Supporting Information for:

A phosphine free, inorganic base free, one-pot tandem Mizoroki-Heck olefination/ direct arylation/ hydrogenation sequence, to give muticyclic alkylated heteroarenes

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Contents

1 Experimental

Solvents and reagents were used as obtained from commercial sources and without purification. Tetrabutylammonium acetate was sourced from Sigma Aldrich. Melting points were measured in a Thomas Hoover Capillary Melting Point apparatus. Infrared spectra were measured on a Perkin Elmer Spectrum Two spectrometer, using universal ATR sampling accessories. Column chromatography was carried out using 60 Å (35–70 µm) silica. Thin-layer chromatography (TLC) was carried out on precoated silica gel plates (Merck 60 PF254). The developed plates were visualized under UV light.

High-resolution precise mass spectra (HRMS) were recorded on a Waters LCT Premier Tof LC-MS instrument in University College Cork. Samples were run in electrospray ionization (ESI) mode using 50% acetonitrile/water containing 0.1% formic acid as an eluent; samples were made up at a concentration of ca. 1 mg mL^{-1}. Samples were run in electrospray ionization (ESI) mode using 50% MeOH/water as eluent; samples were made up at a concentration of ca. 1 mg mL^{-1}. Acquisitions were internally calibrated using sodium formate clusters. Low resolution mass spectra were recorded on a Waters Quattro Micro triple quadrupole spectrometer (QAA1202) in electron spray ionisation mode (ESI) using acetonitrile:water (1:1) containing 0.1% Formic acid as eluent.

Nuclear magnetic resonance (NMR) samples were run in deuterated chloroform ($CDCl_3$). ^{1}H NMR (600 MHz), ^{1}H NMR (500 MHz), ^{1}H NMR (400 MHz), and ^{1}H NMR (300 MHz) spectra were recorded on Bruker Avance III 600, Bruker Avance 500, Bruker Avance 400, and Bruker Avance III 300 NMR spectrometers, respectively, in proton-coupled mode using tetramethysilane (TMS) as the internal standard. Signal assignments were supported by COSY (correlation spectroscopy) or HMBC (Heteronuclear Multiple-Bond Correlation spectroscopy) experiments where necessary. ^{13}C NMR (150.9 MHz), ^{13}C NMR (125 MHz), ^{13}C NMR (100 MHz), and ^{13}C NMR (75.5 MHz) spectra were recorded on Bruker Avance III 600, Bruker Avance 500, Bruker Avance 400, and Bruker Avance III 300 NMR spectrometers, respectively, in proton-decoupled mode at 300 K using TMS as the internal standard. All spectra were assigned with the aid of DEPT (Distortionless Enhancement by Polarisation Transfer) experiments run in DEPT-90, DEPT-135 and DEPT-q modes. Specific assignments were made using HSQC (Heteronuclear Single Quantum Correlation) and HMBC (Heteronuclear Multiple Bond Correlation) experiments. All spectroscopic data for known compounds is in agreement with those previously reported unless otherwise stated. ^{19}F NMR (282 MHz) spectra were recorded on a Bruker Avance III 300 NMR spectrometer in proton-decoupled mode at 300 K. All spectra were run at University College Cork. Chemical shifts (δ) are expressed as parts per million (ppm), positive shift being downfield from TMS; coupling constants (*J*) are expressed in hertz (Hz). Splitting patterns in ^{1}H NMR spectra are designated as follows: s (singlet), br s (broad singlet), d

(doublet), br d (broad doublet), dd (doublet of doublets), ddd (doublet of doublets of doublets), t (triplet), td (triplet of doublets), q (quartet), quin (quintet), and m (multiplet).

The COware apparatus was purchased from Sigma Aldrich and the hydrogen pressure was estimated using PV = *n*RT formula. It is worth noting that a 20 mL COware apparatus was used for these experiments. The COware apparatus has two chambers that are connected by a glass bridge, allowing for *ex situ* gas to be generated in one chamber which can then interact with the reaction mixture in the second chamber (Figure S1). These can be annotated as chamber 'A' and chamber 'B'.

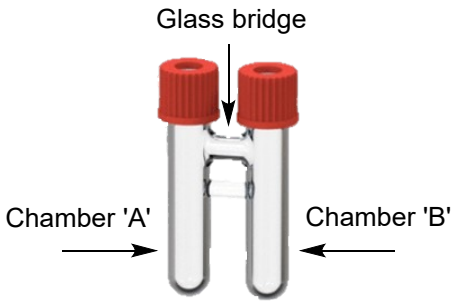


Figure 1S: COware apparatus and set-up.

General Procedure 1: Synthesis of phenoxyquinoline starting materials

A mixture of the 4-chloroquinoline substrate (1 eq.), the phenol (3.5 eq.) and NaOH (1.5 eq., crushed pellets) was stirred at 120 °C until TLC analysis indicated the reaction was complete (2 – 24 hours). The reaction mixture was cooled to room temperature and 10% aqueous NaOH (10 mL) was added and stirred for 30 min. The aqueous layer was extracted with DCM (3 × 15 mL). The organic layers were combined and washed with 6M NaOH (3 × 15 mL), water (10 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo.* Impure products were purified by column chromatography over silica gel using cyclohexane:EtOAc (100:0 - 70:30) or DCM:EtOAc (100:0 - 97:3). The substrate 6-bromo-4-(2-bromo-4-methoxyphenoxy)quinoline **1b** was columned in DCM (100%), followed by a wash of diethyl ether (5 mL).

General Procedure 2: One-pot reaction conditions

To a screw capped vial was added the quinoline/pyridine/diaryl ether substrate (1 eq.), heck coupling partner (1.1 eq.), $Pd(OAc)_2$ (5 mol%) and tetrabutylammonium acetate (5 eq.) which was stirred at 100 °C for 24 hours. The reaction mixture was then purged with hydrogen gas and stirred under a hydrogen atmosphere for a further 24 hours at 100 °C. The crude reaction mixture was loaded directly

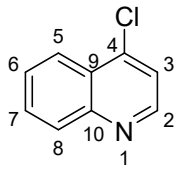
onto silica gel for purification by column chromatography. The benzofuroquinoline and benzofuropyridine products **3**, **4** and **6** eluted in DCM:EtOAc (100:0 – 95:5) or cyclohexane:EtOAc (100:0 - 70:30). The dibenzofuran products **9** eluted in hexane:DCM (100:0 – 80:20) or cyclohexane:EtOAc (100:0 - 90:10).

General Procedure 3: Synthesis of deuterated benzofuroquinoline generating D_2 at 3 atm.

To chamber 'A' of the COware[1] apparatus was put the benzofuroquinoline substrate (1 eq.), Heck coupling partner (1.1 eq.), $Pd(OAc)_2$ (5 mol%) and tetrabutylammonium acetate (5 eq.). To the second chamber 'B' was added Zinc powder (3.65 eq.). Chamber 'A' was placed into an oil bath and was stirred at 100 °C for 24 hours. DCl (4M, 7.3 eq.) was added *via* syringe to chamber 'B' which initiated the D_2 formation and reaction was let stir at 100 °C for a further 24 hours. The crude product was purified by silica gel column chromatography and eluted in a gradient cyclohexane:EtOAc (100:0 - 70:30) or DCM:EtOAc (100:0 – 95:5).

Synthesis of 4-chloroquinoline:

4-Chloroquinoline S1

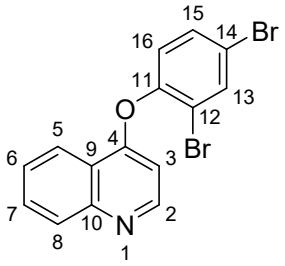


A mixture of 4-quinolinol (2.00 g, 0.0138 mmol) and phosphoryl chloride (6.40 mL, 0.689 mmol) was stirred at 120 °C for 16 hours. The crude mixture was poured onto ice and neutralised with solid sodium bicarbonate. The neutralised aqueous mix was extracted with DCM (3 × 15 mL). The organic layers were combined and washed with aqueous sodium bicarbonate (3 × 15 mL), water (15 mL) and brine (15 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yield the final product. Yellow solid, 80% yield (1.80 g); m.p. 27 – 28 °C (lit. 26 – 28 °C)[2]; IR ν_{max}/cm^{-1}: 2460 (C-H stretch), 1619 (aromatic C=C stretch), 1383 (C=N stretch), 760 (C-Cl stretch); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.79 (d, 1H, *J* 4.6 Hz, H-**2**), 8.25 (dd, 1H, *J* 8.4, 1.0 Hz, H-**5**), 8.14 (dd, 1H, *J* 8.4, 0.6 Hz, H-**8**), 7.79 (ddd, 1H, *J* 8.4, 6.9, 1.4 Hz, H-**7**), 7.66 (ddd, 1H, *J* 8.4, 6.9, 1.4 Hz, H-**6**), 7.50 (d, 1H, *J* 4.6 Hz, H-**3**) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 149.8 (*C*H-**2**), 149.1 (q*C*-**10**), 142.6 (q*C*-**4**), 130.4 (*C*H-**7**), 129.8 (*C*H-**8**), 127.6 (*C*H-**6**), 126.5 (q*C*-**9**), 124.1 (*C*H-**5**), 121.2 (*C*H-**3**) ppm; HRMS (ESI-TOF) *m/z*: [M+H$^+$]: C_9H_7ClN: 164.0267; found: 164.0261.

Syntheis of phenoxyquinoline substrates as per general procedure 1:

4-(2,4-dibromobenzyl)quinoline 1a

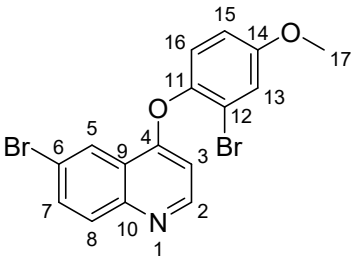
Synthesis of substrate **1a** as per general procedure 1 using 4-chloroquinoline **S1** (1.00 g, 6.14 mmol), 2,4-dibromophenol (5.41 g, 21.48 mmol) and NaOH (0.37 g, 9.21 mmol).



White solid, 95% yield, (2.21 g); m.p. 123 – 125 °C (lit: 125 – 126 °C)[3]; IR ν_{max}/cm^{-1}: 3033 (aromatic C-H stretch), 1594 (C=N stretch), 1563 (aromatic C=C stretch), 1373, 1232 (ether C-O stretch), 677 (C-Br stretch); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.69 (d, 1H, *J* 5.1 Hz, H-**2**), 8.38 (dd, 1H, *J* 8.4 Hz, 0.9 Hz, H-**5**), 8.12 (d, 1H, *J* 8.4 Hz, H-**8**), 7.88 (d, 1H, *J* 2.3 Hz, H-**13**), 7.79 (ddd, 1H, *J* 8.4, 6.9, 1.4, H-**7**), 7.62 (ddd, 1H, *J* 8.3, 7.0, 1.3 Hz, H-**6**), 7.54 (dd, 1H, *J* 8.6, 2.3 Hz, H-**15**), 7.12 (d, 1H, *J* 8.6 Hz, H-**16**), 6.43 (d, 1H, *J* 5.1 Hz, H-**3**) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.3 (qC-**4**), 150.9 (*C*H-**2**), 150.6 (q*C*-**11**), 149.8 (q*C*-**10**), 136.6 (*C*H-**13**), 132.3 (*C*H-**15**), 130.4 (*C*H-**7**), 129.2 (*C*H-**8**), 126.5 (*C*H-**6**), 124.2 (*C*H-**16**), 121.7 (*C*H-**5**), 120.9 (q*C*-**9**), 119.3 (q*C*-**14**), 117.3 (q*C*-**12**), 103.8 (*C*H-**3**) ppm; LRMS m/z (ESI+) 378, 380, 372 [(M+H)+ , 100%].

6-Bromo-4-(2-bromo-4-methoxyphenoxy)quinoline 1b

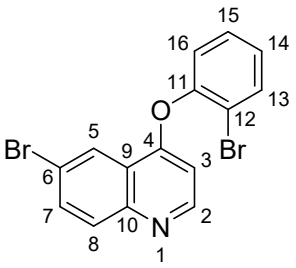
Synthesis of substrate **1b** as per general procedure 1 using 6-bromo-4-chloroquinoline (0.80 g, 3.30 mmol, 1 eq.), with an additional 2 eq. of 4-methoxyphenol (3.30 g, 16.49 mmol, 5 eq.) and NaOH (0.20 g, 4.95 mmol,, 1.5 eq.).



White solid, 25% yield (336 mg); m.p. 122 – 124 °C; IR ν_{max}/cm^{-1}: 3008 (aromatic C-H stretch), 1589 (C=N stretch), 1565 (aromatic C=C stretch), 1349, 1267, 1202 (ether C-O stretch), 673 (C-Br stretch); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.65 (d, 1H, *J* 5.2 Hz, H-**2**), 8.58 (d, 1H, *J* 2.2 Hz, H-**5**), 7.96 (d, 1H, *J* 9.0 Hz, H-**8**), 7.82 (dd, 1H, *J* 9.0, 2.2 Hz, H-**7**), 7.24 (d, 1H, *J* 2.9 Hz, H-**13**), 7.16 (d, 1H, *J* 8.9 Hz, H-**16**), 6.95 (dd, 1H, *J* 8.9, 2.9 Hz, H-**15**), 6.39 (d, 1H, *J* 5.2 Hz, H-**3**), 3.85 (s, 3H, C(**17**)-H_3) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.3 (q*C*-**4**), 158.0 (q*C*-**14**), 151.4 (*C*H-**2**), 148.3 (q*C*-**10**), 144.1 (q*C*-**11**), 133.6 (*C*H-**7**), 130.8 (*C*H-**8**), 124.3 (*C*H-**5**), 123.7 (*C*H-**16**), 122.1 (q*C*-**9**), 120.2 (q*C*-**6**), 119.0 (*C*H-**13**), 116.6 (q*C*-**12**), 115.0 (*C*H-**15**), 103.8 (*C*H-**3**), 55.9 (*C*H_3-**17**) ppm; HRMS (ESI-TOF) *m/z*: [M+H$^+$]: $C_{16}H_{12}Br_2NO_2$: 407.9229; found: 407.9227.

6-Bromo-4-(2-bromophenoxy)quinoline 1c

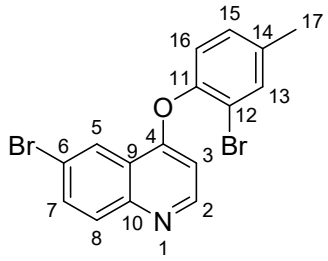
Synthesis of substrate **1c** as per general procedure 1 using 6-Bromo-4-chloroquinoline (1.00 g, 4.12 mmol), 2-bromophenol (2.49 g, 14.43 mmol) and NaOH (0.25 g, 6.19 mmol).



Off-white solid, 88% yield (2.03 g); m.p. 92 - 94 °C (lit. 97 – 98 °C)[3]; IR ν_{max}/cm^{-1}: 3070 (aromatic C-H stretch), 1589 (C=N stretch), 1560 (aromatic C=C stretch), 1348, 1223 (ether C-O stretch), 658 (C-Br stretch); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67 (d, 1H, *J* 5.1 Hz, H-**2**), 8.60 (d, 1H, *J* 2.1 Hz, H-**5**), 8.02 (d, 2H, *J* 9.0 Hz, H-**8**), 7.86 (dd, 1H, *J* 9.0, 2.2 Hz, H-**7**), 7.72 – 7.76 (m, 1H, H-**13**), 7.45 (ddd, 1H, *J* 8.8, 7.4, 1.4 Hz, H-**15**), 7.21 – 7.28 (m, 2H, H-**14**, H-**16**), 6.42 (d, 1H, *J* 5.1 Hz, H-**3**) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2 (q*C*-**4**), 151.0 (*C*H-**2**), 150.6 (q*C*-**11**), 147.8 (q*C*-**10**), 134.4 (*C*H-**13**), 134.0 (*C*H-**7**), 130.5 (*C*H-**8**), 129.4 (*C*H-**15**), 127.7 (*C*H-**14**), 124.4 (*C*H-**5**), 123.3 (*C*H-**16**), 122.1 (q*C*-**9**), 120.6 (q*C*-**6**), 116.3 (q*C*-**12**), 104.2 (*C*H-**3**) ppm; LRMS m/z (ESI+) 378, 380, 372 [(M+H)+ , 100%].

6-Bromo-4-(2-bromo-4-methylphenoxy)quinoline 1d

Synthesis of substrate **1d** as per general procedure 1 using 6-Bromo-4-chloroquinoline (1.00 g, 4.12 mmol), 4-bromo-2-methylphenol (2.70 g, 14.43 mmol) and NaOH (0.25 g, 6.19 mmol).

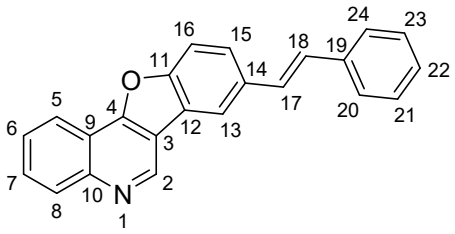


Light-brown solid, 88% yield (1.42 g); m.p. 94 – 95 °C; IR ν_{max}/cm^{-1}: 2964 (aromatic C-H stretch), 2922 (methyl C-H stretch), 1587 (C=N stretch), 1563 (aromatic C=C stretch), 1351, 1205 (ether C-O stretch), 670 (C-Br stretch); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.65 (d, 1H, *J* 5.1 Hz, H-**2**), 8.58 (d, 1H, *J* 2.2, H-**5**), 7.96 (d, 1H, *J* 9.0 Hz, H-**8**), 7.83 (dd, 1H, *J* 9.0, 2.2 Hz, H-**7**), 7.54 (d, 1H, *J* 2.0 Hz, H-**13**), 7.22 (ddd, 1H, *J* 8.2, 2.0, 0.6 Hz, H-**16**), 7.11 (d, 1H, *J* 8.2 Hz, H-**15**), 6.40 (d, 1H, *J* 5.1 Hz, H-**3**), 2.41 (s, 3H, C(**17**)-H_3) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ = 160.1 (q*C*-**4**), 151.3 (*C*H-**2**), 148.3 (q*C*-**11**), 148.2 (q*C*-**10**), 137.9 (q*C*-**14**), 134.6 (*C*H-**13**), 133.7 (*C*H-**7**), 130.8 (*C*H-**8**), 129.9 (*C*H-**16**), 124.4 (*C*H-**5**), 122.9 (*C*H-**15**), 122.1 (q*C*-**9**), 120.3 (q*C*-**6**), 115.9 (q*C*-**12**), 104.0 (*C*H-**3**), 20.7 (*C*H_3-**17**) ppm; HRMS (ESI-TOF) *m/z*: [M+H$^+$]: $C_{16}H_{12}Br_2NO$: 391.9280; found: 391.9278.

Synthesis of direct-arylation/Heck intermediate:

(*E*)-8-Styrylbenzofuro[3,2-c]quinoline 2a

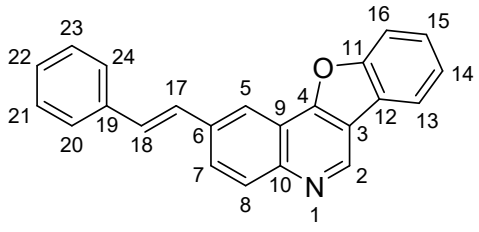
To a screw capped vial was added the quinoline substrate **1a** (200.0 mg, 0.53 mmol), styrene (66 µL, 0.58 mmol), $Pd(OAc)_2$ (5.92 mg, 5 mol%) and tetrabutylammonium acetate (795.4 mg, 2.64 mmol) which was stirred at 100 °C for 24 hours. The crude reaction mixture was loaded directly onto silica gel for purification by column chromatography and eluted in DCM:EtOAc (100:0 – 95:5).



Off-white solid, 86% yield (146 mg); m.p. 202 – 204 °C (lit: 200 – 203 °C)[3]; IR ν_{max}/cm^{-1}: 1651 (*trans* alkene C=C stretch), 1597 (C=N stretch), 1568 (aromatic C=C stretch), 1327, 1195 (ether C-O stretch); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.50 (s, 1H, (H-**2**), 8.39 (dd, 1H, *J* 8.1, 1.3 Hz, H-**5**), 8.27 (d, 1H, *J* 8.5 Hz, H-**8**), 8.19 (s, 1H, H-**13**), 7.63 – 7.83 (m, 4H, H-**6**, H-**7**, H-**15**, H-**16**), 7.52 – 7.61 (m, 2H, H-**20**, H-**24**), 7.14 – 7.44 (m, 5H, H-**17**, H-**18**, H-**21**, H-**22**, H-**23**) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 158.0 (q*C*-**4**), 155.6 (q*C*-**11**), 147.5 (q*C*-**10**), 144.4 (*C*H-**2**), 137.2 (q*C*-**19**), 133.9 (q*C*-**14**), 129.9 (*C*H-**8**), 129.4 (*C*H-**7**), 128.9 (*C*H-**18**), 128.8 (2 × *C*H-**21**, *C*H-**24**), 128.1 (*C*H-**17**), 127.1 (*C*H-**6**), 126.5 (2 × *C*H-**20**, *C*H-**24**), 126.0 (*C*H-**15**), 123.3 (q*C*-**12**), 120.8 (*C*H-**5**), 118.2 (*C*H-**13**), 117.2 (q*C*-**9**), 116.2 (q*C*-**3**), 112.2 (*C*H-**16**) ppm; LRMS m/z (ESI+) 322 [$(M+H)^+$, 100%].

(*E*)-2-Styrylbenzofuro[3,2-c]quinoline 2b

To a screw capped vial was added the quinoline substrate **1c** (200.0 mg, 0.53 mmol), styrene (66 µL, 0.58 mmol), $Pd(OAc)_2$ (5.92 mg, 5 mol%) and tetrabutylammonium acetate (795.4 mg, 2.64 mmol) which was stirred at 100 °C for 24 hours. The crude reaction mixture was loaded directly onto silica gel for purification by column chromatography and eluted in DCM:EtOAc (100:0 – 95:5).



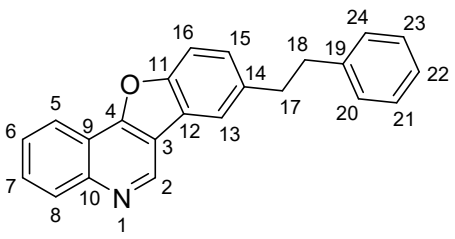
White solid, 88% yield (149 mg); m.p. 202–204 °C (lit: 201 – 202 °C)[3]; IR ν_{max}/cm^{-1}: 1666 (trans alkene C=C stretch), 1650 (C=N stretch), 1560 (aromatic C=C stretch), 1375, 1180 (ether C-O stretch); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.41 (s, 1H, H-**2**), 8.39 (d, 1H, *J* 1.8 Hz, H-**5**), 8.22 (d, 1H, *J* 8.9 Hz, H-**8**), 8.07 (dd, 1H, *J* 7.6, 0.8 Hz, H-**13**), 7.98 (dd, 1H, *J* 8.9, 2.0 Hz, H-**7**), 7.76 (d, 1H, *J* 8.1 Hz, H-**16**), 7.66–7.22 (m, 9H, H-**14**, H-**15**, H-**17**, H-**18**, H-**20**, H-**21**, H-**22**, H-**23**, H-**24**) ppm; ^{13}C NMR (75.5 MHz,

$CDCl_3$) δ: 157.4 (q*C*-**4**), 156.0 (q*C*-**11**), 147.0 (q*C*-**10**), 143.9 *C*H-**2**), 137.0 (q*C*-**19**), 136.1 (q*C*-**6**), 130.6 *C*H-**18**), 130.1 *C*H-**8**), 128.8 (2 × *C*H-**21**, *C*H-**23**), 128.1 (*C*H-**22**), 127.8 (*C*H-**17**), 127.3 (*C*H-**15**), 127.2 (*C*H-**7**), 126.8 (2 × *C*H-**20**, *C*H-**24**),124.1 (*C*H-**14)**, 122.7 (q*C*-**12**), 120.7 (*C*H-**13**), 118.6 (*C*H-**5**), 117.4 (q*C*-**9**), 116.7 (q*C*-**3**), 112.1 (*C*H-**16**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd. for $C_{23}H_{16}NO$: 322.1226; found: 322.1223.

<u>One-pot products as per general procedure 2:</u>

8-Phenethylbenzofuro[3,2-c]quinoline 3a

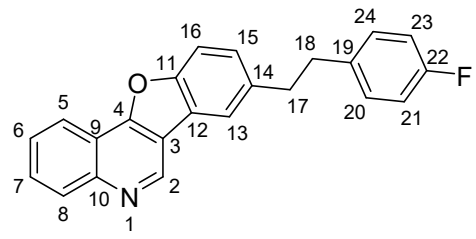
Synthesis of product **3a** as per general procedure 2 using **1a** (100 mg, 0.26 mmol), $Pd(OAc)_2$ (2.96 mg, 5 mol%), TBAOAc (398 mg, 1.32 mmol), styrene (33.0 µL, 0.29 mmol) and one hydrogen balloon.



White solid, 81% yield (69 mg); m.p. 129 – 131 °C; IR ν_{max}/cm^{-1}: 2925 (alkyl C-H stretch), 1600 (C=N stretch), 1567 (aromatic C=C stretch), 1341, 1193 (ether C-O stretch); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.46 (s, 1H, H-**2**), 8.40 (d, 1H, *J* 8.1 Hz, H-**5**), 8.30 (d, 1H, *J* 8.1 Hz, H-**8**), 7.87 (d, 1H, *J* 1.2 Hz, H-**13**), 7.75 – 7.80 (m, 1H, H-**7**), 7.68 (t, 1H, *J* 8.1 Hz, H-**6**), 7.63 (d, 1H, *J* 8.4 Hz, H-**16**), 7.33 (dd, 1H, *J* 8.4, 1.7 Hz, H-**15**), 7.18 – 7.31 (m, 5H, H-**20**, H-**21**, H-**22**, H-**23**, H-**24**), 2.99 – 3.17 (m, 4H, C(**17**)-H_2, C(**18**)-H_2) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 157.8 (q*C*-**4**), 154.6 (q*C*-**11**), 147.1 (q*C*-**10**), 144.3 (*C*H-**2**), 141.4 (q*C*-**19**), 137.8 (q*C*-**14**), 129.7 (*C*H-**8**), 129.3 (*C*H-**7**), 128.5 (2 × *C*H-**20**, *C*H-**24**), 128.4 (2 × *C*H-**21**, *C*H-**23**), 128.0 (*C*H-**15**), 127.0 (*C*H-**6**), 126.1 (*C*H-**22**), 122.7 (q*C*-**12**), 120.8 (*C*H-**5**), 120.1 (*C*H-**13**), 117.3 (q*C*-**9**), 116.4 (q*C*-**3**), 111.7 (*C*H-**16**), 38.5 (*C*H_2-**17**), 37.9 (*C*H_2-**18**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{23}H_{18}NO$: 324.1383, found: 324.1385.

8-(4-Fluorophenethyl)benzofuro[3,2-c]quinoline 3b

Synthesis of product **3b** as per general procedure 2 using **1a** (100 mg, 0.26 mmol), $Pd(OAc)_2$ (2.96 mg, 5 mol%), TBAOAc (398 mg, 1.32 mmol), 4-fluorostyrene (33.6 µL, 0.29 mmol) and one hydrogen balloon.

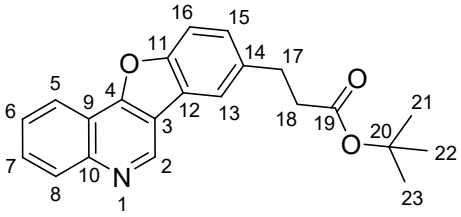


White solid, 79% yield (71 mg); m.p. 162 – 163 °C; IR ν_{max} /cm^{-1}: 2919 (aromatic C-H stretch), 1603 (C=N stretch), 1565 (aromatic C=C stretch), 1320, 1213 (ether C-O stretch), 1050 (C-F stretch); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.48 (br s, 1H, H-**2**), 8.42 (br d, 1H, *J* 6.1 Hz, H-**5**), 8.31 (br d, 1H, *J* 6.1 Hz, H-**8**),

7.86 (s, 1H, H-**13**), 7.80 (t, 1H, *J* 7.0 Hz, H-**7**), 7.70 (t, 1H, *J* 7.0 Hz, H-**6**), 7.64 (d, 1H, *J* 8.3 Hz, H-**16**), 7.30 (dd, 1H, *J* 8.3, 1.3 Hz, H-**15**), 7.13 (m, 2H, H-**20**, H-**24**), 6.97 (m, 2H, H-**21**, H-**23**), 2.97 – 3.13 (m, 4H, C(**17**)-H_2, C(**18**)-H_2) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 161.4 (d, $^1J_{(C, F)}$ = 244 Hz, *C*(**22**)-F), 157.9 (q*C*-**4**), 154.7 (q*C*-**11**), 146.9 (q*C*-**10**), 144.0 (*C*H-**2**), 137.6 (q*C*-**14**), 136.9 (d, $^4J_{(C, F)}$ = 3 Hz, q*C*-**19**), 129.9 (d, $^3J_{(C, F)}$ = 8 Hz, 2 × *C*H-**20**, *C*H-**24**), 129.5 (2 × *C*H-**7,** *C*H-**8**), 128.0 (*C*H-**15**), 127.2 (*C*H-**6**), 122.7 (q*C*-**12**), 120.9 (*C*H-**5**), 120.2 (*C*H-**13**), 117.3 (q*C*-**9**), 116.4 (q*C*-**3**), 115.1 (d, $^2J_{(C, F)}$ = 21 Hz, 2 × *C*H-**21**, *C*H-**23**), 111.8 (*C*H-**16**), 38.0 (CH_2-**17**), 37.6 (CH_2-**18**) ppm; ^{19}F NMR (282 MHz, CDCl3): δ = -117.3 ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{23}H_{17}FNO$: 342.1289; found: 342.1298.

tert-Butyl 3-(benzofuro[3,2-c]quinolin-8-yl)propanoate 3c

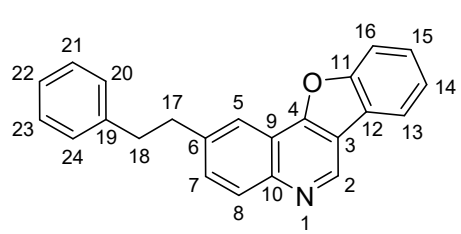
Synthesis of product **3c** as per general procedure 2 using **1a** (100 mg, 0.26 mmol), $Pd(OAc)_2$ (2.96 mg, 5 mol%), TBAOAc (398 mg, 1.32 mmol), *tert*-butylacrylate (42.0 µL, 0.29 mmol) and one hydrogen balloon.



White solid, 75% yield (69 mg); m.p. 105 – 106 °C; IR ν_{max}/cm^{-1}: 2973 (alkyl C-H stretch), 1716 (ester C=O stretch), 1565 (C=N stretch), 1478 (aromatic C=C stretch), 1367, 1204 (ether C-O stretch), 1140 (ester C-O stretch); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.48 (s, 1H, H-**2**), 8.42 (dd, 1H, *J* 8.2, 0.9 Hz, H-**5**), 8.32 (d, 1H, *J* 8.2 Hz, H-**8**), 7.94 (d, 1H, *J* 1.4 Hz, H-**13**), 7.77 – 7.85 (m, 1H, H-**7**), 7.70 – 7.75 (m, 1H, H-**6**), 7.67 (d, 1H, *J* 8.7 Hz, H-**16**), 7.40 (dd, 1H, *J* 8.7, 1.8 Hz, H-**15**), 3.13 (t, 2H, *J* 7.7 Hz, C(**17**)-H_2), 2.66 (t, 2H, *J* 7.7 Hz, C(**18**)-H_2), 1.42 (s, 9H, 3 × C(**21**)-H_3, C(**22**)-H_3, C(**23**)-H_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.0 (q*C*-**19**), 158.1 (q*C*-**4**), 154.8 (q*C*-**11**), 146.7 (q*C*-**10**), 143.8 (*C*H-**2**), 137.2 (q*C*-**14**), 129.6 (*C*H-**7**), 129.3 (*C*H-**8**), 128.0 (*C*H-**15**), 127.3 (*C*H-**6**), 122.7 (q*C*-**12**), 120.9 (*C*H-**5**), 120.2 (*C*H-**13**), 117.3 (q*C*-**9**), 116.4 (q*C*-**3**), 111.9 (*C*H-**16**), 80.6 (q*C*-**20**), 37.5 (CH_2-**18**), 31.1 (CH_2-**17**), 28.1 (3 × CH_3-**21**, CH_3-**22**, CH_3-**23**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{22}H_{22}NO_3$: 348.1594; found: 348.1598.

2-Phenethylbenzofuro[3,2-c]quinoline 4a

Synthesis of product **4a** as per general procedure 2 using **1c** (100 mg, 0.26 mmol), $Pd(OAc)_2$ (2.96 mg, 5 mol%), TBAOAc (398 mg, 1.32 mmol), styrene (33.0 µL, 0.29 mmol) and one hydrogen balloon.

