An Efficient Domino Sonogashira/Double Carbopalladation/C–H Activation Reaction Leading To Fluoresecent Polycyclic Aromatic Hydrocarbons

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Supporting Information

General methods

Experimental methods: All air-sensitive reactions were performed under an argon atmosphere in flame-dried flasks and the reactants were introduced by syringe or transfer cannula. All solvents were dried by standard methods and the reagents obtained from commercial sources were used without further purification. Thin-layer chromatography was performed on precoated silica gel plates (SIL G/UV_{254}, Machery-Nagel GmbH & Co. Kg). Silica gel 60 (0.032–0.064 mm, Merck) was used for column chromatography.

NMR spectroscopy: NMR spectra were recorded with a Varian Mercury-300, Unity-300, Inova-500 and Inova-600 spectrometer and a Bruker AMX-300 spectrometer in $CDCl_3$; chemical shifts are given in ppm relative to tetramethylsilane (TMS), coupling constants *J* in Hertz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. The multiplicities of first order were assigned as: s (singlet), s_{br} (broad singlet), d (doublet), t (triplet), q (quartet), p (pentet), dd (doublet of doublets), etc. Signals of higher orders were assigned as m (multiplet) respectively m_C (centered multiplet).

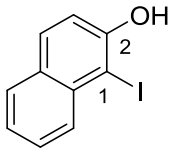
IR spectroscopy: IR spectra were recorded with a JASCO FT/IR-4100 spectrometer. All substances were applied neat on an ATR unit.

UV spectroscopy: UV spectra were recorded with a JASCO V-630 spectrometer.

Mass spectrometry: ESI-MS and ESI-HRMS spectra were recorded with a Bruker Daltronik Apex IV, EI-MS and EI-HRMS spectra were recorded with a Thermo Finnigan MAT 95.

The following abbreviations were used: aq. (aqueous), DMF (dimethyl formamide), DMSO (dimethyl sulfoxide), EtOAc (ethyl acetate), MTBE (methyl *tert*butyl ether), PE (petroleum ether, bp = 40–60 °C), r.t. (room temperature), sat. (saturated).

1-Iodo-2-naphthol (8)[1]



A solution of H_2SO_4 (5.5 mL, 10 g, 104 mmol, 1.5 equiv.) in MeOH (200 mL) was charged with 2-naphthol **7** (10.0 g, 69.4 mmol, 1.00 equiv.), KI (11.5 g, 69.4 mmol, 1.00 equiv.) and 30% aq. H_2O_2 solution (37.4 mL, 139 mmol, 2.00 equiv.) at 0 °C and stirred at this temperature for 1 h. After addition of sat. aq. $NaHSO_3$ solution (200 mL) and H_2O (100 mL) the mixture was extracted with CH_2Cl_2 (300 mL), the organic layer was washed with H_2O (300 mL), dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. Column chromatography (*n*-pentane/CH_2Cl_2 5:1) yielded iodide **8** as a yellow solid (13.5 g, 50.0 mmol, 72 %).

TLC: R_f = 0.25 (*n*-pentane/CH_2Cl_2, 5:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 231 (4.772), 282 (3.744), 294 (3.673), 324 (3.408), 334 (3.476).

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 3233, 1621, 1599, 1494, 1344, 1206, 806, 742.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.77 (s, 1 H, OH), 7.24 (d, *J* = 8.9 Hz, 1 H, 3-H), 7.36 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1 H, 5-H), 7.53 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1 H, 6-H), 7.69–7.75 (m, 2 H, 7-H, 8-H) 7.91 (dd, *J* = 8.5, 0.9 Hz, 1 H, 4-H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 86.2 (C-1), 116.4 (C-3), 124.2 (C-6), 128.2 (C-5), 128.3 (C-7), 129.7 (C-4a), 130.2 (C-8), 130.6 (C-4), 134.8 (C-8a), 153.7 (C-2).

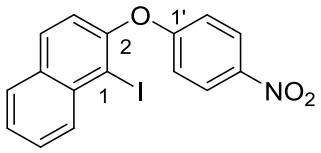
MS (EI): *m*/*z* = 143.0 (25) $[M-I]^+$, 270.0 (100) $[M]^+$.

HRMS (EI): *m*/*z* = found: 269.9533, calcd.: 269.9542 $[M]^+$.

$C_{10}H_7IO$ (270.07).

[1] For original procedure see: T. Kometani *et al*, *J. Org. Chem*. **1985**, *50*, 5384–5387.
Experimental Data from: T. Hungerland, *Dissertation*, Georg-August-Universität, Göttingen, **2013**; M. A. Düfert, *Dissertation*, Georg-August-Universität, Göttingen, **2010**.

1-Iodo-2-(4-nitrophenoxy)naphthalene (1a)[2]



A mixture of 1-iodo-2-naphthol **8** (5.00 g, 18.5 mmol, 1.00 equiv.) and K_2CO_3 (7.67 g, 55.5 mmol, 3.00 equiv.) in DMSO (50 mL) was stirred at 95 °C for 15 min. 4-Fluoronitrobenzene **9** (1.96 mL, 2.61 g, 18.5 mmol, 1.00 equiv.) was added and the reaction mixture was stirred at 95 °C for 24 h. After the addition of H_2O (200 mL) the mixture was extracted with MTBE (4 × 200 mL), the combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. Recrystallization from *n*-hexane (300 mL) and CH_2Cl_2 (100 mL) yielded biarylic ether **1a** as a brown solid (5.69 g, 14.5 mmol, 78 %).

TLC: R_f = 0.19 (*n*-pentane/CH_2Cl_2, 5:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 228 (4.686), 291 (4.245).

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 1583, 1504, 1484, 1331, 1237, 1108, 842, 798, 746.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.96–7.01 (m, 2 H, 2'-H, 6'-H), 7.21 (d, *J* = 8.7 Hz, 1 H, 3-H), 7.56 (t, *J* = 7.5 Hz, 1 H, 6-H), 7.64 (t, *J* = 7.7 Hz, 1 H, 7-H), 7.85 (d, *J* = 8.7 Hz, 1 H, 5-H), 7.90 (d, *J* = 8.7 Hz, 1 H, 4-H), 7.85 (d, *J* = 8.7 Hz, 1 H, 5-H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 94.1 (C-1), 116.6 (C-2', C-6'), 120.3 (C-3), 126.0 (C-3', C-5'), 126.6 (C-6), 128.4 (C-5), 128.6 (C-7), 131.2 (C-4), 131.9 (C-4a), 132.0 (C-8), 135.7 (C-8a), 142.9 (C-4'), 152.6 (C-2), 162.4 (C-1').

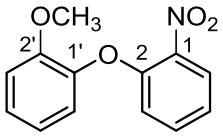
MS (EI): *m*/*z* = 218.1 (43) $[M\text{-}I\text{-}NO_2]^+$, 263.1 (6) $[M\text{-}I]^+$, 391.0 (100) $[M]^+$.

HRMS (EI): *m*/*z* = found: 390.9689, calcd.: 390.9705 $[M]^+$.

$C_{16}H_{10}INO_3$ (391.16).

[2] Original procedure and experimental data from: T. Hungerland, *Dissertation*, Georg-August-Universität, Göttingen, **2013**.

1-Methoxy-2-(2-nitrophenoxy)benzene (13)[3]



A mixture of 2-methoxyphenol (1.80 mL, 2.00 g, 16.1 mmol, 1.00 equiv.), 2-fluoronitrobenzene (1.70 mL, 2.27 g, 16.1 mmol, 1.00 equiv.) and K_2CO_3 (4.45 g, 32.2 mmol, 2.00 equiv.) in DMSO (40 mL) was stirred at 95 °C for 20 h. After cooling to r.t. the mixture was treated with H_2O (100 mL) and the insoluble parts were filtered off and kept, as they contained the final product. The filtrate was extracted with MTBE (3 × 100 mL). The combined organic extracts were washed with brine (200 mL), dried over Na_2SO_4, filtered and the solvent was removed *in vacuo* to yield biarylic ether **13** as a yellow oil (3.96 g, quant.) with little impurities.

TLC: R_f = 0.35 (*n*-pentane/EtOAc, 10:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 194 (4.7202), 264 (3.7487), 319 (3.4631).

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 1606, 1584, 1523, 1496, 1480, 1471, 1455, 1439, 1349, 1305, 1263, 1231, 1197, 1175, 1163, 1147, 1111, 1089, 1043, 1018, 883, 846, 801, 770, 746, 738, 694, 665.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.75 (s, 3 H, OCH_3), 6.80 (dd, *J* = 8.5, 1.2 Hz, 1 H), 6.94 (td, *J* = 7.7, 1.4 Hz, 1 H), 6.99 (dd, *J* = 8.2, 1.4 Hz, 1 H), 7.06 (dd, *J* = 8.0, 1.7 Hz, 1 H), 7.08 (td, *J* = 7.9, 1.2 Hz, 1 H), 7.18 (td, *J* = 7.8, 1.6 Hz, 1 H), 7.39 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1 H) 7.92 (dd, *J* = 8.2, 1.7 Hz, 1 H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 55.9 (OCH_3), 113.2, 118.1, 121.3, 121.8, 122.0, 125.6, 126.3, 133.9, 140.0, 143.3, 151.3, 151.7.

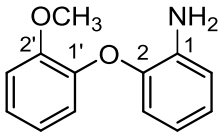
MS (ESI): *m*/*z* (%) = 246.1 (100) $[M+H]^+$, 263.1 (94) $[M+Na]^+$, 268.1 (92) $[M+Na]^+$.

HRMS (ESI): *m*/*z* = found: 246.0763, calcd.: 246.0761 $[M+H]^+$.

$C_{13}H_{11}NO_4$ (245.23).

[3] For original procedure see: J. A. De la Fuente, *J. Med. Chem*. **2003**, *46*, 5208–5221.

2-(2-Methoxyphenoxy)aniline (14)[4]



Conc. HCl (50 mL) and afterwards conc. AcOH (50 mL) were added drop wise to a solution of 1-methoxy-2-(2-nitrophenoxy)benzene **13** (3.95 g, 17.0 mmol, 1.00 equiv.) in EtOAc (100 mL) at 0 °C. Zinc powder (33.3 g, 510 mmol, 30.0 equiv.) was added in portions, the solution was warmed to r.t. and stirred at this temperature for 30 min. The reaction mixture was cooled to 0 °C and 33 % aq. NH_3 solution (200 mL) was added drop wise. The mixture was extracted with CH_2Cl_2 (3 × 300 mL) and the combined organic extracts were dried over Na_2SO_4 and filtered. Removal of the solvent *in vacuo* yielded amine **14** as a brown solid (3.39 g, 15.7 mmol, 92 %) with little impurities.

TLC: R_f = 0.20 (*n*-pentane/EtOAc, 10:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 196 (4.6806), 279 (3.6116).

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 3446, 3360, 1627, 1592, 1580, 1493, 1452, 1438, 1329, 1299, 1249, 1210, 1190, 1181, 1162, 1149, 1113, 1042, 1024, 883, 785, 745, 722, 681, 671, 586, 572, 551, 530.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.71 (s_{br}, 2 H, NH_2), 3.86 (s, 3 H, OCH_3), 6.67 (ddd, *J* = 7.9, 7.4, 1.5 Hz, 1 H, 4-H), 6.76 (dd, *J* = 8.1, 1.4 Hz, 1 H, 3-H), 6.81 (dd, *J* = 7.9, 1.5 Hz, 1 H, 6-H), 6.84–6.87 (m, 2 H, 5'-H, 6'-H), 6.92 (td, *J* = 7.6, 1.4 Hz, 1 H, 5-H), 6.97 (d, *J* = 8.1 Hz, 1 H, 3'-H), 7.05 (dt, *J* = 8.0, 4.4 Hz, 1 H, 4'-H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 56.0 (OCH_3), 112.6 (C-3'), 116.4 (C-6), 118.5, 118.8, 118.8 (C-3, C-4, C-5'/C-6'), 121.0 (C-5'/C-6'), 123.9 (C-4'), 124.1 (C-5), 137.6 (C-1), 144.3 (C-2), 145.8 (C-2'), 150.5 (C-2).

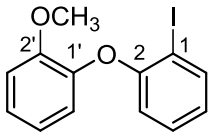
MS (ESI): *m*/*z* (%) = 216.1 (100) $[M+H]^+$, 238.1 (13) $[M+Na]^+$.

HRMS (ESI): *m*/*z* = found: 216.1018, calcd.: 216.1019 $[M+Na]^+$.

$C_{13}H_{13}NO_2$ (215.25).

[4] For original procedure see: F. Wen *et al*., *Pestic. Biochem. Physiol.* **2010**, *98*, 248–253.

