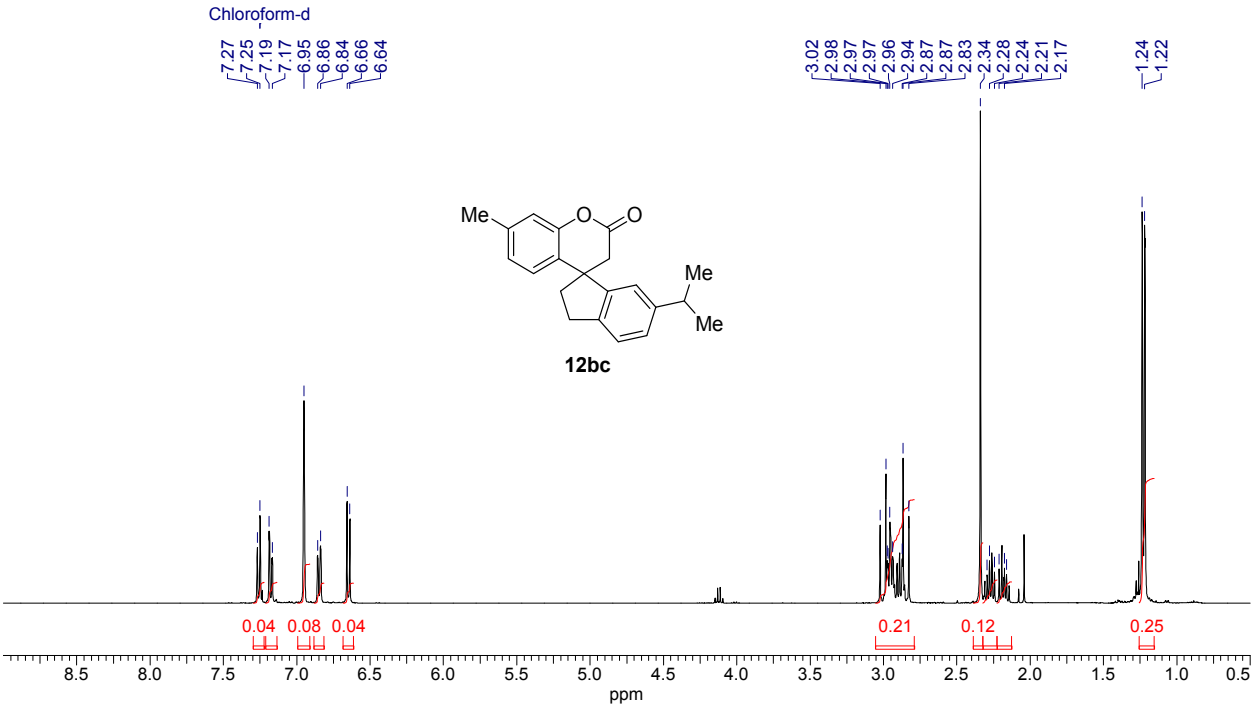
^{13}C NMR (100 MHz) spectrum of **12af** in $CDCl_3$



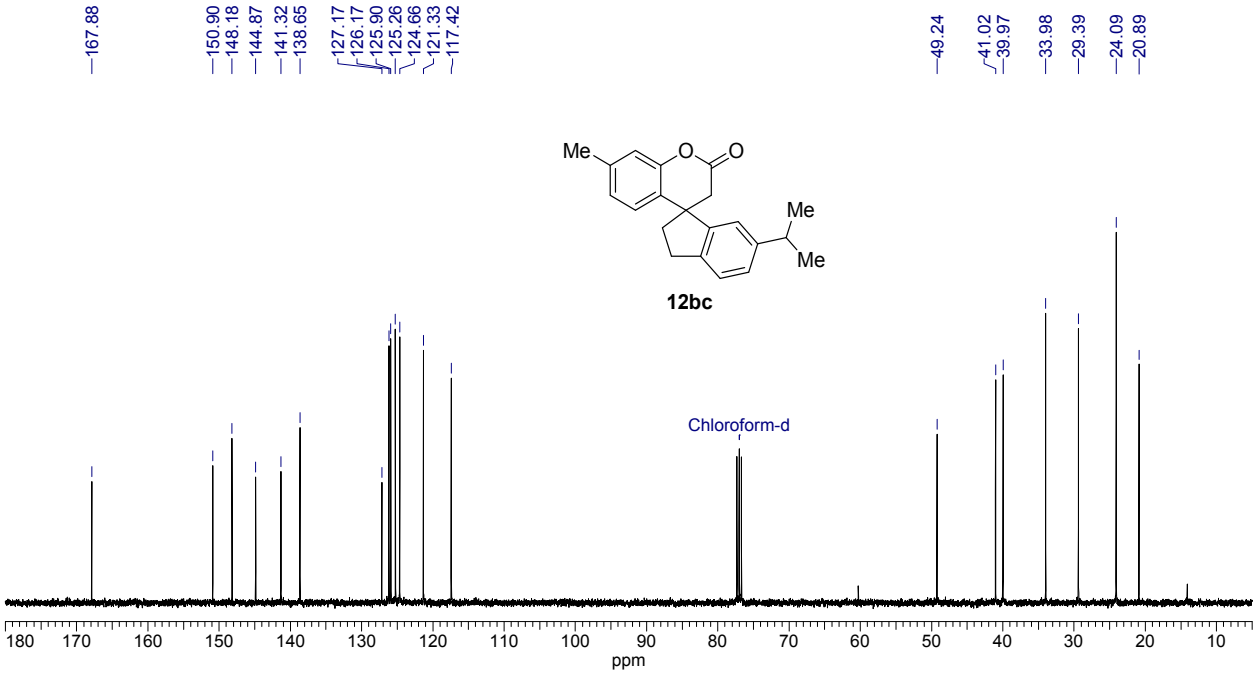
^{1}H NMR (400 MHz) spectrum of **12bb** in $CDCl_3$