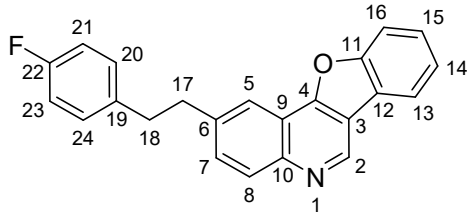


White solid, 79% yield (67 mg); m.p. 112 – 113 °C; IR ν_{max}/cm^{-1}: 3023 (aromatic C-H stretch), 2922 (alkyl C-H stretch), 1589 (C=N stretch), 1562 (aromatic C=C stretch), 1370, 1188 (ether

C-O stretch); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.42 (br s, 1H, H-**2**), 8.15 – 8.21 (m, 2H, H-**5**, H-**8**), 8.06 (d, 1H, *J* 7.7 Hz, H-**13**), 7.72 (d, 1H, *J* 7.7 Hz, H-**16**), 7.60 (dd, 1H, *J* 8.5, 1.4 Hz, H-**7**), 7.52 (t, 1H, *J* 7.7 Hz, H-**15**), 7.45 (t, 1H, *J* 7.7 Hz, H-**14**), 7.17 – 7.32 (m, 5H, H-**20**, H-**21**, H-**22**, H-**23**, H-**24**), 3.03 – 3.24 (m, 4H, C(**17**)-H_2, C(**18**)-H_2) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.3 (q*C*-**4**), 156.0 (q*C*-**11**), 146.1 (q*C*-**10**), 143.5 (*C*H-**2**), 141.3 (q*C*-**6**), 141.0 (q*C*-**19**), 130.9 (*C*H-**7**), 129.6 (*C*H-**8**), 128.5 (4 × *C*H-**20**, *C*H-**21**, *C*H-**23**, *C*H-**24**), 127.2 (*C*H-**15**), 126.1 (*C*H-**22**), 124.1 (*C*H-**14**), 122.8 (q*C*-**12**), 120.6 (*C*H-**13**), 119.3 (*C*H-**5**), 117.1 (q*C*-**9**), 116.4 (q*C*-**3**), 112.1 (*C*H-**16**), 38.1 (CH_2-**17**), 37.7 (CH_2**18**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{23}H_{18}NO$: 324.1383; found: 324.1390.

2-(4-Fluorophenethyl)benzofuro[3,2-c]quinoline 4b

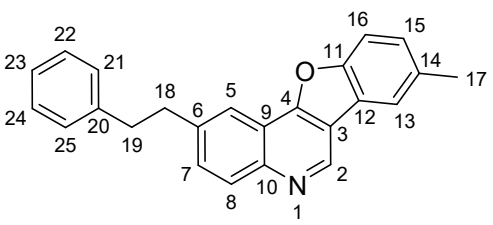
Synthesis of product **4b** as per general procedure 2 using **1c** (100 mg, 0.26 mmol), $Pd(OAc)_2$ (2.96 mg, 5 mol%), TBAOAc (398 mg, 1.32 mmol), 4-fluorostyrene (33.6 µL, 0.29 mmol) and one hydrogen balloon.



White solid, 81% yield (73 mg); m.p. 130 – 131 °C; IR ν_{max}/cm^{-1}: 3038 (aromatic C-H stretch), 2923 (alkyl C-H stretch), 1598 (C=N stretch), 1564 (aromatic C=C stretch), 1346, 1218 (ether C-O stretch), 1014 (C-F stretch); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.45 (br s, 1H, H-**2**), 8.22 (d, 1H, *J* 8.5 Hz, H-**8**), 8.16 (s, 1H, H-**5**), 8.08 (d, 1H, *J* 7.2 Hz, H-**13**), 7.74 (d, 1H, *J* 8.3 Hz, H-**16**), 7.59 (dd, 1H, *J* 8.5, 1.7 Hz, H-**7**), 7.52 – 7.56 (m, 1H, H-**15**), 7.45 – 7.49 (m, 1H, H-**14**), 7.12 – 7.17 (m, 2H, H-**20**, H-**24**), 6.94 – 6.99 (m, 2H, H-**21**, H-**23**), 3.02 – 3.21 (m, 4H, C(**17**)-H_2, C(**18**)-H_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.4 (d, $^{1}J_{(C,F)}$ = 244 Hz, *C*(**22**)**-F**), 157.4 (q*C*-**4**), 156.0 (q*C*-**11**), 145.8 (q*C*-**10**), 143.4 (*C*H-**2**), 140.8 (q*C*-**6**), 136.7 (d, $^{4}J_{(C,F)}$ = 3 Hz, q*C*-**19**), 130.9 (*C*H-**7**), 129.9 (d, $^{3}J_{(C,F)}$ = 8 Hz, 2 × *C*H-**20**, *C*H-**24**), 129.5 (*C*H-**8**), 127.3 (*C*H-**15**), 124.2 (*C*H-**14**), 122.7 (q*C*-**12**), 120.7 (*C*H-**13**), 119.4 (*C*H-**5**), 117.0 (q*C*-**9**), 116.4 (q*C*-**3**), 115.2 (d, $^{2}J_{(C,F)}$ = 21 Hz, 2 × *C*H-**21**, *C*H-**23**), 112.1 (*C*H-**16**), 38.1 (CH_2-**18**), 36.8 (CH_2-**17**) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -117.2 ppm; (HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{23}H_{17}FNO$: 342.1289; found: 342.1294.

8-Methyl-2-phenethylbenzofuro[3,2-c]quinoline 4c

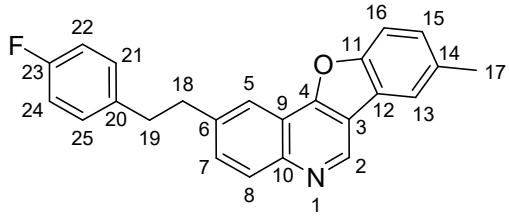
Synthesis of product **4c** as per general procedure 2 using **1d** (100 mg, 0.25 mmol), $Pd(OAc)_2$ (2.86 mg, 5 mol%), TBAOAc (383.5 mg, 1.27 mmol), styrene (32.0 µL, 0.28 mmol) and one hydrogen balloon.



White solid; 75% (64 mg); m.p. 157 – 158 °C, IR ν_{max}/cm^{-1}: 3026 (aromatic C-H stretch), 2920 (alkyl C-H stretch), 2857 (methyl C-H stretch), 1593 (C=N stretch), 1565 (aromatic C=C stretch), 1325, 1188 (ether C-O stretch); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.39 (s, 1H, H-**2**), 8.09 – 8.25 (m, 2H, H-**5**, H-**8**), 7.85 (s, 1H, H-**13**), 7.60 (d, 1H, *J* 8.4 Hz, H-**16**), 7.16 – 7.36 (m, 6H, H-**15**, H-**21**, H-**22**, H-**23**, H-**24**, H-**25**), 3.03 – 3.25 (m, 4H, H-**18**, H-**19**), 2.55 (s, 3H, C(**17**)-H_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.6 (q*C*-**4**), 154.4 (q*C*-**11**), 145.8 (q*C*-**10**), 143.4 (*C*H-**2**), 141.3 (q*C*-**20**), 141.0 (q*C*-**6**), 133.8 (q*C*-**14**), 130.9 (*C*H-**7**), 129.4 (*C*H-**8**), 128.5 (3 × *C*H-**22**, *C*H-**23**, *C*H-**24**) , 128.4 (*C*H-**15**), 126.1 (2 × *C*H-**21**, *C*H-**25**), 122.7 (q*C*-**12**), 120.6 (*C*H-**13**), 119.3 (*C*H-**5**), 117.2 (q*C*-**9**), 116.4 (q*C*-**3**), 111.6 (*C*H-**16**), 38.1 (*C*H_2-**18**), 37.7 (*C*H_2-**19**), 21.5 (*C*H_3-**17**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{24}H_{20}NO_2$: 338.1539; found: 338.1544.

2-(4-Fluorophenethyl)-8-methylbenzofuro[3,2-c]quinoline 4d

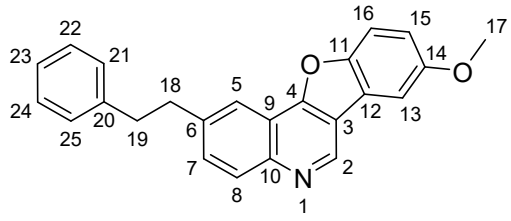
Synthesis of product **4d** as per general procedure 2 using **1d** (100 mg, 0.25 mmol), $Pd(OAc)_2$ (2.86 mg, 5 mol%), TBAOAc (383.5 mg, 1.27 mmol), 4-fluorostyrene (33.4 µL, 0.28 mmol) and one hydrogen balloon.



White solid; 76% yield (68 mg); m.p. 151 - 153 °C; IR ν_{max}/cm^{-1}: 2921 (alkyl C-H stretch), 2855 (methyl C-H stretch), 1597 (C=N stretch), 1565 (aromatic C=C stretch), 1324, 1218 (ether C-O stretch), 1185 (C-F stretch); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.38 (s, 1H, H-**2**), 8.17 (d, 1H, *J* 8.7 Hz, H-**8**), 8.12 (s, 1H, H-**5**), 7.84 (s, 1H, H-**13**), 7.58 (d, 1H, *J* 8.4 Hz, H-**16**), 7.56 (dd, 1H, *J* 8.7, 1.9 Hz, H-**7**), 7.31 (dd, 1H, *J* 8.4, 1.3 Hz, H-**15**), 7.11-7.16 (m, 2H, H-**21**, H-**25**), 6.93 – 6.98 (m, 2H, H-**22**, H-**24**), 3.10 (m, 4H, H-**18**, H-**19**), 2.53 (s, 3H, C(**17**)-H_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.4 (d, $^{1}J_{(C,F)}$ = 248 Hz, *C*(**23**)-F), 157.5 (q*C*-**4**), 154.4 (q*C*-**11**), 145.9 (q*C*-**10**), 143.4 (*C*H-**2**), 140.6 (q*C*-**6**), 136.8 (d, $^{4}J_{(C,F)}$ = 3 Hz q*C*-**20**), 133.8 (q*C*-**14**), 130.7 (*C*H-**7**), 129.8 (d, $^{3}J_{(C,F)}$ = 8 Hz, 2 × *C*H-**21**, *C*H-**25**), 129.5 (*C*H-**8**), 128.4 (*C*H-**15**), 122.7 (q*C*-**12**), 120.6 (*C*H-**13**), 119.4 (*C*H-**5**), 117.2 (q*C*-**9**), 116.4 (q*C*-**3**), 115.2 (d, $^{2}J_{(C,F)}$ = 22 Hz, 2 × *C*H-**22**, *C*H-**24**), 111.6 (*C*H-**16**), 38.1 (*C*H_2-**18**), 36.8 (*C*H_2-**19**), 21.4 (*C*H_3-**17**) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -117.2 ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{24}H_{19}FNO$: 356.1445; found: 356.1447.

8-Methoxy-2-phenethylbenzofuro[3,2-c]quinoline 4e

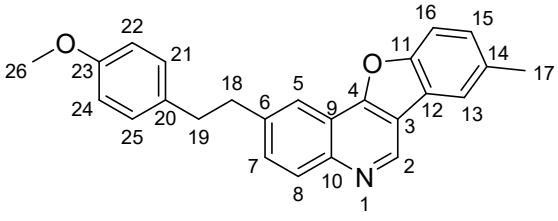
Synthesis of product **4e** as per general procedure 2 using **1b** (100 mg, 0.24 mmol), $Pd(OAc)_2$ (2.74 mg, 5 mol%), TBAOAc (369 mg, 1.22 mmol), styrene (31.0 µL, 0.27 mmol) and one hydrogen balloon.



White solid, 78% yield (68 mg), m.p. 152-153; IR ν_{max}/cm^{-1}: 3030 (aromatic C-H stretch), 2920 (alkyl C-H stretch), 2830 (methoxy C-H stretch), 1594 (C=N stretch), 1568 (aromatic C=C stretch), 1319, 1267, 1228 (ether C-O stretch); ^{1}H NMR (400 MHz, $CDCl_3$): δ =9.41 (s, 1H, H-**2**), 8.21 (d, 1H, *J* 8.7 Hz, H-**8**), 8.17 (s, 1H, H-**5**), 7.63 (d, 1H, *J* 9.0 Hz, *H*-**16,** overlapping with H-**7**), 7.62 (dd, 1H, *J* 8.4, 1.8 Hz, H-**7,** overlapping with H-**16**), 7.52 (d, 1H, *J* 2.5 Hz, H-**13**), 7.19 – 7.34 (m, 5H, H-**21**, H-**22**, H-**23**, H-**24**, H-**25**), 7.12 (dd, 1H, *J* 9.0 Hz, 2.5, H-**15**), 3.95 (s, 3H, C(17)-H_3), 3.05 – 3.25 (m, 4H, C(**18**)-H_2, C(**19**)-H_2) ppm; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 158.2 (q*C*-**4**), 156.9 (q*C*-**11**), 150.7 (q*C*-**14**), 145.4 (q*C*-**10**), 143.1 (*C*H-**2**), 141.2 (2 × q*C*-**6**, q*C*-**20**), 131.1 (*C*H-**7**), 129.1 (*C*H-**8**), 128.5 (3 × *C*H-**22**, *C*H-**23**, *C*H-**24**), 126.2 (2 × *C*H-**21**, *C*H-**25**), 123.2 (q*C*-**12**), 119.4 (*C*H-**5**), 117.2 (q*C*-**9**), 116.7 (q*C*-**3**), 115.7 (*C*H-**15**), 112.7 (*C*H-**16**), 103.3 (*C*H-**13**), 56.1 (CH_3-**17**), 38.1 (CH_2-**18**), 37.7 (CH_2-**19**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{24}H_{20}NO_2$: 354.1489; found: 354.1489.

2-(4-Methoxyphenethyl)-8-methylbenzofuro[3,2-c]quinoline 4f

Synthesis of product **4f** as per general procedure 2 using **1d** (100 mg, 0.25 mmol), $Pd(OAc)_2$ (2.86 mg, 5 mol%), TBAOAc (383.5 mg, 1.27 mmol), 4-methoxystyrene (37.2 µL, 0.28 mmol) and one hydrogen balloon.

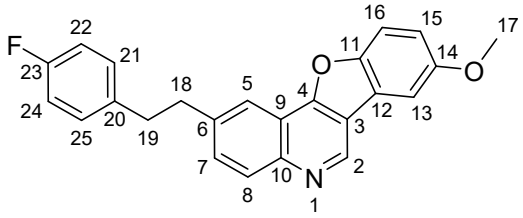


White solid; 82% yield (77 mg); m.p. 156-158 °C; IR ν_{max}/cm^{-1}: 2960 (alkyl C-H stretch), 2875 (methyl C-H stretch), 2837 (methoxy C-H stretch), 1611 (C=N stretch), 1563 (aromatic C=C stretch), 1367, 1187, 1175 (ether C-O stretch); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.41 (s, 1H, H-**2**), 8.19 (d, 1H, H-**8**, overlapping with H-**5**), 8.18 (s, 1H, H-**5,** overlapping with H-**8**), 7.90 (s, 1H, H-**13**), 7.62 (d, 1H, *J* 8.4, H-**16,** overlapping with H-**7**), 7.60 (d, 1H, H-**7** overlapping with H-**16**), 7.35 (dd, 1H, *J* 8.4, 1.5, H-**15**), 7.10 – 7.16 (m, 2H, H-**21**, H-**25**), 6.80 – 6.86 (m, 2H, H-**22**, H-**24**), 3.79 (s, 3H, C(**26**)-H_3), 3.01 – 3.20 (m, 4H, H-**19**, H-**18**), 2.56 (s, 3H, C(**17**)-H_3) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 157.9 (q*C*-**23**), 157.6 (q*C*-**4**), 154.4 (q*C*-**11**), 145.7 (q*C*-**10**), 143.3 (*C*H-**2**), 141.1 (q*C*-**6**), 133.9 (q*C*-**14**), 133.3 (q*C*-**20**), 131.0 (*C*H-**7**), 129.4 (2 × *C*H-**21**, *C*H-**25**), 129.3 (*C*H-**8**), 128.4 (*C*H-**15**), 122.7 (q*C*-

12), 120.6 (*C*H-**13**), 119.4 (*C*H-**5**), 117.2 (q*C*-**9**), 116.4 (q*C*-**3**), 113.8 (2 × *C*H-**22**, *C*H-**24**), 111.6 (*C*H-**16**), 55.3 (CH_3-**26**), 38.3 (CH_2-**18**), 36.8 (CH_2-**19**), 21.5 (CH_3-**17**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{25}H_{22}NO_2$: 368.1645; found: 368.1656.

2-(4-Fluorophenethyl)-8-methoxybenzofuro[3,2-c]quinoline 4g

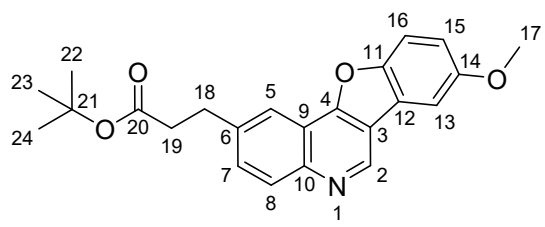
Synthesis of product **4g** as per general procedure 2 using **1b** (100 mg, 0.24 mmol), $Pd(OAc)_2$ (2.74 mg, 5 mol%), TBAOAc (369 mg, 1.22 mmol), 4-fluorostyrene (32.9 µL, 0.27 mmol) and one hydrogen balloon.



White solid, 83% yield (75 mg); m.p. 170 – 171 °C; IR ν_{max}/cm^{-1}: 2944 (alkyl C-H stretch), 2861 (methoxy C-H stretch), 1600 (C=N stretch), 1565 (aromatic C=C stretch), 1368, 1245, 1219 (ether C-O stretch), 1049 (C-F stretch); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.38 (s, 1H, H-**2**), 8.15 (d, 1H, *J* 8.6 Hz, H-**8**), 8.11 (s, 1H, H-**5**), 7.60 (d, 1H, *J* 9.0 Hz, H-**16**), 7.56 (dd, 1H, *J* 8.6, 1.8 Hz, H-**7**), 7.50 (d, 1H, *J* 2.6 Hz, H-**13**), 7.12 – 7.17 (m, 2H, H-**21**, H-**25**), 7.10 (dd, 1H, *J* 9.0, 2.6 Hz, H-**15**), 6.93 – 6.99 (m, 2H, H-**22**, H-**24**), 3.94 (s, 3H, C(**17**)-H_3), 3.01 – 3.19 (m, 4H, H-**18**, H-**19**) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.4 (d, $^1J_{(C,F)}$ = 244 Hz, C(**23**)-F), 157.9 (q*C*-**4**), 156.9 (q*C*-**11**), 150.7 (q*C*-**14**), 146.1 (q*C*-**10**), 143.6 (*C*H-**2**), 140.5 (q*C*-**6**), 136.8 (d, $^4J_{(C,F)}$ = 3 Hz, q*C*-**20**), 130.7 (*C*H-**7**), 129.8 (d, $^3J_{(C,F)}$ = 8 Hz, *C*H-**21**, *C*H-**25**), 129.8 (*C*H-**8**), 123.3 (q*C*-**12**), 119.3 (*C*H-**5**), 117.2 (q*C*-**9**), 116.7 (q*C*-**3**), 115.5 (*C*H-**15**), 115.2 (d, $^2J_{(C,F)}$ = 22 Hz, *C*H-**22**, *C*H-**24**), 112.6 (*C*H-**16**), 103.4 (*C*H-**13**), 56.1 (CH_3-**17**), 38.1 (CH_2-**18**), 36.8 (CH_2-**19**) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -117.2 ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{24}H_{19}FNO_2$: 372.1399; found: 372.1394.

***tert*-Butyl 3-(8-methoxybenzofuro[3,2-c]quinolin-2-yl)propanoate 4h**

Synthesis of product **4h** as per general procedure 2 using **1b** (100 mg, 0.24 mmol), $Pd(OAc)_2$ (2.74 mg, 5 mol%), TBAOAc (369 mg, 1.22 mmol), *tert*-butylacrylate (39.4 µL, 0.27 mmol) and one hydrogen balloon.

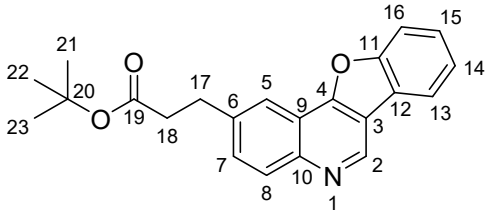


White solid, 81% yield (75 mg); m.p. 119-120 °C; IR ν_{max}/cm^{-1}: 2981 (alkyl C-H stretch), 2830 (methoxy C-H stretch), 1717 (ester C=O stretch), 1594 (C=N stertch), 1567 (aromatic C=C stretch), 1367, 1205 (ether C-O stretch), 1147 (ester C-O stretch), 1028

(ether C-O stretch); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.37 (s, 1H, H-**2**), 8.13 – 8.21 (m, 2H, H-**5**, H-**8**), 7.63 (d, 1H, *J* 7.2 Hz, H-**7**), 7.60 (d, 1H, *J* 9.0 Hz, H-**16**), 7.46 (d, 1H, *J* 2.5 Hz, H-**13**), 7.09 (dd, 1H, *J* 9.0, 2.5 Hz, H-**15**), 3.93 (s, 3H, C(**17**)-H_3), 3.18 (t, 2H, *J* 7.7 Hz, H-**18**), 2.71 (t, 2H, *J* 7.7 Hz, H-**19**), 1.43 (s, 9H, 3 × C(**22**)-H_3, C(**23**)-H_3, C(**24**)-H_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.9 (q*C*-**20**), 157.9 (q*C*-**4**), 156.8 (q*C*-**11**), 150.7 (q*C*-**14**), 146.1 (q*C*-**10**), 143.5 (*C*H-**2**), 139.9 (q*C*-**6**), 130.5 (*C*H-**7**), 129.8 (*C*H-**8**), 123.3 (q*C*-**12**), 119.3 (*C*H-**5**), 117.2 (q*C*-**9**), 116.7 (q*C*-**3**), 115.5 (*C*H-**15**), 112.6 (*C*H-**16**), 103.3 (*C*H-**13**), 80.6 (q*C*-**21**), 56.0 (CH_3-**17**), 36.7 (CH_2-**19**), 31.2 (CH_2-**18**), 28.1 (3 × CH_3-**22**, CH_3-**23**, CH_3-**24**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{23}H_{24}NO_4$: 378.1700; found: 378.1703.

tert-Butyl 3-(benzofuro[3,2-c]quinolin-2-yl)propanoate 4i

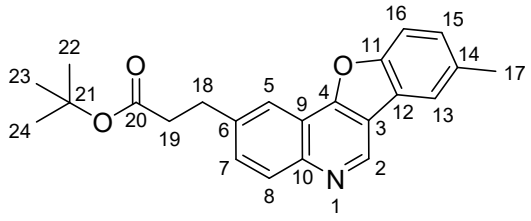
Synthesis of product **4i** as per general procedure 2 using **1c** (100 mg, 0.26 mmol), $Pd(OAc)_2$ (2.96 mg, 5 mol%), TBAOAc (398 mg, 1.32 mmol), *tert*-butylacrylate (42.0 µL, 0.29 mmol) and one hydrogen balloon



White solid, 76% yield (DCM:EtOAc, 70 mg), 73% yield (cyclohexane:EtOAc, 67 mg); m.p. 109 – 110 °C; IR ν_{max}/cm^{-1}: 2923 (alkyl C-H stretch), 1728 (ester C=O stretch), 1599 (C=N stretch), 1462 (aromatic C=C stretch), 1368, 1270 (ether C-O stretch), 1150 (ester C-O stretch); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.43 (s, 1H, H-**2**), 8.16 – 8.24 (m, 2H, H-**5**, H-**8**), 8.10 (dd, 1H, *J* 7.7, 0.6 Hz, H-**13**), 7.72 (d, 1H, *J* 8.4 Hz, H-**16**), 7.64 (br d, 1H, *J* 6.8 Hz, H-**7**), 7.50 – 7.54 (m, 1H, H-**15**), 7.42 – 7.47 (m, 1H, H-**14**), 3.19 (t, 2H, *J* 7.8 Hz, C(**17**)-H_2), 2.72 (t, 2H, *J* 7.8 Hz, C(**18**)-H_2), 1.43 (s, 9H, C(**21**)-H_3, C(**22**)-H_3, C(**23**)-H_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.9 (q*C*-**19**), 157.3 (q*C*-**4**), 156.0 (q*C*-**11**), 146.0 (q*C*-**10**), 143.5 (*C*H-**2**), 140.1 (q*C*-**6**), 130.7 (*C*H-**7**), 129.6 (*C*H-**8**), 127.3 (*C*H-**15**), 124.1 (*C*H-**14**), 122.7 (q*C*-**12**), 120.6 (*C*H-**13**), 119.3 (*C*H-**5**), 117.1 (q*C*-**9**), 116.5 (q*C*-**3**), 112.1 (*C*H-**16**), 80.6 (q*C*-**20**), 36.7 (CH_2-**18**), 31.2 (CH_2-**17**), 28.1 (3 × CH_3-**21**, CH_3-**22**, CH_3-**23**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{22}H_{22}NO_3$: 348.1594; found: 348.1585.

tert-Butyl 3-(8-methylbenzofuro[3,2-c]quinolin-2-yl)propanoate 4j

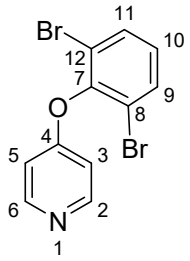
Synthesis of product **4j** as per general procedure 2 using **1d** (100 mg, 0.25 mmol), $Pd(OAc)_2$ (2.86 mg, 5 mol%), TBAOAc (383.5 mg, 1.27 mmol), *tert*-butylacrylate (41.0 µL, 0.28 mmol) and one hydrogen balloon.



White solid; 76% yield (70 mg); m.p. 115-116 °C; IR ν_{max}/cm^{-1}: 2962 (alkyl C-H stretch), 2873 (methyl C-H stretch), 1731 (ester C=O stretch), 1594 (C=N stretch), 1567 (aromatic C=C stretch), 1302, 1255 (ether C-O stretch), 1190 (ester C-O stretch); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.39 (s, 1H, H-**2**), 8.20 (s, 1H, H-**5**), 8.18 (d, 1H, *J* 8.5 Hz, H-**8**), 7.86 (s, 1H, H-**13**), 7.63 (dd, 1H, *J* 8.5, 1.8 Hz, H-**7**), 7.60 (d, 1H, *J* 8.4 Hz, H-**16**), 7.33 (dd, 1H, *J* 8.4, 1.2 Hz, H-**15**), 3.19 (t, 1H, *J* 7.7 Hz, H-**18**), 2.71 (t, 1H, *J* 7.7 Hz, H-**19**), 2.55 (s, 3H, C(**17**)-H_3), 1.43 (s, 9H, C(**22**)-H_3, C(**23**)-H_3, C(**24**)-H_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.0 (q*C*-**20**), 157.5 (q*C*-**4**), 154.4 (q*C*-**11**), 146.1 (*C*H-**10**), 143.6 (*C*H-**2**), 140.0 (q*C*-**6**), 133.8 (q*C*-**14**), 130.5 (*C*H-**7**), 129.7 (*C*H-**8**), 128.4 (*C*H-**15**), 122.7 (q*C*-**12**), 120.5 (*C*H-**13**), 119.3 (*C*H-**5**), 117.2 (q*C*-**9**), 116.4 (q*C*-**3**), 111.6 (*C*H-**16**), 80.6 (q*C*-**21**), 36.8 (**C**H_2-**19**), 31.2 (*C*H_2-**18**), 28.1 (3 × *C*H_3-**22**, *C*H_3-**23**, *C*H_3-**24**), 21.4 (*C*H_3-**17**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{23}H_{24}NO_3$: 362.1751; found: 362.1757.

Synthesis of phenenoxypyridine starting material:

4-(2,6-Dibromophenoxy)pyridine 5

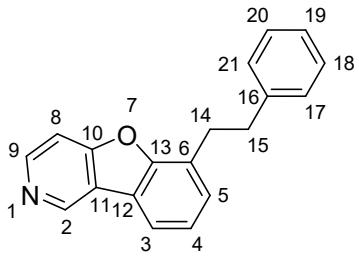


A mixture of 4-chloropyridine hydrochloride (1.0 g, 6.67 mmol) and 2,6-dibromophenol (5.8 g, 23.3 mmol) were stirred 130 °C 24 hours. The reaction mixture was cooled to room temperature and 10% aqueous NaOH (10 mL) was added and stirred for 30 min. The aqueous layer was extracted with DCM (3 × 15 mL). The organic layers were combined and washed with 6M NaOH (3 × 15 mL), water (10 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo.* The crude product was recrystallised from cyclohexane if necessary. White solid, 46% yield (1.01 g); m.p. 92 – 93 °C (lit: 91 – 93 °C)[3]; IR ν_{max}/cm^{-1}: 1578 (C=N stretch), 1257, 1202 (ether C-O stretch), 667 (C-Br stretch); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.49 (d, 2H, *J* 5.2 Hz, H-**2**, H-**6**), 7.63 (d, 2H, *J* 8.1 Hz, H-**9**, H-**11**), 7.07 (t, 1H, *J* 8.1 Hz, H-**10**), 6.72 – 6.77 (m, 2H, H-**3**, H-**5**) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 162.5 (q*C*-**4**), 151.5 (2 × *C*H-**2**, *C*H-**6**), 147.7 (q*C*-**7**), 133.1 (2 × *C*H-**9**, *C*H-**11**), 128.3 (*C*H-**10**), 118.3 (2 × q*C*-**8**, q*C*-**12**), 110.8 (2 × *C*H-**3**, *C*H-**5**) ppm; LRMS m/z (ESI+) 328, 330, 332 [$(M+H)^+$, 100%].

One-pot pyridine products:

6-Phenethylbenzofuro[3,2-c]pyridine 6a

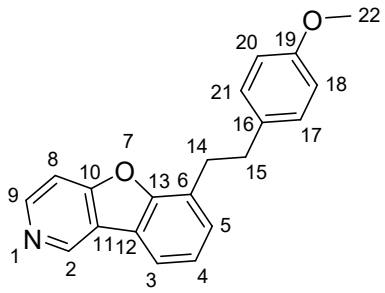
Synthesis of product **6a** as per general procedure 2 using **5** (100 mg, 0.30 mmol), $Pd(OAc)_2$ (3.41 mg, 5 mol%), TBAOAc (458.2 mg, 1.51 mmol), styrene (38.3 µL, 0.33 mmol) and one hydrogen balloon.



Colourless oil, 66% yield (55 mg); IR ν_{max}/cm^{-1}: 3022 (aromatic C-H stretch), 2921 (alkyl C-H stretch), 1599 (C=N stretch), 1494 (aromatic C=C stretch), 1346, 1244 (ether C-O stretch); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.35 (br s, 1H, H-**2**), 8.75 (br s, 1H, H-**9**), 7.87 (dd, 1H, *J* 7.4, 1.0 Hz, H-**4**), 7.57 (br s, 1H, H-**8**), 7.17 – 7.35 (m, 7H, H-**3**, H-**5**, H-**17**, H-**18**, H-**19**, H-**20**, H-**21**), 3.05 – 3.32 (m, 4H, C(**14**)-H_2, C(**15**)-H_2) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 160.8 (q*C*-**10**), 154.5 (q*C*-**13**), 146.8 (*C*H-**9**), 143.2 (*C*H-**2**), 141.3 (q*C*-**16**), 128.6 (*C*H-**5**), 128.5 (*C*H-**17**, *C*H-**21**), 128.4 (*C*H-**18**, *C*H-**20**), 126.2 (q*C*-**6**), 126.1 (*C*H-**19**), 124.0 (*C*H-**3**), 121.3 (2 × q*C*-**11**, q*C*-**12**), 118.9 (*C*H-**4**), 108.0 (*C*H-**8**), 36.1 (CH_2-**15**), 31.9 (CH_2-**14**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{19}H_{16}NO$: 273.1274; found: 273.1286.

6-(4-Methoxyphenethyl)benzofuro[3,2-c]pyridine 6b

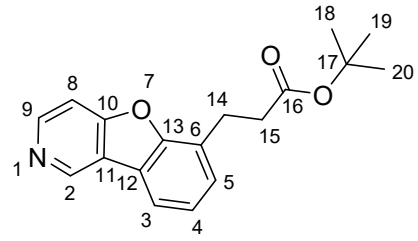
Synthesis of product **6b** as per general procedure 2 using **5** (100 mg, 0.30 mmol), $Pd(OAc)_2$ (3.41 mg, 5 mol%), TBAOAc (458.2 mg, 1.51 mmol), 4-methoxystyrene (44.5 µL, 0.33 mmol) and one hydrogen balloon.



Colourless oil, 65% yield (60 mg); IR ν_{max}/cm^{-1}: 3031 (aromatic C-H stretch), 2925 (alkyl C-H stretch), 2855 (methoxy C-H stretch), 1594 (C=N stretch), 1575 (aromatic C=C stretch), 1340, 1243 (ether C-O stretch); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.27 (br s, 1H, H-**2**), 8.67 (br s, 1H, H-**9**), 8.87 (dd, 1H, *J* 7.3, 1.7 Hz, H-**4**), 7.53 (br d, 1H, *J* 3.9 Hz, H-**9**), 7.26 – 7.36 (m, 2H, H-**3**, H-**5**), 7.10 – 7.16 (m, 2H, H-**17**, H-**21**), 6.82 (m, 2H, H-**18**, H-**20**), 3.78 (s, 3H, C(**22**)-H_3), 2.97 – 3.31 (m, 4H, C(**14**)-H_2, C(**15**)-H_2) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 160.8 (q*C*-**19**), 157.9 (q*C*-**10**), 154.5 (q*C*-**13**), 147.1 (*C*H-**9**), 143.5 (*C*H-**2**), 133.5 (q*C*-**16**), 129.4 (2 × *C*H-**17**, *C*H-**21**), 128.6 (*C*H-**5**), 126.2 (q*C*-**6**), 123.9 (*C*H-**3**), 122.1 (q*C*-**11**), 121.2 (*C*H-**12**), 118.8 (*C*H-**4**), 113.8 (2 × *C*H-**18**, *C*H-**19**), 107.6 (*C*H-**8**), 55.3 (CH_3-**22**), 35.2 (CH_2-**15**), 32.2 (CH_2-**14**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{20}H_{18}NO_2$: 304.1332; found: 304.1336.