1-Iodo-2-(2-methoxyphenoxy)benzol (1d)[5]



A solution of KI (5.18 g, 31.2 mmol, 2.00 equiv.) and $NaNO_2$ (2.15 g, 31.2 mmol, 2.00 equiv.) in H_2O (50 mL) was added drop wise to a solution of 2-(2-methoxyphenoxy)aniline **14** (3.11 g, 15.6 mmol, 1.00 equiv.) and *p*-TsOH·H_2O (8.90 g, 46.8 mmol, 3.00 equiv.) in CH_3CN (100 mL) and stirred at r.t. for 2 h. The reaction mixture was treated with sat. aq. $NaHCO_3$ solution (100 mL) and extracted with CH_2Cl_2 (3 × 300 mL). The combined organic extracts were concentrated *in vacuo*, diluted in CH_2Cl_2 (200 mL), washed with sat. aq. $Na_2S_2O_3$ solution (100 mL), dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. Column chromatography (SiO_2, *n*-pentane/EtOAc 100:1→50:1) yielded aryl iodide **1d** as a yellow oil (4.54 g, 13.9 mmol, 89 %).

TLC: R_f = 0.33 (*n*-pentane/EtOAc, 100:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 275 (3.6968).

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 1600, 1572, 1497, 1462, 1437, 1304, 1258, 1222, 1197, 1174, 1158, 1109, 1040, 1017, 878, 802, 770, 741, 712, 646.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.82 (s, 3 H, OCH_3), 6.66 (dd, *J* = 8.2, 1.4 Hz, 1 H, 3-H), 6.75–6.82 (m, 1 H, 5-H), 6.88–6.93 (m, 2 H, 5'-H, 6'-H), 6.97–7.02 (m, 1 H, 3'-H), 7.13 (ddd, *J* = 8.1, 5.2, 3.9 Hz, 1 H, 4'-H), 7.19 (ddd, *J* = 8.1, 7.3, 1.5 Hz, 1 H, 4-H), 7.81 (dd, *J* = 7.8, 1.5 Hz, 1 H, 6-H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 56.0 (OCH_3), 112.6 (C-3'), 116.4 (C-6), 118.5, 118.8, 118.8 (C-3, C-4, C-5'/C-6'), 121.0 (C-5'/C-6'), 123.9 (C-4'), 124.1 (C-5), 137.6 (C-1), 144.3 (C-1'), 145.8 (C-2'), 150.5 (C-2).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 56.2 (OCH_3), 87.1 (C-1), 113.2 (C-3'), 116.8 (C-3), 120.7, 121.1 (C-5', C-6'), 124.3 (C-5), 125.1 (C-4'), 129.3 (C-4), 139.6 (C-6), 144.9 (C-1'), 151.2 (C-2'), 157.1 (C-2).

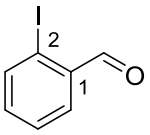
MS (ESI): *m*/*z* (%) = 349.0 (100) $[M+Na]^+$.

HRMS (ESI): *m*/*z* = found: 348.9699, calcd.: 348.9696 $[M+Na]^+$.

$C_{13}H_{11}IO_2$ (326.13).

[5] General method from: E. A. Krasnokutskaya, N. I. Semenischeva, V. D. Filimonov, P. Knochel, *Synthesis* **2007**, 81–84.

2-Iodobenzaldehyde (15)[6]



MnO_2 (12.3 g, 141 mmol, 30.0 equiv.) was added in portions to a solution of (2-Iodophenyl)methanol (1.10 g, 4.70 mmol, 1.00 equiv.) in CH_2Cl_2 (50 mL) and the resulting mixture was stirred at r.t. for 6.5 h. Column filtration (SiO_2, EtOAc) yielded aldehyde **15** as a yellow oil (841 mg, 3.62 mmol, 77 %).

TLC: R_f = 0.13 (*n*-pentane).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.21–7.34 (m, 1 H, 4-H), 7.45 (tt, *J* = 7.7, 1.0 Hz, 1 H, 5-H), 7.86 (dd, *J* = 7.8, 1.8 Hz, 1 H, 3-H), 7.93 (dd, *J* = 7.9, 1.1 Hz, 1 H, 6-H), 10.05 (d, *J* = 0.8 Hz, 1 H, CHO).

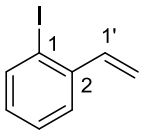
^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 100.6 (C-2), 128.7, 130.2 (C-4, C-5), 135.1 (C-1), 135.4, 140.6 (C-3, C-6), 195.7 (CHO).

HRMS (ESI): *m*/*z* = found: 232.9457, calcd.: 232.9458 $[M+H]^+$.

C_7H_5IO (232.02).

[6] For original procedure see: W. S. Rapson, R. G. Shuttleworth, *J. Chem. Soc*. **1941**, 487–490.

1-Iodo-2-vinylbenzene (1f)[7]



n-Butyllithium (2.5 M in *n*-hexane, 1.59 mL, 3.98 mmol, 1.10 equiv.) was added drop wise to a suspension of $MePPh_3^+Br^-$ (1.55 g, 4.34 mmol, 1.20 equiv.) in THF (60 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min, a solution of **15** (841 mg, 3.62 mmol, 1.00 equiv.) in THF (10 mL) was added and the mixture was warmed to r.t. over 15 h. After addition of H_2O (100 mL) the mixture was extracted with CH_2Cl_2 (3 × 100 mL), the combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. Column chromatography (SiO_2, *n*-pentane) yielded alkene **1f** as a colourless oil (678 mg, 2.95 mmol, 81 %).

TLC: R_f = 0.68 (*n*-pentane).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 221 (4.2637), 245 (4.0409).

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 3057, 2921, 1951, 1915, 1836, 1802, 1623, 1582, 1556, 1461, 1433, 1412, 1275, 1202, 1009, 982, 914, 760, 726, 646, 570.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.31 (dd, J = 10.9, 1.0 Hz, 1 H, 2'-H_a), 5.62 (dd, J = 17.3, 1.0 Hz, 1 H, 2'-H_b), 6.83–6.90 (m, 1 H), 6.90–6.97 (m, 1 H) (4-H, 5-H), 7.30 (dddd, J = 7.8, 7.3, 1.3, 0.6 Hz, 1 H, 1'-H), 7.50 (dd, J = 7.8, 1.7 Hz, 1 H, 6-H), 7.82 (dd, J = 8.0, 1.3 Hz, 1 H, 3-H).

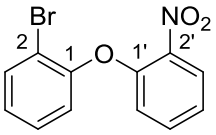
^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 99.6, 116.8, 126.3, 128.3, 129.2, 139.4, 140.6, 140.7.

MS (EI): *m*/*z* (%) = 230.0 (100) $[M]^+$, 77.0 (61) $[C_6H_5]^+$.

C_8H_7I (230.05).

[7] For original procedure see: M. R. Acheson, G. C. M. Lee, *J. Chem. Soc., Perkin Trans. 1* **1987**, *11*, 2321–2332. Method applied from: D. Sun *et al.*, *Synth. Commun*. **2007**, *37*, 2989–2994.

1-Bromo-2-(2-nitrophenoxy)benzene (16)[8]



A mixture of 2-bromophenol **10** (750 µL, 1.12 g, 6.47 mmol, 1.00 equiv.), 2-fluoronitrobenzene **11** (860 µL, 913 mg, 1.00 equiv.) and K_2CO_3 (1.79, g, 12.9 mmol, 2.00 equiv.) in DMSO (13 mL) was stirred at 95 °C for 23 h. After cooling to r.t. the mixture was poured into H_2O (100 mL) and extracted with CH_2Cl_2 (4 × 30 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. Column chromatography (SiO_2, PE/EtOAc 10:1) yielded biarylic ether **16** (2.04 g, quant.) which was used in the next step without further purification.

TLC: R_f = 0.32 (PE/EtOAc, 10:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 194 (4.7724), 255 (3.6540), 313 (3.3391).

IR (Film): $\tilde{\nu}$ (cm^{-1}) = 1606, 1586, 1524, 1468, 1351, 1264, 1242, 1121, 1046, 882, 844, 798, 744.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.83 (dd, J = 8.4, 1.2 Hz, 1 H, 6'-H), 7.03 (dd, J = 8.1, 1.5 Hz, 1 H, 6-H), 7.09 (dt, J = 8.1, 1.5 Hz, 1 H, 4-H), 7.19 (dt, J = 8.4, 1.0 Hz, 1 H, 4'-H), 7.31 (dt, J = 8.1, 1.7 Hz, 1 H, 5-H), 7.47 (dt, J = 8.4, 1.7 Hz, 1 H, 5'-H), 7.64 (dd, J = 7.9, 1.7 Hz, 1 H, 3-H), 7.96 (dd, J = 8.2, 1.7 Hz, 1 H, 3'-H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 115.2 (C-2), 119.0 (C-6'), 121.2 (C-6), 123.1 (C-4'), 125.8 (C-3'), 126.3 (C-4), 128.9 (C-5), 134.1 (C-3), 134.(C-5'), 140.5 (C-2'), 150.1 (C-1'), 152.0 (C-1).

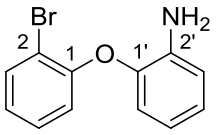
MS (ESI): *m/z* (%) = 318.0 (87) $[M+Na]^+$, 333.9 (81) $[M+K]^+$, 610.9 (100) $[2M+Na]^+$, 626.9 (46) $[2M+K]^+$.

HRMS (ESI): *m/z* = found: 315.9579, calcd.: 315.9580 $[M+Na]^+$.

$C_{12}H_8BrNO_3$ (294.10).

[8] For original procedure see: C. Bjorklund, R. Wahren, Robert, *Acta Chem. Scand.* **1976**, *B30*, 6, 576–578; Experimental data from: M. A. Düfert, *Disseration*, Georg-August-Universität, Göttingen, **2010**.

1-Bromo-2-(2-aminophenoxy)benzene (17)[9]



Conc. HCl (50 mL) and afterwards conc. AcOH (50 mL) were added drop wise to a solution of **16** (2.04 g, 6.94 mmol, 1.00 equiv.) in EtOAc (20 mL) at 0 °C. Zinc powder (13.2 g, 202 mmol, 30.0 equiv.) was added in portions over 1 h and the resulting mixture was warmed to r.t. and stirred at this temperature for 15 min. After cooling to 0 °C 33% aq. NH_3 solution (105 mL) was added drop wise and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. Column chromatography (SiO_2, PE/EtOAc 10:1, 1 vol% NEt_3) yielded amine **17** as a yellow oil (1.57 g, 5.94 mmol, 86 %).

TLC: R_f = 0.38 (PE/EtOAc, 10:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 196 (4.6688), 281 (3.5327).

IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3460, 3374, 1617, 1497, 1469, 1439, 1315, 1267, 1228, 1185, 1131, 1031, 884, 821, 776, 753, 455, 434.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.84 (s_{br}, 2 H, NH_2), 6.71 (dt, *J* = 8.0, 1.5 Hz, 1 H, 4-H), 6.84 (dt, *J* = 8.0, 1.5 Hz, 3 H, 3-H, 6-H, 6'-H), 6.93–7.03 (m, 2 H, 5-H, 4'-H), 7.16–7.24 (m, 1 H, 5'-H), 7.62 (dd, *J* = 7.9, 1.5 Hz, 1 H, 3'-H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 113.1 (C-2'), 116.4 (C-6), 117.9 (C-6'), 118.5 (C-4), 119.5 (C-3), 124.0 (C-4'), 125.0 (C-4), 128.4 (C-5'), 133.5 (C-3'), 138.2 (C-2), 142.7 (C-1), 153.7 (C-1').

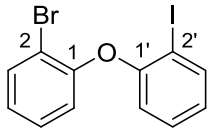
MS (ESI): *m/z* (%) = 266.0 (93) $[M+H]^+$, 286.0 (24) $[M+Na]^+$, 303.9 (31) $[M+K]^+$, 529.0 (100) $[2M+H]^+$, 551.0 (29) $[2M+Na]^+$.

HRMS (ESI): *m/z* = found: 285.9837, calcd.: 285.9838 $[M+Na]^+$.

$C_{12}H_{10}BrNO$ (264.12).

[9] For original procedure see: J. F. K. Wilshire, *Aust. J. Chem*. **1988**, *41*, 6, 995–1001.
Experimental data from: M. A. Düfert, *Disseration*, Georg-August-Universität, Göttingen, **2010**.