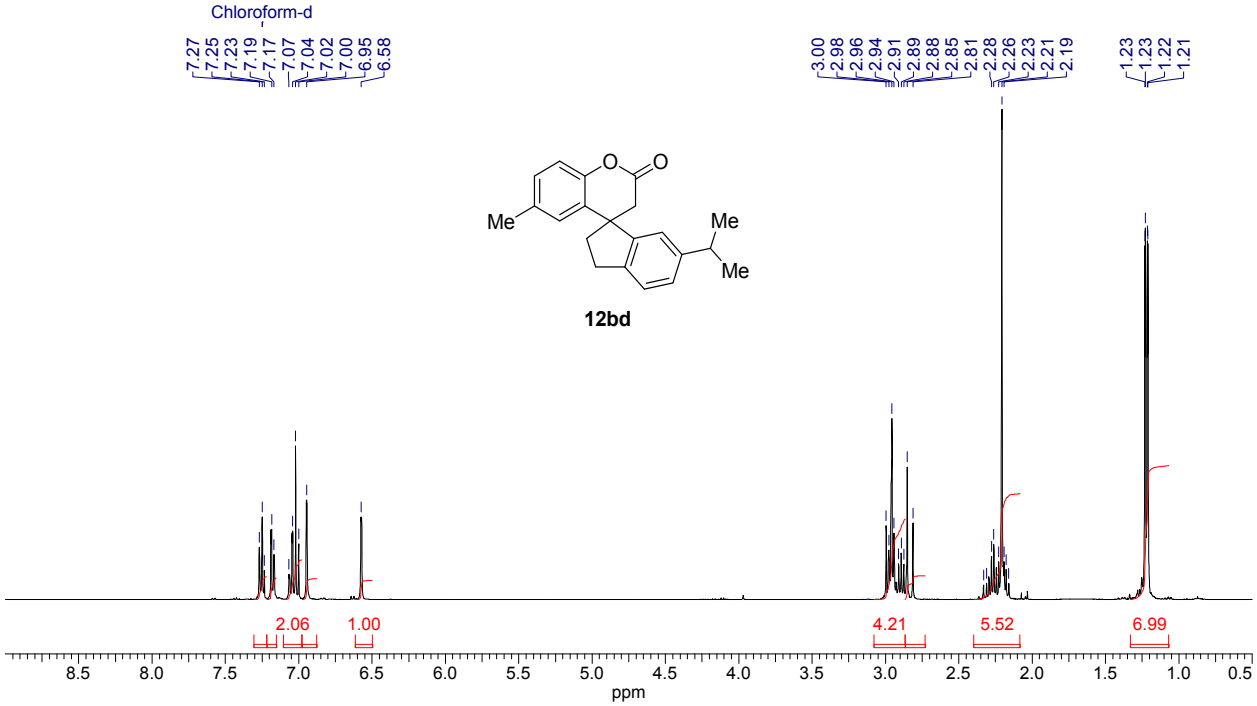
^{13}C NMR (100 MHz) spectrum of **12bb** in $CDCl_3$



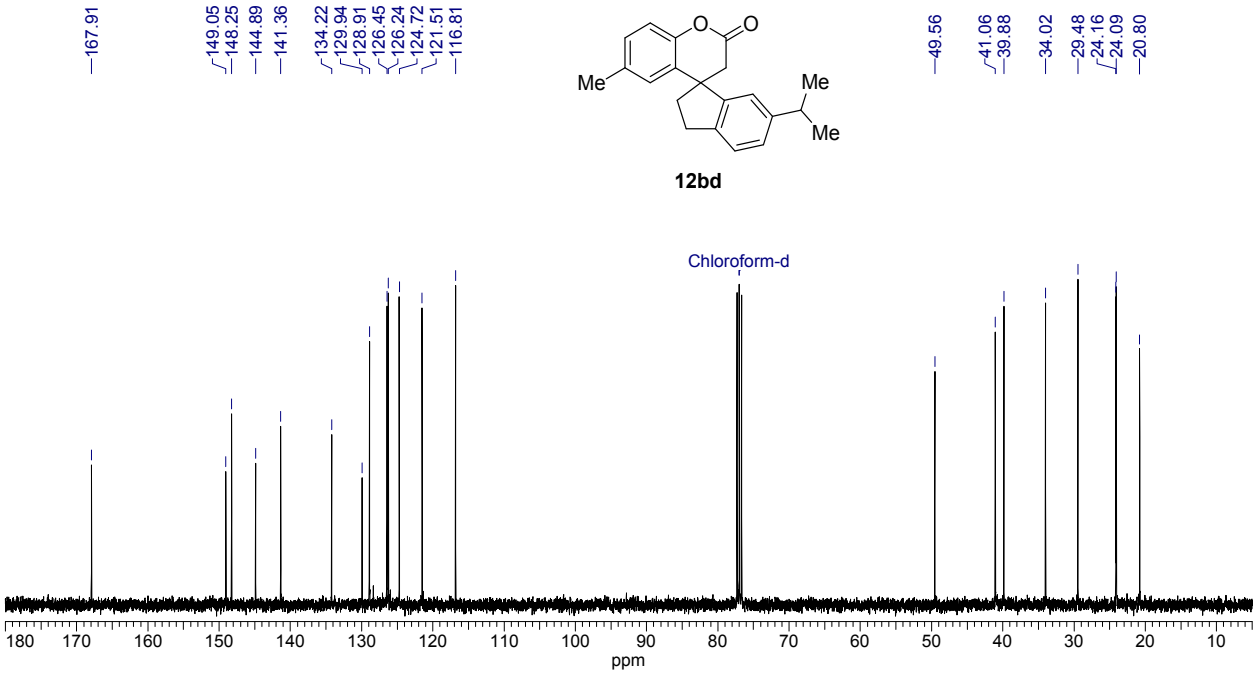