***tert*-Butyl 3-(benzofuro[3,2-c]pyridin-6-yl)propanoate 6c**

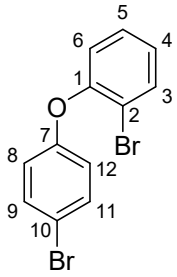
Synthesis of product **6c** as per general procedure 2 using **5** (100 mg, 0.30 mmol), $Pd(OAc)_2$ (3.41 mg, 5 mol%), TBAOAc (458.2 mg, 1.51 mmol), *tert*-butylacrylate (49.0 µL, 0.33 mmol) and one hydrogen balloon.



Colourless oil, 73% yield (66 mg); IR ν_{max}/cm^{-1}: 2976 (alkyl C-H stretch), 1724 (ether C=O stretch), 1593 (C=N stretch), 1575 (aromatic C=C stretch), 1367, 1209 (ether C-O stretch), 1145 (ester C-O stretch); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.24 (s, 1H, H-**2**), 8.65 (d, 1H, *J* 5.9 Hz, H-**9**), 7.88 (dd, 1H, *J* 6.9, 2.1 Hz, H-**4**), 7.54 (dd, 1H, *J* 5.7, 0.8 Hz, H-**8**), 7.31 – 7.40 (m, 2H, H-**3**, H-**5**), 3.28 (t, 2H, *J* 7.6 Hz, C(**14**)-H_2), 2.74 (t, 2H, *J* 7.6 Hz, C(**15**)-H_2), 1.41 (s, 9H, C(**18**)-H_3, C(**19**)-H_3, C(**20**)-H_3) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 172.0 (q*C*-**16**), 160.9 (q*C*-**10**), 154.5 (q*C*-**13**), 147.0 (*C*H-**9**), 143.4 (*C*H-**2**), 128.6 (*C*H-**5**), 125.2 (q*C*-**6**), 124.1 (*C*H-**3**), 122.0 (q*C*-**11**), 121.3 (q*C*-**12**), 119.2 (*C*H-**4**), 107.7 (*C*H-**8**), 80.6 (q*C*-**17**), 35.3 (CH_2-**15**), 28.1 (3 × CH_3-**18**, CH_3-**19**, CH_3-**20**), 25.4 (CH_2-**14**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{18}H_{20}NO_3$: 298.1438; found: 298.1436.

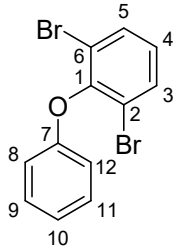
Synthesis of diaryl ether starting materials:

1-Bromo-2-(4-bromophenoxy)benzene 7



A mixture of 2-bromophenol (361.8 mg, 2.1 mmol), 4-bromophenylboronic acid (840.0, 4.18 mmol), $Cu(OAc)_2$ (363.0 mg, 2.0 mmol), Et_3N (1.4 mL, 10 mmol), 3 Å molecular sieves (250 mg) was added to DCM (20 mL) and stirred at room temperature for 72 hours. The reaction mixture was diluted with hexane, filtered through celite, and concentrated *in vacuo*. The crude product was purified by column chromatography over silica gel and eluted with hexane (100%). Colourless oil, 48% yield (332 mg); IR ν_{max}/cm^{-1}: 3065 (aromatic C-H stretch), 1575 (aromatic C=C stretch), 1232, 1163 (ether C-O stretch), 659 (C-Br stretch); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.63 (dd, 1H, *J* 7.9, 1.5 Hz, H-**3**), 7.38 – 7.45 (m, 2H, H-**9**, H-**11**), 7.27 (td, 1H, *J* 8.0, 8.0, 1.6 Hz, H-**5**), 7.04 (td, 1H, *J* 8.0, 8.0, 1.6 Hz, H-**4**), 6.97 (dd, 1H, *J* 8.1, 1.4, H-**6**), 6.79 – 6.85 (m, 2H, H-**8**, H-**12**) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 156.3 (q*C*-**7**), 153.1 (q*C*-**1**), 134.1 (*C*H-**3**), 132.8 (2 × *C*H-**9**, *C*H-**11**), 128.9 (*C*H-**5**), 125.7 (*C*H-**4**), 121.1 (*C*H-**6**), 119.6 (*C*H-**8**), 115.8 (*C*H-**10**), 115.3 (*C*H-**2**) ppm; LRMS m/z (ESI+) 329 [(M+H)+ , 10%].

1,3-Dibromo-2-phenoxybenzene 8

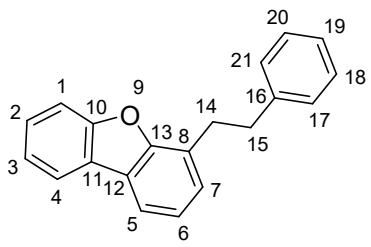


To a solution of 2,6-dibromophenol (600 mg, 2.38 mmol) in THF (21 mL) at 0 °C was added ^{t}BuOK (354 mg, 2.62 mmol) and stirred for 15 min. The iodonium salt (1.05 g, 2.86 mmol) was added to the mixture and was let stir at room temperature for five days. The solvent was then removed *in vacuo* and water (15 mL) was added. The aqueous phase was extracted with DCM (3 × 15 mL) and the organic layers were combined. The organic layers were washed with water (3 × 15 mL) and brine (15 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Light brown solid, 38% yield (299 mg); m.p. 55 – 57 °C; IR ν_{max}/cm^{-1}: 3072 (aromatic C-H stretch), 1589 (aromatic C=C stretch), 1242, 1194 (ether C-O stretch), 686 (C-Br stretch); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.60 (d, 2H, *J* 8.0 Hz, H-**3**, H-**5**), 7.23 – 7.34 (m, 2H, H-**9**, H-**11**), 6.97 – 7.08 (m, 2H, H-**4**, H-**10**), 6.77 – 6.84 (m, 2H, H-**8**, H-**12**) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 156.5 (q*C*-**7**), 149.2 (q*C*-**1**), 133.1 (2 × *C*H-**3**, *C*H-**5**), 129.7 (*C*H-**9**, *C*H-**11**), 127.4 (*C*H-**4**), 122.5 (*C*H-**10**), 119.0 (2 × *C*H-**2**, *C*H-**6**), 115.1 (*C*H-**8**, *C*H-**12**) ppm; LRMS m/z (ESI+) 327 [(M-H)$^-$, 55%].

One-pot diarylether products

4-Phenethyldibenzo[b,d]furan 9a

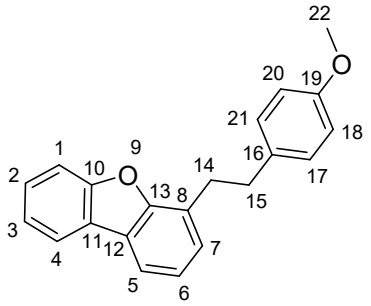
Synthesis of product **9a** as per general procedure 2 using **8** (100.0 mg, 0.30 mmol), $Pd(OAc)_2$ (3.42 mg, 5 mol%), TBAOAc (459.6 mg, 1.52 mmol), styrene (39.0 µL, 0.34 mmol) and one hydrogen balloon.



White solid, 69% (57 mg); m.p. 51 – 53 °C; IR ν_{max}/cm^{-1}: 3028 (aromatic C-H stretch), 2923 (alkyl C-H stretch), 1586 (aromatic C=C stretch) 1182 (ether C-O stretch); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (dd, 1H, *J* 0.7 Hz, H-**12**), 7.79 (dd, 1H, *J* 6.7, 2.2 Hz, H-**6**), 7.58 (d, 1H, *J* 8.2 Hz, H-**1**), 7.41 – 7.48 (m, 1H, H-**2**), 7.14 – 7.37 (m, 8H, H-**3**, H-**5**, H-**7**, H-**17**, H-**18**, H-**19**, H-**20**, H-**21**), 3.05 – 3.33 (m 4H, C(**14**)-H_2, C(**15**)-H_2) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 156.0 (q*C*-**10**), 154.7 (q*C*-**13**), 141.8 (q*C*-**16**), 128.5 (2 × *C*H-**17**, *C*H-**21**), 128.3 (2 × *C*H-**18**, *C*H-**20**), 127.3 (*C*H-**7**), 126.9 (*C*H-**2**), 126.0 (*C*H-**19**), 125.7 (q*C*-**8**), 124.5 (q*C*-**12**), 123.9 (q*C*-**11**), 122.7 (*C*H-**5**), 122.6 (*C*H-**3**), 120.7 (*C*H-**4**), 118.4 (*C*H-**6**), 111.7 (*C*H-**1**), 36.1 (CH_2-**15**), 32.0 (CH_2-**14**) ppm; HRMS (ESI-TOF) *m/z*: [M+H$^+$]: $C_{20}H_{17}O$: 273.1274; found: 273.1262.

4-(4-Methoxyphenethyl)dibenzo[b,d]furan 9b

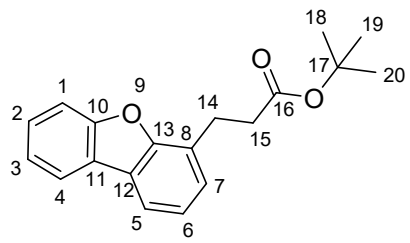
Synthesis of product **9b** as per general procedure 2 using **8** (100.0 mg, 0.30 mmol), $Pd(OAc)_2$ (3.42 mg, 5 mol%), TBAOAc (459.6 mg, 1.52 mmol), 4-methoxystyrene (45.2 µL, 0.34 mmol) and one hydrogen balloon.



White solid, 71% yield (65 mg); m.p. 78 – 80 °C; IR ν_{max}/cm^{-1}: 3026 (aromatic C-H stretch), 2910 (alkyl C-H stretch), 2833 (methoxy C-H stretch), 1510 (aromatic C=C stretch), 1303, 1241, 1180 (ether C-O stretch); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (ddd, 1H, *J* 7.6, 1.2, 0.6 Hz, H-**7**), 7.79 (dd, 1H, *J* 7.0, 1.9 Hz, H-**6**), 7.59 (d, 1H, *J* 8.2 Hz, H-**1**), 7.41 – 7.48 (m, 1H, H-**2**), 7.29 – 7.36 (m, 1H, H-**3**), 7.20 – 7.25 (m, 2H, H-**5**, H-**7**), 7.16 (m, 2H, H-**17**, H-**21**), 6.79 – 6.86 (m, 2H, H-**18**, H-**20**), 3.78 (s, 3H, C(**22**)-H_3), 2.99 – 3.29 (m, 4H, C(**14**)-H_2, C(**15**)-H_2) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 157.9 (q*C*-**19**), 156.1 (q*C*-**10**), 154.8 (q*C*-**13**), 133.9 (q*C*-**16**), 129.4 (2 × *C*H-**17**, *C*H-**21**), 127.4 (*C*H-**7**), 126.9 (*C*H-**2**), 125.9 (q*C*-**8**), 124.6 (q*C*-**11**), 123.9 (q*C*-**12**), 122.7 (*C*H-**5**), 122.6 (CH-**3**), 120.7 (*C*H-**4**), 118.4 (*C*H-**6**), 113.8 (2 × *C*H-**18**, *C*H-**20**), 111.7 (*C*H-**1**), 55.3 (CH_3-**22**), 35.2 (CH_2-**15**), 32.3 (CH_2-**14**) ppm; HRMS (ESI-TOF) *m/z*: [M+H$^+$]: $C_{21}H_{19}O_2$: 303.1380; found: 303.1393.

***tert*-Butyl 3-(dibenzo[b,d]furan-4-yl)propanoate 9c**

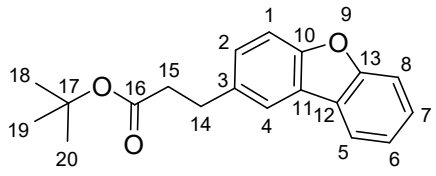
Synthesis of product **9c** as per general procedure 2 using **8** (100.0 mg, 0.30 mmol), $Pd(OAc)_2$ (3.48 mg, 5 mol%), TBAOAc (459.6 mg, 1.52 mmol), *tert*-butylacrylate (49.1 µL, 0.34 mmol) and one hydrogen balloon.



Colourless oil, 74% yield (67 mg), IR ν_{max}/cm^{-1}: 2976 (alkyl C-H stretch), 1724 (ester C=O stretch), 1587 (aromatic C=C stretch), 1350, 1184 (ether C-O stretch), 1144 (ester C-O stretch); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (dd, 1H, *J* 7.8, 0.6 Hz, H-**4**), 7.79 (dd, 1H, *J* 7.1, 1.7 Hz, H-**6**), 7.58 (d, 1H, *J* 8.2 Hz, H-**1**), 7.44 (m, 1H, H-**2**), 7.21 – 7.35 (m, 3H, H-**3**, H-**5**, H-**7**), 3.27 (t, 2H, *J* 7.7 Hz, C(**14**)-H_2), 2.74 (t, 2H, *J* 7.7 Hz, C(**15**)-H_2), 1.41 (s, 9H, C(**18**)-H_3, C(**19**)-H_3, C(**20**)-H_3) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 172.3 (q*C*-**16**), 156.0 (q*C*-**10**), 154.7 (q*C*-**13**), 131.4 (q*C*-**8**), 127.3 (*C*H-**7**), 127.0 (*C*H-**2**), 124.8 (q*C*-**12**), 124.5 (q*C*-**11**), 122.8 (*C*H-**5**), 122.6 (*C*H-**3**), 120.7 (*C*H-**4**), 118.7 (*C*H-**6**), 111.7 (*C*H-**1**), 80.4 (q*C*-**17**), 35.5 (CH_2-**15**), 28.1 (3 × CH_3-**18**, CH_3-**19**, CH_3-**20**), 25.6 (CH_2-**14**) ppm; HRMS (ESI-TOF) *m/z*: [M+Na$^+$]: $[C_{19}H_{20}O_3][Na]^+$: 319.1305; found: 319.1306.

***tert*-Butyl 3-(dibenzo[b,d]furan-2-yl)propanoate 9d**

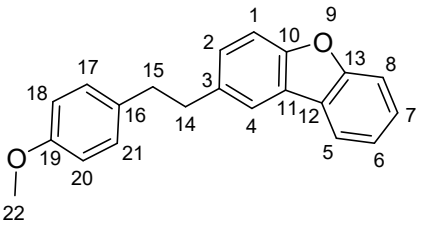
Synthesis of product **9d** as per general procedure 2 using **8** (100.0 mg, 0.30 mmol), $Pd(OAc)_2$ (3.48 mg, 5 mol%), TBAOAc (459.6 mg, 1.52 mmol), *tert*-butylacrylate (49.1 µL, 0.34 mmol) and one hydrogen balloon.



Colourless oil, 68% yield (61 mg); IR ν_{max}/cm^{-1}: 2976 (alkyl C-H stretch), 1724 (ester C=O stretch), 1366, 1194 (ether C-O stretch), 1141 (ester C-O stretch); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (dd, 1H, *J* 7.6, 0.7 Hz, H-**5**), 7.78 (d, 1H, *J* 1.3 Hz, H-**4**), 7.55 (d, 1H, *J* 8.2, H-**8**), 7.40 – 7.49 (m, 2H, H-**1**, H-**7**), 7.27 – 7.36 (m, 2H, H-**2**, H-**6**), 3.07 (t, 2H, *J* 7.7 Hz, C(**14**)-H_2), 2.62 (t, 2H, *J* 7.7 Hz, C(**15**)-H_2), 1.42 (s, 9H, 3 × C(**18**)-H_3, C(**19**)-H_3, C(**20**)-H_3) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 172.2 (q*C*-**16**), 156.6 (q*C*-**13**), 154.9 (q*C*-**10**), 135.3 (q*C*-**3**), 127.6 (*C*H-**2**), 127.0 (*C*H-**7**), 124.3 (q*C*-**11**), 124.2 (q*C*-**12**), 122.6 (*C*H-**6**), 120.5 (*C*H-**5**), 120.1 (*C*H-**4**), 111.7 (*C*H-**8**), 111.4 (*C*H-**1**), 80.4 (q*C*-**17**), 37.7 (CH_2-**15**), 31.1 (CH_2-**14**), 28.1 (3 × CH_3-**18**, CH_3-**19**, CH_3-**20**); HRMS (ESI-TOF) *m/z*: [M+Na$^+$]: $[C_{19}H_{20}O_3][Na^+]$: 319.1307; found: 319.1305

2-(4-Methoxyphenethyl)dibenzo[b,d]furan 9e

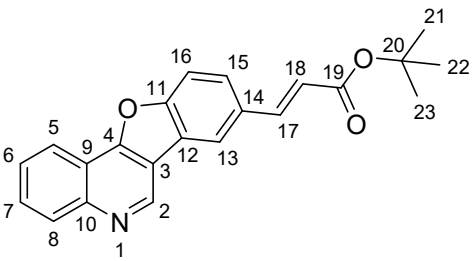
Synthesis of product **9e** as per general procedure 2 using **8** (100.0 mg, 0.30 mmol), $Pd(OAc)_2$ (3.48 mg, 5 mol%), TBAOAc (459.6 mg, 1.52 mmol), *tert*-butylacrylate (45.1 µL, 0.34 mmol) and one hydrogen balloon.



Colourless oil, 65% yield (DCM:EtOAC, 60 mg), 70% (cyclohexane,EtOAc, 65 mg); IR ν_{max}/cm^{-1}: 3039 (aromatic C-H stretch), 2857 (alkyl C-H stertch), 2839 (methoxy C-H stretch), 1510 (aromatic C=C stretch), 1300, 1244, 1175 (ether C-O stretch); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (ddd, 1H, *J* 7.6, 1.3, 0.6 Hz, H-**5**), 7.73 (dd, 1H, *J* 1.8, 0.4 Hz, H-**4**), 7.55 (ddd, 1H, *J* 8.1, 1.0, 0.7 Hz, H-**8**), 7.40 – 7.48 (m, 2H, H-**1**, H-**7**), 7.34 (dd, 1H, *J* 7.6, 1.0 Hz, H-**6**), 7.22 – 7.26 (m, 1H, H-**2**), 7.07 – 7.14 (m, 2H, H-**17**, H-**21**), 6.79 – 6.86 (m, 2H, H-**18**, H-**20**), 3.79 (s, 3H, C(**22**)-H_3)2.89 – 3.10 (m, 4H, C(**14**)-H_2, C(**15**)-H_2) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 157.9 (q*C*-**19**), 156.5 (q*C*-**13**), 154.8 (q*C*-**10**), 136.4 (q*C*-**3**), 133.8 (q*C*-**16**), 129.4 (2 × *C*H-**17**, *C*H-**21**), 127.8 (*C*H-**2**), 127.0 (*C*H-**7**), 124.3 (q*C*-**11**), 124.2 (qC-**12**), 122.5 (*C*H-**6**), 120.6 (*C*H-**5**), 120.2 (*C*H-**4**), 113.8 (2 × *C*H-**18**, *C*H-**20**), 111.6 (*C*H-**8**), 111.2 (*C*H-**1**), 55.3 (CH_3-**22**), 38.1 (CH_2-**14**), 37.6 (CH_2-**15**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{21}H_{19}O_2$: 303.1016; found: 303.1011.

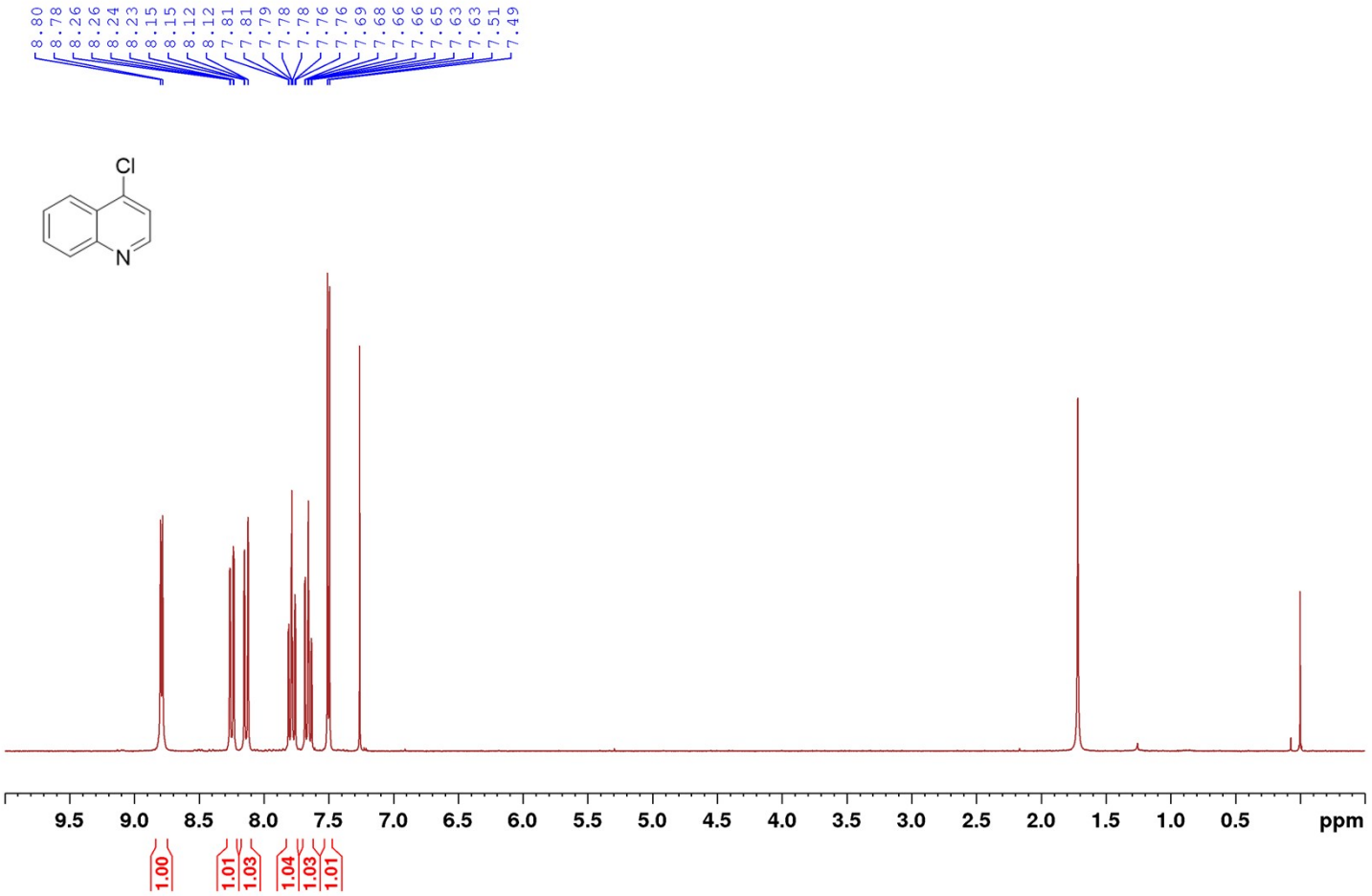
***tert*-Butyl (*E*)-3-(benzofuro[3,2-c]quinolin-8-yl)acrylate S2**

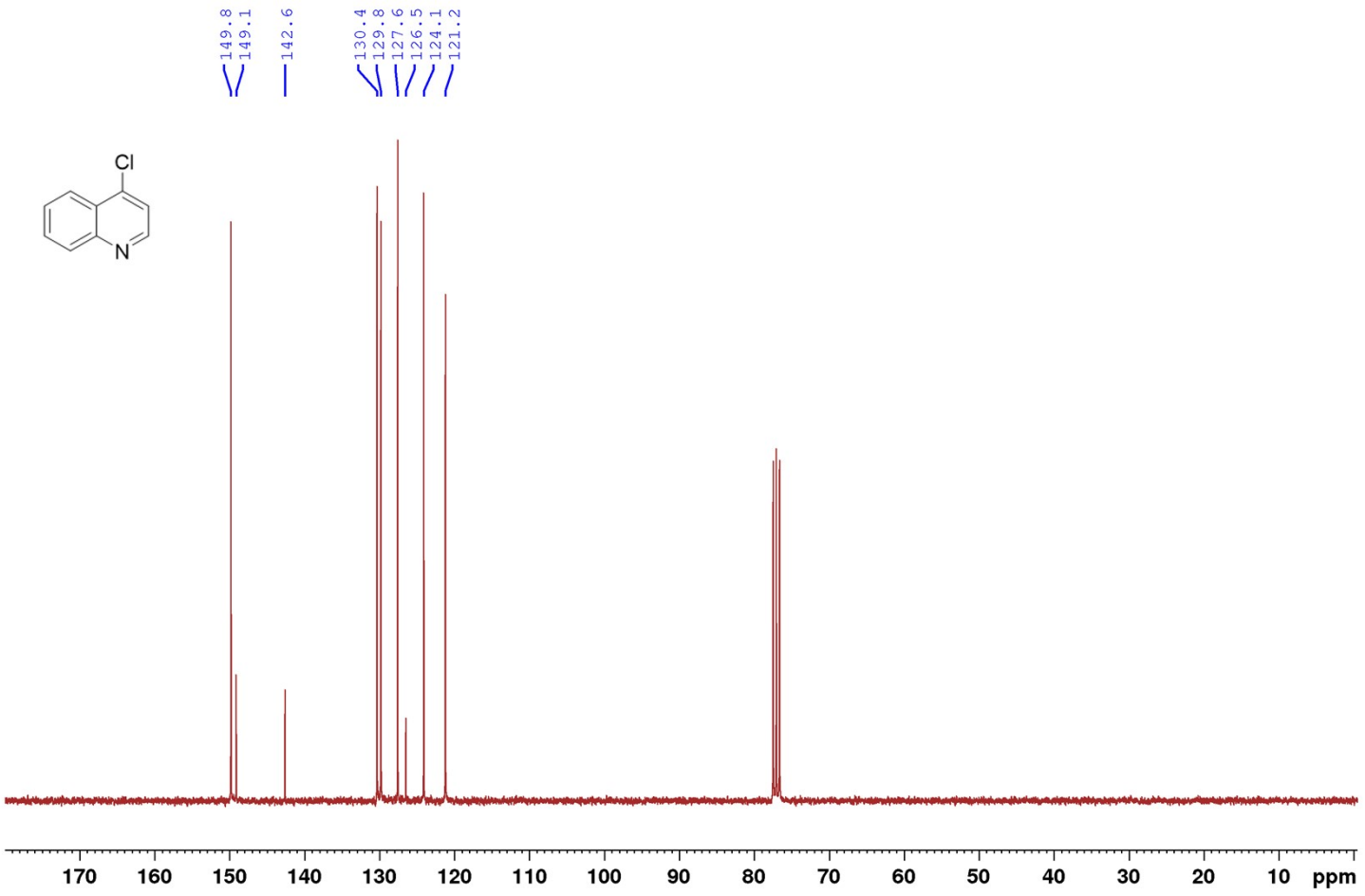
Synthesis of product **S2** as per general procedure 1 using **1a** (1.00 g, 2.64 mmol), $Pd(OAc)_2$ (29.6 mg, 5 mol%), TBAOAc (3.97 g, 13.19 mmol), *tert*-butylacrylate (425 µL, 2.90 mmol) and hydrogen balloons.



white solid, 88% yield (802 mg); m.p. 155–157 °C; IR ν_{max}/cm^{-1}: 1704 (ester C=O stretch), 1668 (trans alkene C=C stretch), 1599 (C=N stretch), 1565 (aromatic C=C stretch), 1337, 1208 (ether C-O stretch), 1149 (ester C-O stretch); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.45 (s, 1H, H-**2**), 8.36 (dd, 1H, *J* 8.1, 1.1 Hz, H-**5**), 8.25 (d, 1H, *J* 8.4, H-**8**), 8.17 (s, 1H, H-**13**), 7.83–7.62 (m, 5H, H-**6**, H-**7**, H-**15**, H-**16**, H-**17**), 6.47 (d, *J* = 15.9 Hz, 1H, H-**18**), 1.58 (s, 9H, C(**21**)-***H***$_3$, C(**22**)-H_3, C(**23**)-H_3) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = : 166.2 (q*C*-**19**), 158.2 (q*C*-**4**), 156.7 (q*C*-**11**), 147.7 (q*C*-**10**), 144.3 (*C*H-**2**), 143.0 (*C*H-**17**), 131.2 (q*C*-**14**), 130.0 (*C*H-**8**), 129.6 (*C*H-**7**), 127.24 (*C*H-**6**), 127.21 (*C*H-**15**), 123.5 (q*C*-**12**), 120.8 (*C*H-**5**), 120.3 (*C*H-**18**), 120.2 (*C*H-**13**), 117.1 (q*C*-**9**), 115.9 (q*C*-**3**), 112.5 (*C*H-**16**), 80.7 (q*C*-**20**), 28.2 (× 3 CH_3-**21**, CH_3-**22**, CH_3-**23**) ppm; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ $C_{22}H_{20}NO_3$: 346.1438; found: 346.1430.