1-Iodo-2-(2-bromophenoxy)benzene (12)[10]



A solution of KI (47.3 g, 285 mmol, 2.64 equiv.) and $NaNO_2$ (15.8 g, 229 mmol, 2.12 equiv.) in H_2O (370 mL) was added drop wise to a solution of **17** (28.5 g, 108 mmol, 1.00 equiv.) and *p*-$TsOH \cdot H_2O$ (65.0 g, 342 mmol, 3.17 equiv.) in CH_3CN (700 mL). The mixture was stirred at r.t. for 30 min and the reaction mixture was adjusted to pH 9–10 by the addition of sat. aq. $NaHCO_3$ solution. After the addition of 1 M $Na_2S_2O_3$ solution (800 mL) the mixture was extracted with EtOAc (5 × 300 mL), the combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. Column chromatography (SiO_2, PE) yielded aryl iodide **12** as a colourless oil (35.2 g, 93.9 mmol, 87 %).

TLC: R_f = 0.23 (PE).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 195 (4.6866), 275 (3.3713), 282 (3.2932).

IR (Film): $\tilde{\nu}$ (cm^{-1}) = 1572, 1463, 1437, 1237, 1118, 1045, 1020, 878, 798, 749, 685.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.74 (dd, *J* = 8.1, 1.4 Hz, 1 H, 6‘-H), 6.86 (m_C, 2 H, 3-H, 4‘-H), 7.02 (ddd, *J* = 7.9, 7.5, 1.5 Hz, 1 H, 5-H), 7.21–7.29 (m, 2 H, 4-H, 4‘-H), 7.63 (dd, *J* = 7.9, 1.6 Hz, 1 H, 6-H), 7.86 (dd, *J* = 7.8, 1.6 Hz, 1 H, 3‘-H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 88.0 (C-2), 114.5 (C-2‘), 118.3 (C-6‘), 119.9 (C-3), 125.2 (C-5), 125.3 (C-4‘), 128.6 (C-4), 129.6 (C-5‘), 133.9 (C-6), 140.0 (C-3‘), 153.2 (C-1‘), 156.0 (C-1).

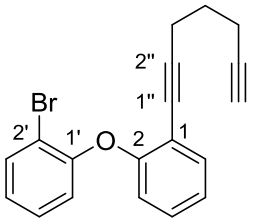
MS (EI): *m/z* (%) = 168.1 (100) $[M\text{-}C_6H_4I]^+$, 373.9 (48) $[M]^+$.

HRMS (EI): *m/z* = found: 373.8806, calcd.: 373.8803 $[M]^+$.

$C_{12}H_8BrIO$ (375.00).

[10] For original procedure see: M. W. P. Bebbington *et al*, *Eur. J. Org. Chem*. **2007**, *27*, 4483–4486.
Experimental data from: M. A. Düfert, *Disseration*, Georg-August-Universität, Göttingen, **2010**.
General method from: E. A. Krasnokutskaya, N. I. Semenischeva, V. D. Filimonov, P. Knochel, *Synthesis* **2007**, 81–84.

1-Bromo-2-(2-(hepta-1,6-diyn-1-yl)phenoxy)benzene (2)



A mixture of **12** (656 mg, 1.75 mmol, 1.00 equiv.), 1,6-heptadiyne (1.00 mL, 805 mg, 8.74 mmol, 5.00 equiv.), $PdCl_2(PPh_3)_2$ (61.5 mg, 87.6 µmol, 0.05 equiv.) and CuI (33.5 mg, 176 µmol, 0.10 equiv.) in degassed NEt_3 (8.5 mL) was stirred at r.t. for 17 h. The solvent was removed *in vacuo*. Column chromatography (SiO_2, *n*-pentane/CH_2Cl_2 5:1) yielded dialkyne **2** as a yellow oil (427 mg, 1.26 mmol, 72 %).

TLC: R_f = 0.29 (*n*-pentane/CH_2Cl_2, 5:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 252 (4.2065), 282 (3.4500).

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 3294, 1568, 1485, 1470, 1440, 1253, 1228, 1196, 1157, 1104, 1045, 1029, 871, 798, 748, 630.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.65 (p, *J* = 7.0 Hz, 2 H, 4''-H_2), 1.92 (t, *J* = 2.6 Hz, 1 H, 7''-H), 2.18 (td, *J* = 7.1, 2.7 Hz, 2 H, 5''-H_2), 2.43 (t, *J* = 6.9 Hz, 2 H, 3''-H_2), 6.75 (dd, *J* = 8.2, 1.5 Hz, 1 H, 6'-H), 6.86–7.00 (m, 2 H, 5-H, 3'-H), 7.08 (td, *J* = 7.5, 1.2 Hz, 1 H, 4-H), 7.15–7.27 (m, 2 H, 4'-H, 5'-H), 7.44 (dd, *J* = 7.6, 1.7 Hz, 1 H, 3-H), 7.60 (dd, *J* = 7.9, 1.6 Hz, 1 H, 6-H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 17.4 (C-5''), 18.6 (C-3''), 27.4 (C-4''), 68.7 (C-7''), 76.3 (C-6''), 83.7 (C-2''), 94.7 (C-1'') , 113.5 (C-2'), 116.5 (C-1), 118.5 (C-6'), 119.5 (C-3'), 124.0, 124.1 (C-4, C-5), 128.4, 129.0 (C-4', C-5'), 133.6, 133.7 (C-3, C-6), 154.2 (C-1'), 156.5 (C-2).

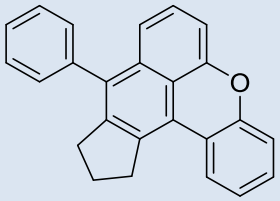
MS (ESI): *m*/*z* (%) = 341.0 (40) $[M+H]^+$, 356.1 (56) $[M+NH_4]^+$, 363.0 (100) $[M+Na]^+$.

HRMS (ESI): *m*/*z* = found: 339.0378, calcd.: 339.0379 $[M(^{79}Br)+H]^+$; found: 341.0354, calcd.: 341.0359 $[M(^{81}Br)+H]^+$.

$C_{19}H_{15}BrO$ (339.23).

General procedure for the domino reaction:

A mixture of **1** (1.00 equiv.), **2** (1.09 equiv.), $Pd(OAc)_2$ (0.10 equiv.), PPh_3 (0.50 equiv.) and $(n\text{Bu})_4\text{NOAc}$ (6.00 equiv.) in degassed DMF (3 mL) was stirred at 100 °C for 14.5–21 h. The reaction mixture was filtered through SiO_2, flushed with EtOAc and the solvent was removed *in vacuo*. Column chromatography (SiO_2) yielded domino product **3** as a yellow solid.

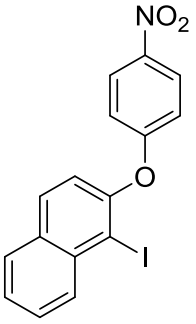


3

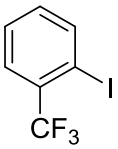
Entry	Sustrate 1	Product	Yield [mg]	Yield [%]
1[a]	**1a**	**3a**	79.9	81
2	**1b**	**3b**	45.9	97
3	**1c**	**3c**	35.3	90
4	**1d**	**3d**	43.1	80
5	**1e**	**3e**	29.4	64
6[b]	**1f**	**3f**	42.5	54

[a] **2** (1.05 equiv.), DMF (5 mL); [b] **2** (1.20 equiv.).

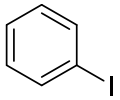
Substrates:



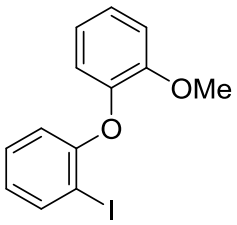
1a



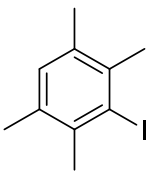
1b



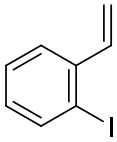
1c



1d

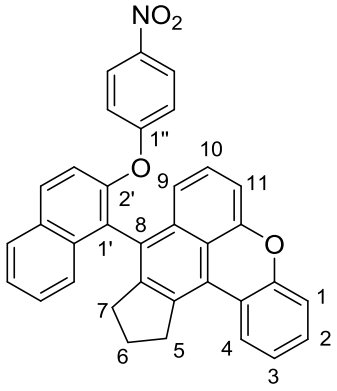


1e



1f

9-(2-(4-Nitrophenoxy)naphthalene-1-yl)-11,12-dihydro-10*H*-indeno[6,5,4-*kl*]xanthene (3a)



TLC: R_f = 0.40 (*n*-pentane/EtOAc, 20:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 193 (4.9352), 223 (4.3783), 256 (3.8842), 286 (3.6870), 350 (3.4956), 367 (3.4858).

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 1580, 1509, 1485, 1463, 1442, 1338, 1307, 1279, 1240, 1166, 1128, 1110, 1066, 1045, 1028, 1012, 958, 860, 852, 836, 821, 808, 768, 761, 750, 734, 703, 688, 667, 645, 629, 618, 530, 522, 514.

^{1}H-NMR (600 MHz, C_6D_6): δ (ppm) = 1.58–1.70 (m, 2 H, 6-H_2), 2.33 (ddd, *J* = 16.2, 8.4, 6.2 Hz, 1 H, 7-H_a), 2.50 (dt, *J* = 15.9, 7.9 Hz, 1 H, 7-H_b), 2.87 (dt, *J* = 15.6, 7.5 Hz, 1 H, 5-H_a), 2.94 (ddd, *J* = 15.8, 8.2, 5.9 Hz, 1 H, 5-H_b), 6.37 (d, *J* = 9.2 Hz, 2 H, 2''-H, 6''-H), 6.77 (dd, *J* = 7.9, 1.6 Hz, 1 H, 11-H), 6.84–6.92 (m, 3 H, 3-H, 9-H, 10-H), 6.97 (ddd, *J* = 8.3, 7.3, 1.4 Hz, 1 H, 2-H), 7.03–7.09 (m, 2 H, 3-H, 1-H), 7.14 (m_C, 1 H, 7'-H), 7.26 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1 H, 6'-H), 7.43 (dd, *J* = 8.5, 1.1 Hz, 1 H, 8'-H), 7.59 (d, *J* = 9.2 Hz, 2 H, 3''-H, 5''-H), 7.67 (d, *J* = 8.9 Hz, 1 H, 4'-H), 7.71 (d, *J* = 8.4 Hz, 1 H, 4-H), 7.73 (d, *J* = 8.4 Hz, 1 H, 5'-H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) = 25.5 (C-6), 32.2 (C-7), 35.3 (C-5), 108.1 (C-9), 117.0 (C-2'', C-6''), 117.2 (C-1), 118.2 (C-11), 120.7 (C-3'), 122.4, 122.6 (C-4a), 123.1 (C-3), 123.3 (C-4b), 125.5 (C-3'', C-5''), 125.7, 126.1 (C-6', C-8'), 127.0, 127.1, 127.6 (C-4, C-10, C-7'), 127.9 (C-1'), 128.3, 128.6 (C-5'), 129.6 (C-2), 130.2 (C-4'), 132.0 (C-4'a), 133.9 (C-8'a, C-4c /C-7a), 134.1 (C-8a), 143.0 (C-1''), 146.4 (C-4c /C-7a), 150.2 (C-2'), 151.7 (C-11a), 153.4 (C-11b), 162.7 (C-1).

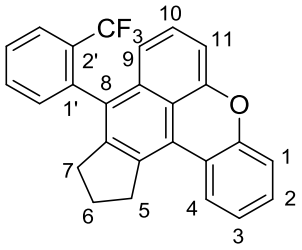
Further signals could not be assigned.

MS (ESI): *m*/*z* (%) = 544.2 (41) $[M+Na]^+$.

HRMS (ESI): *m*/*z* = found: 544.1505, calcd.: 544.1519 $[M+Na]^+$.

$C_{35}H_{23}NO_4$ (521.64).

9-(2-(Trifluoromethyl)phenyl)-11,12-dihydro-10*H*-indeno[6,5,4-*kl*]xanthene (3b)



TLC: R_f = 0.28 (*n*-pentane/CH_2Cl_2, 10:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 223 (4.6371), 254 (4.4498), 262 (4.4393), 286 (3.7312), 296 (3.6610), 307 (3.5173), 350 (4.0726), 365 (4.0931), 381 (3.9509).

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 1601, 1587, 1486, 1444, 1388, 1311, 1280, 1259, 1173, 1131, 1118, 1105, 1066, 1052, 1036, 812, 766, 746, 734, 683, 661, 647, 635, 598.