^{1}H NMR (400 MHz) spectrum of **12bc** in $CDCl_3$



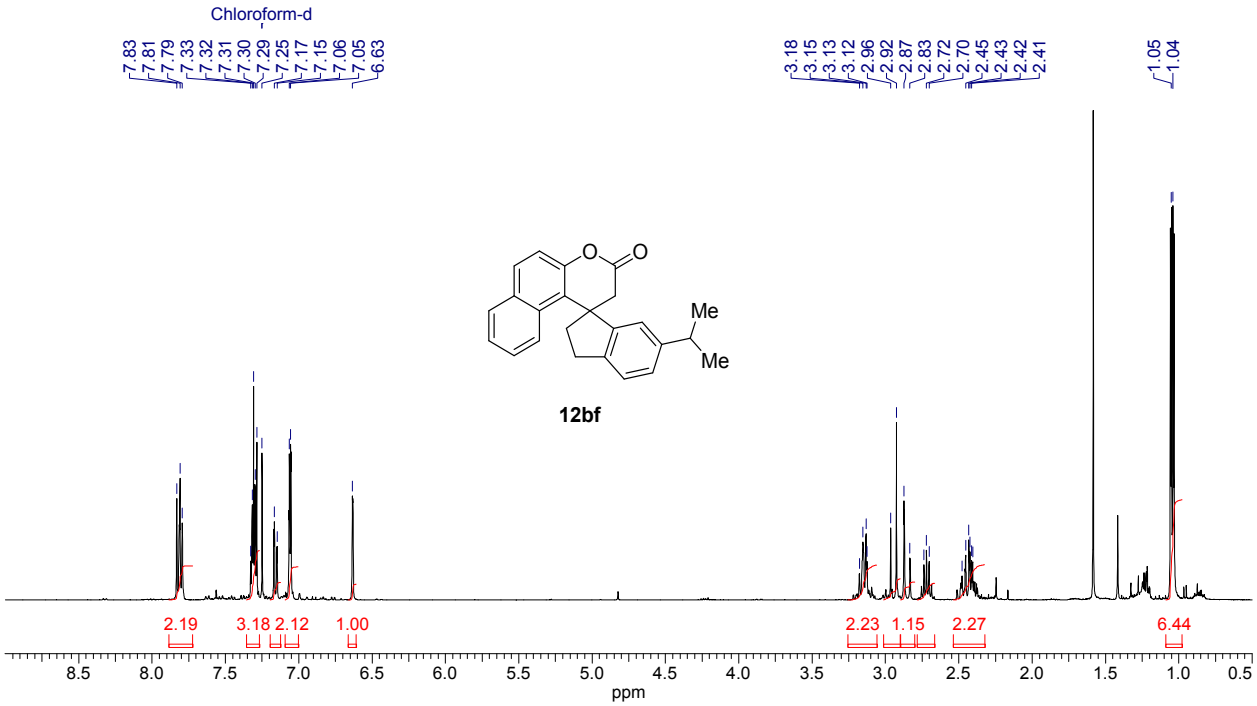
^{13}C NMR (100 MHz) spectrum of **12bc** in $CDCl_3$



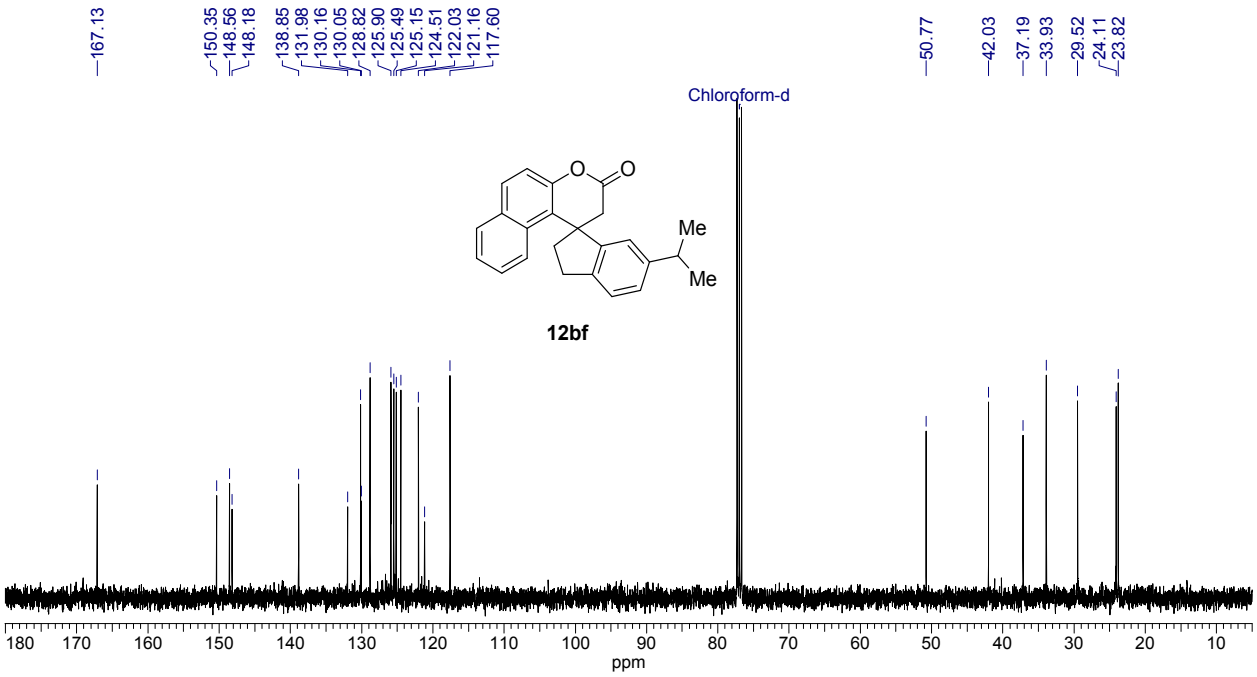