4-Chloroquinoline S1

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127.6
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124.1
121.2
Cl
N
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160
150
140
130
120
110
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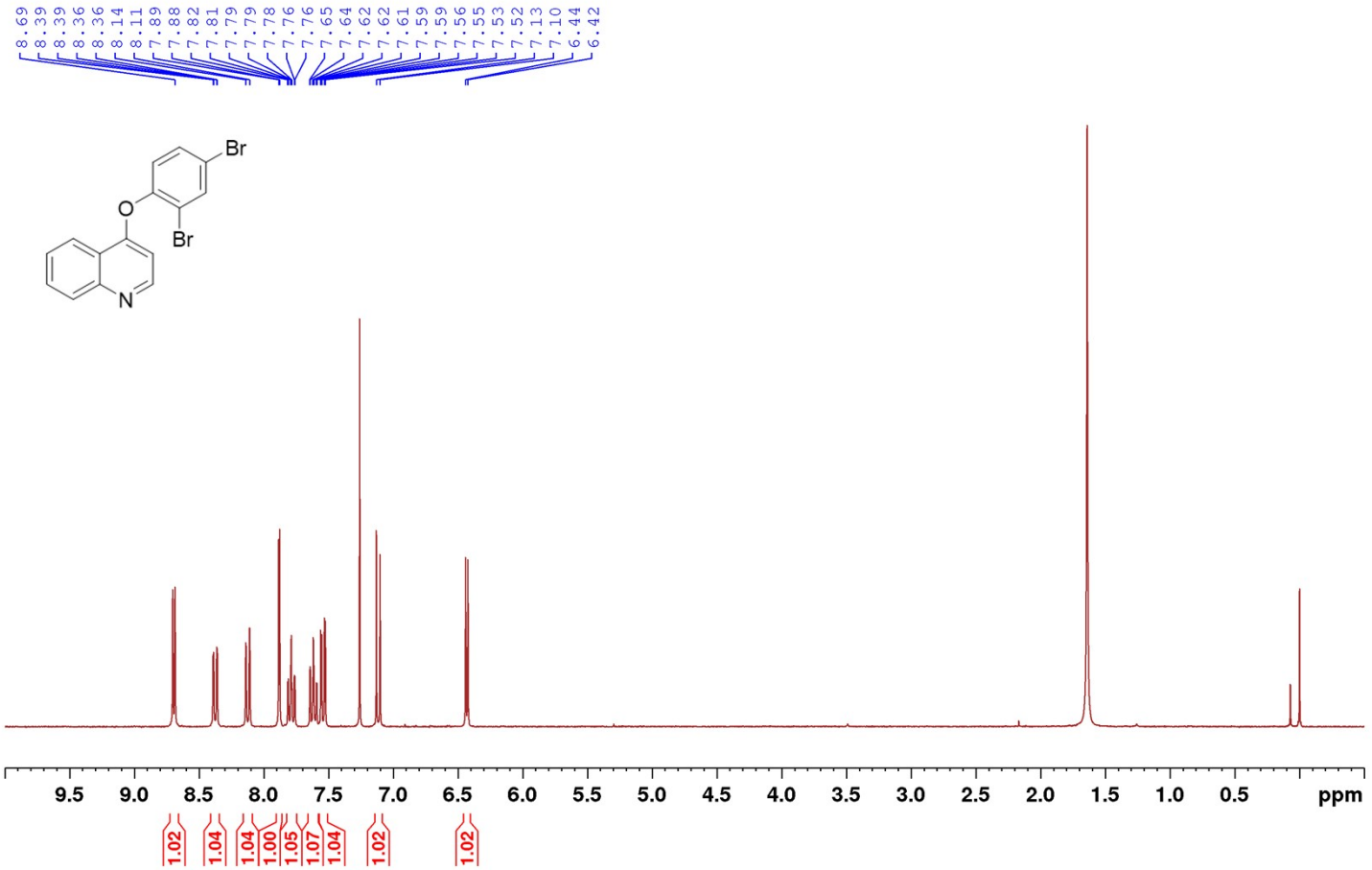
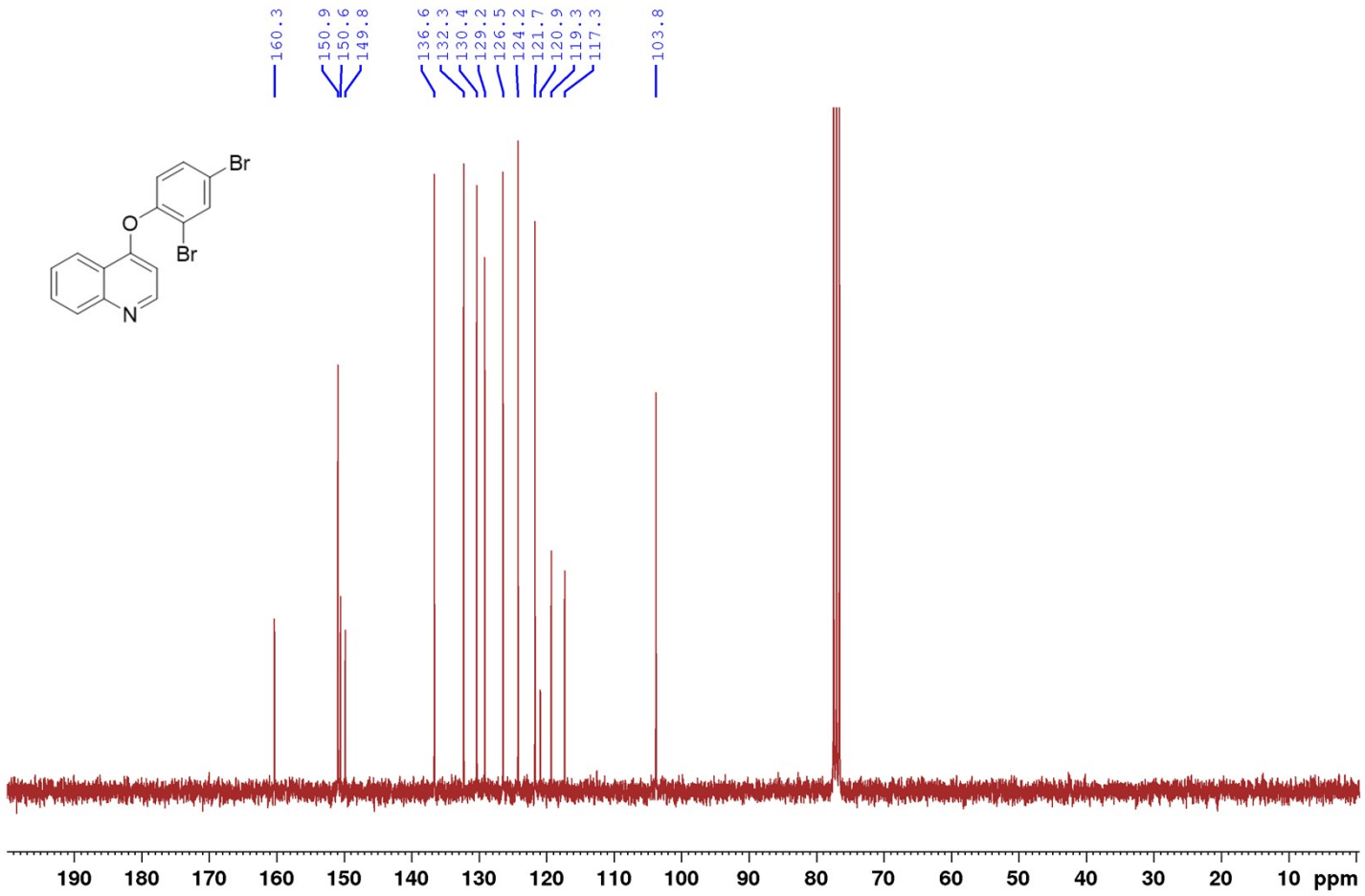
90
80
70
60
50
40
30
20
10
ppm

4-(2,4-Dibromophenoxy)quinoline 1a

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117.3
103.8
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O
Br
N
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180
170
160
150
140
130
120
110
100
90
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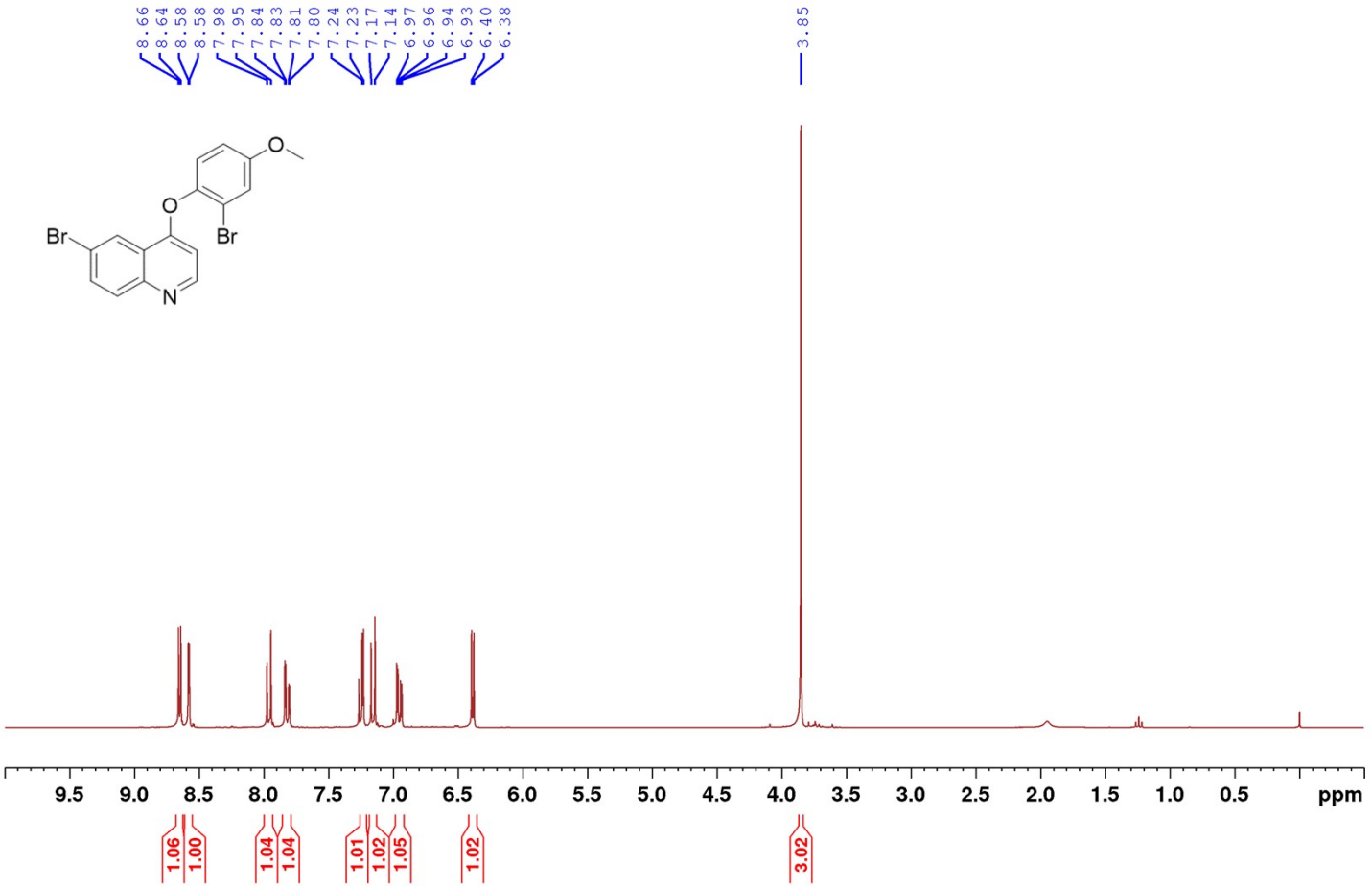
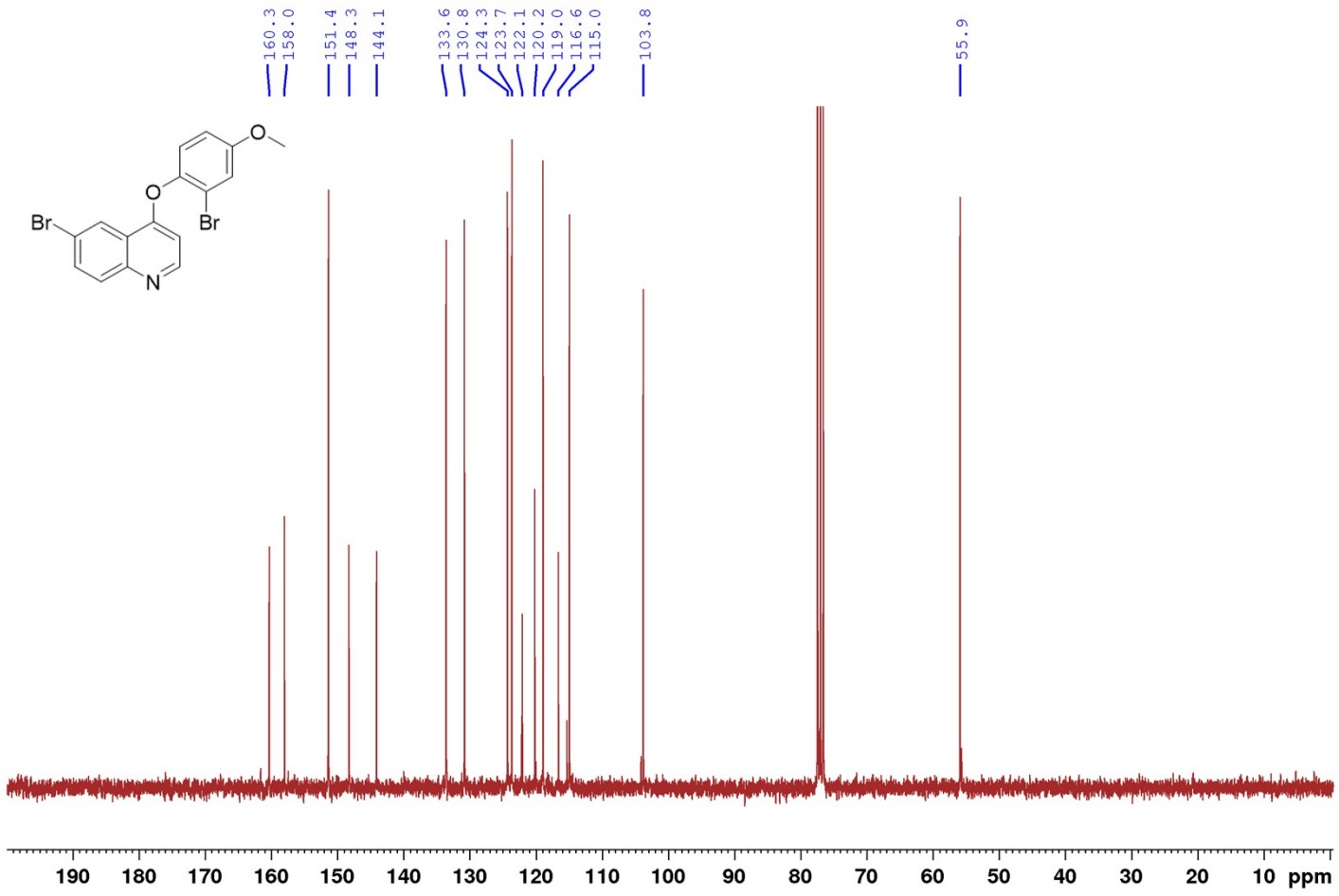
70
60
50
40
30
20
10
ppm

6-Bromo-4-(2-bromo-4-methoxyphenoxy)quinoline 1b

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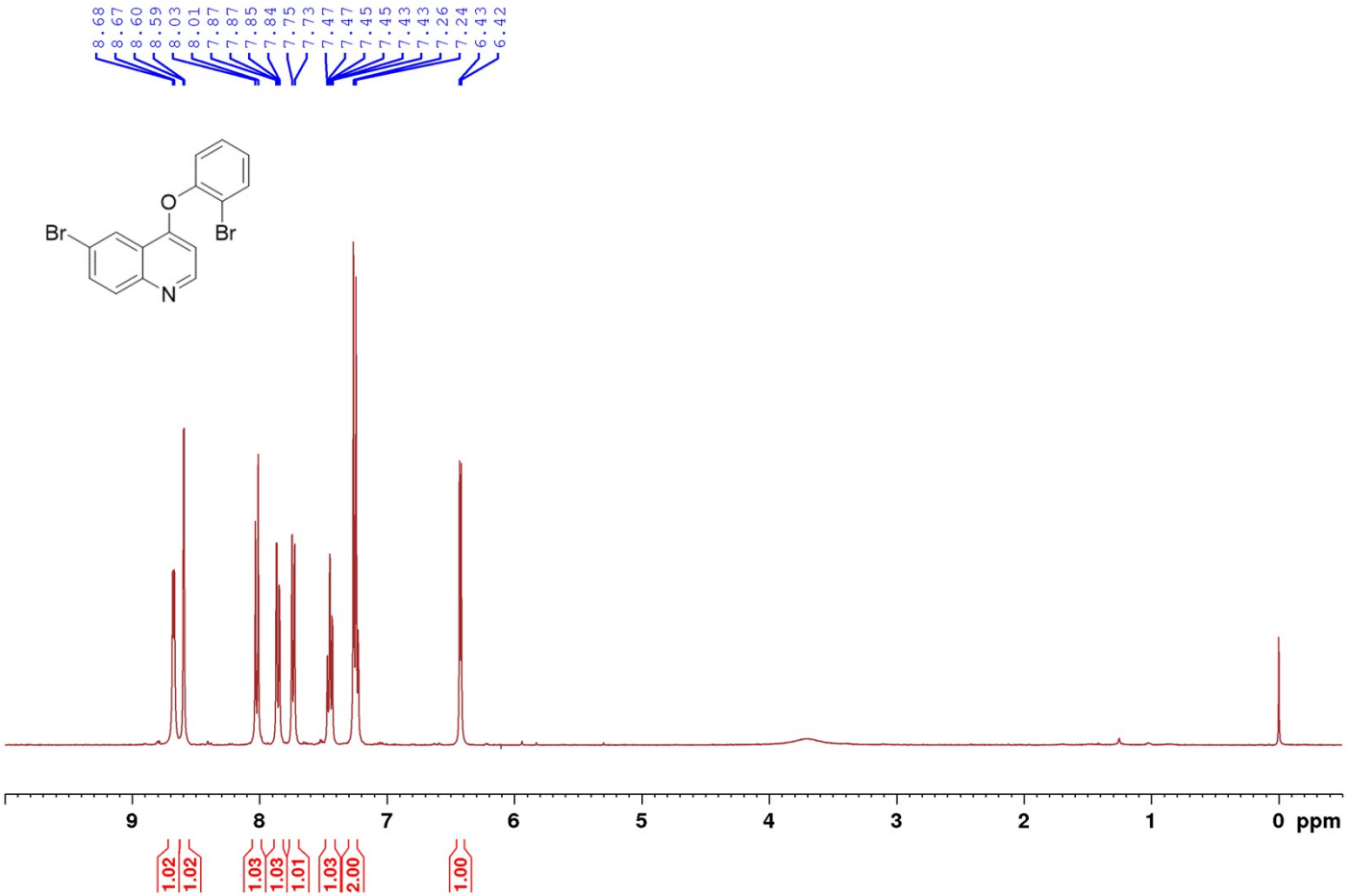
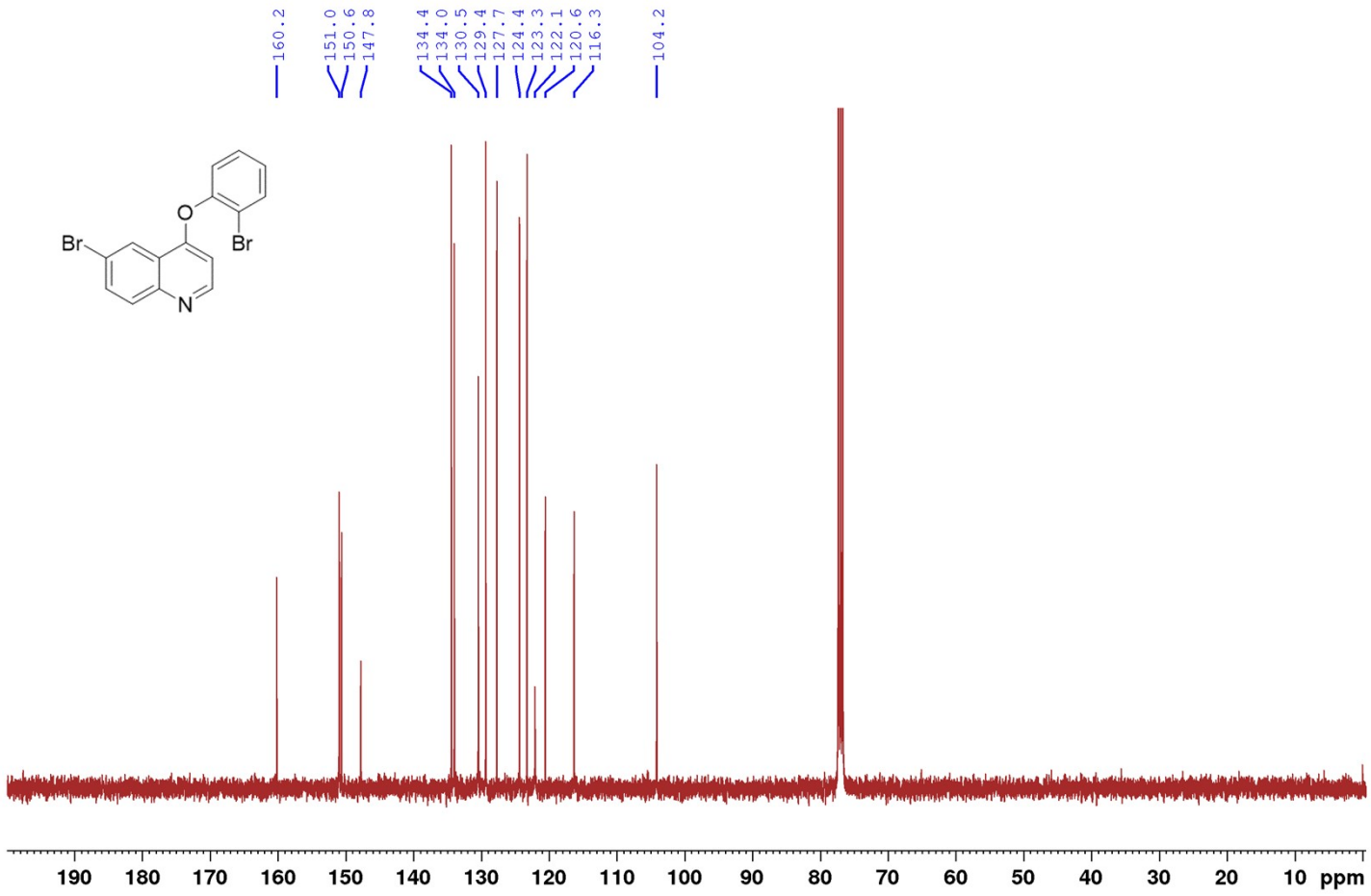
115.0
103.8
55.9
Br
Br
O
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

6-Bromo-4-(2-bromophenoxy)quinoline 1c

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Br
O
Br
N
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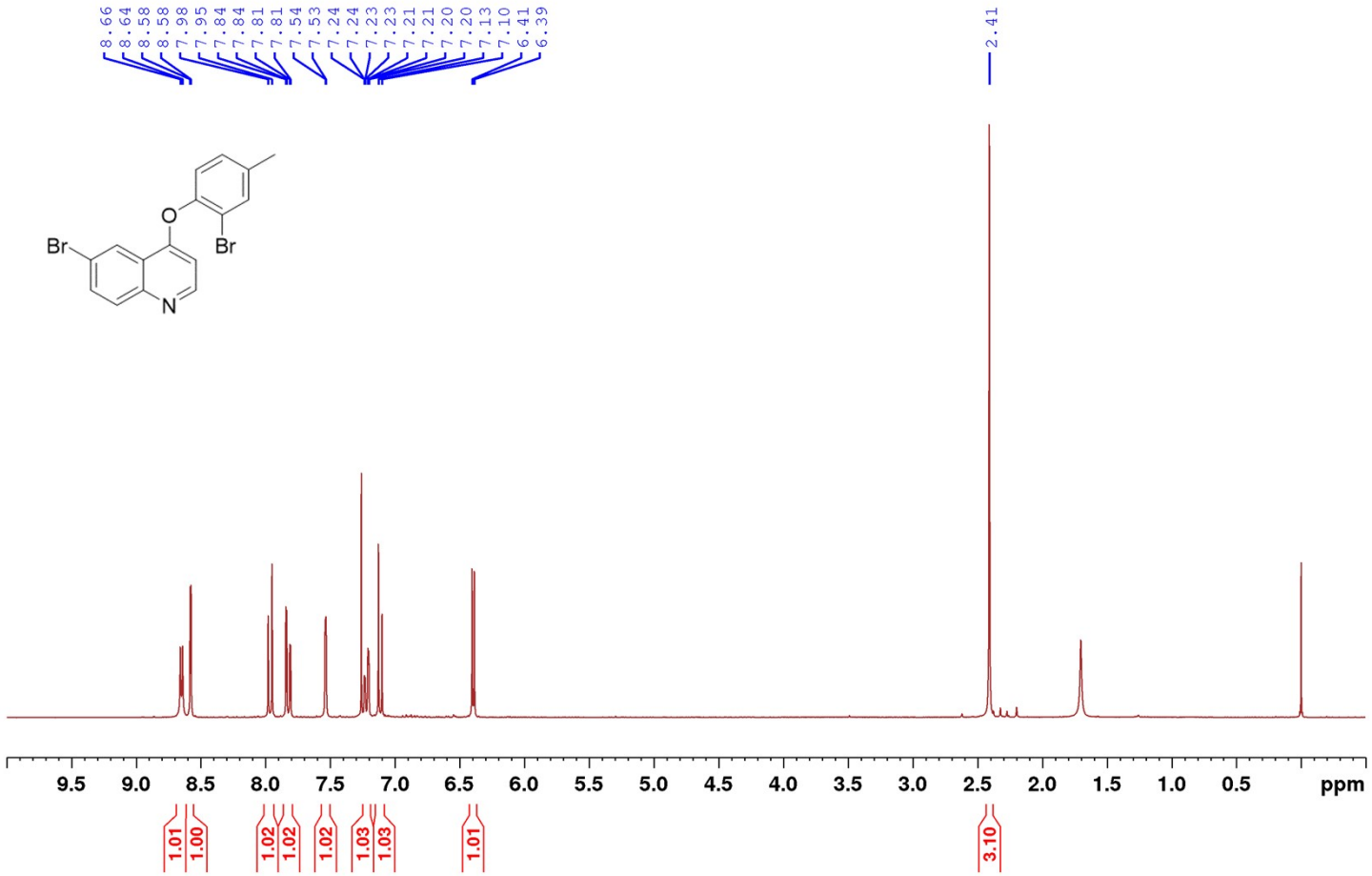
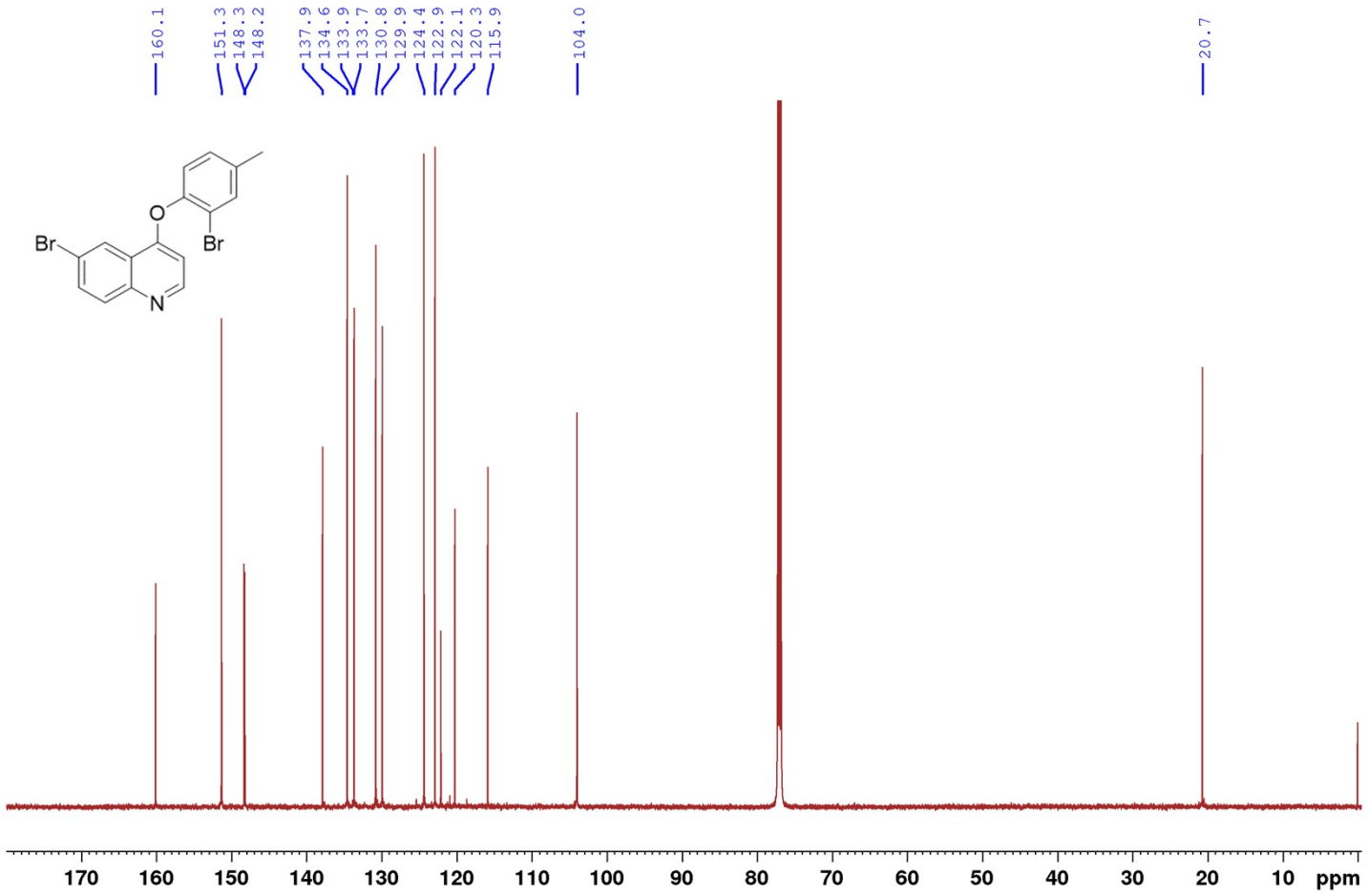
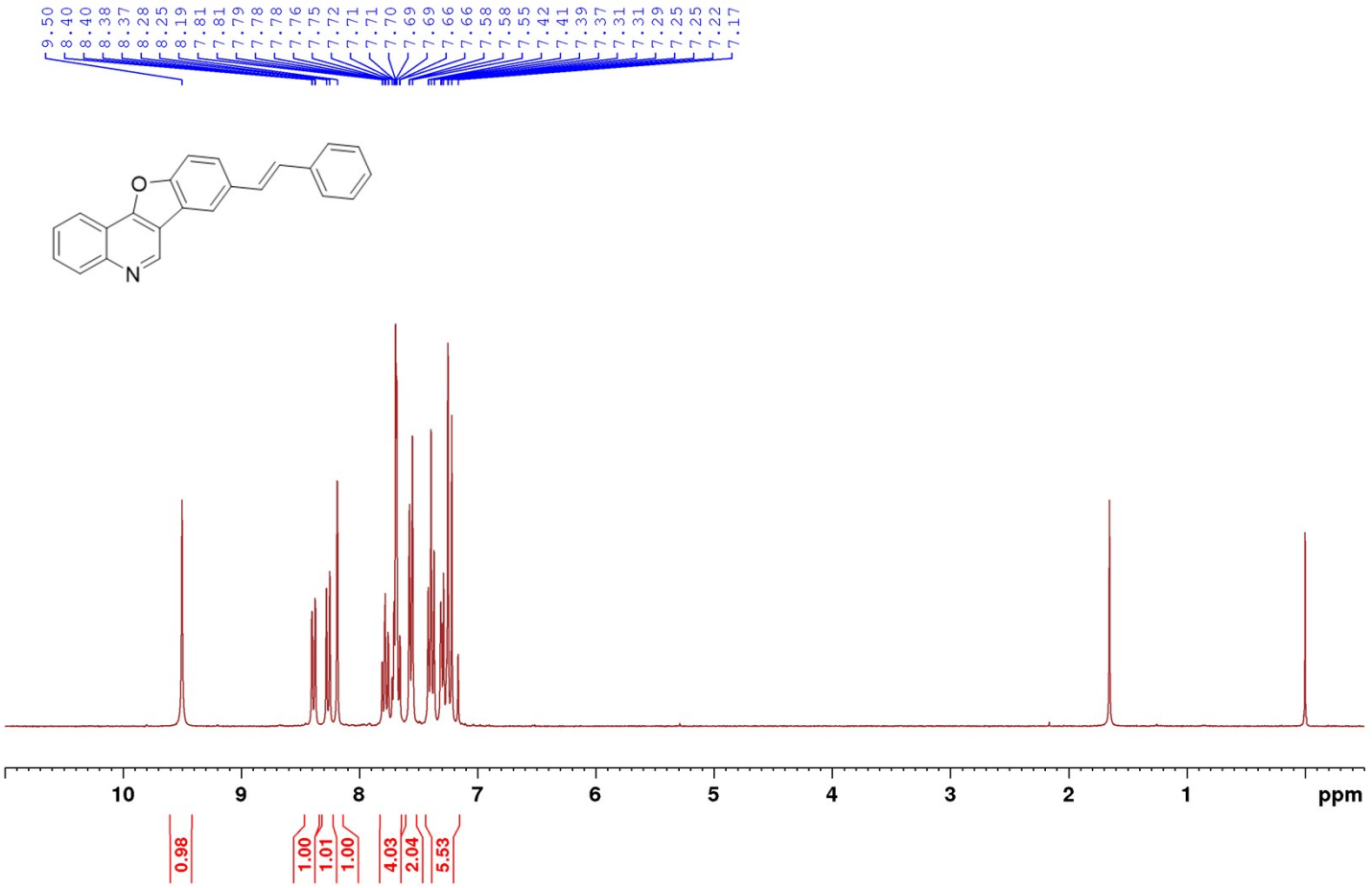
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

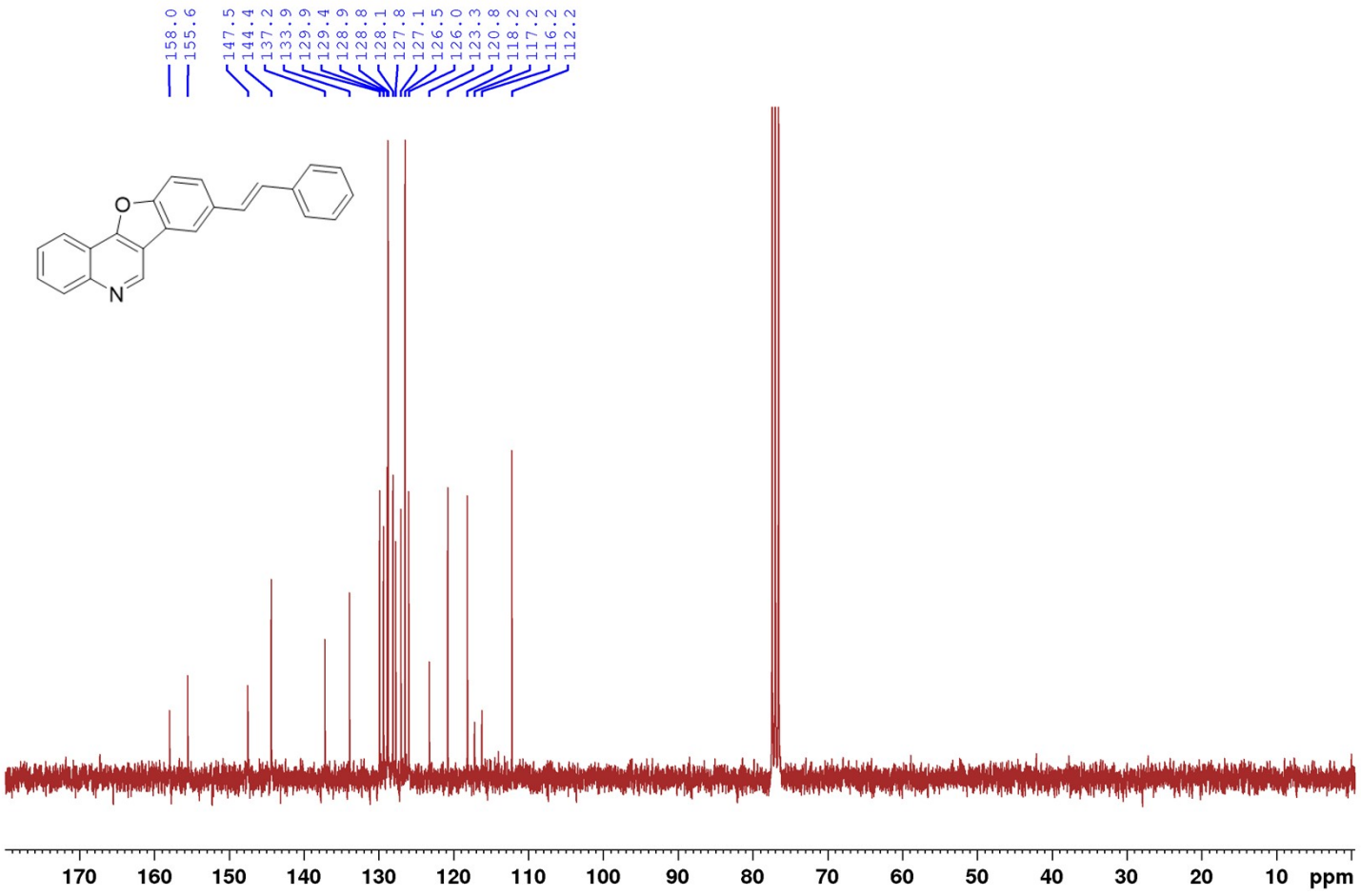
6-Bromo-4-(2-bromo-4-methylphenoxy)quinoline **1d**