^{1}H-NMR (600 MHz, C_6D_6): δ (ppm) = 1.63–1.72 (m, 1 H, 6-H_a), 1.72–1.82 (m, 1 H, 6-H_b), 2.37 (ddd, *J* = 15.9, 8.5, 6.2 Hz, 1 H, 5-H_a), 2.58–2.64 (m, 1 H, 5-H_b), 2.85–2.97 (m, 2 H, 7-H_2), 6.75 (d, *J* = 8.0 Hz, 1 H, 9-H), 6.87–6.90 (m, 1 H, 3-H), 6.91 (dd, *J* = 7.7, 1.1 Hz, 1 H, 11-H), 6.95 (d, *J* = 7.4 Hz, 1 H, 6'-H), 6.97–7.04 (m, 3 H, 2-H, 10-H, 4'-H), 7.07 (dd, *J* = 8.1, 1.4 Hz, 1 H, 1-H), 7.10–7.19 (m, 1 H, 5'-H), 7.62 (d, *J* = 7.7 Hz, 1 H, 3'-H), 7.73 (dd, *J* = 8.0, 1.0 Hz, 1 H, 4-H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) = 25.7 (C-6), 32.1 (C-7), 35.3 (C-5), 107.9 (C-11), 117.1 (C-1), 118.5 (C-9), 122.1 (C-8b), 122.8 (C-4a), 123.0 (C-3, C-4b), 123.6 (CF_3), 126.7 (C-10/C-4', C-3'), 127.2 (C-4), 127.8 (C-10/C-4'), 129.4 (C-2), 129.8 (C-2'), 130.3 (C-8), 132.2 (C-6'), 132.3 (C-5'), 133.7 (C-7a), 134.4 (C-8a), 139.0 (C-1'), 145.0 (C-4c), 151.4 (C-11a), 153.5 (C-11b).

^{13}C multiplets could not be assigned properly.

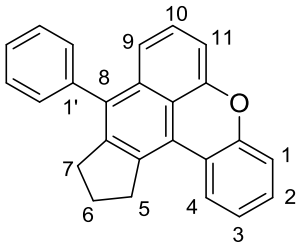
^{19}F-NMR (282 MHz, C_6D_6): δ (ppm) = -60.14 (s).

MS (EI): *m*/*z* (%) = 402.1 (100) $[M]^+$.

HRMS (EI): *m*/*z* = found: 402.1221, calcd.: 402.1231 $[M]^+$.

$C_{26}H_{17}F_3O$ (402.42).

9-Phenyl-11,12-dihydro-10*H*-indeno[6,5,4-*kl*]xanthene (3c)



TLC: R_f = 0.26 (*n*-pentane/CH_2Cl_2, 10:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 223 (4.0123), 256 (4.3790), 261 (3.7720), 352 (3.4143), 367 (3.4312).

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 1625, 1592, 1584, 1565, 1485, 1460, 1437, 1390, 1369, 1342, 1306, 1281, 1261, 1228, 1210, 1118, 1071, 1065, 865, 839, 808, 755, 741, 726, 704, 645, 633, 615, 537.

^{1}H-NMR (600 MHz, C_6D_6): δ (ppm) = 1.69 (p, *J* = 7.5 Hz, 2 H, 6-H_2), 2.57 (t, *J* = 7.6 Hz, 2 H, 7-H_2), 2.94 (t, *J* = 7.3 Hz, 2 H, 5-H_2), 6.88–6.93 (m, 1 H, 3-H), 6.94 (dd, *J* = 7.5, 1.0 Hz, 1 H, 11-H), 6.97–7.01 (m, 1 H, 2-H), 7.00–7.03 (m, 1 H, 10-H), 7.09 (dd, *J* = 8.1, 1.3 Hz, 1 H, 1-H), 7.19–7.23 (m, 2 H, 9-H, 4'-H), 7.25 (dt, *J* = 7.6, 1.7 Hz, 2 H, 2'-H, 6'-H), 7.28–7.32 (m, 2 H, 3'-H, 5'-H), 7.78 (dd, *J* = 7.9, 0.9 Hz, 1 H, 4-H).

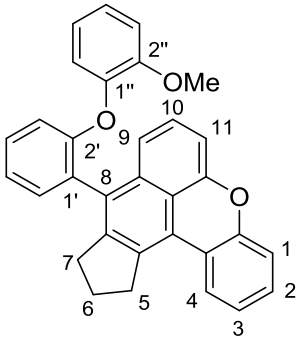
^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) = 25.7 (C-6), 32.3 (C-7), 35.4 (C-5), 107.9 (C-11), 117.1 (C-1), 118.5 (C-9), 122.2 (C-4b), 122.5 (C-8b), 123.0 (C-4a), 123.1 (C-3), 126.6 (C-10), 127.1, 127.3 (C-4, C-4'), 128.9 (C-3', C-5'), 129.3 (C-4b), 130.0 (C-2', C-6'), 133.4 (C-8), 134.1 (C-7a, C-8a), 140.2 (C-1'), 144.4 (C-4c), 151.6 (C-11a), 153.5 (C-11b).

MS (EI): *m*/*z* (%) = 334.1 (100) $[M]^+$.

HRMS (EI): *m*/*z* = found: 334.1343, calcd.: 334.1358 $[M]^+$.

$C_{25}H_{18}O$ (334.42).

9-(2-(2-Methoxyphenoxy)phenyl)-11,12-dihydro-10*H*-indeno[6,5,4-*kl*]xanthene (3d)



TLC: R_f = 0.46 (*n*-pentane/CH_2Cl_2, 2:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 195 (4.9575), 222 (4.7106), 256 (4.4021), 263 (4.3996), 351 (4.0466), 367 (4.0849), 384 (3.9530).

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 1599, 1584, 1573, 1497, 1482, 1456, 1442, 1391, 1373, 1343, 1305, 1259, 1229, 1215, 1175, 1156, 1114, 1108, 1038, 1019, 884, 810, 800, 759, 731, 644, 633.

^{1}H-NMR (600 MHz, C_6D_6): δ (ppm) = 1.74–1.89 (m, 2 H, 6-H_2), 2.71–2.80 (m, 1 H, 7-H_a), 2.86–2.94 (m, 1 H, 7-H_b), 2.95–3.02 (m, 1 H, 5-H_a), 3.06–3.13 (m, 1 H, 5-H_b), 3.11 (d, *J* = 1.6 Hz, 3 H, OCH_3), 6.42 (dt, *J* = 8.1, 1.5 Hz, 1 H, 3''-H), 6.60 (ddt, *J* = 9.3, 7.9, 1.6 Hz, 1 H, 5''-H), 6.73–6.78 (m, 1 H, 4''-H), 6.85–6.91 (m, 3 H, 3-H, 3'-H, 6''-H), 6.93–7.02 (m, 3 H, 2-H, 5'-H, 9-H), 7.05–7.12 (m, 3 H, 1-H, 10-H, 4'-H), 7.26 (dt, *J* = 7.4, 1.6 Hz, 1 H, 6'-H), 7.35 (dt, *J* = 8.4, 1.2 Hz, 1 H, 11-H), 7.74 (d, *J* = 8.0 Hz, 1 H, 4-H).

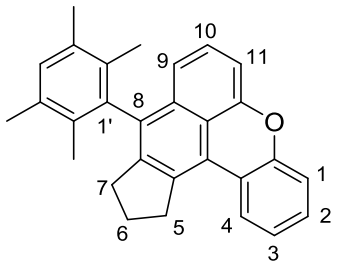
^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) = 25.6 (C-6), 32.3 (C-7), 35.5 (C-5), 55.3 (OCH_3), 107.6 (C-9), 113.9 (C-3''), 116.5 (C-3/C-3'), 117.0 (C-1), 118.9 (C-11), 121.2 (C-5''), 122.1 (C-6''), 122.2 (C-1'), 122.5, 122.6 (C-4b, C-8b), 122.9 (C-3/C-3'), 123.1 (C-4a), 124.9 (C-4''), 126.2 (C-10), 127.1 (C-4), 128.9, 129.1 (C-2, C-4'), 129.6, 129.7 (C-8, C-5'), 132.1 (C-6'), 134.1 (C-7a), 134.4 (C-8a), 145.4 (C-1''), 145.7 (C-4c), 151.6 (C-11a), 152.0 (C-2''), 153.5 (C-11b), 156.7 (C-2').

MS (ESI): *m*/*z* (%) = 457.2 (38) $[M+H]^+$, 474.2 (9) $[M+NH_4]^+$, 479.2 (17) $[M+Na]^+$

HRMS (ESI): *m*/*z* = found: 457.1778, calcd.: 457.1798 $[M+H]^+$.

$C_{32}H_{24}O_3$ (456.54).

9-(2,3,5,6-Tetramethylphenyl)-11,12-dihydro-10*H*-indeno[6,5,4-*kl*]xanthene (3e)



TLC: R_f = 0.28 (*n*-pentane/CH_2Cl_2, 10:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 221 (4.0004), 254 (3.7245), 262 (3.6995), 351 (3.3814), 364 (3.4002), 379 (3.2602).

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 1584, 1462, 1442, 1381, 1366, 1343, 1307, 1282, 1270, 1258, 1210, 1114, 1005, 806, 760, 743, 729, 583.

^{1}H-NMR (600 MHz, C_6D_6): δ (ppm) = 1.74 (p, J = 7.4 Hz, 2 H, 6-H_2), 1.87 (s, 6 H, 2'-CH_3, 6'-CH_3), 2.21 (s, 6 H, 3'-CH_3, 5'-CH_3), 2.46 (t, J = 7.6 Hz, 2 H, 7-H_2), 2.98 (t, J = 7.3 Hz, 1 H, 5-H_2), 6.90–6.95 (m, 2 H, 3-H, 9-H), 6.96–7.03 (m, 3 H, 2-H, 10-H, 11-H), 7.05 (s, 1 H, 6'-H), 7.11 (dd, J = 8.1, 1.3 Hz, 1 H, 1-H), 7.80 (dd, J = 7.9, 1.0 Hz, 1 H, 4-H).

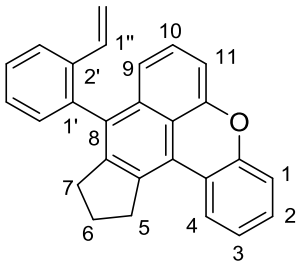
^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) = 16.3 (2'-CH_3, 6'-CH_3), 20.3 (3'-CH_3, 5'-CH_3), 25.6 (C-6), 32.0 (C-7), 35.5 (C-5), 108.1 (C-9), 117.1 (C-1), 117.9 (C-11), 121.9 (C-4b), 122.5 (C-8b), 123.0 (C-3), 123.2 (C-4a), 126.9, 127.0 (C-4, C-10), 129.2 (C-2), 131.1 (C-4'), 132.2 (C-2', C-6'), 133.4 (C-8), 133.8 (C-8a), 134.1 (C-7a, C-3', C-5'), 138.8 (C-1'), 144.4 (C-4c), 151.8 (C-11a), 153.5 (C-11b).

MS (EI): *m*/*z* (%) = 390.2 (100) $[M]^+$.

HRMS (ESI): *m*/*z* = found: 390.1980, calcd.: 390.1984 $[M+Na]^+$.

$C_{29}H_{26}O$ (390.53).

9-(2-Vinylphenyl)-11,12-dihydro-10*H*-indeno[6,5,4-*kl*]xanthene (3f)



TLC: R_f = 0.24 (*n*-pentane/CH_2Cl_2, 20:1).

UV/Vis (CH_3CN): λ_{max} (nm) (lg ε) = 199 (4.4754), 222 (4.3067), 254 (4.1417), 352 (3.6848), 366 (3.7017), 383 (3.5689).

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 2953, 2935, 2922, 2846, 1625, 1593, 1584, 1562, 1479, 1459, 1442, 1432, 1386, 1370, 1341, 1306, 1277, 1260, 1243, 1230, 1209, 1196, 1119, 1105, 985, 912, 866, 810, 764, 744, 732, 704, 678, 650, 645, 634.