^{1}H NMR (400 MHz) spectrum of **12bd** in $CDCl_3$



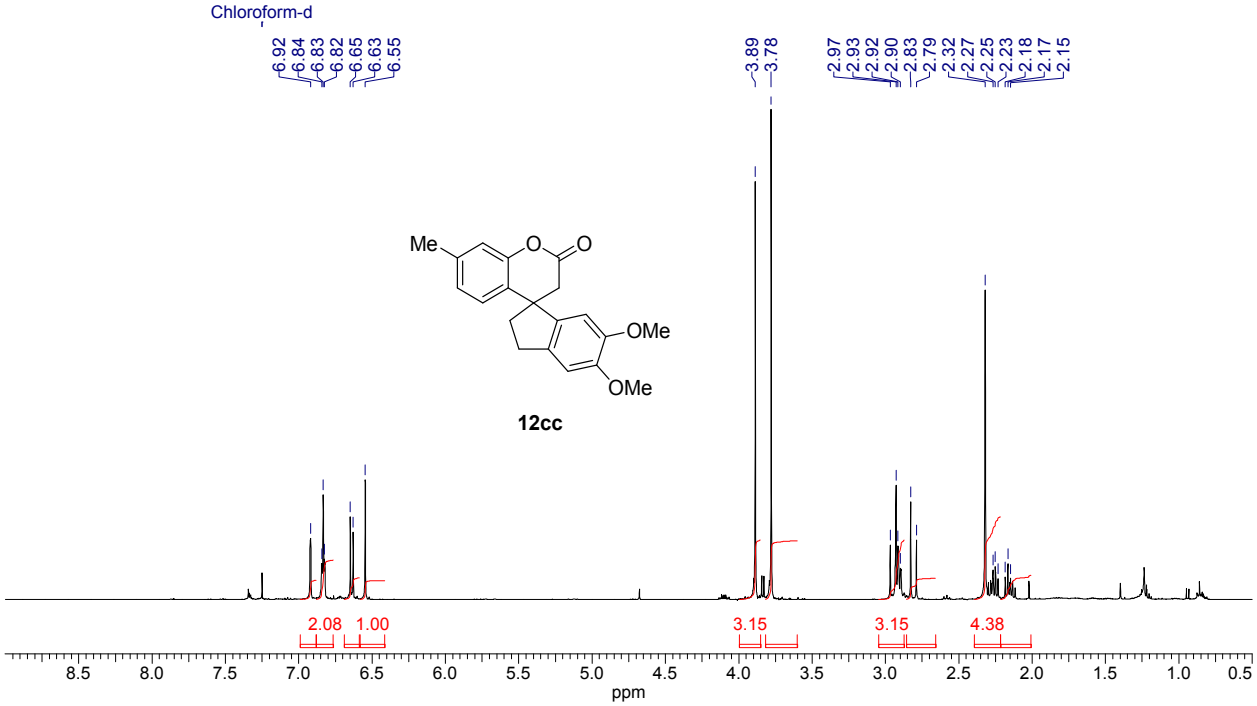
^{13}C NMR (100 MHz) spectrum of **12bd** in $CDCl_3$