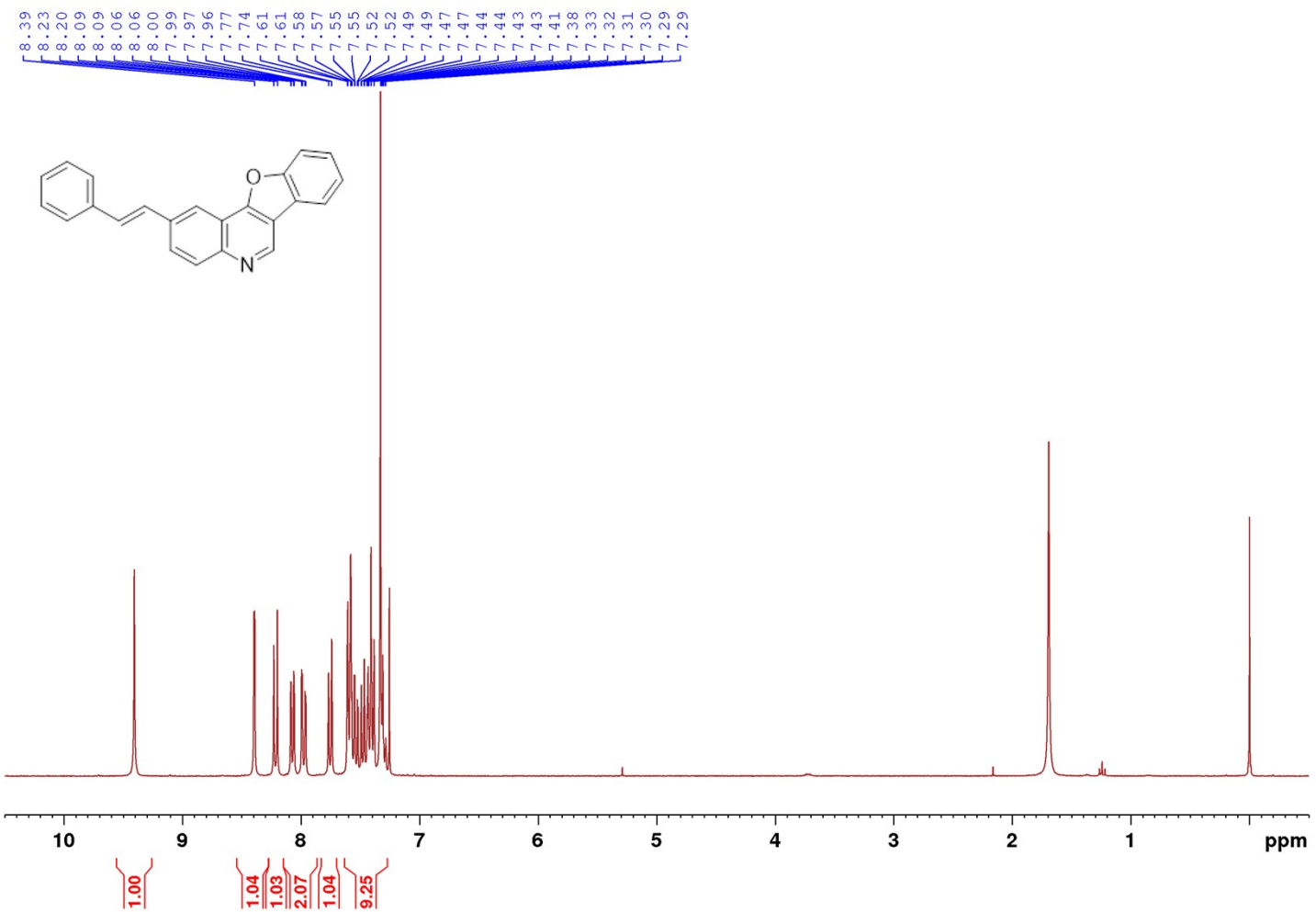

160.1
151.3
148.3
148.2
137.9
134.6
133.9
133.7
130.8
129.9
124.4
122.9
122.1
120.3
115.9
104.0
20.7
Br
O
Br
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

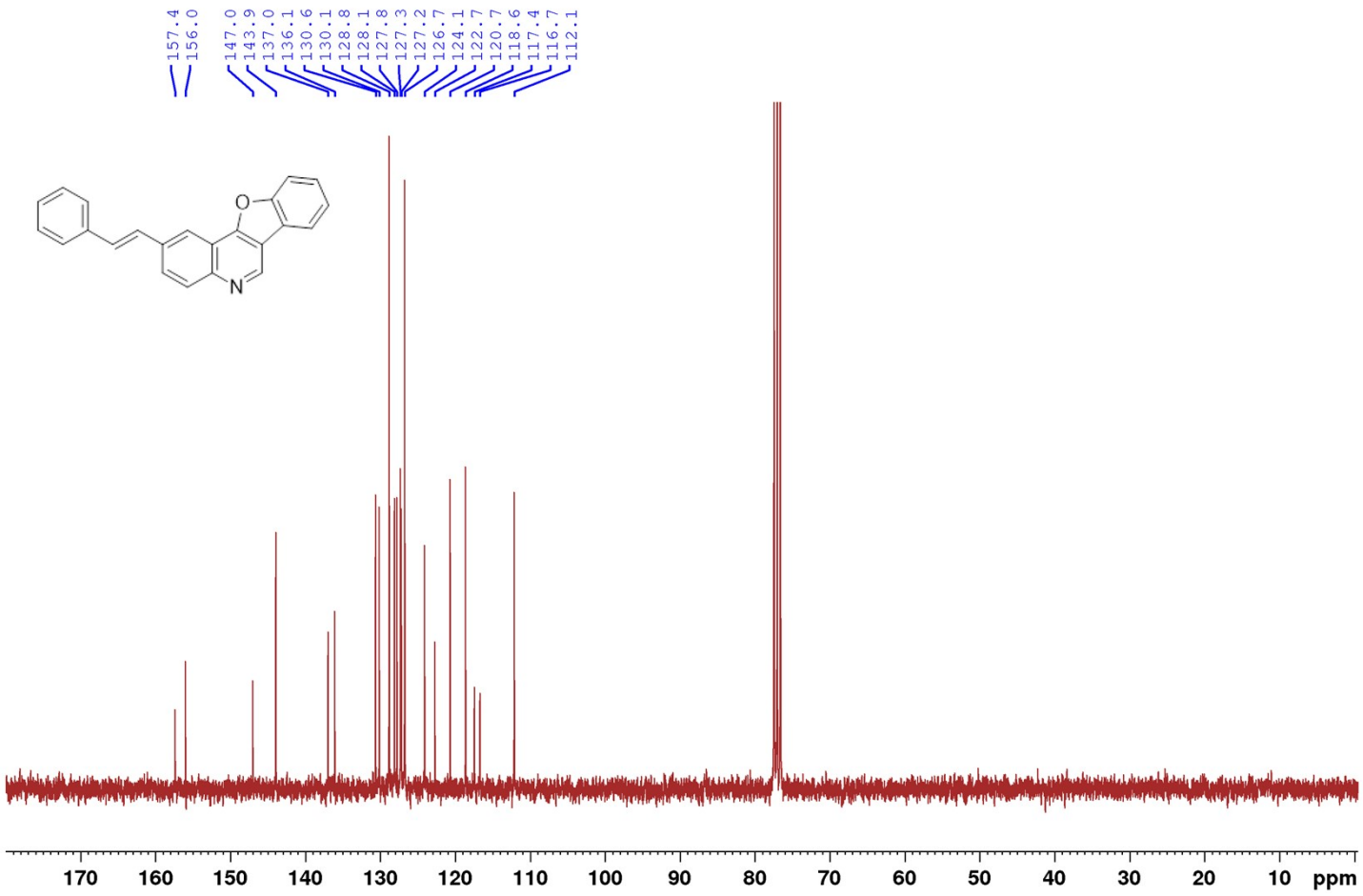
(*E*)-8-Styrylbenzofuro[3,2-c]quinoline 2a



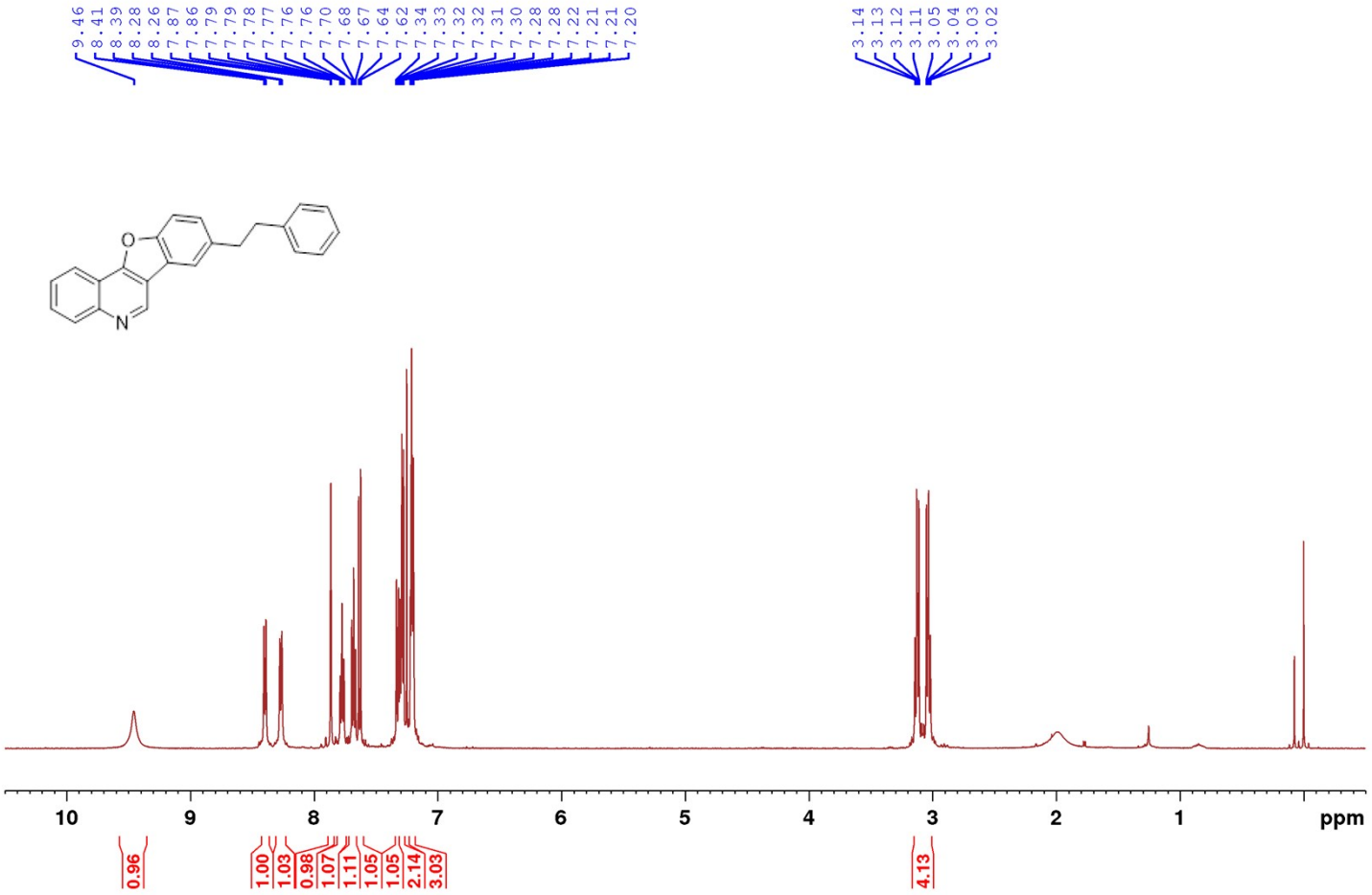

158.0
155.6
147.5
144.4
137.2
133.9
129.9
129.4
128.9
128.8
128.1
127.8
127.1
126.5
126.0
123.3
120.8
118.2
117.2
116.2
112.2
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

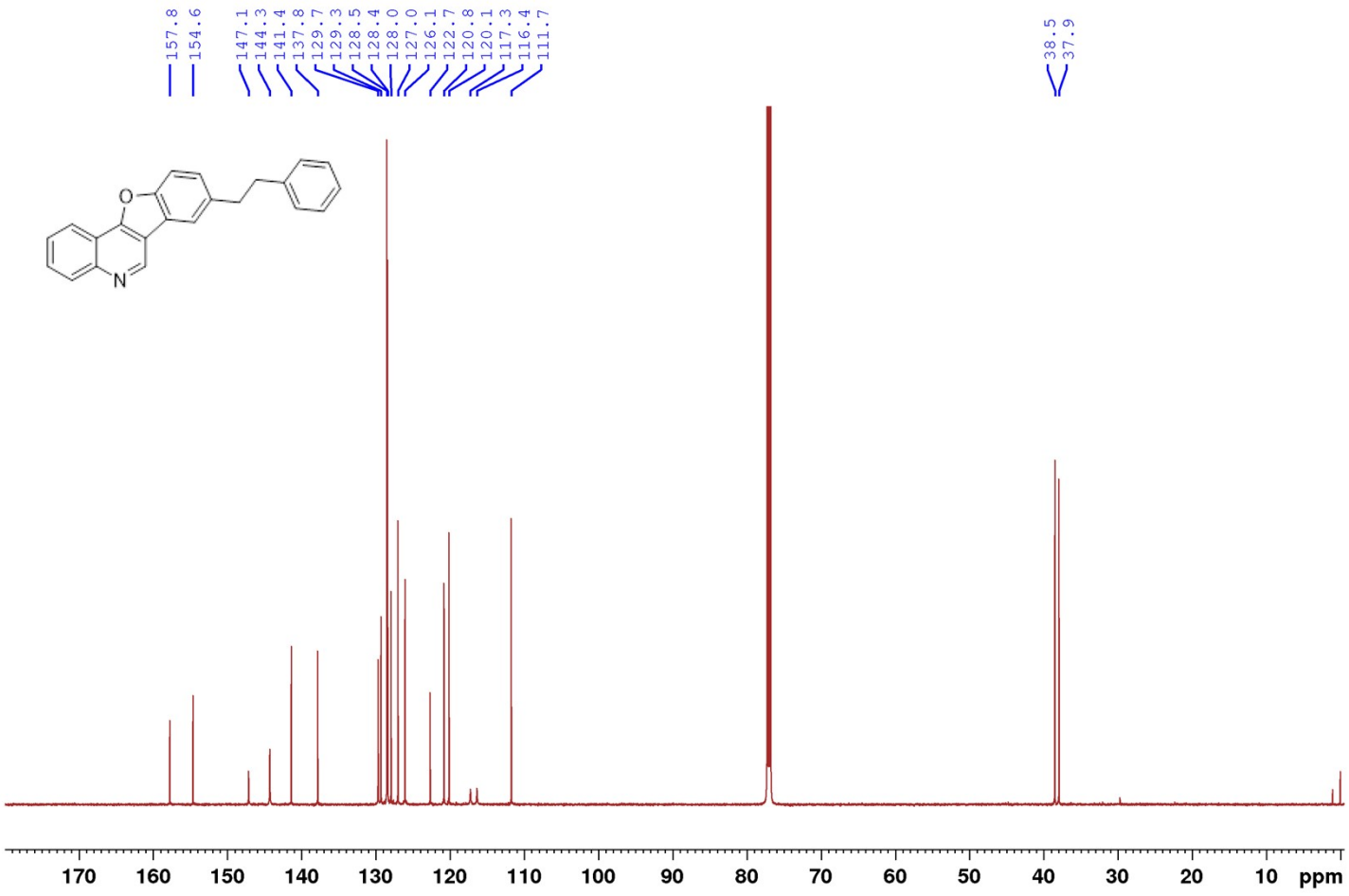
(*E*)-2-Styrylbenzofuro[3,2-c]quinoline 2b



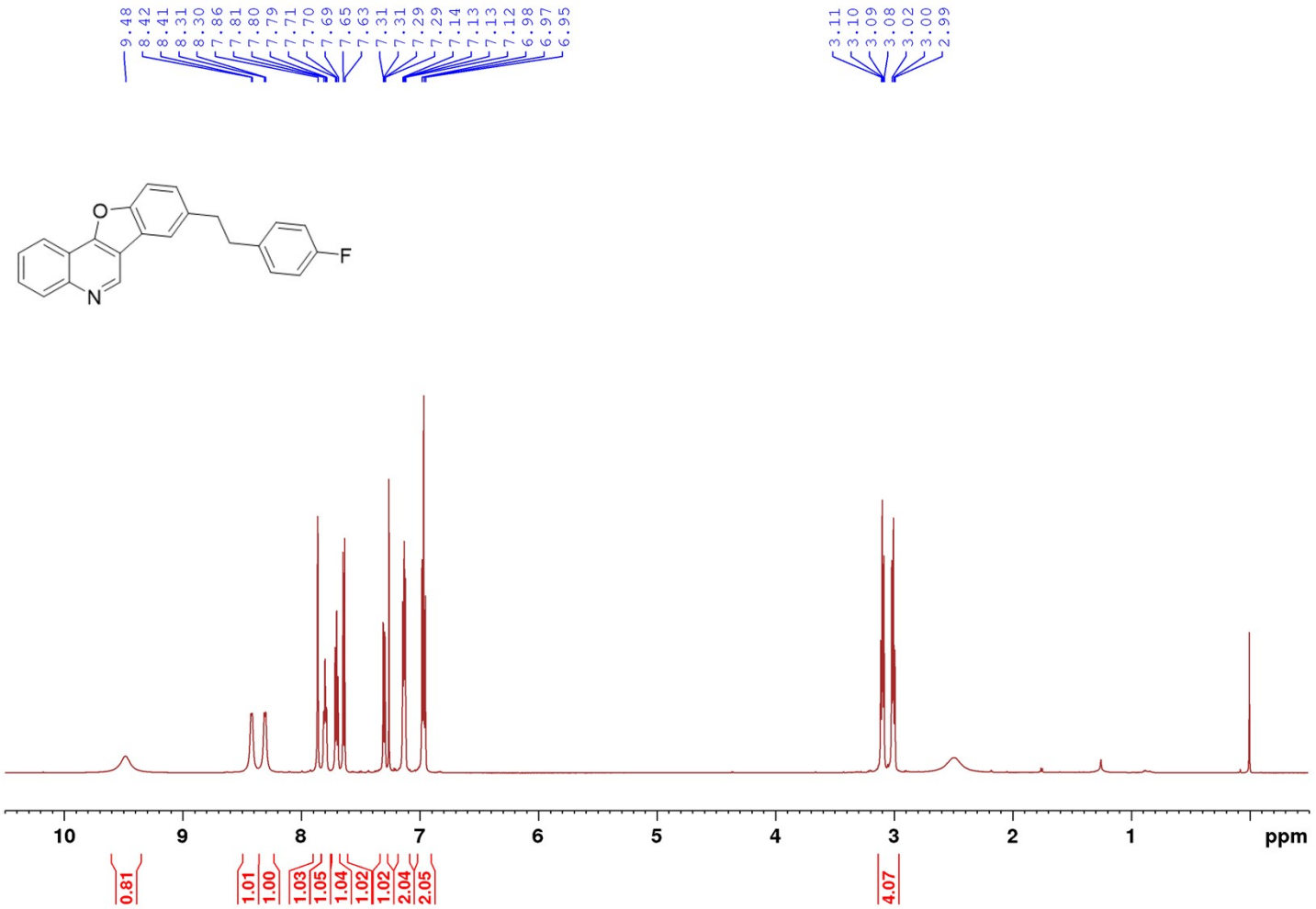

157.4
156.0
147.0
143.9
137.0
136.1
130.6
130.1
128.8
128.1
127.8
127.3
127.2
126.7
124.1
122.7
120.7
118.6
117.4
116.7
112.1
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

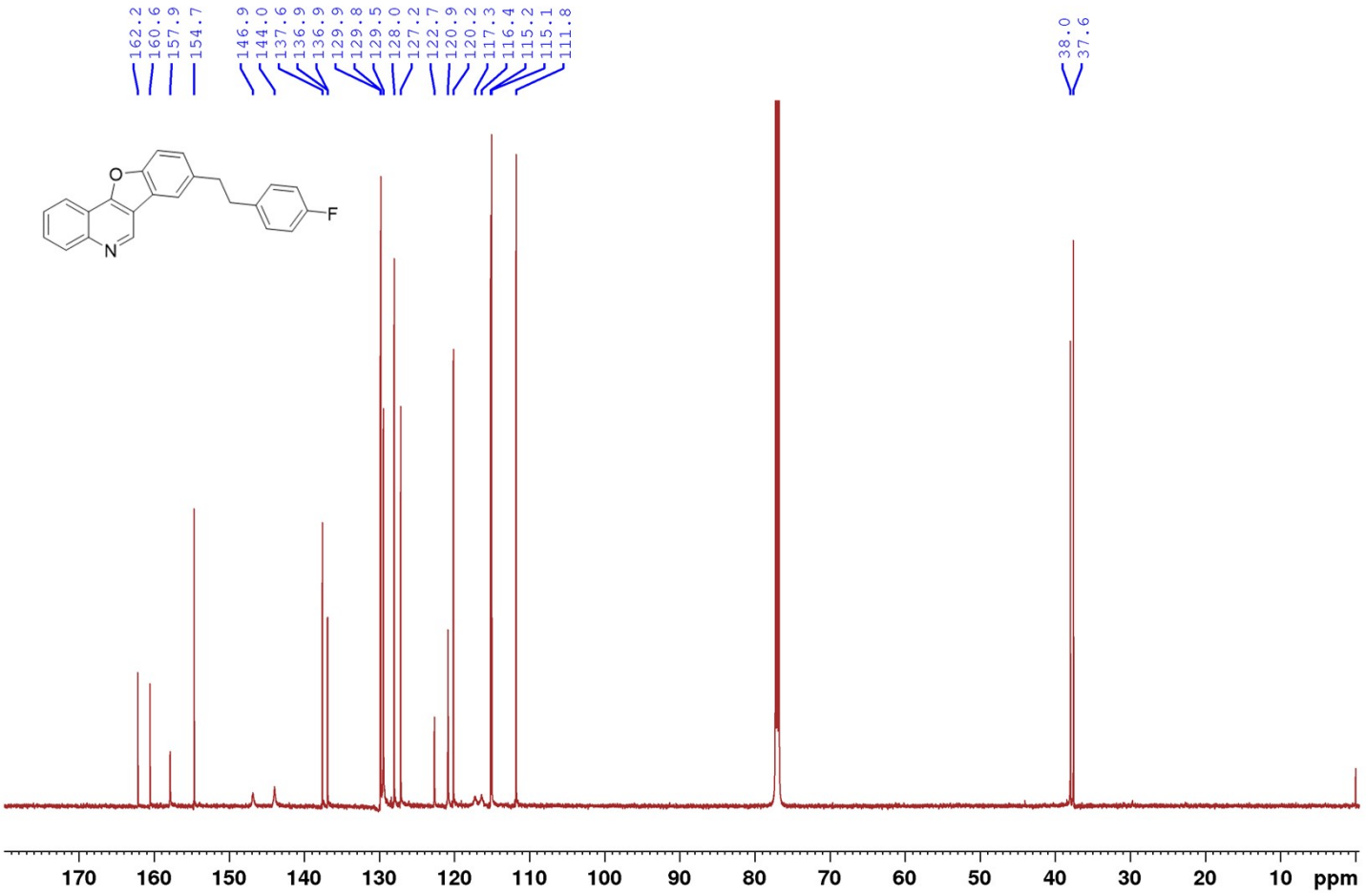
8-Phenethylbenzofuro[3,2-c]quinoline 3a

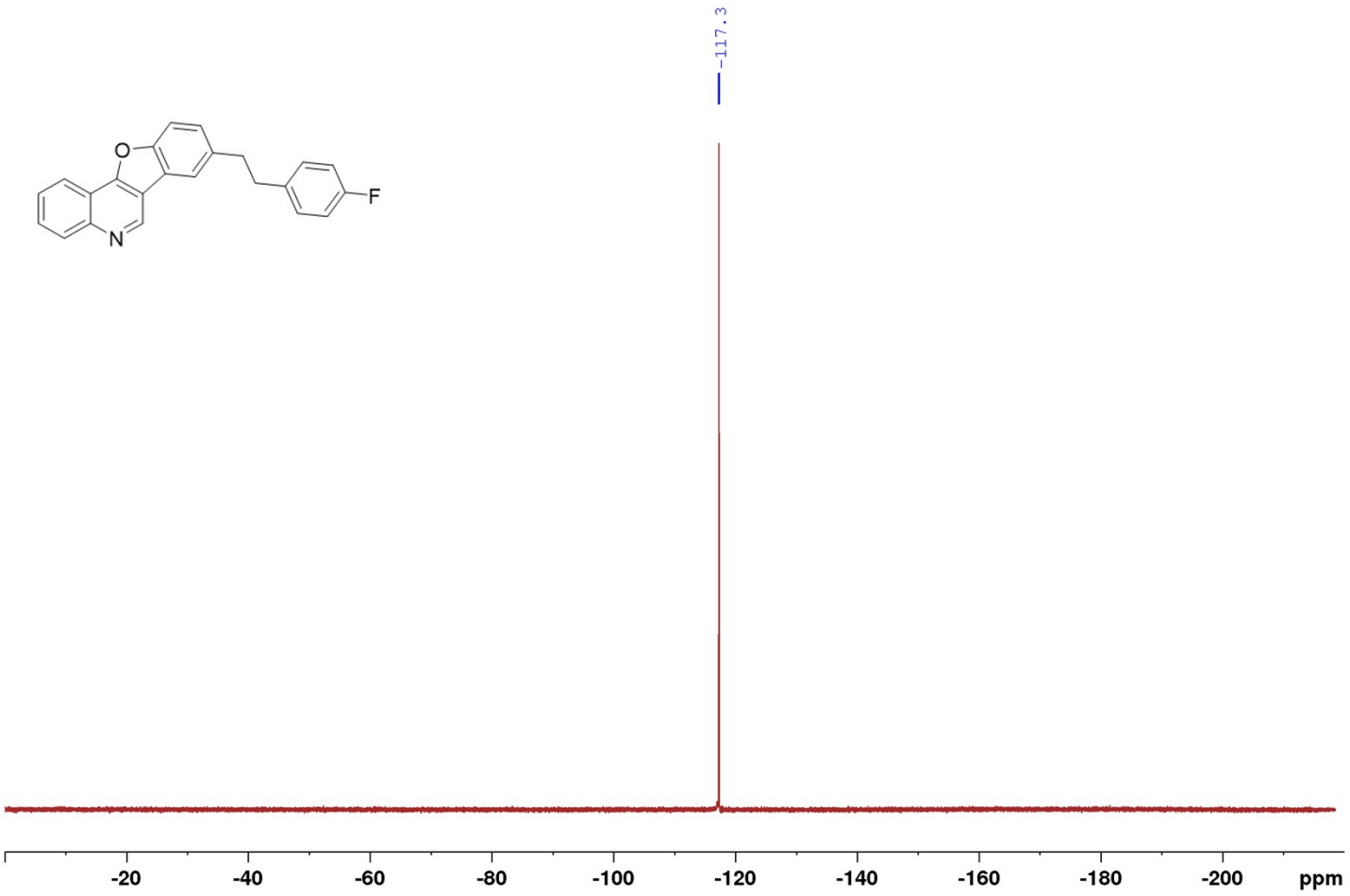



157.8
154.6
147.1
144.3
141.4
137.8
129.7
129.3
128.5
128.4
128.0
127.0
126.1
122.7
120.8
120.1
117.3
116.4
111.7
38.5
37.9
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

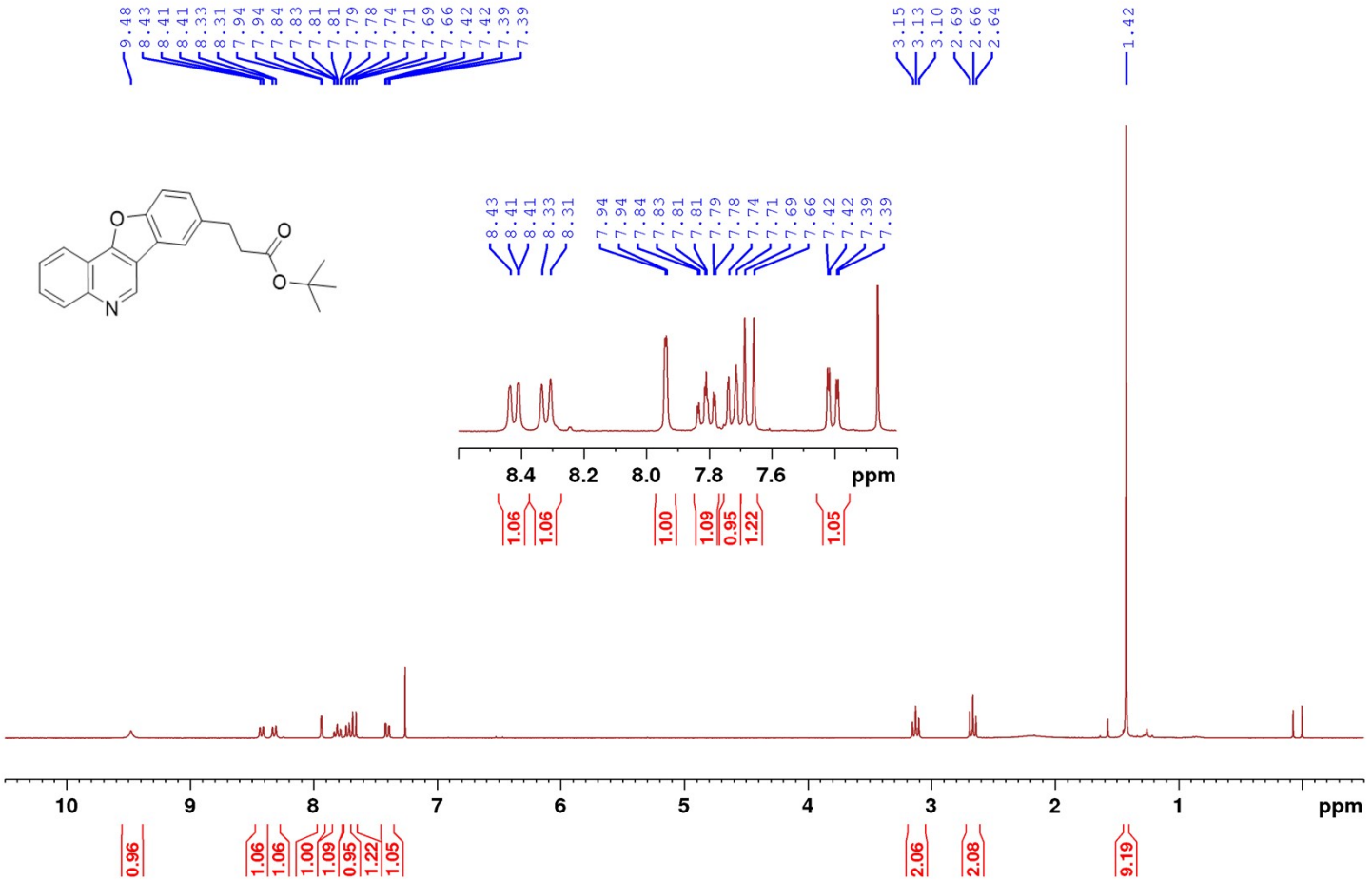
8-(4-Fluorophenethyl)benzofuro[3,2-c]quinoline 3b