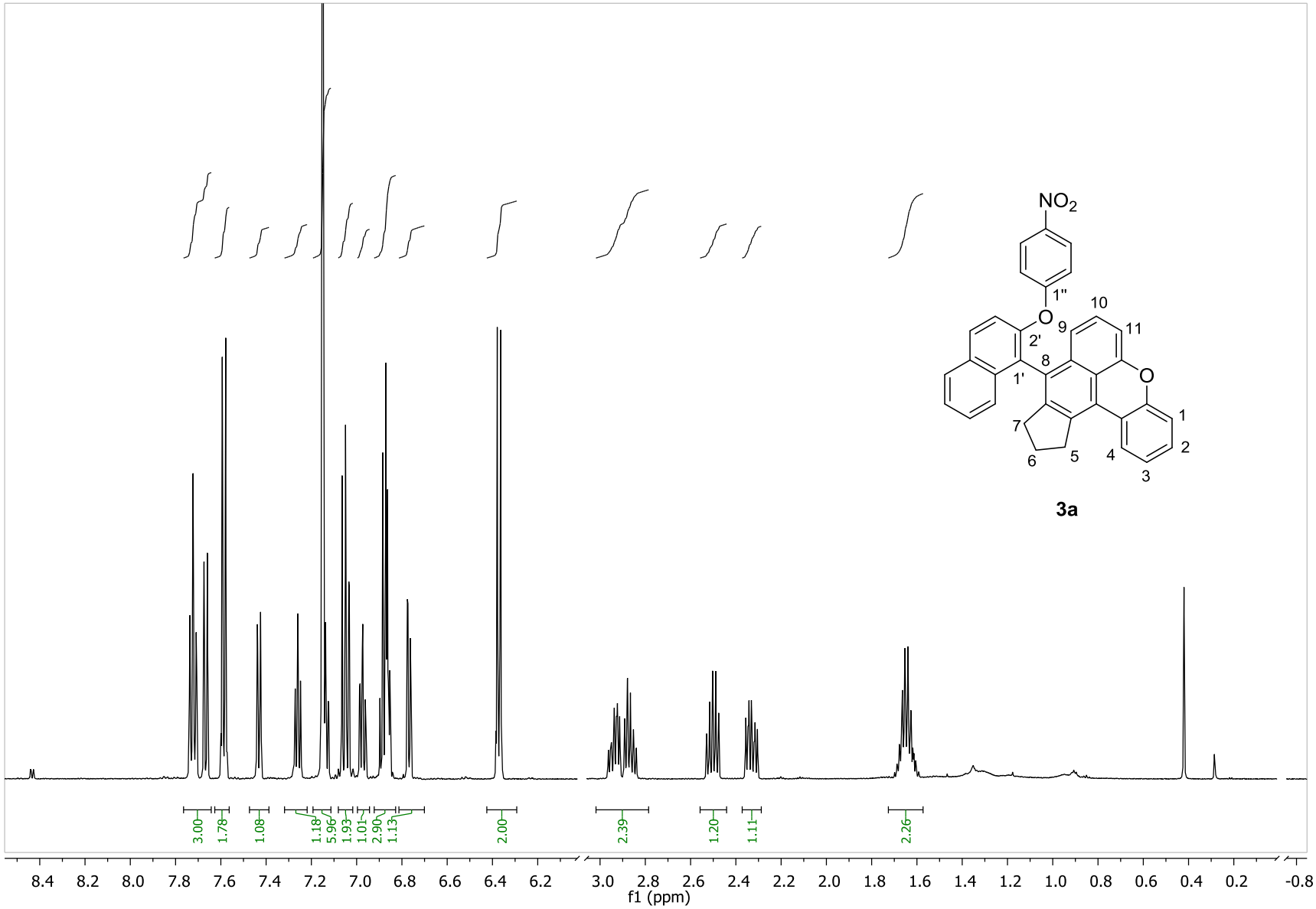
^{1}H-NMR (600 MHz, C_6D_6): δ (ppm) = 1.69 (p, *J* = 7.5 Hz, 2 H, 6-H_2), 2.51 (dd, *J* = 8.1, 7.1 Hz, 2 H, 7-H_2), 2.93 (td, *J* = 7.3, 1.9 Hz, 2 H, 5-H_2), 4.90 (dd, *J* = 10.9, 1.2 Hz, 1 H, 2''-H_a), 5.60 (dd, *J* = 17.5, 1.2 Hz, 1 H, 2''-H_b), 6.51 (dd, *J* = 17.5, 11.0 Hz, 1 H, 1''-H), 6.88–6.94 (m, 2 H, 3-H, 9-H), 6.96–7.02 (m, 3 H, 2-H, 10-H, 11-H), 7.09 (dd, *J* = 8.2, 1.4 Hz, 1 H, 1-H), 7.12 (dd, *J* = 7.2, 1.7 Hz, 1 H, 6'-H), 7.18–7.25 (m, 2 H, 3'-H, 5'-H), 7.68 (dd, *J* = 7.6, 1.6 Hz, 1 H, 4'-H), 7.77 (dd, *J* = 7.9, 1.4 Hz, 1 H, 4-H).

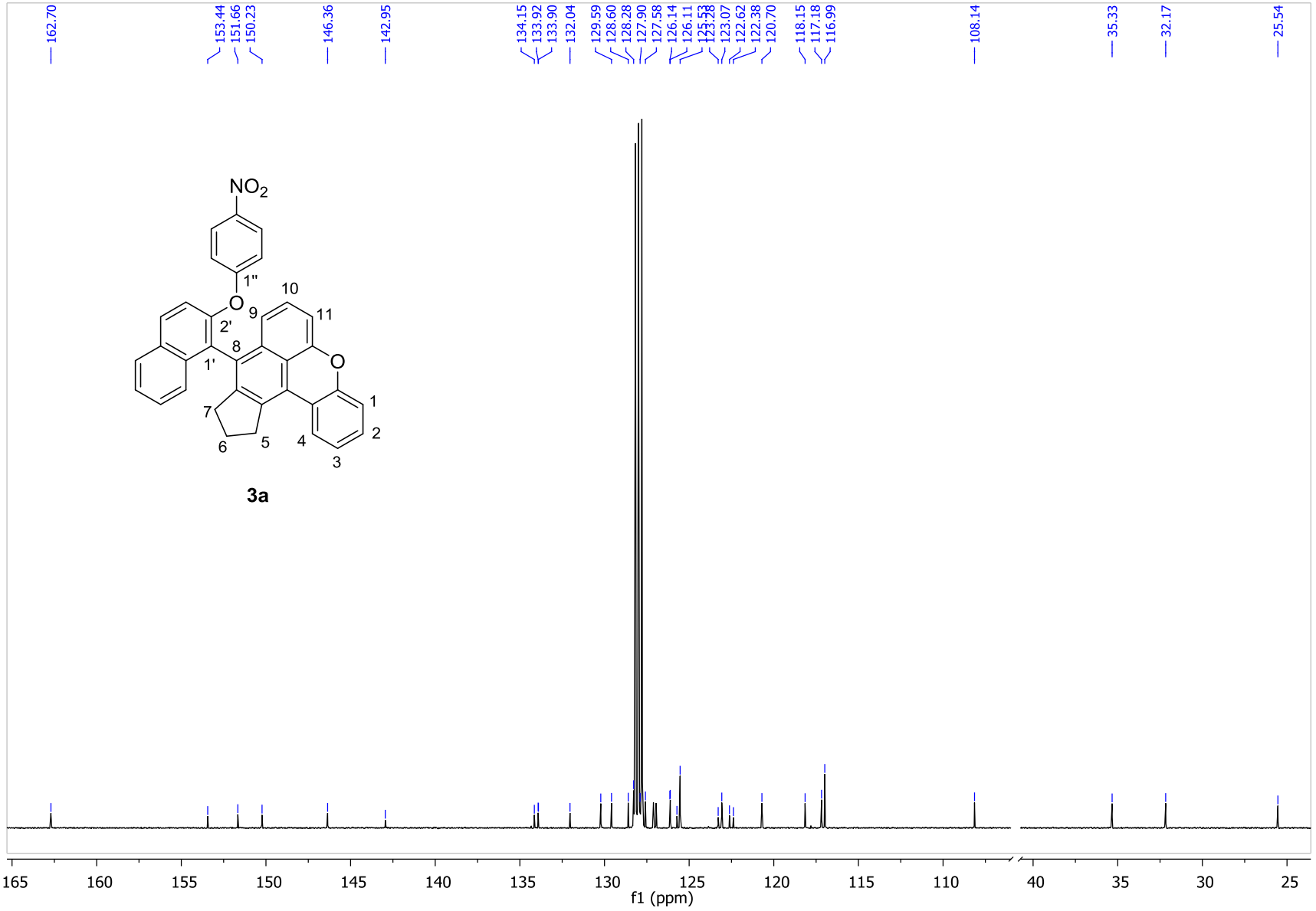
^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) = 25.5 (C-6), 32.1 (C-7), 35.4 (C-5), 108.0 (C-9), 114.6 (C-2''), 117.1 (C-1), 118.6 (C-11), 122.3, 122.4 (C-4b, C-8b), 123.0 (C-3, C-4a), 125.5 (C-4'), 126.9 (C-10), 127.1 (C-4), 127.9 (C-3'/C-5'), 128.4 (C-3'/C-5'), 129.3 (C-2), 130.6 (C-6'), 131.8 (C-8), 133.9 (C-7a), 134.2 (C-8a), 135.2 (C-1''), 136.8 (C-2'), 138.8 (C-1'), 145.1 (C-4c), 151.6 (C-11a), 153.5 (C-11b).

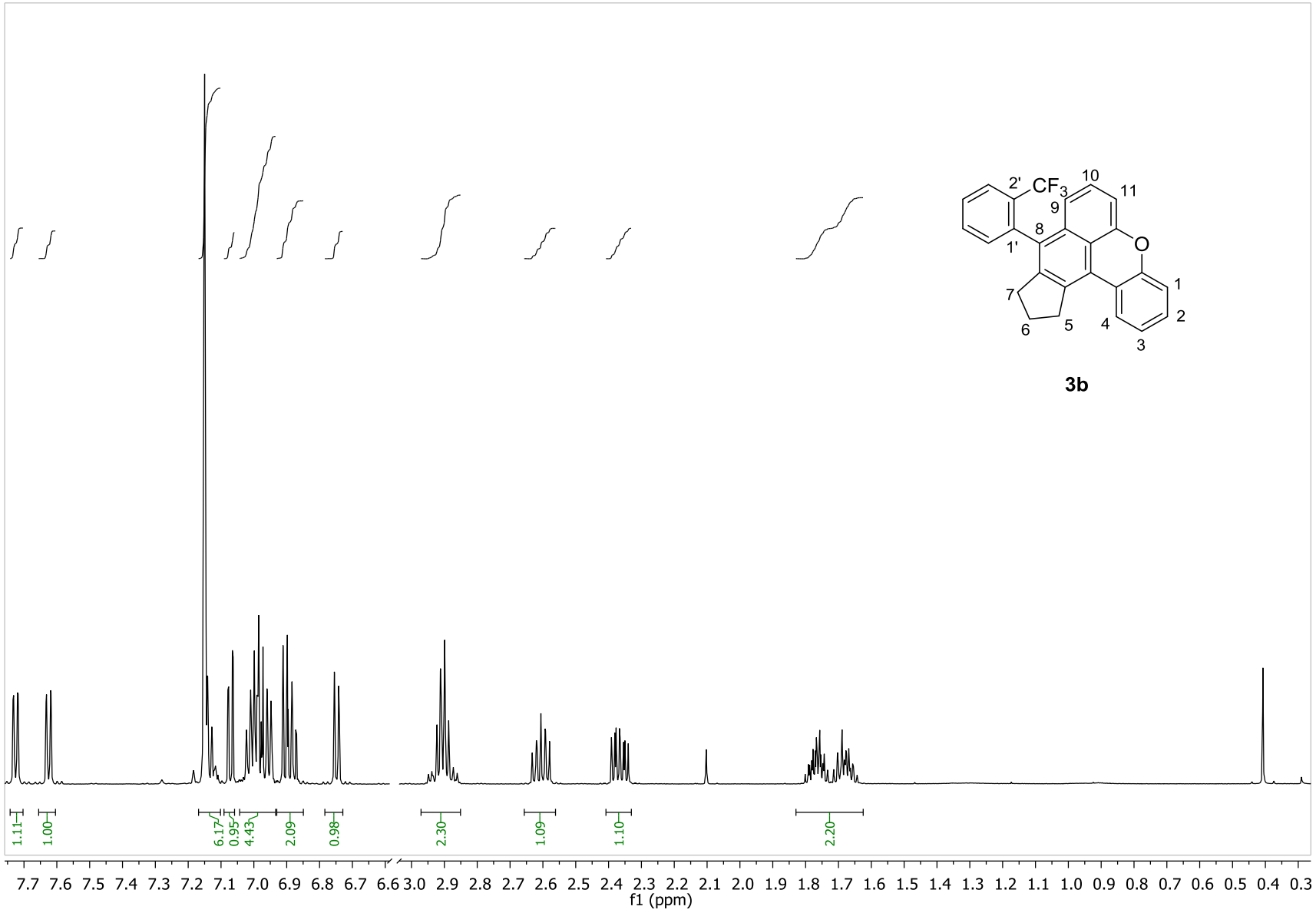
MS (EI): *m*/*z* (%) = 360.1 (100) $[M]^+$.