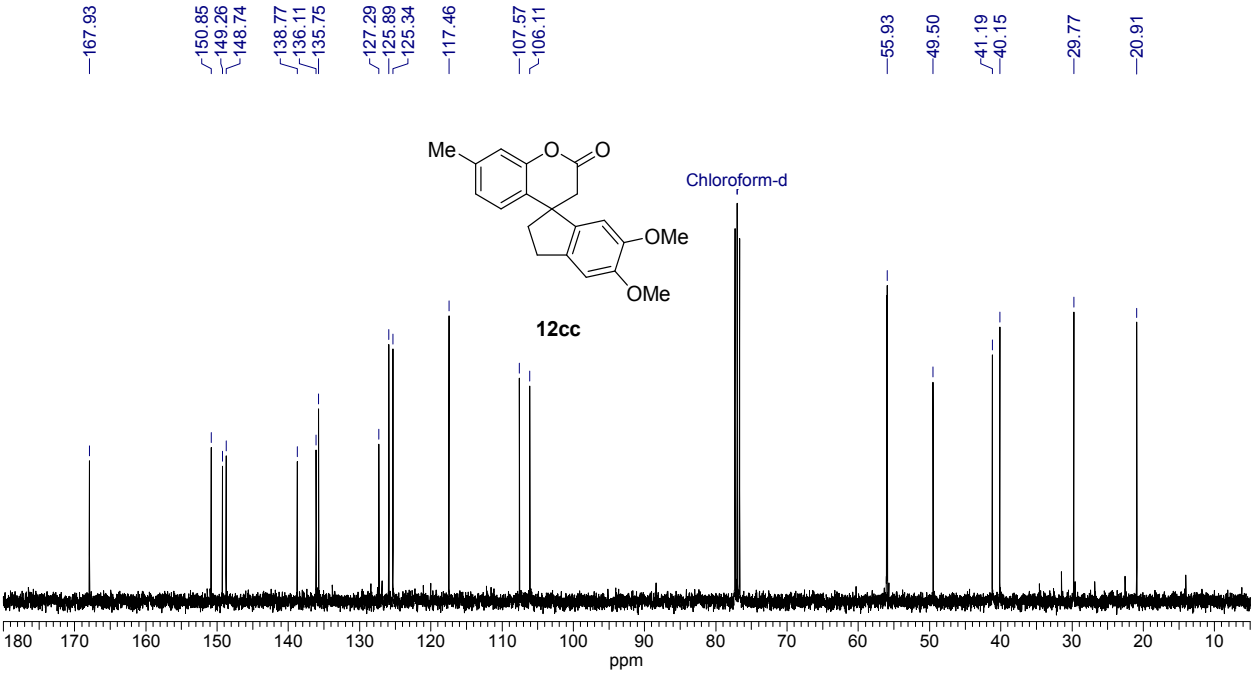
^{1}H NMR (400 MHz) spectrum of **12bf** in $CDCl_3$



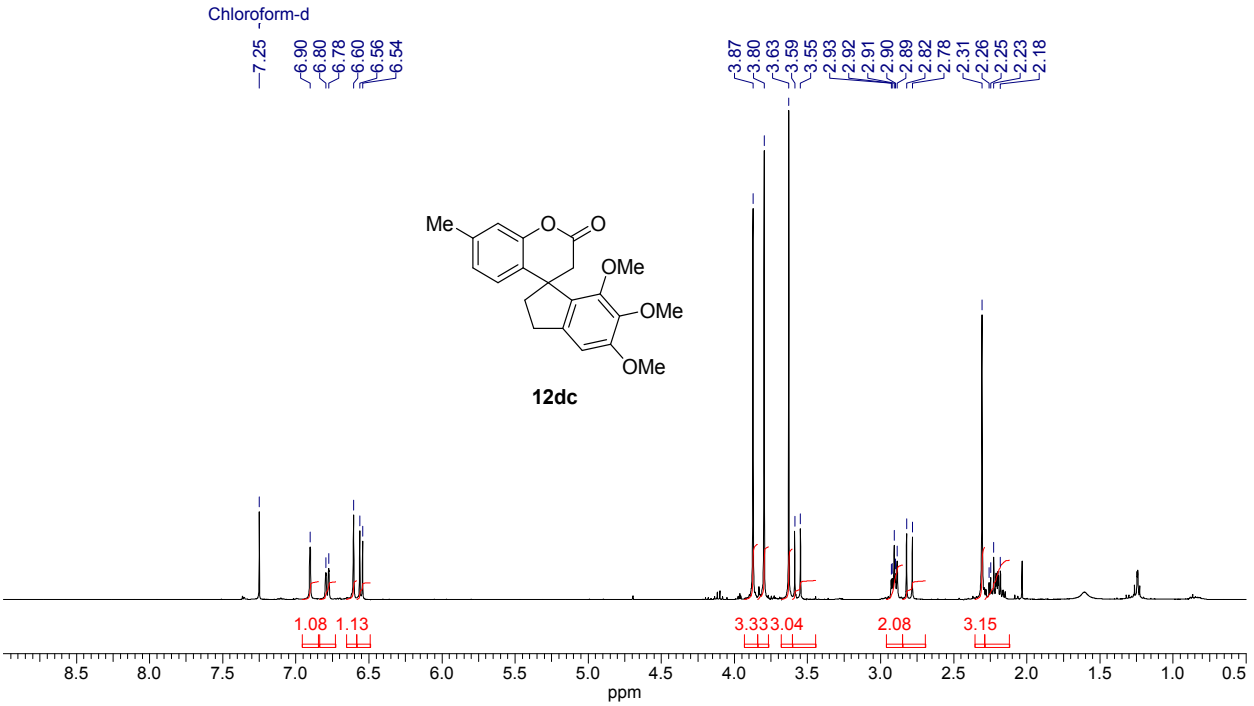
^{13}C NMR (100 MHz) spectrum