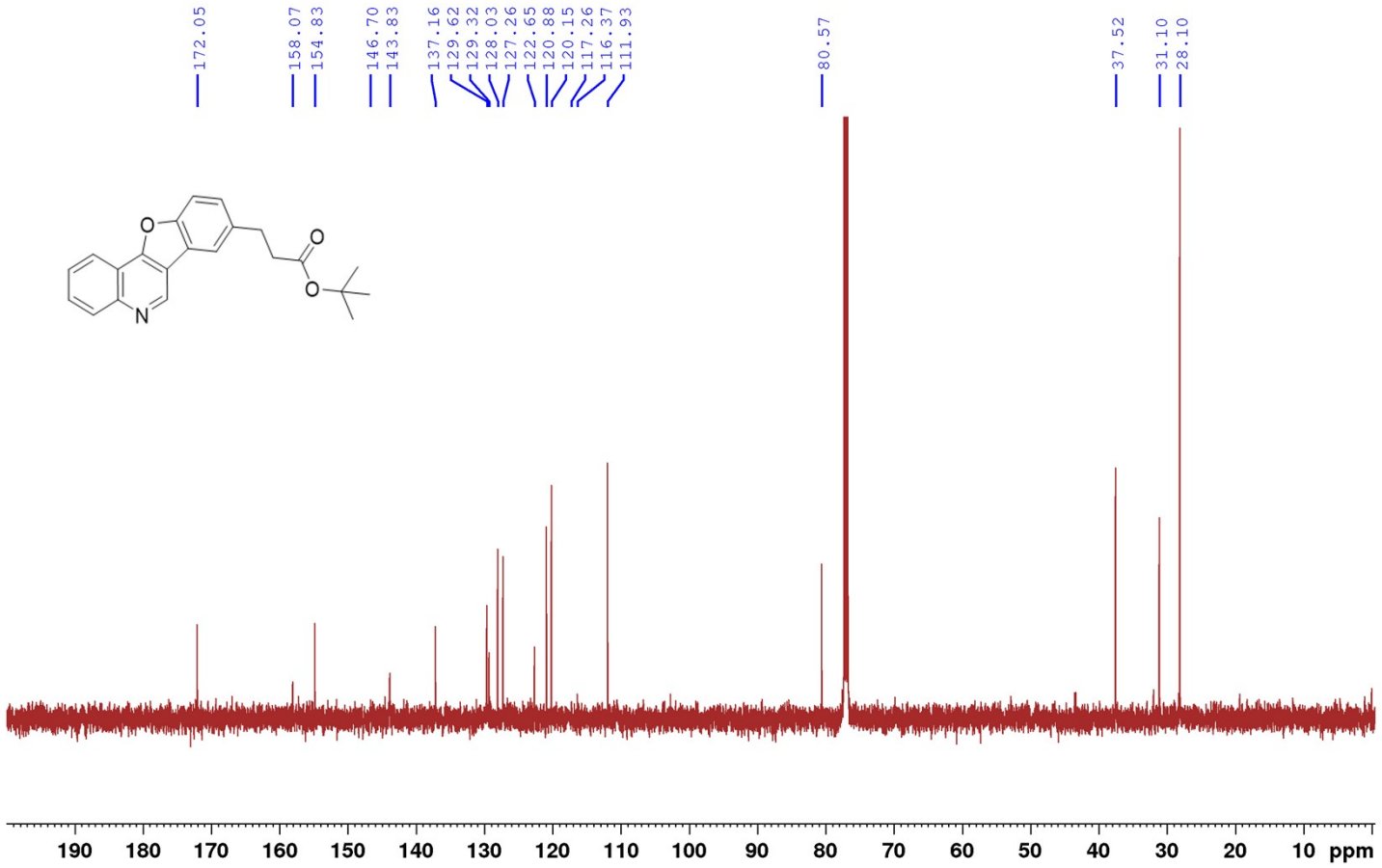



162.2
160.6
157.9
154.7
146.9
144.0
137.6
136.9
136.9
129.9
129.8
129.5
128.0
127.2
122.7
120.9
120.2
117.3
116.4
115.2
115.1
111.8
38.0
37.6
O
F
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

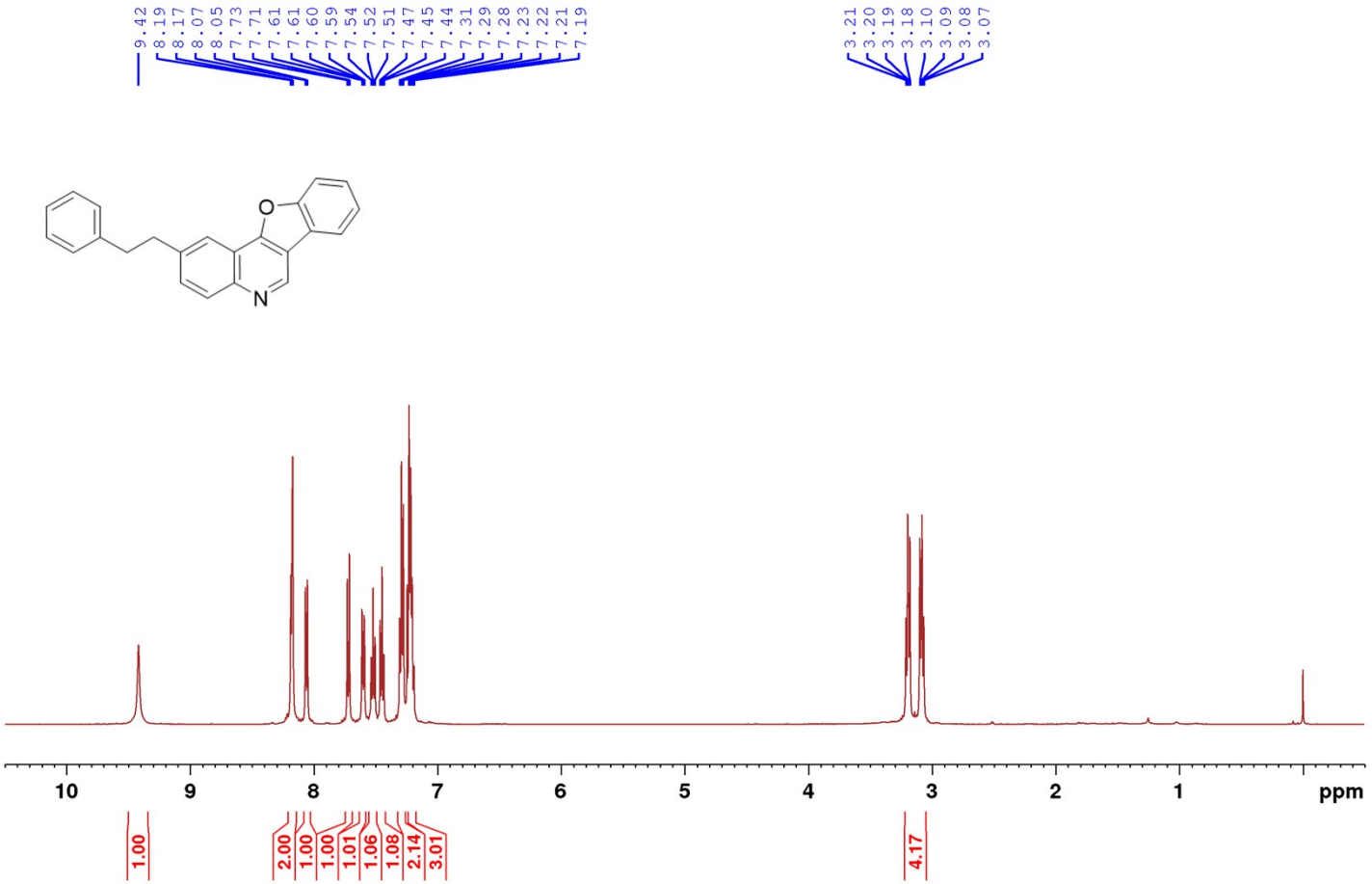

-117.3
O
F
N
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

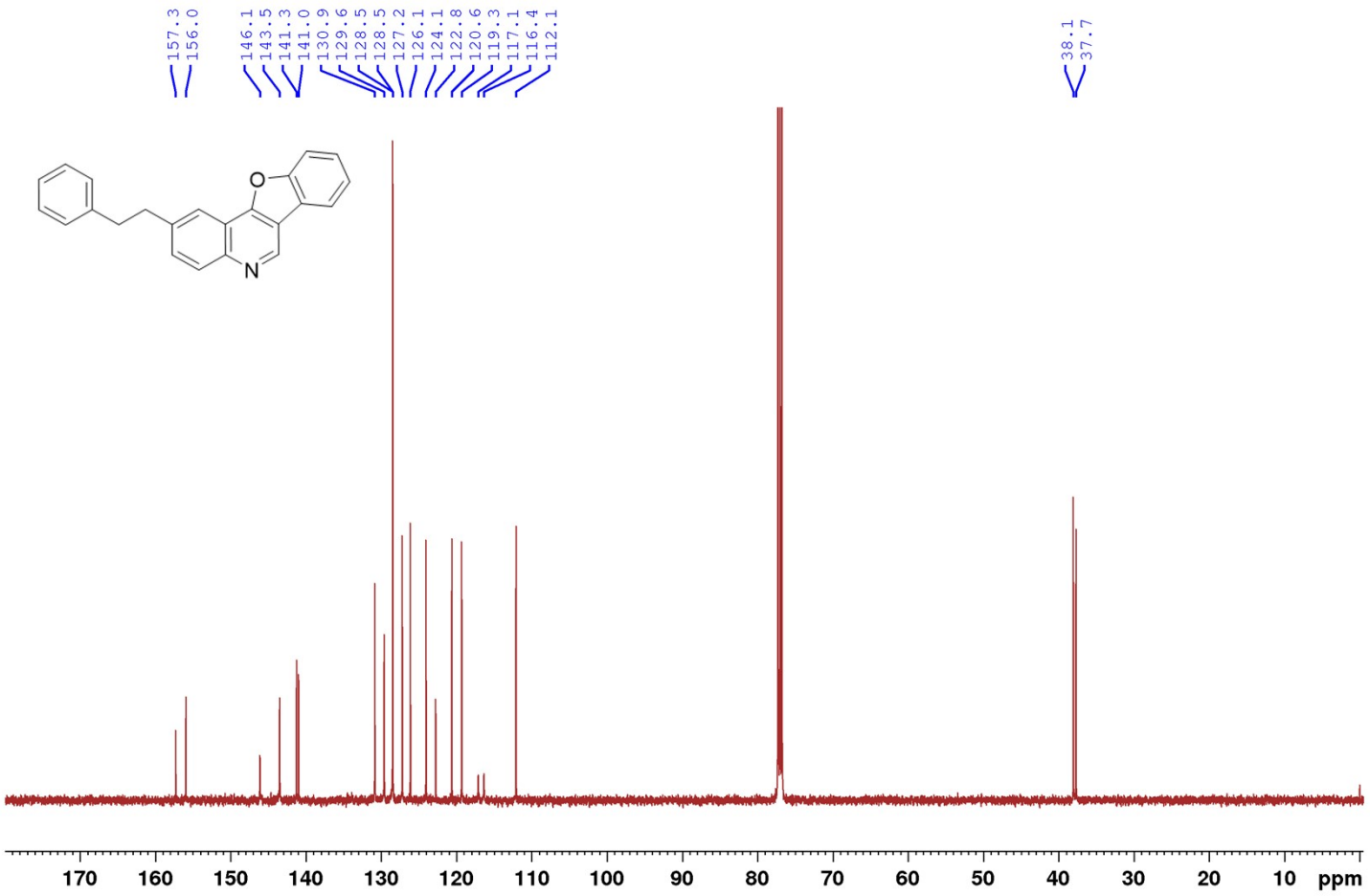
***tert*-Butyl 3-(benzofuro[3,2-c]quinolin-8-yl)propanoate 3c**



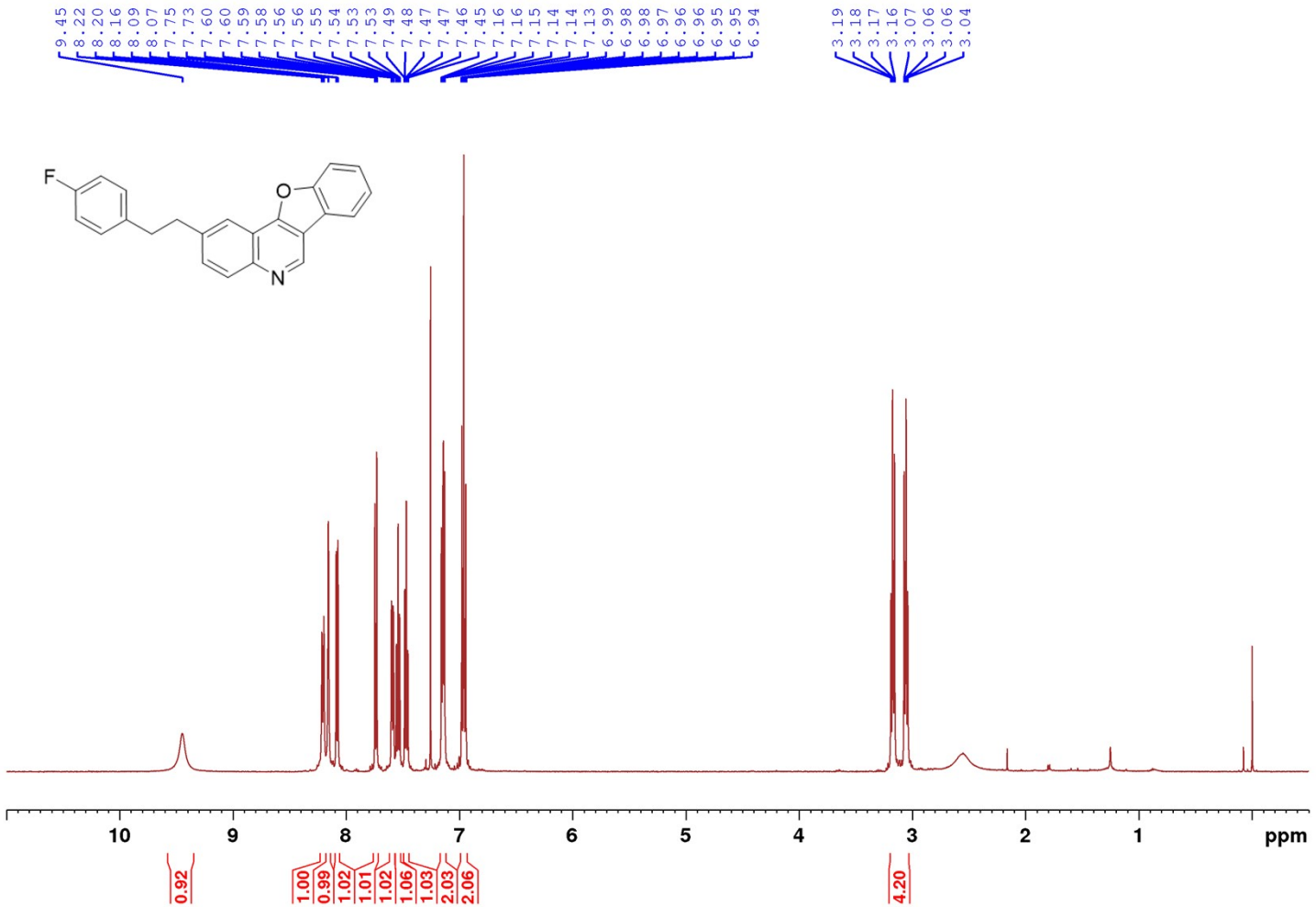

172.05
158.07
154.83
146.70
143.83
137.16
129.62
129.32
128.03
127.26
122.65
120.88
120.15
117.26
116.37
111.93
80.57
37.52
31.10
28.10
O
O
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

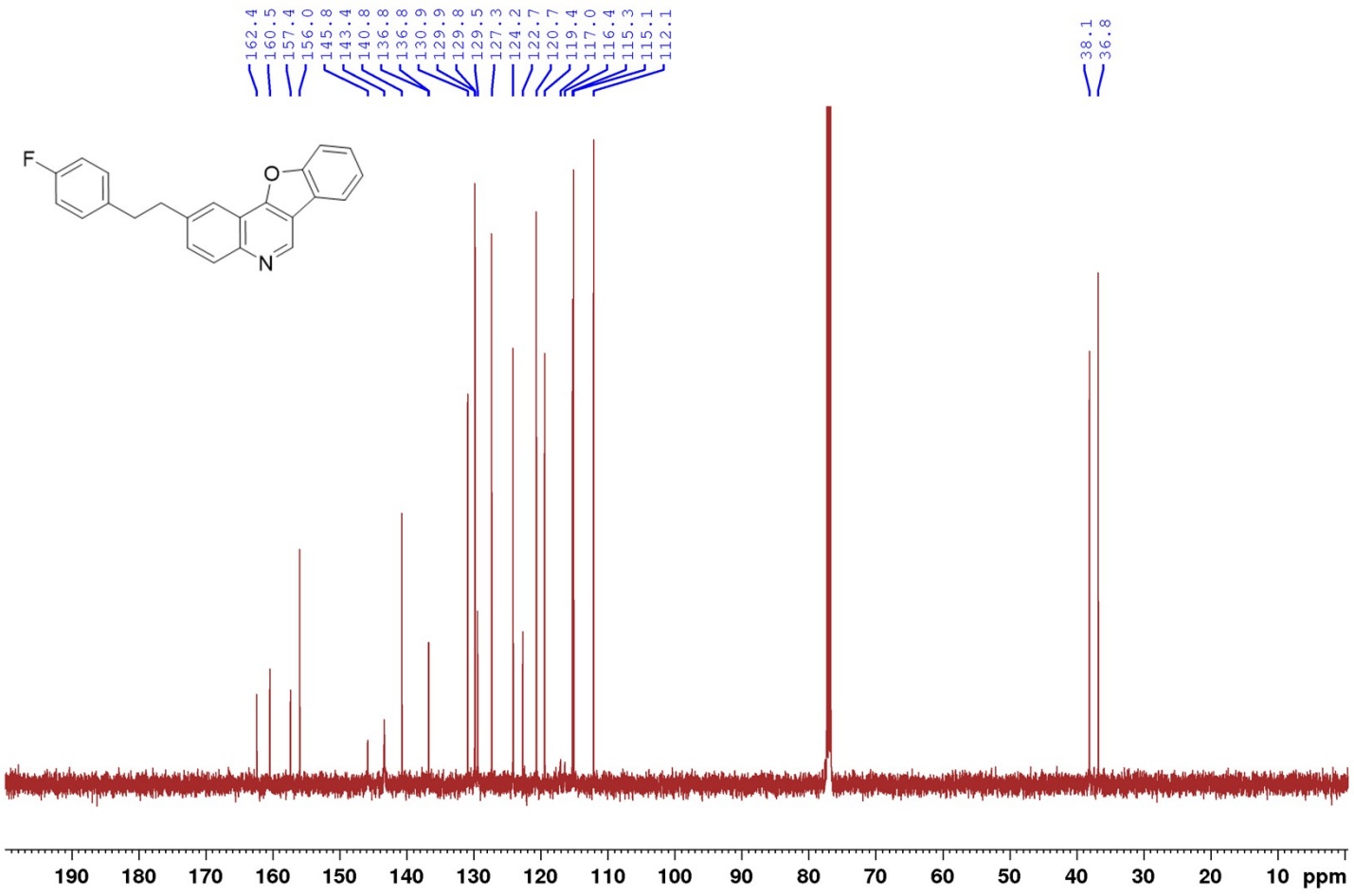
2-Phenethylbenzofuro[3,2-c]quinoline 4a

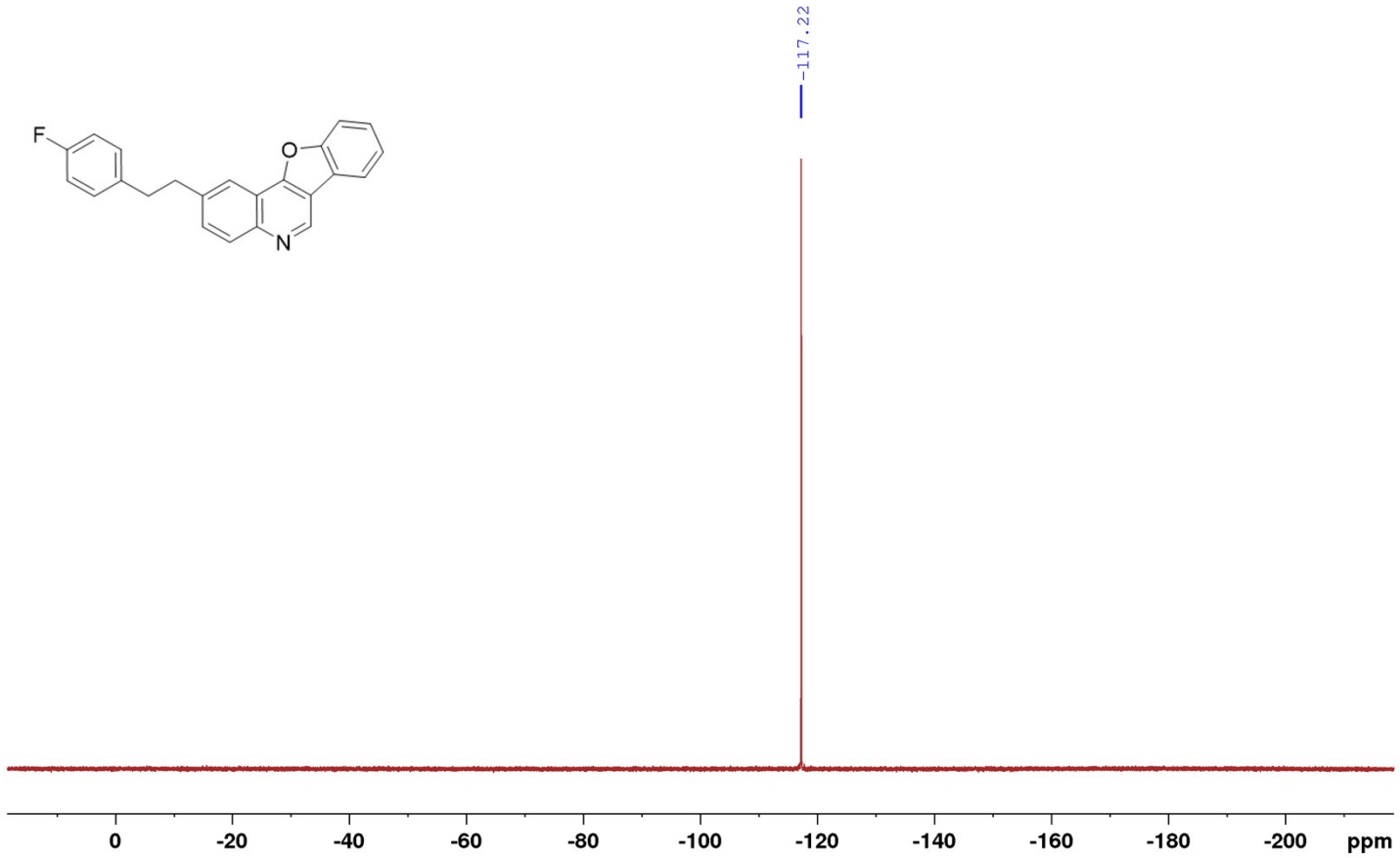



157.3
156.0
146.1
143.5
141.3
141.0
130.9
129.6
128.5
128.5
127.2
126.1
124.1
122.8
120.6
119.3
117.1
116.4
112.1
38.1
37.7
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

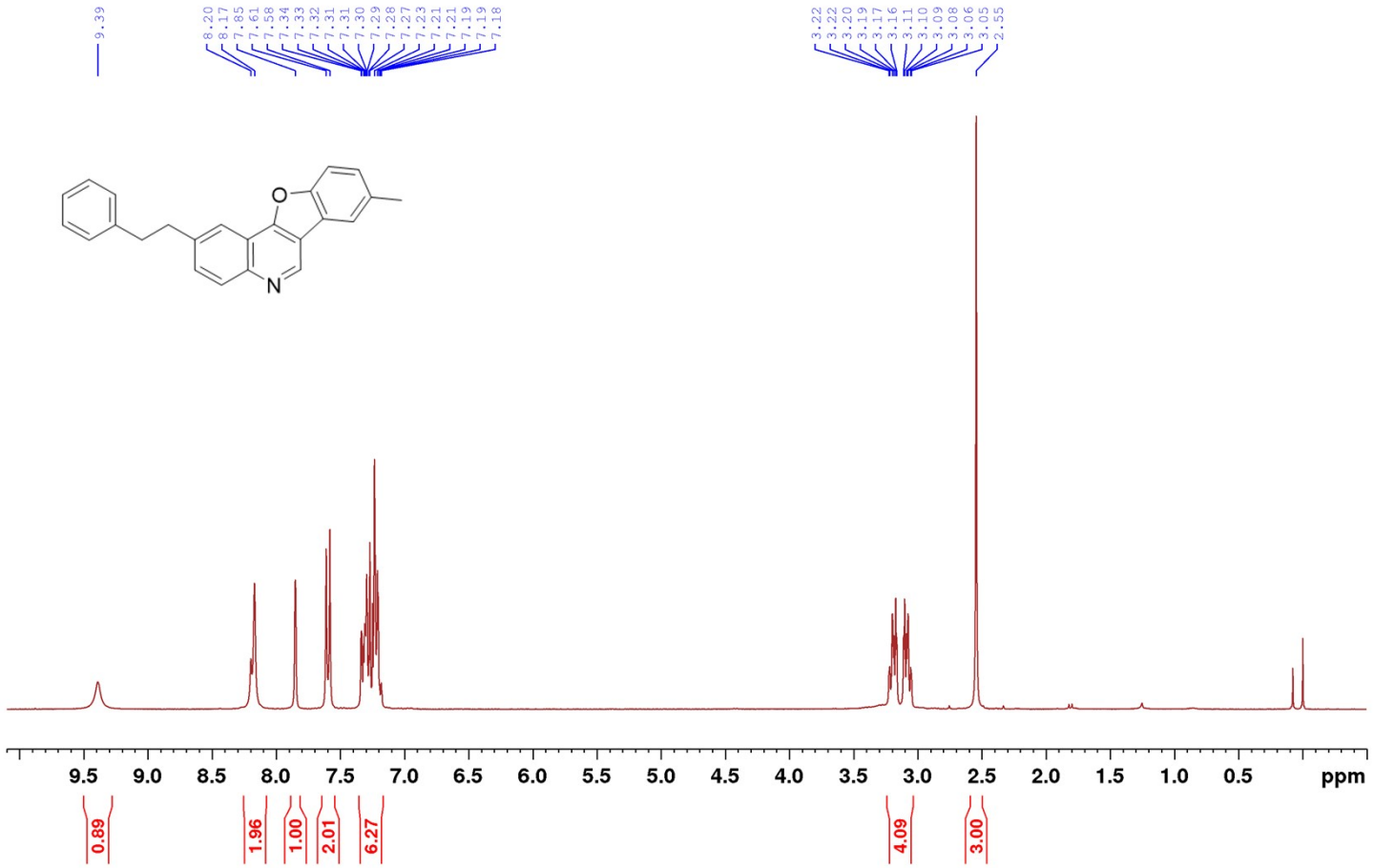
2-(4-Fluorophenethyl)benzofuro[3,2-c]quinoline 4b

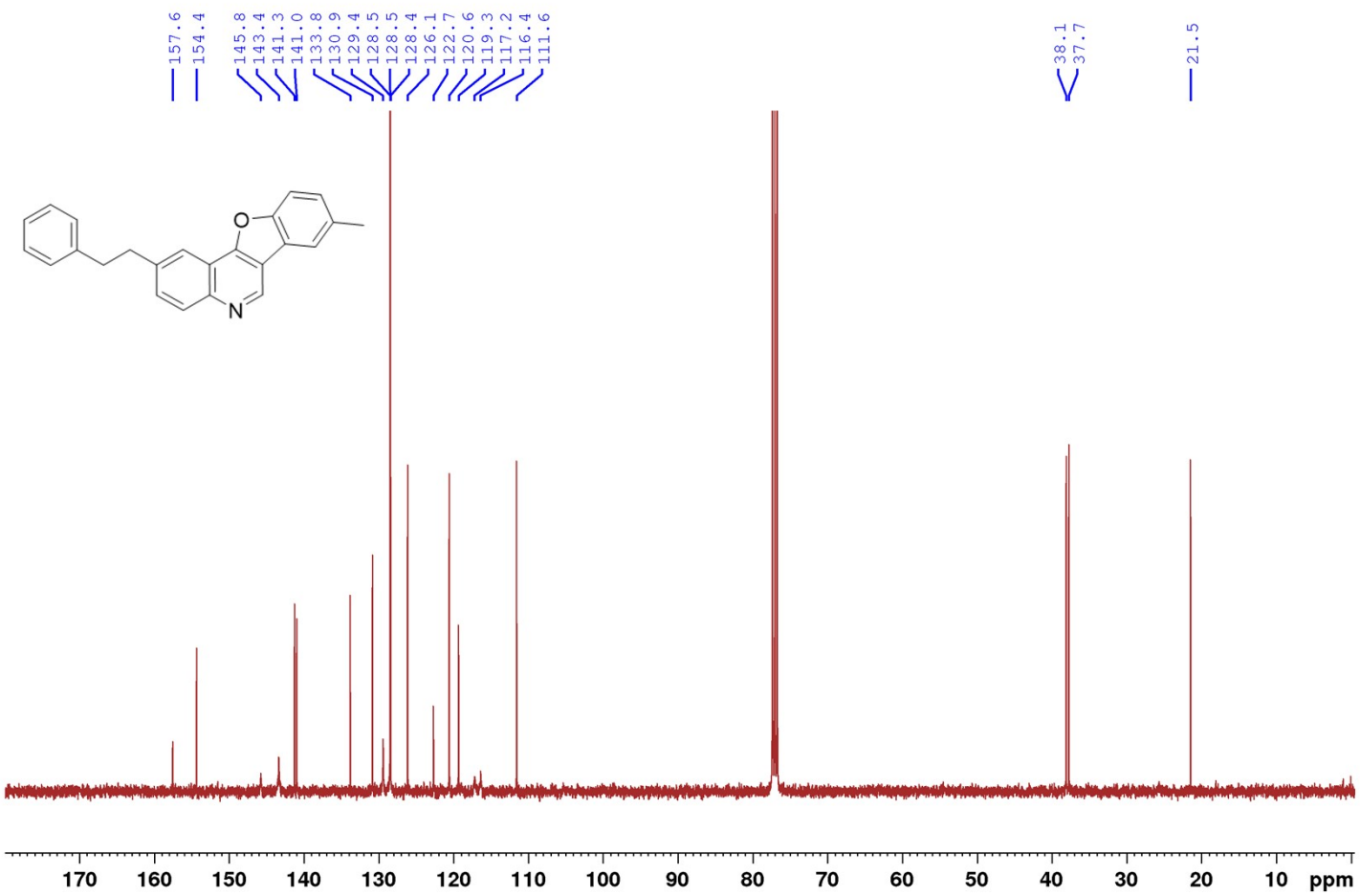



162.4
160.5
157.4
156.0
145.8
143.4
140.8
136.8
136.8
130.9
129.9
129.8
129.5
127.3
124.2
122.7
120.7
119.4
117.0
116.4
115.3
115.1
112.1
38.1
36.8
F
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