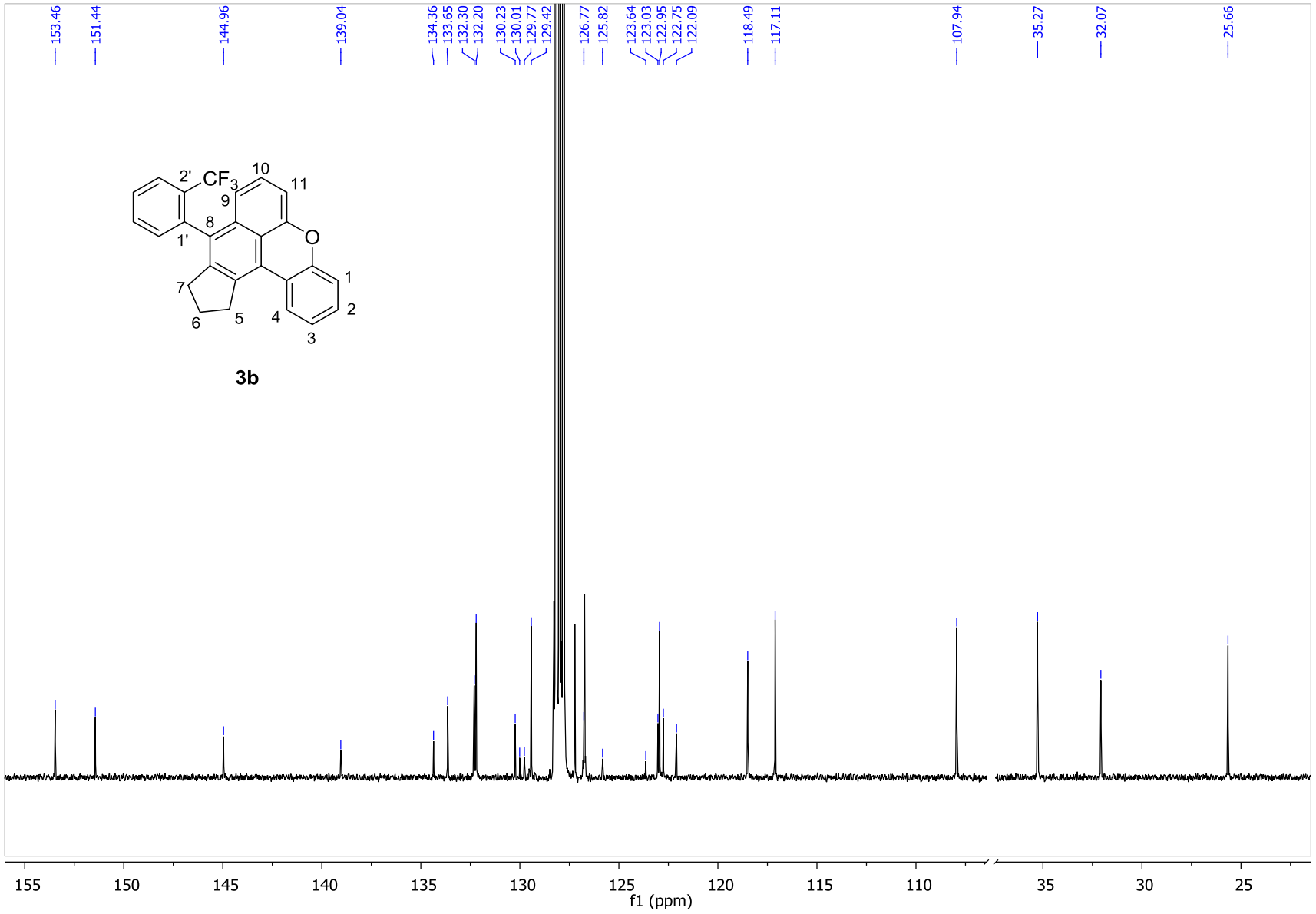
HRMS (ESI): *m*/*z* = found: 360.1499, calcd.: 360.1509 $[M+H]^+$.

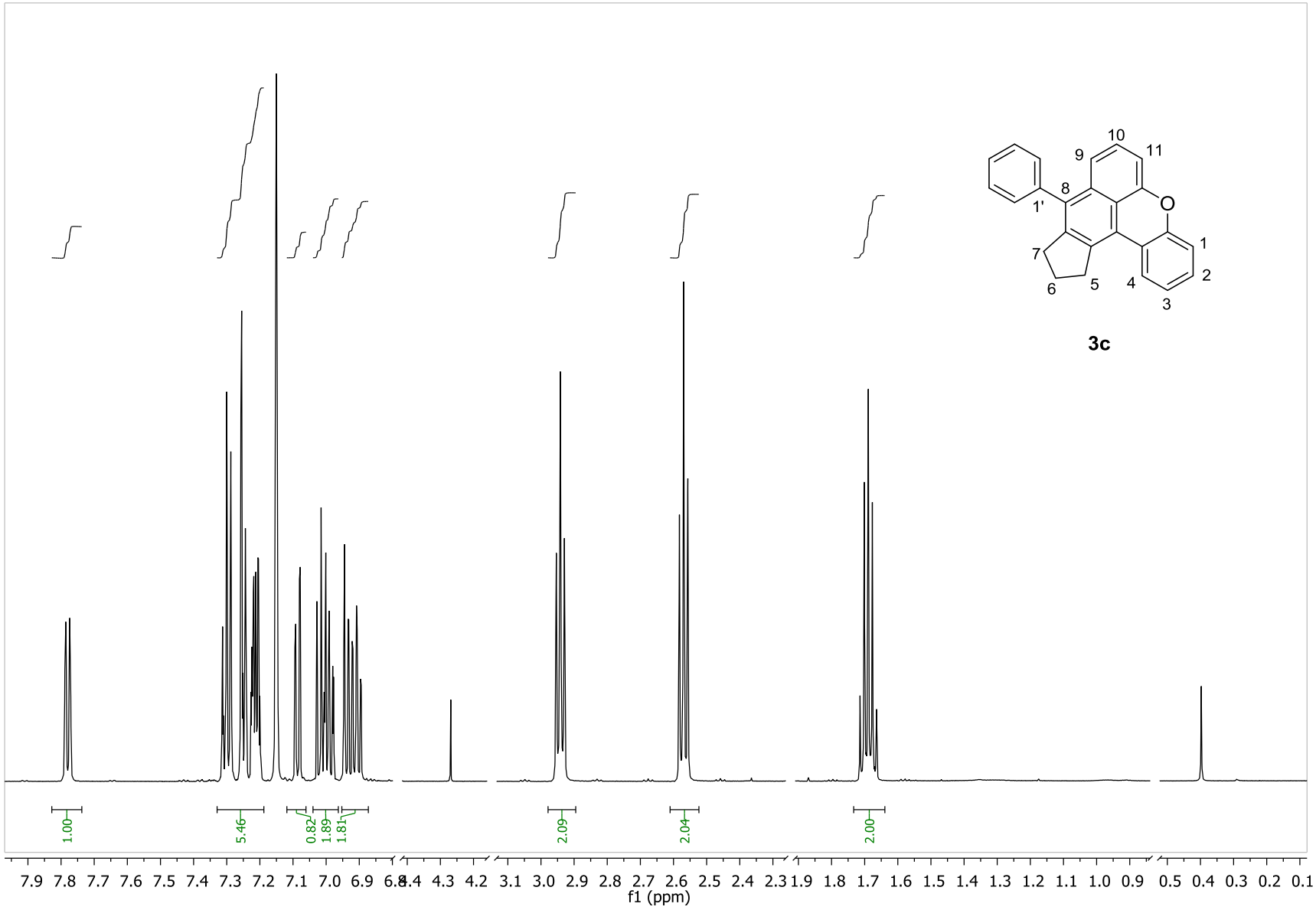
$C_{27}H_{20}O$ (360.46).

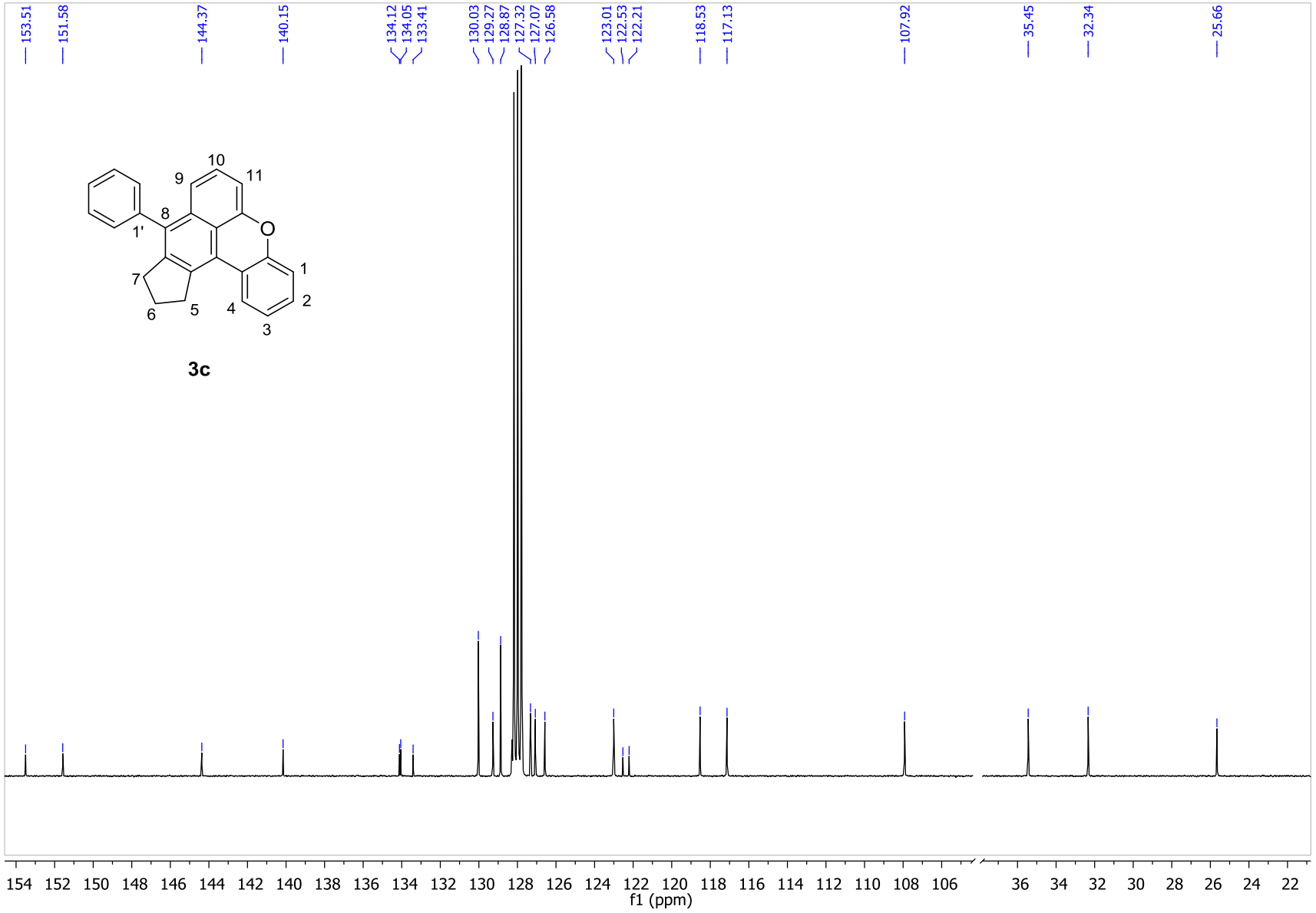

NO2
1"
O
9
10
11
2'
8
1'
O
1
2
3
4
5
6
7
3a
3.00
1.78
1.08
1.18
5.96
1.93
1.01
2.90
1.13
2.00
2.39
1.20
1.11
2.26
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 -0.8
f1 (ppm)