of **12bf** in $CDCl_3$



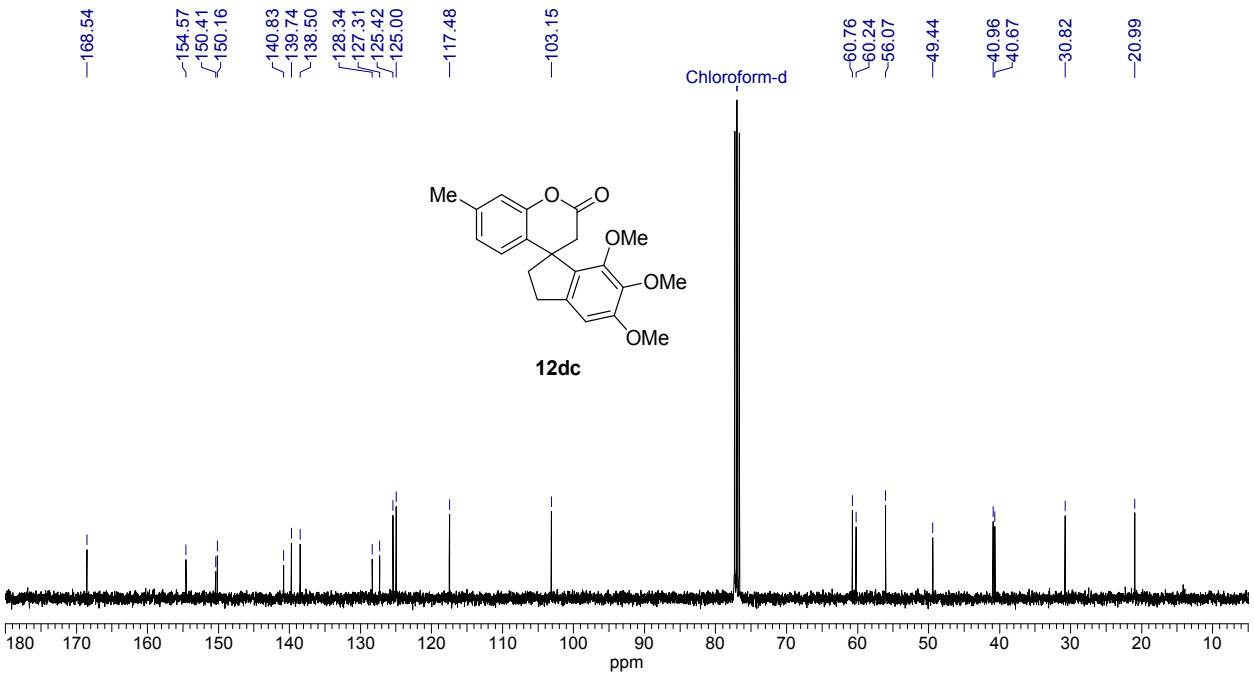
^{1}H NMR (400 MHz) spectrum of **12cc** in $CDCl_3$



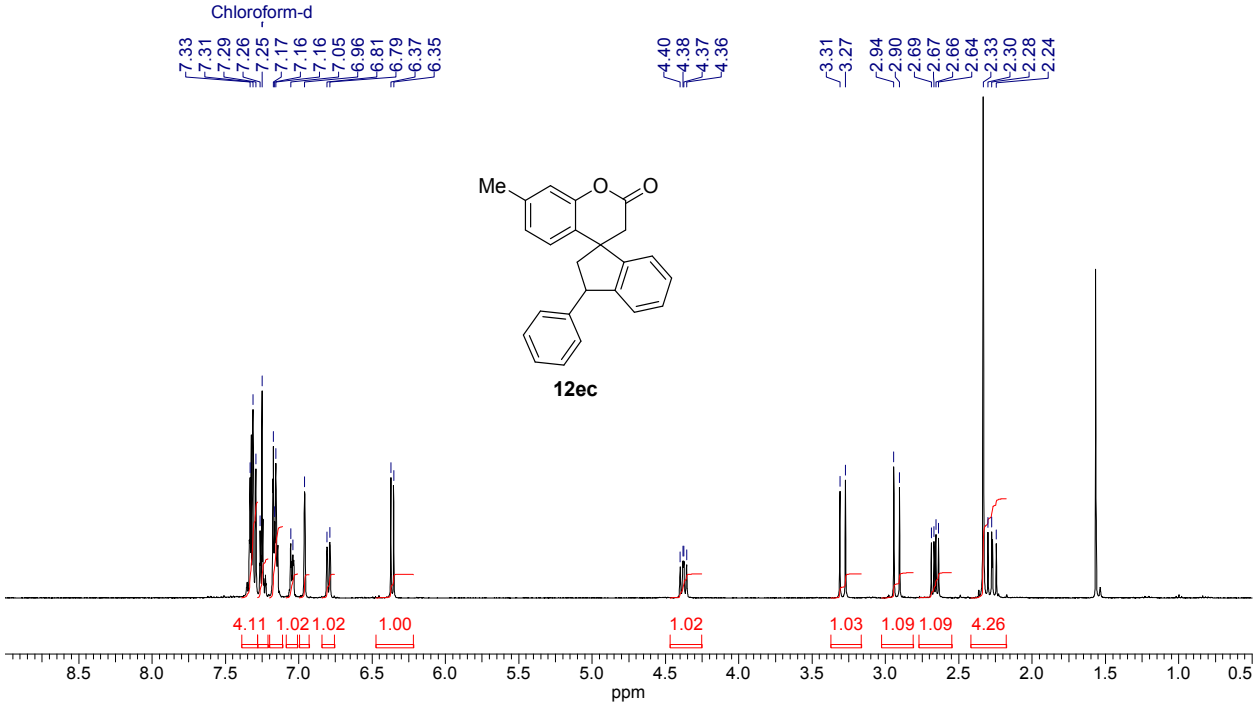