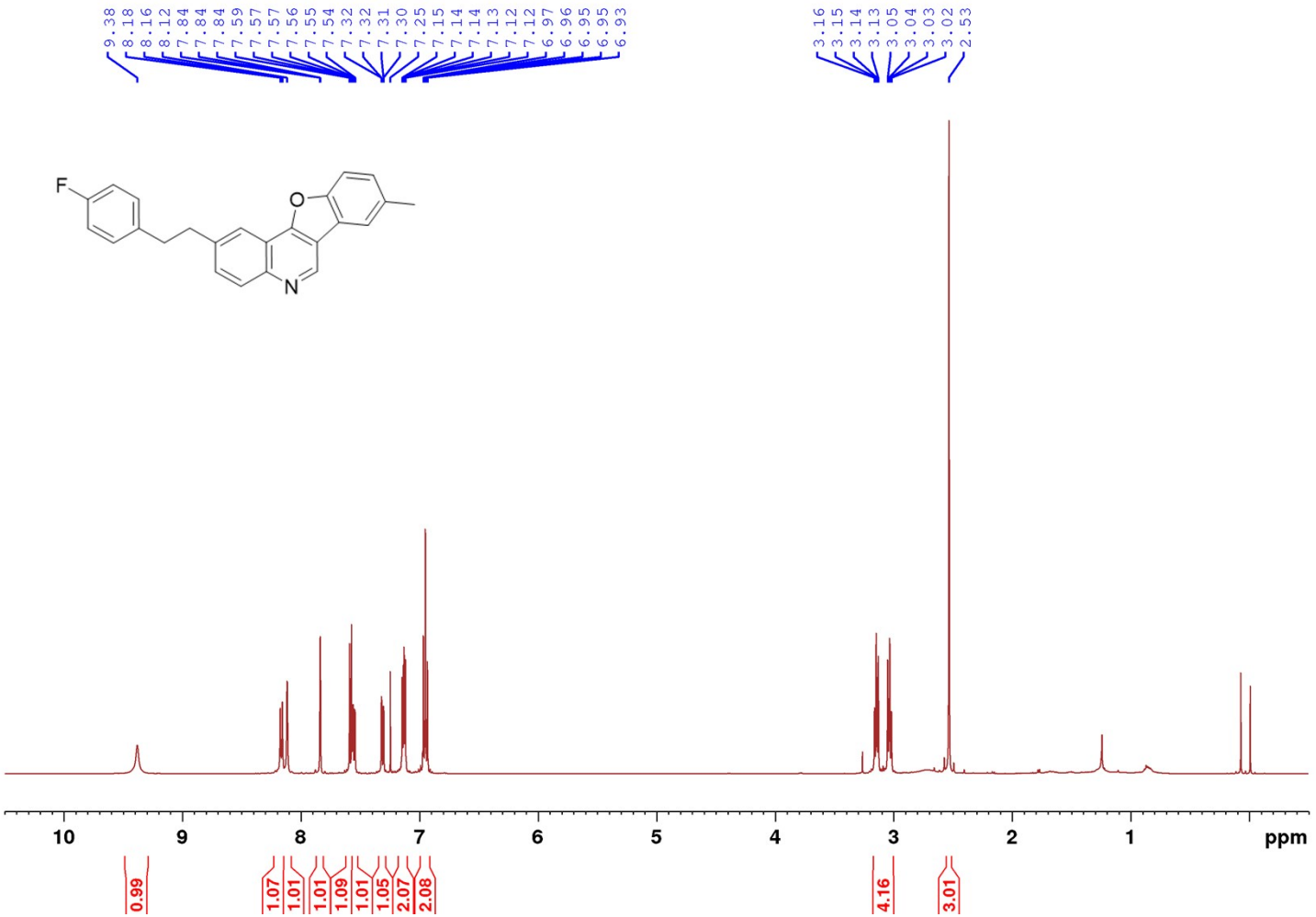

F
O
N
-117.22
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

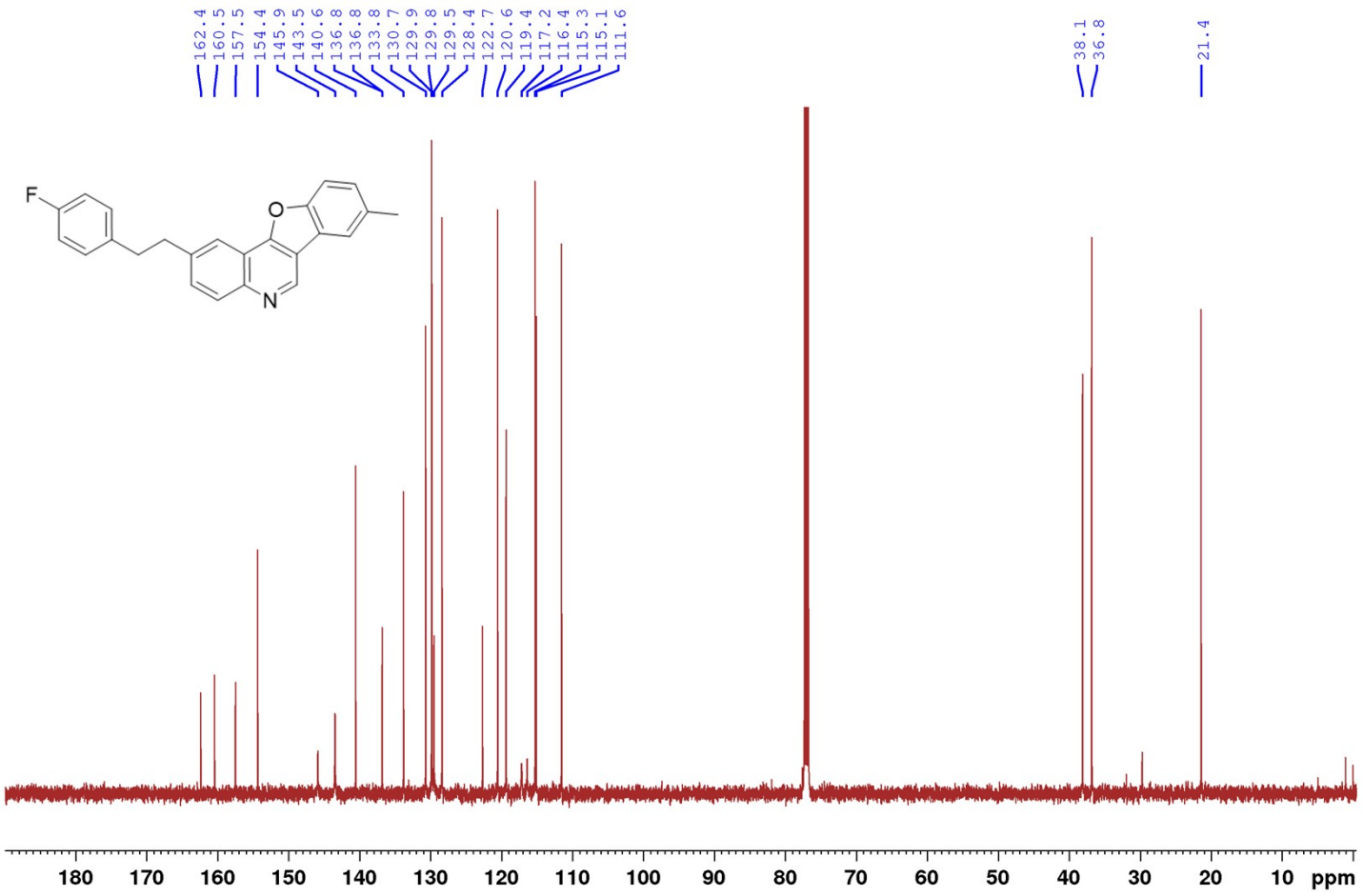
8-Methyl-2-phenethylbenzofuro[3,2-c]quinoline 4c

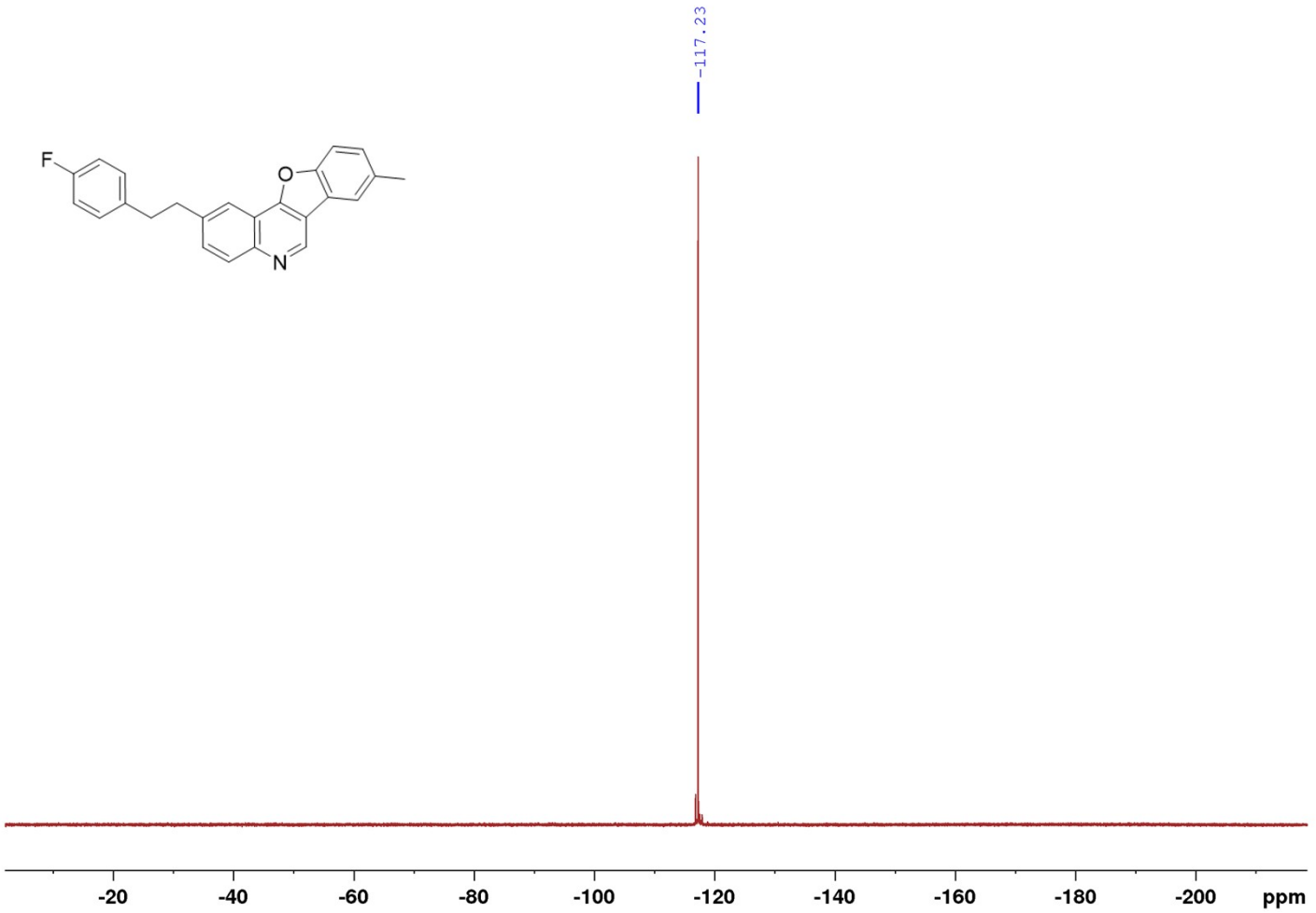



157.6
154.4
145.8
143.4
141.3
141.0
133.8
130.9
129.4
128.5
128.5
128.4
126.1
122.7
120.6
119.3
117.2
116.4
111.6
38.1
37.7
21.5
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

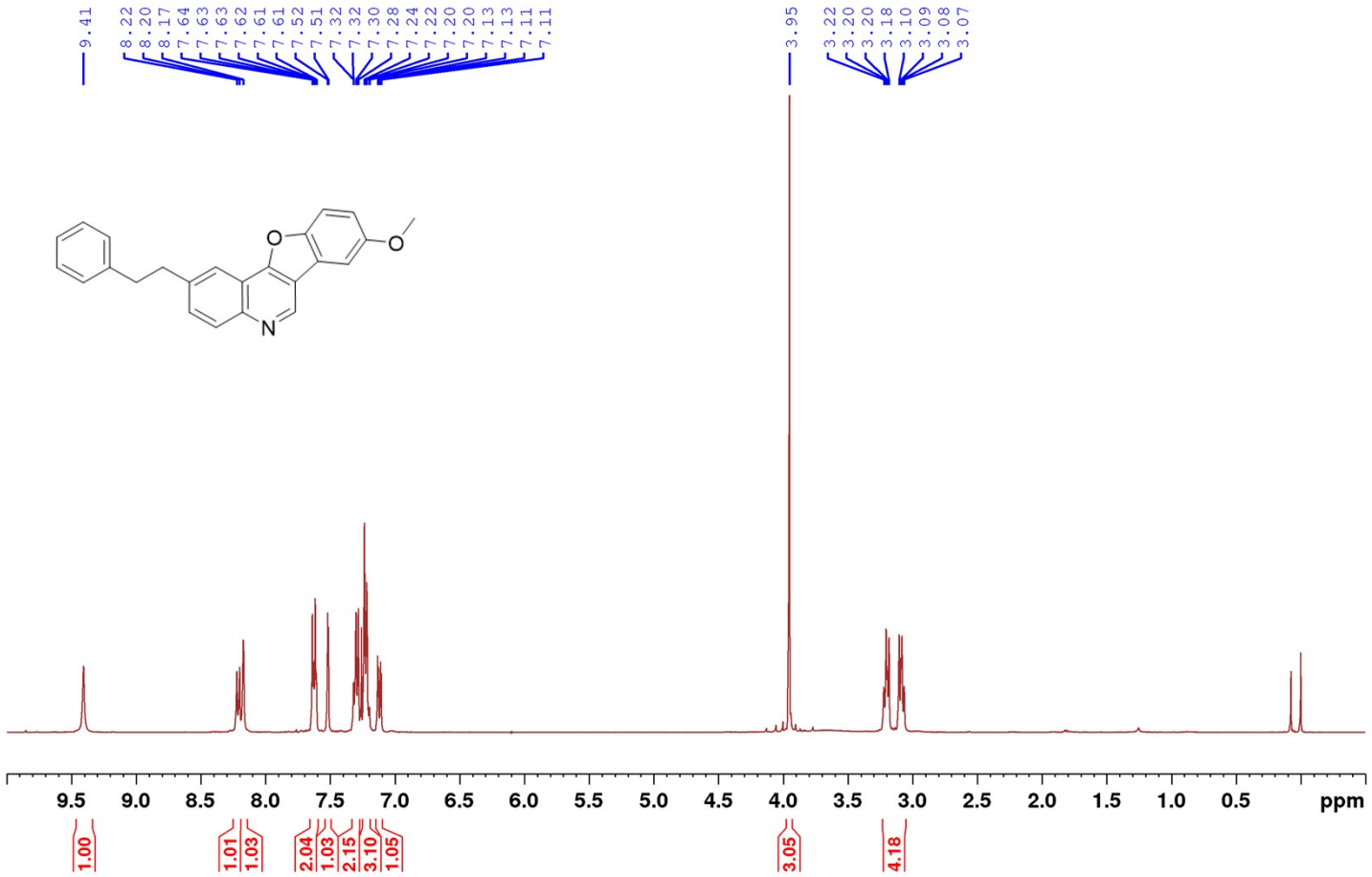
2-(4-Fluorophenethyl)-8-methylbenzofuro[3,2-c]quinoline 4d

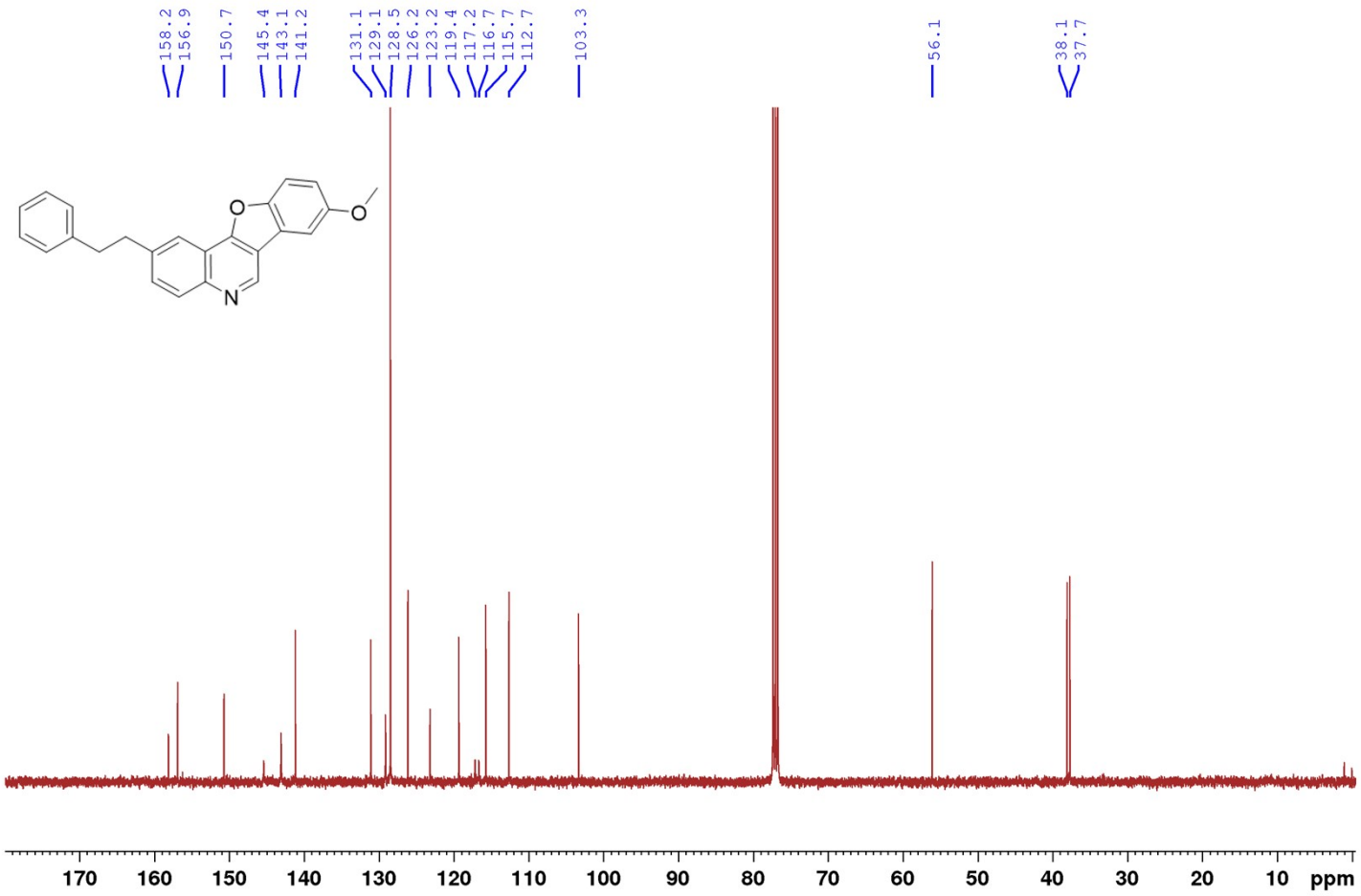



162.4
160.5
157.5
154.4
145.9
143.5
140.6
136.8
136.8
133.8
130.7
129.9
129.8
129.5
128.4
122.7
120.6
119.4
117.2
116.4
115.3
115.1
111.6
38.1
36.8
21.4
F
O
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

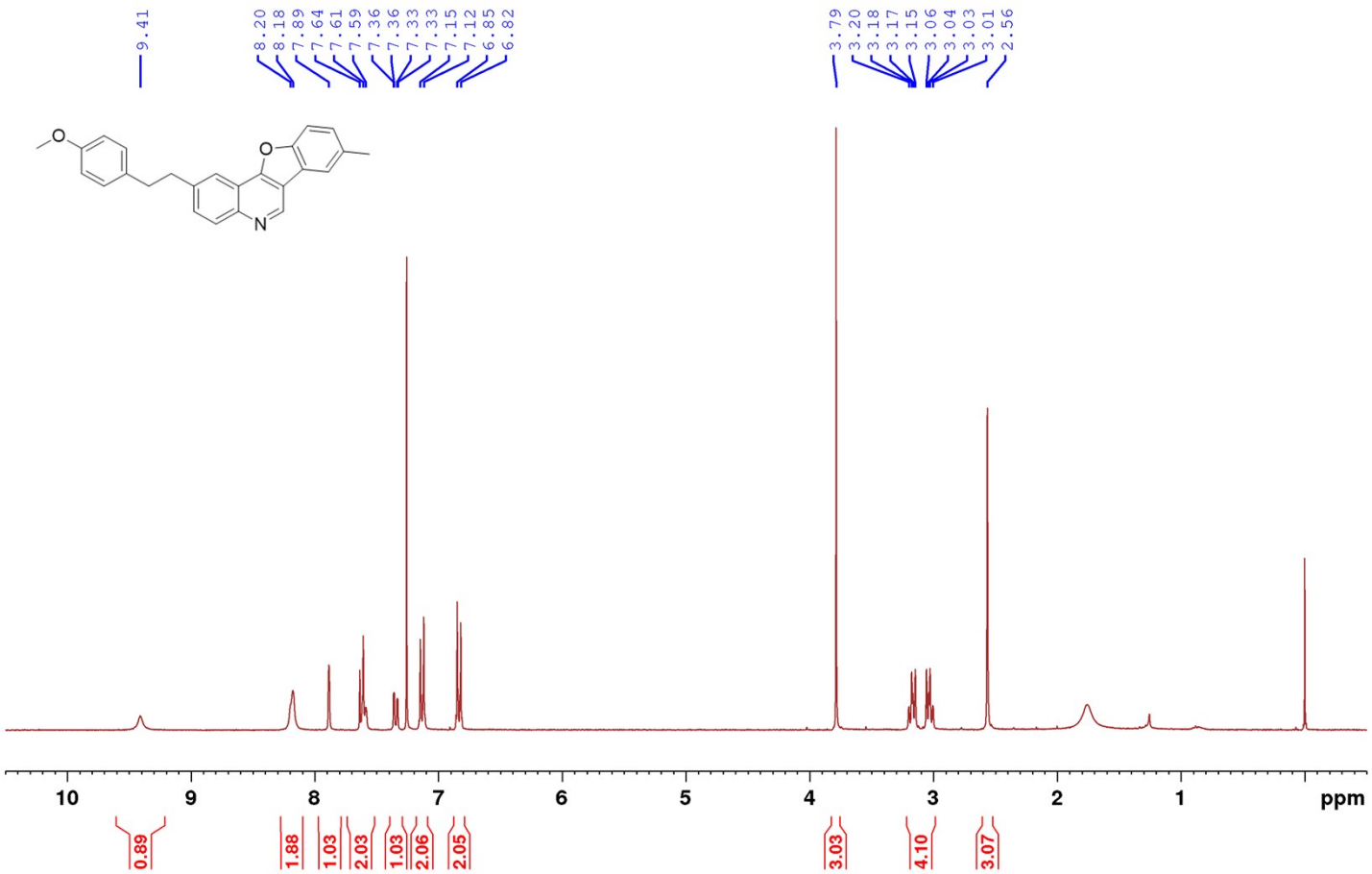

-117.23
F
O
N
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

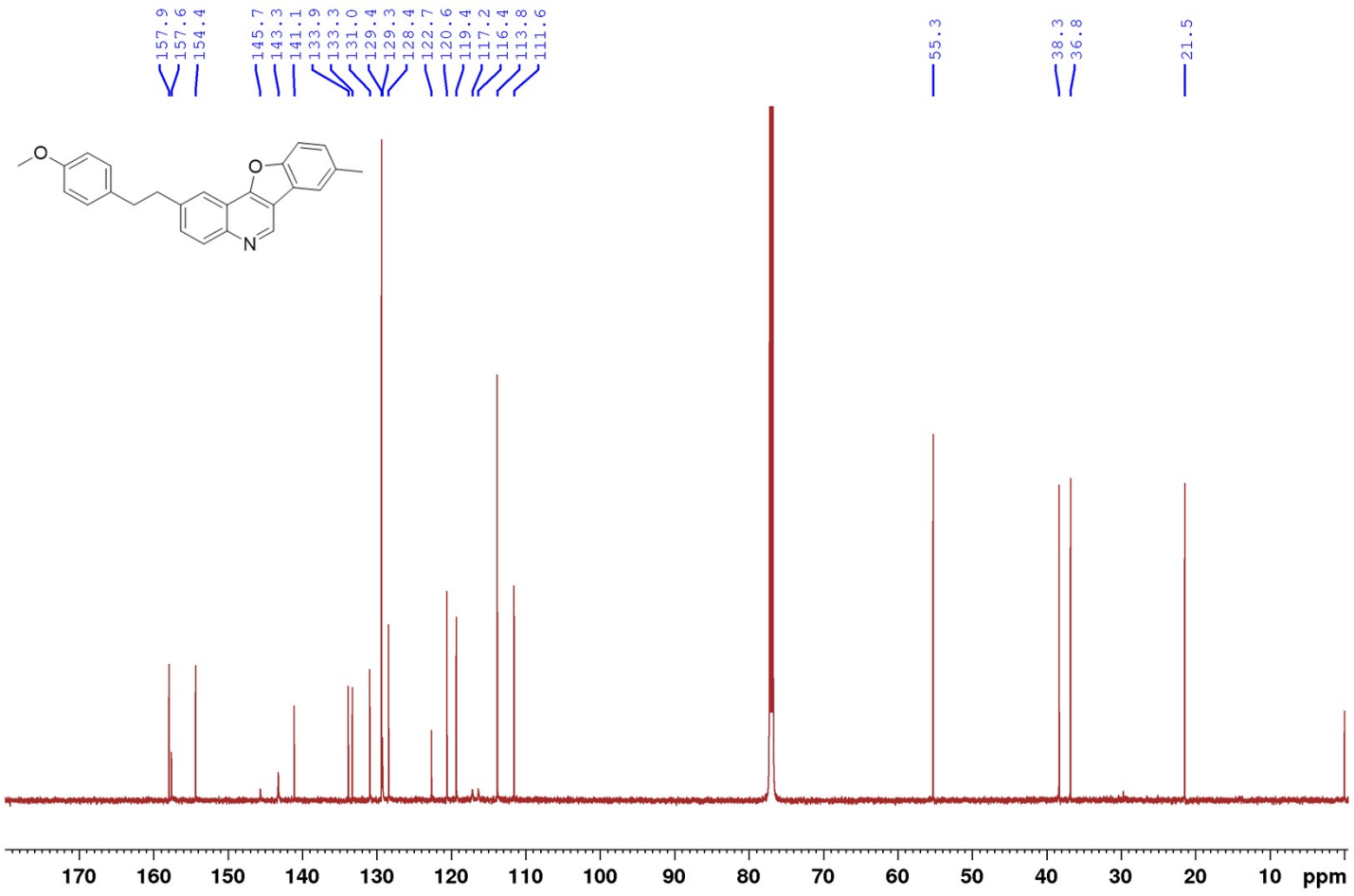
8-Methoxy-2-phenethylbenzofuro[3,2-c]quinoline 4e



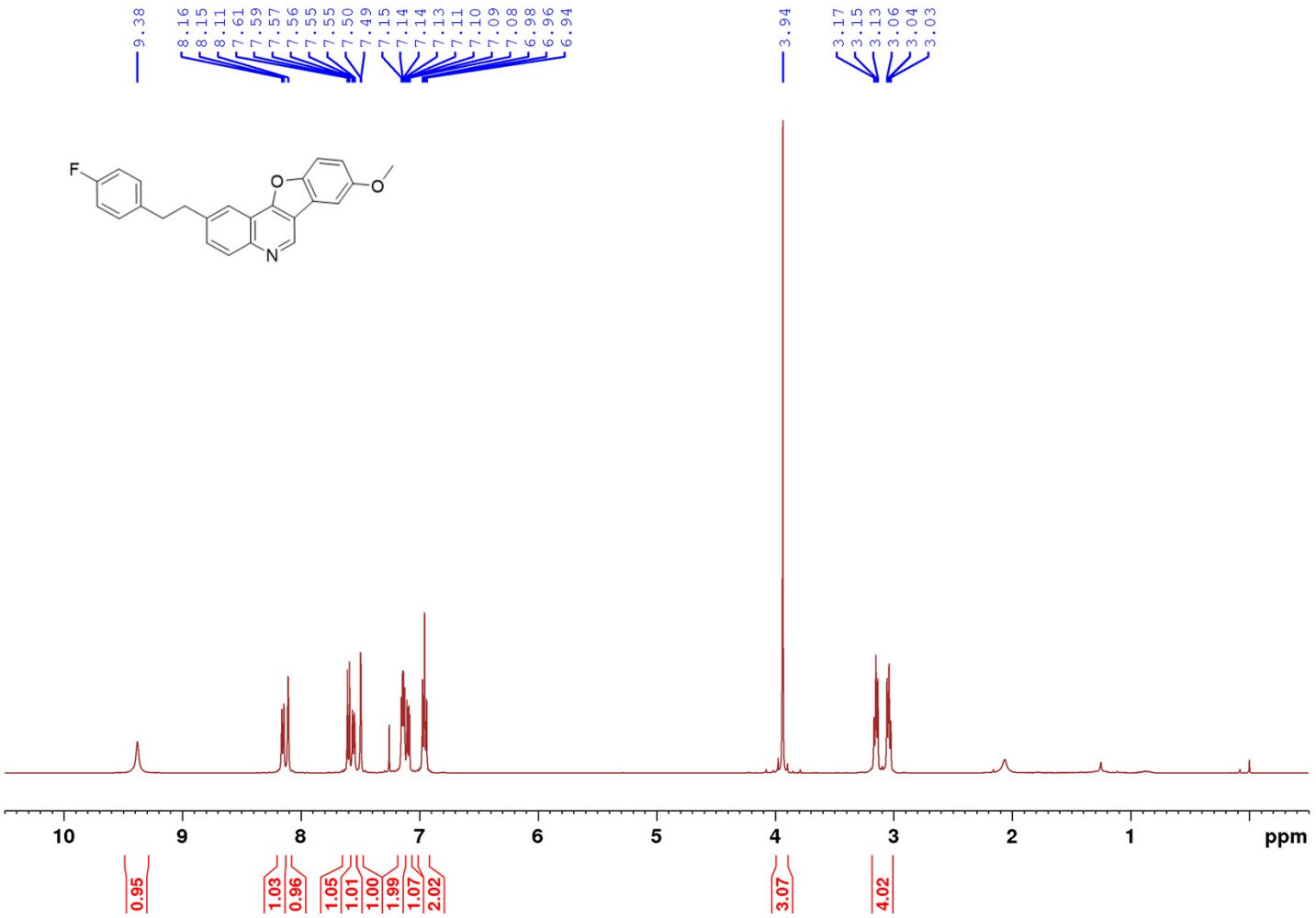

158.2
156.9
150.7
145.4
143.1
141.2
131.1
129.1
128.5
126.2
123.2
119.4
117.2
116.7
115.7
112.7
103.3
56.1
38.1
37.7
O
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

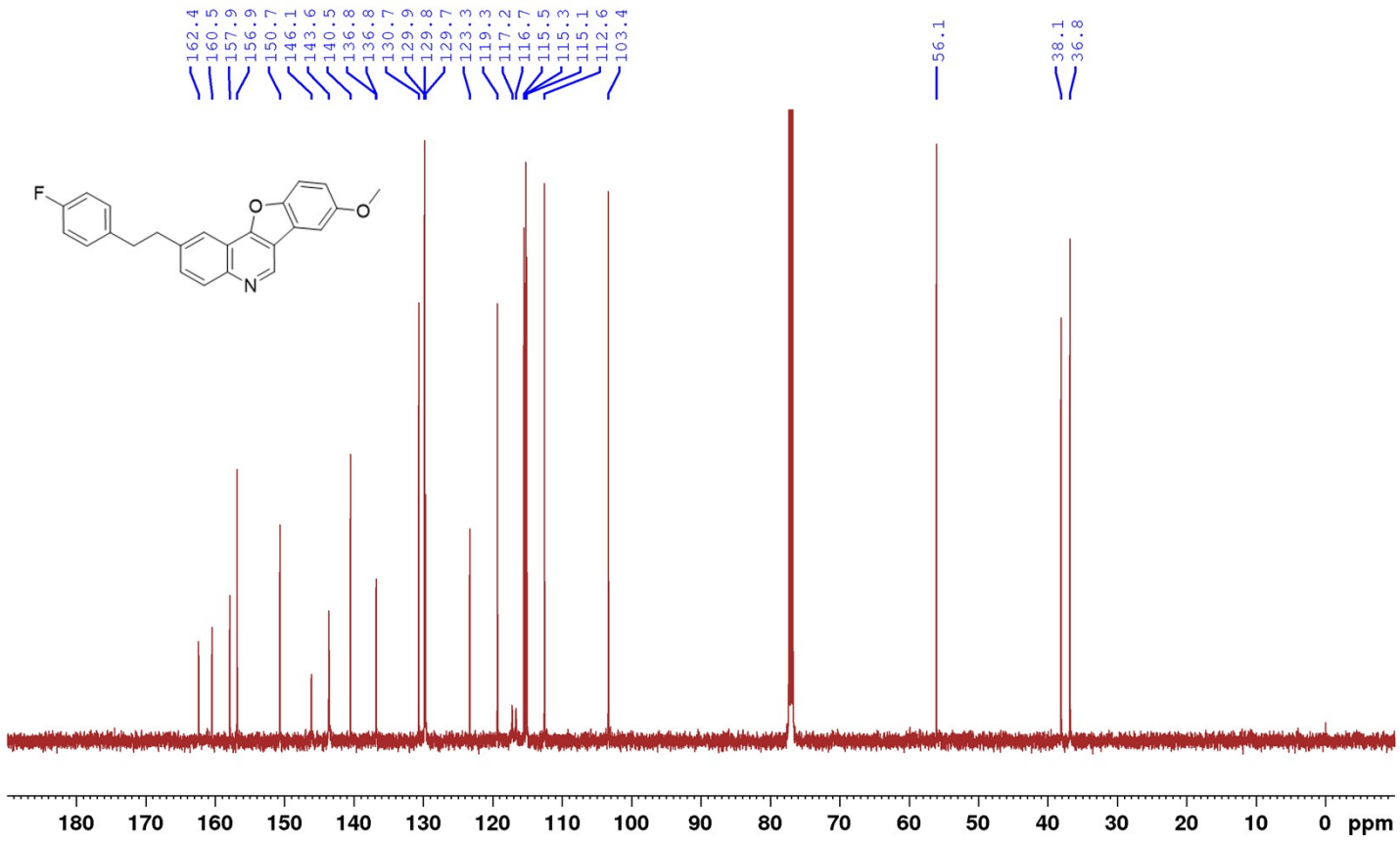
2-(4-Methoxyphenethyl)-8-methylbenzofuro[3,2-c]quinoline 4f

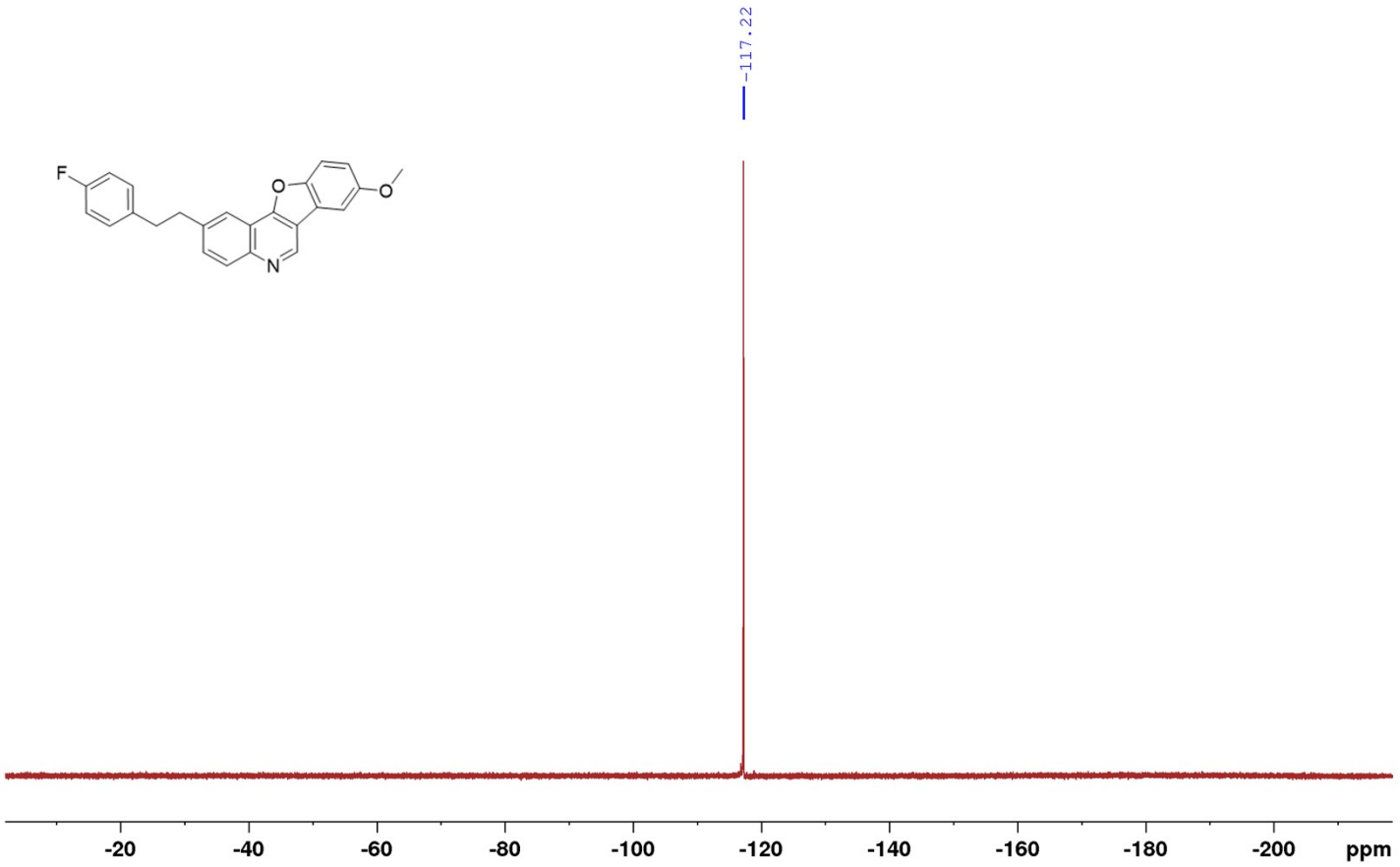



157.9
157.6
154.4
145.7
143.3
141.1
133.9
133.3
131.0
129.4
129.3
128.4
122.7
120.6
119.4
117.2
116.4
113.8
111.6
55.3
38.3
36.8
21.5
O
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