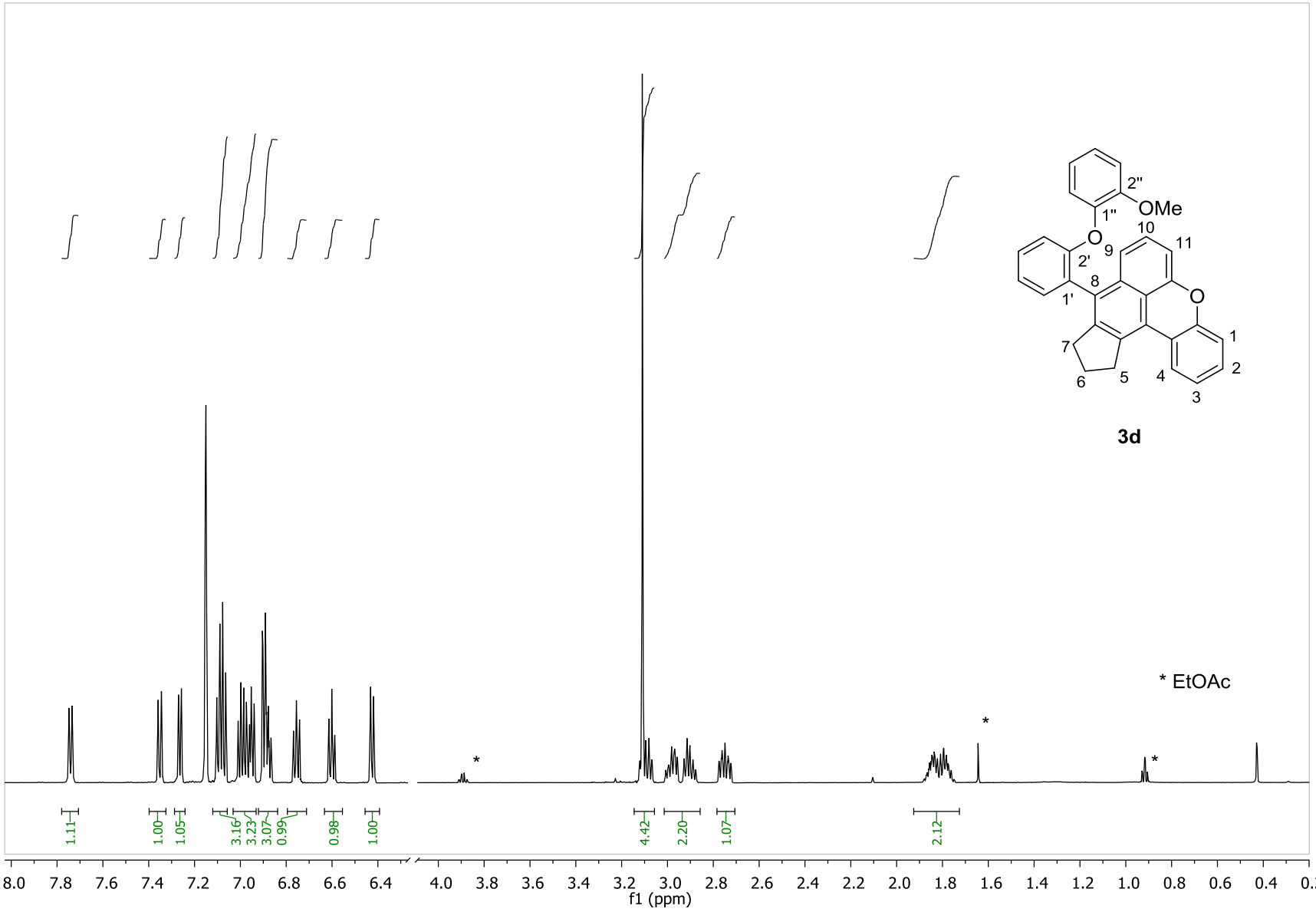

162.70
153.44
151.66
150.23
146.36
142.95
134.15
133.92
133.90
132.04
129.59
128.60
128.28
127.90
127.58
126.14
126.11
125.53
123.28
123.07
122.62
122.38
120.70
118.15
117.18
116.99
108.14
35.33
32.17
25.54
NO2
1"
O
10
9
11
2'
8
1'
O
7
1
2
6
5
4
3
3a
165
160
155
150
145
140
135
130
125
120
115
110
40
35
30
25
f1 (ppm)

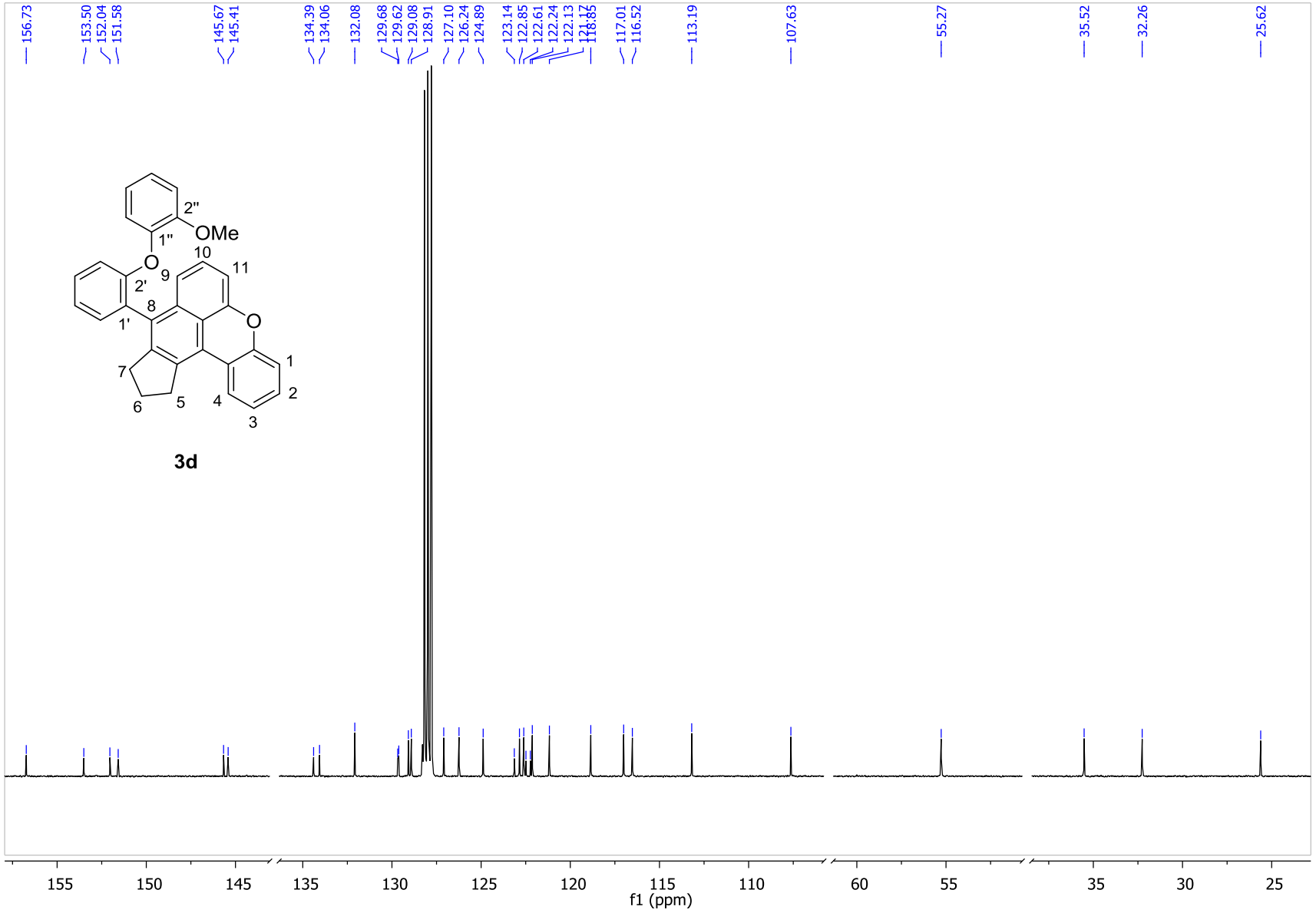

2'
CF3
10
11
9
8
1'
O
1
2
3
4
5
6
7
3b
1.11
1.00
6.17
0.95
4.43
2.09
0.98
2.30
1.09
1.10
2.20
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3
f1 (ppm)


153.46
151.44
144.96
139.04
134.36
133.65
132.30
132.20
130.23
130.01
129.77
129.42
126.77
125.82
123.64
123.03
122.95
122.75
122.09
118.49
117.11
107.94
35.27
32.07
25.66
2'
CF3
10
11
9
8
1'
O
1
2
3
4
5
6
7
3b
155
150
145
140
135
130
125
120
115
110
35
30
25
f1 (ppm)

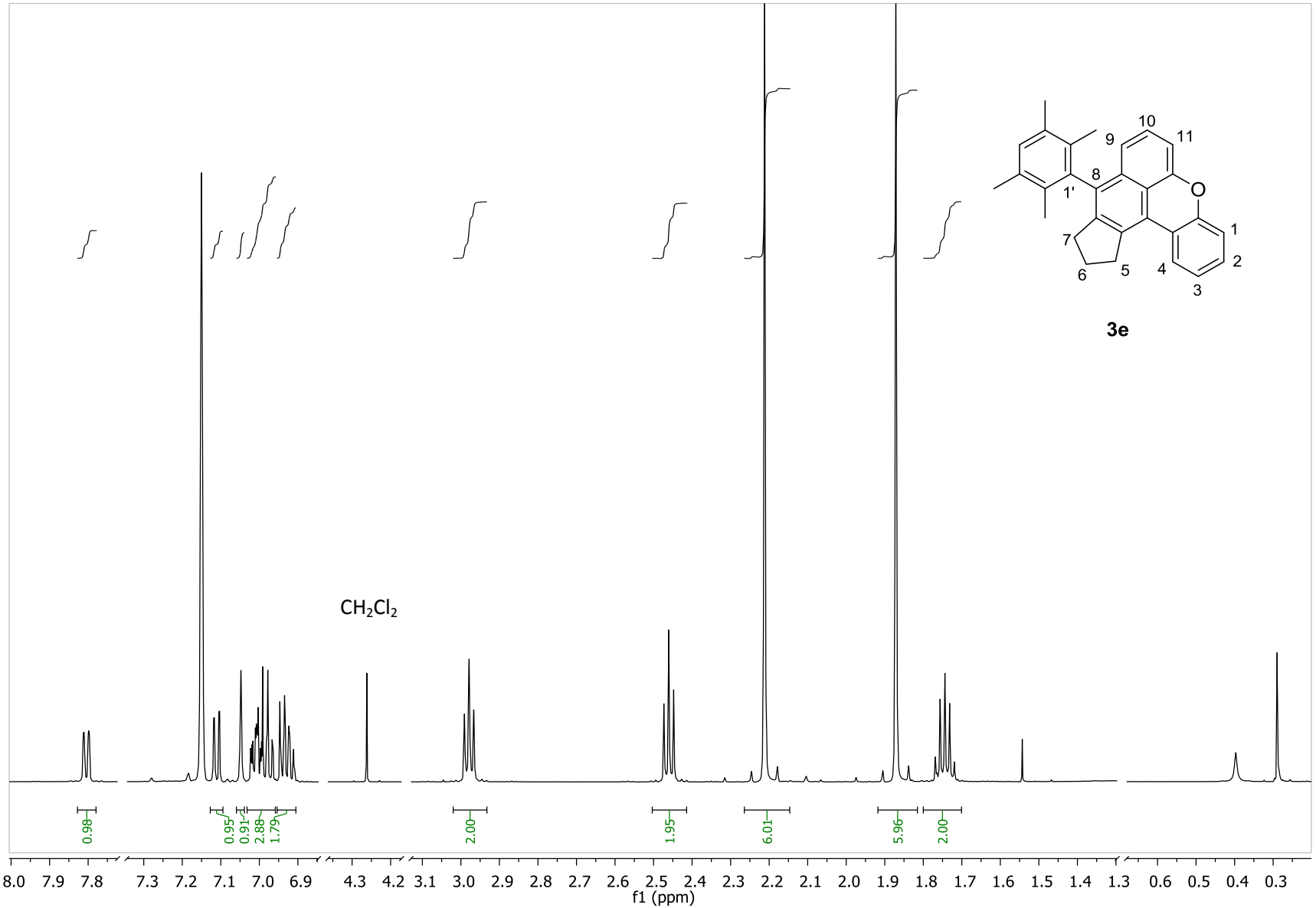

10
11
9
8
1'
O
1
7
2
6
5
4
3
3c
1.00
5.46
0.82
1.89
1.81
2.09
2.04
2.00
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 4.4 4.3 4.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.5 0.4 0.3 0.2 0.1
f1 (ppm)