^{13}C NMR (100 MHz) spectrum of **12cc** in $CDCl_3$



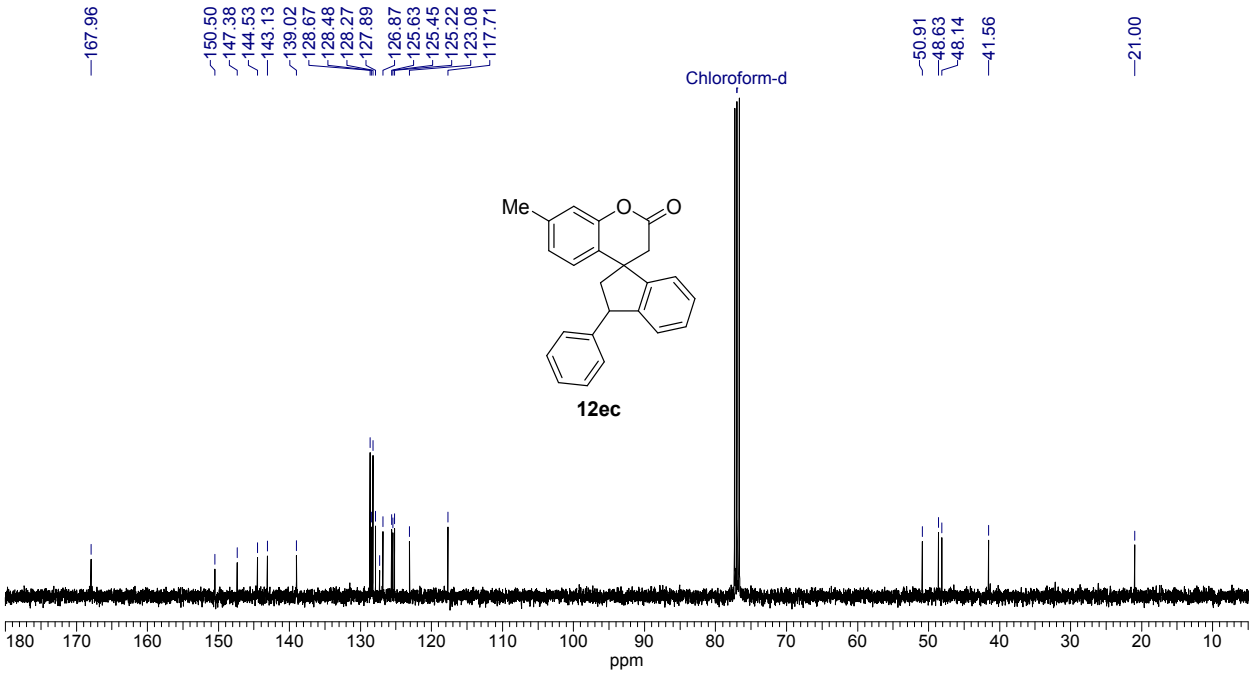
^{1}H NMR (400 MHz) spectrum of **12dc** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of **12dc** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of **12ec** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of **12ec** in $CDCl_3$