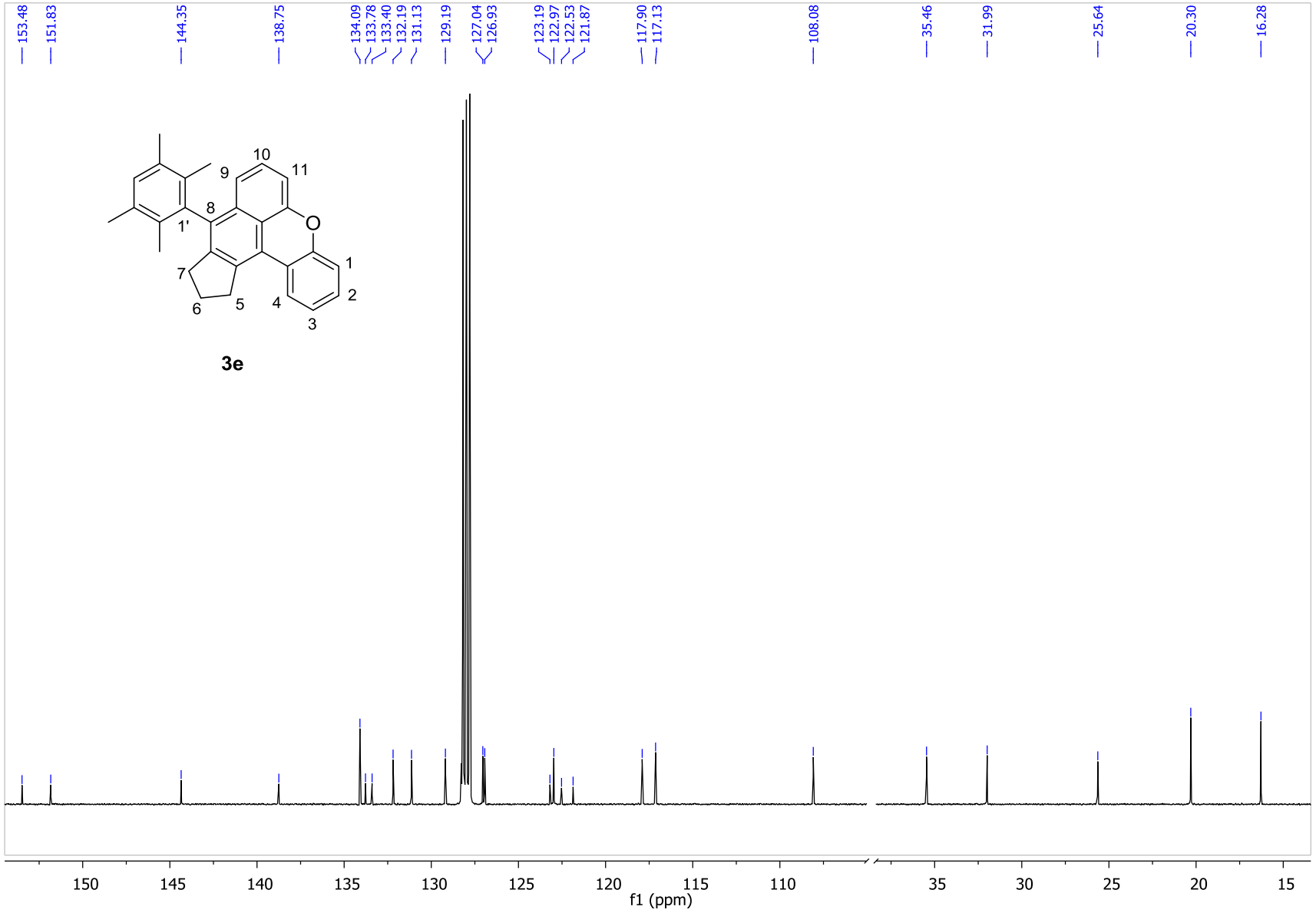

153.51
151.58
144.37
140.15
134.12
134.05
133.41
130.03
129.27
128.87
127.32
127.07
126.58
123.01
122.53
122.21
118.53
117.13
107.92
35.45
32.34
25.66
10
9
11
8
1'
O
1
7
2
6
5
4
3
3c
154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106
36 34 32 30 28 26 24 22
f1 (ppm)

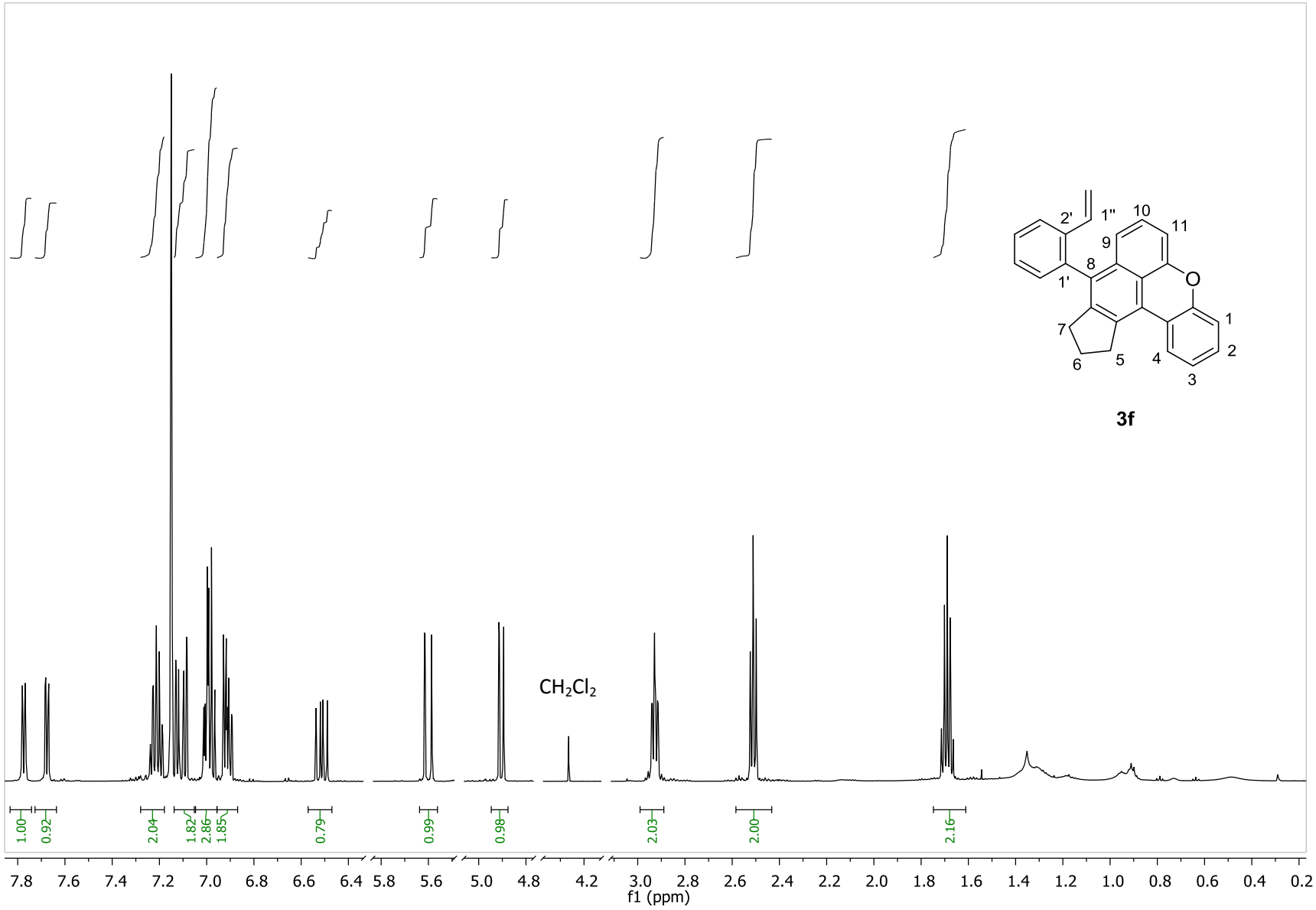

2"
OMe
1"
10
O
9
11
2'
8
1'
O
1
7
2
6
5
4
3
3d
* EtOAc
*
*
*
1.11
1.00
1.05
3.16
3.23
3.07
0.99
0.98
1.00
4.42
2.20
1.07
2.12
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
f1 (ppm)

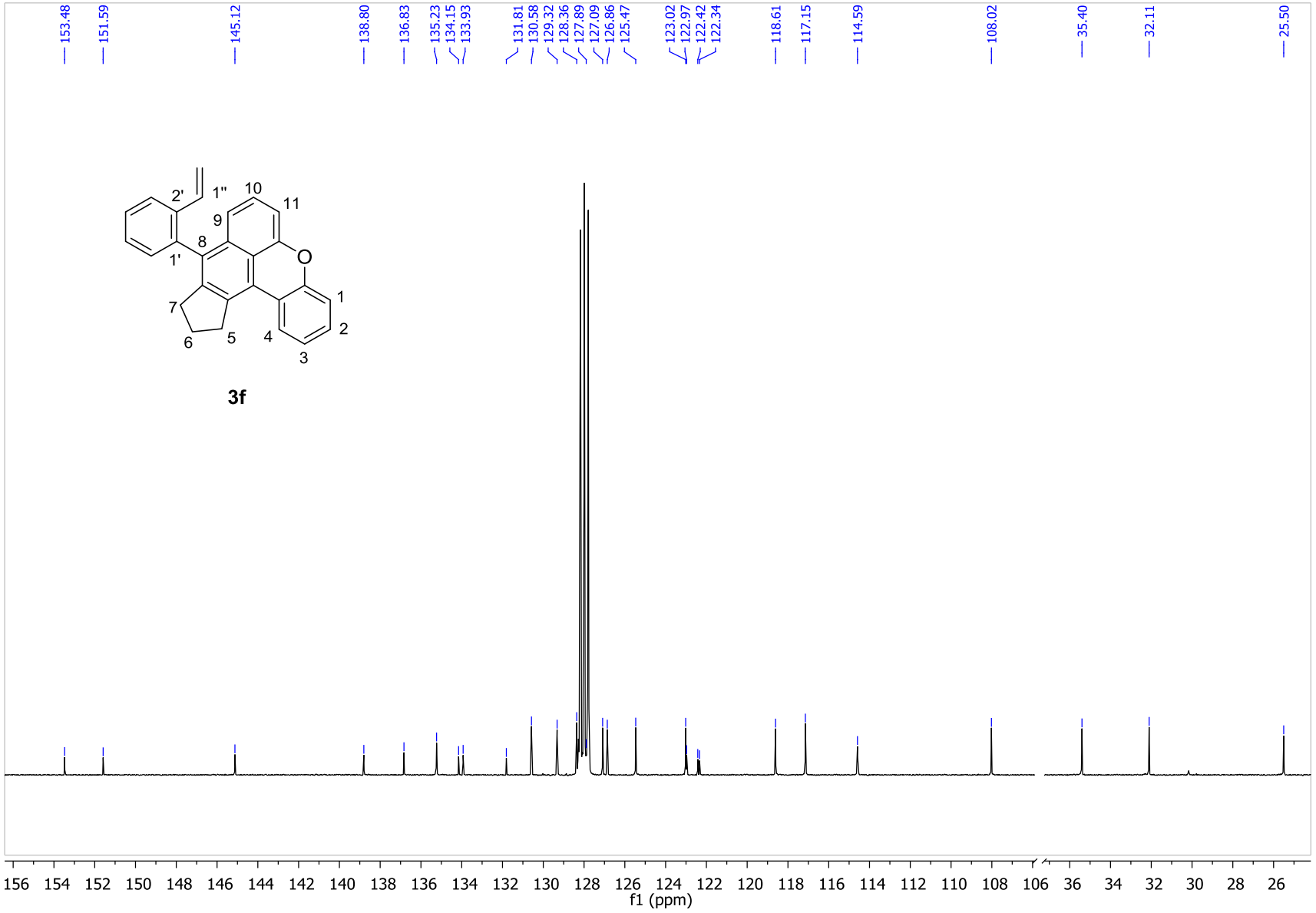

156.73
153.50
152.04
151.58
145.67
145.41
134.39
134.06
132.08
129.68
129.62
129.08
128.91
127.10
126.24
124.89
123.14
122.85
122.61
122.24
122.13
117.01
116.52
113.19
107.63
55.27
35.52
32.26
25.62
2"
OMe
1"
10
11
O
9
2'
8
1'
O
1
7
2
6
5
4
3
155
150
145
135
130
125
120
115
110
60
55
35
30
25
f1 (ppm)

3d


10
9
11
8
1'
O
1
7
2
6
5
4
3
3e
CH2Cl2
0.98
0.95
0.91
2.88
1.79
2.00
1.95
6.01
5.96
2.00
8.0 7.9 7.8 7.3 7.2 7.1 7.0 6.9 4.3 4.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 0.6 0.5 0.4 0.3
f1 (ppm)


153.48
151.83
144.35
138.75
134.09
133.78
133.40
132.19
131.13
129.19
127.04
126.93
123.19
122.97
122.53
121.87
117.90
117.13
108.08
35.46
31.99
25.64
20.30
16.28
10
9
11
8
1'
O
7
1
2
6
5
4
3
3e
150
145
140
135
130
125
120
115
110
35
30
25
20
15
f1 (ppm)


2'
1''
10
11
9
8
1'
O
1
7
2
6
5
4
3
3f
CH2Cl2
1.00
0.92
2.04
1.82
2.86
1.85
0.79
0.99
0.98
2.03
2.00
2.16
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
5.8
5.6
5.0
4.8
4.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
f1 (ppm)


153.48
151.59
145.12
138.80
136.83
135.23
134.15
133.93
131.81
130.58
129.32
128.36
127.89
127.09
126.86
125.47
123.02
122.97
122.42
122.34
118.61
117.15
114.59
108.02
35.40
32.11
25.50
2'
1"
10
11
9
8
1'
O
1
2
7
6
5
4
3
3f
156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 36 34 32 30 28 26
f1 (ppm)