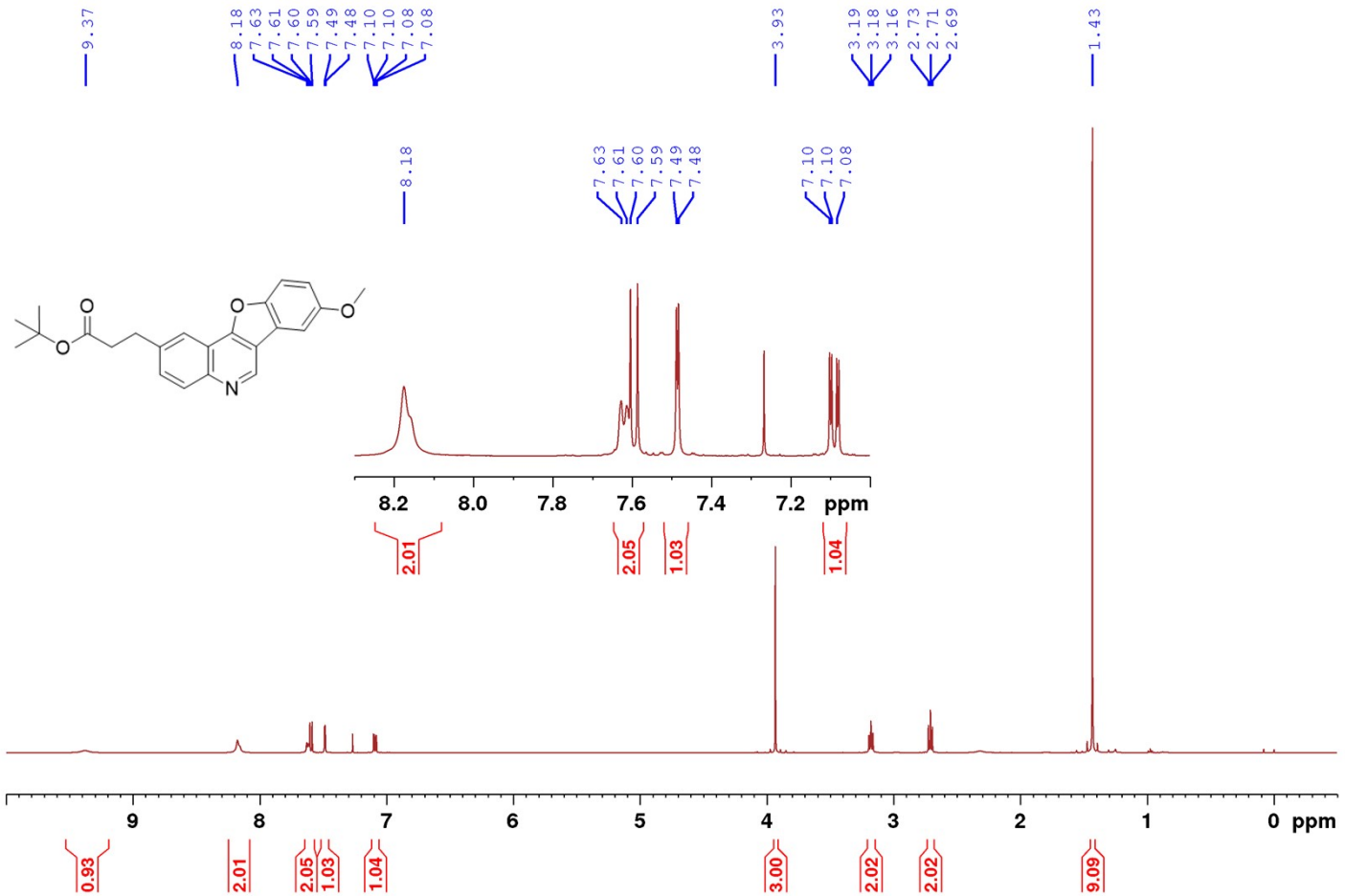
2-(4-Fluorophenethyl)-8-methoxybenzofuro[3,2-c]quinoline 4g

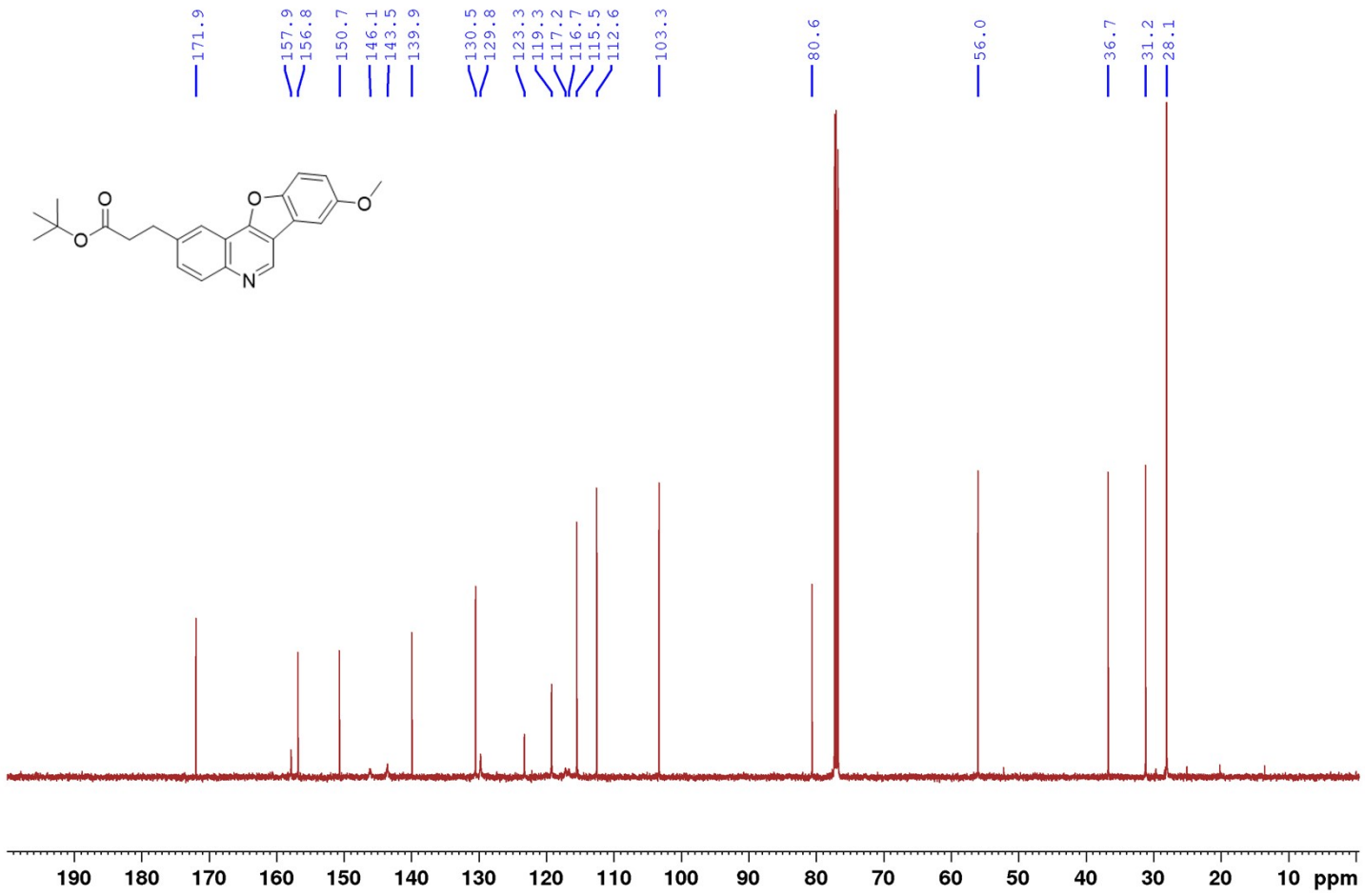



162.4
160.5
157.9
156.9
150.7
146.1
143.6
140.5
136.8
136.8
130.7
129.9
129.8
129.7
123.3
119.3
117.2
116.7
115.5
115.3
115.1
112.6
103.4
56.1
38.1
36.8
F
O
O
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

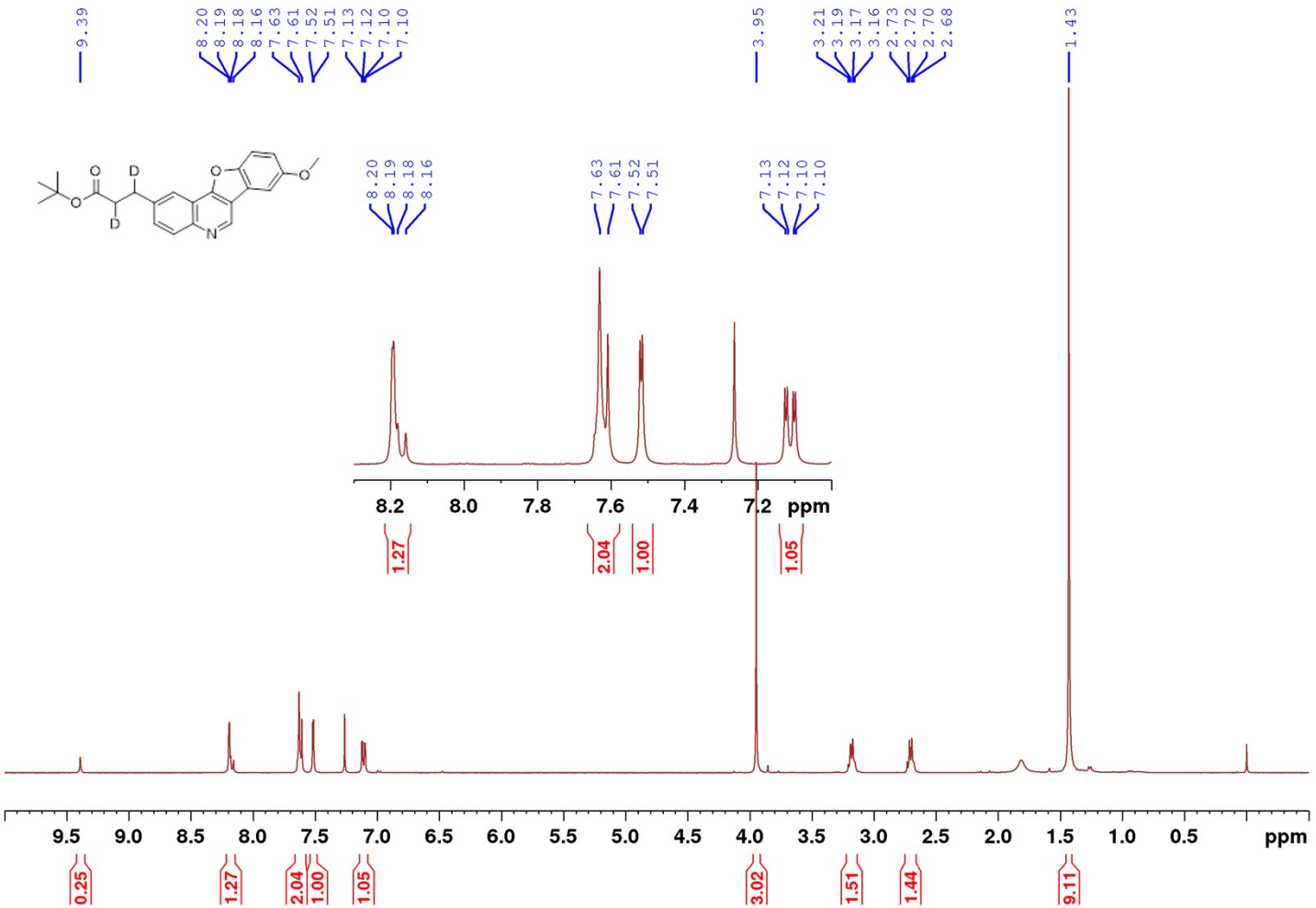

-117.22
F
O
O
N
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

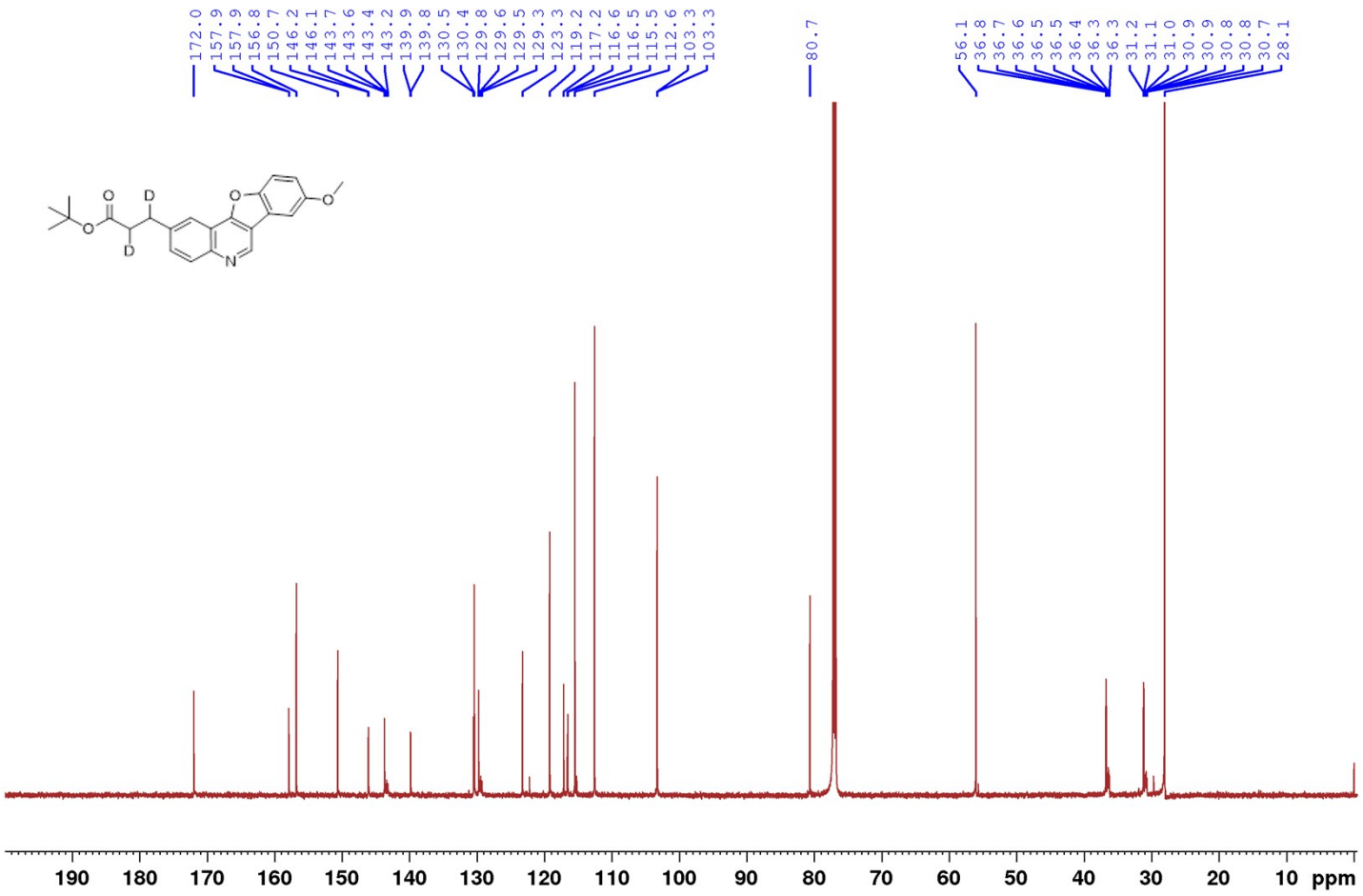
***tert*-Butyl 3-(8-methoxybenzofuro[3,2-c]quinolin-2-yl)propanoate 4h**



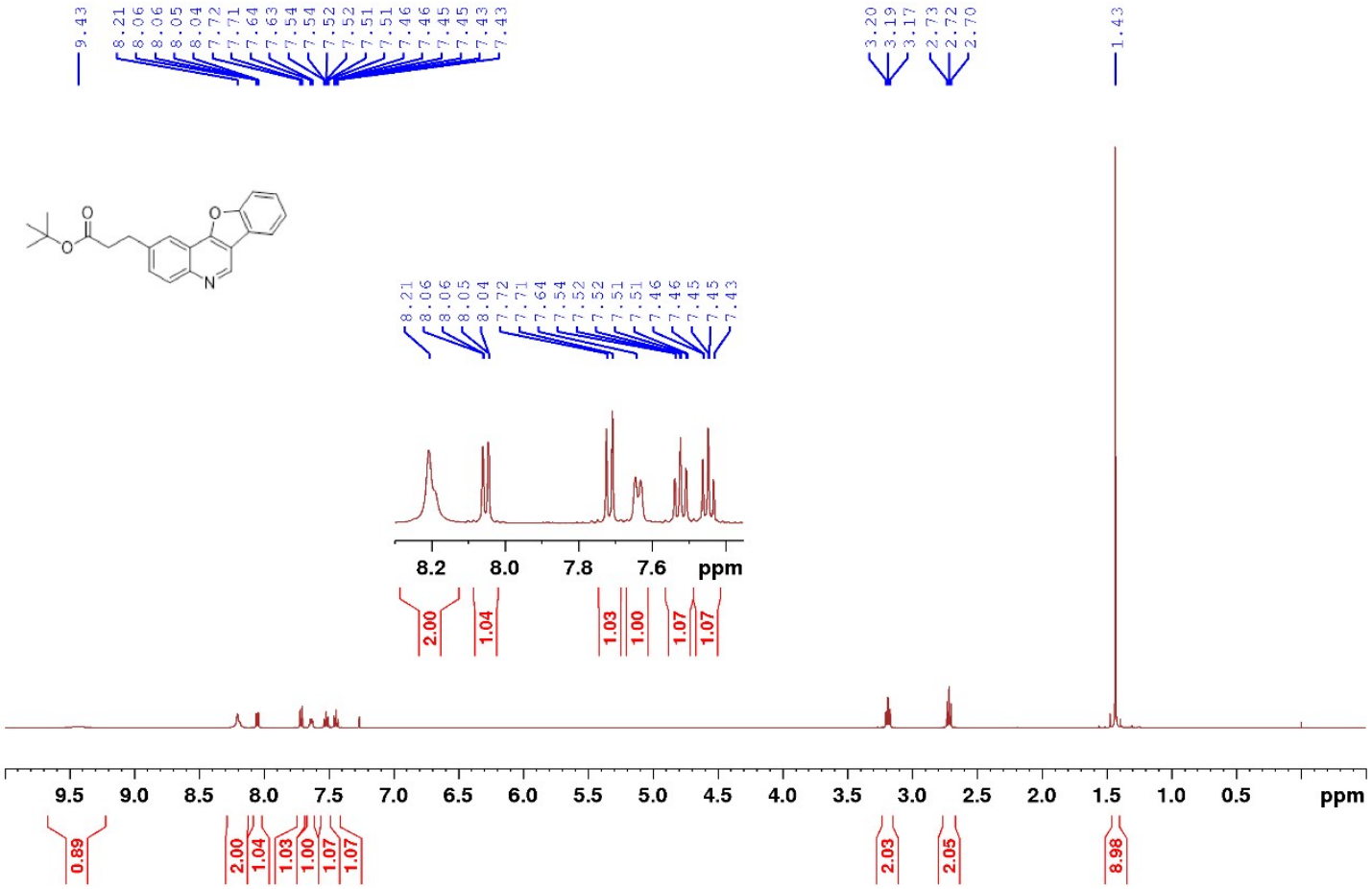

171.9
157.9
156.8
150.7
146.1
143.5
139.9
130.5
129.8
123.3
119.3
117.2
116.7
115.5
112.6
103.3
80.6
56.0
36.7
31.2
28.1
O
O
O
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

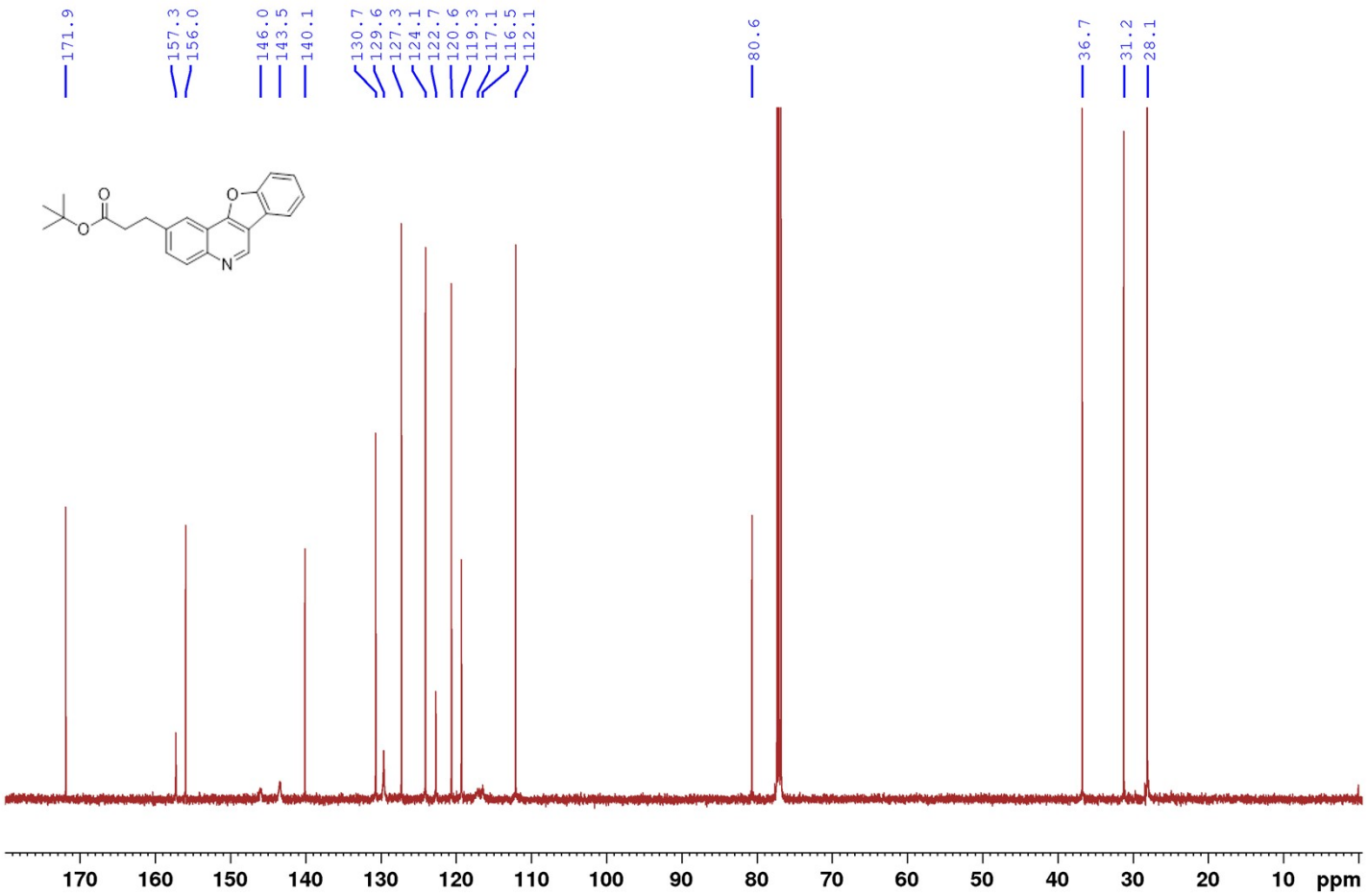
tert-butyl (3R)-3-(8-methoxybenzofuro[3,2-c]quinolin-2-yl-4,6-d2)propanoate-2,3-d2 4h-d_4



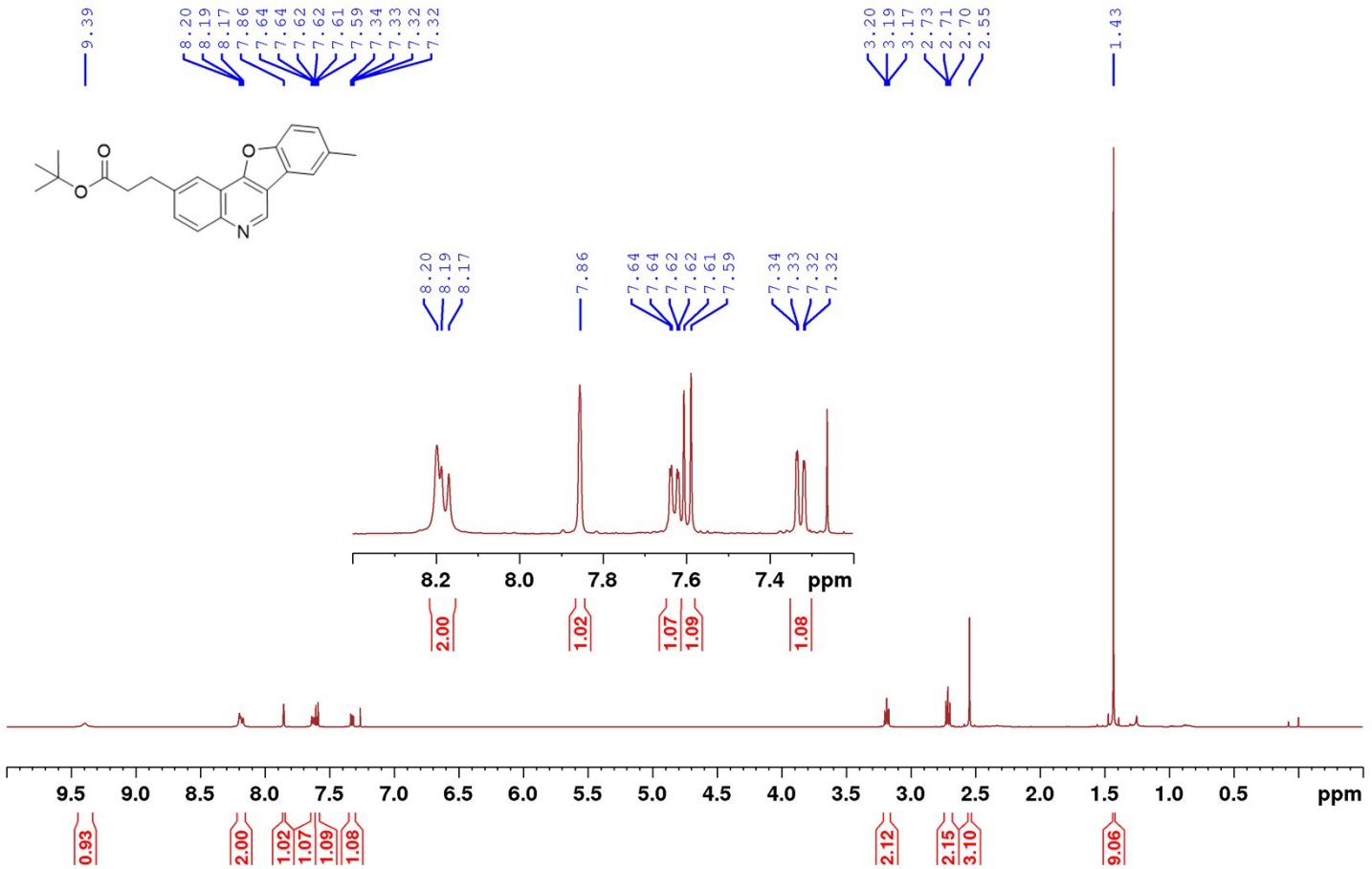

172.0
157.9
157.9
156.8
150.7
146.2
146.1
143.7
143.6
143.4
143.2
139.9
139.8
130.5
130.4
129.8
129.6
129.5
129.3
123.3
119.2
117.2
116.6
116.5
115.5
112.6
103.3
103.3
80.7
56.1
36.8
36.7
36.6
36.5
36.5
36.4
36.3
36.3
31.2
31.1
31.0
30.9
30.9
30.8
30.8
30.7
28.1
O
D
O
O
D
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

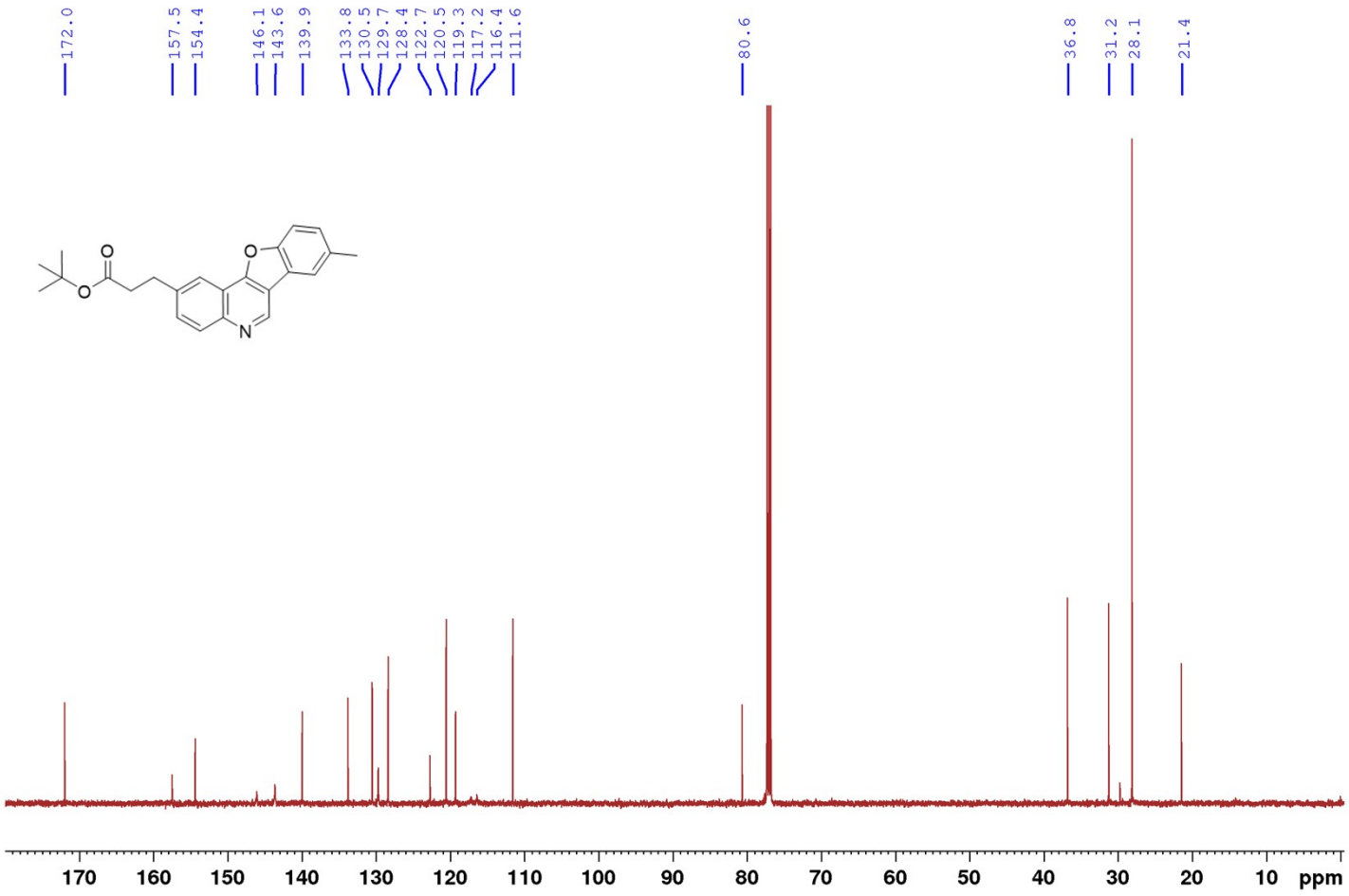
tert-Butyl 3-(benzofuro[3,2-c]quinolin-2-yl)propanoate 4i



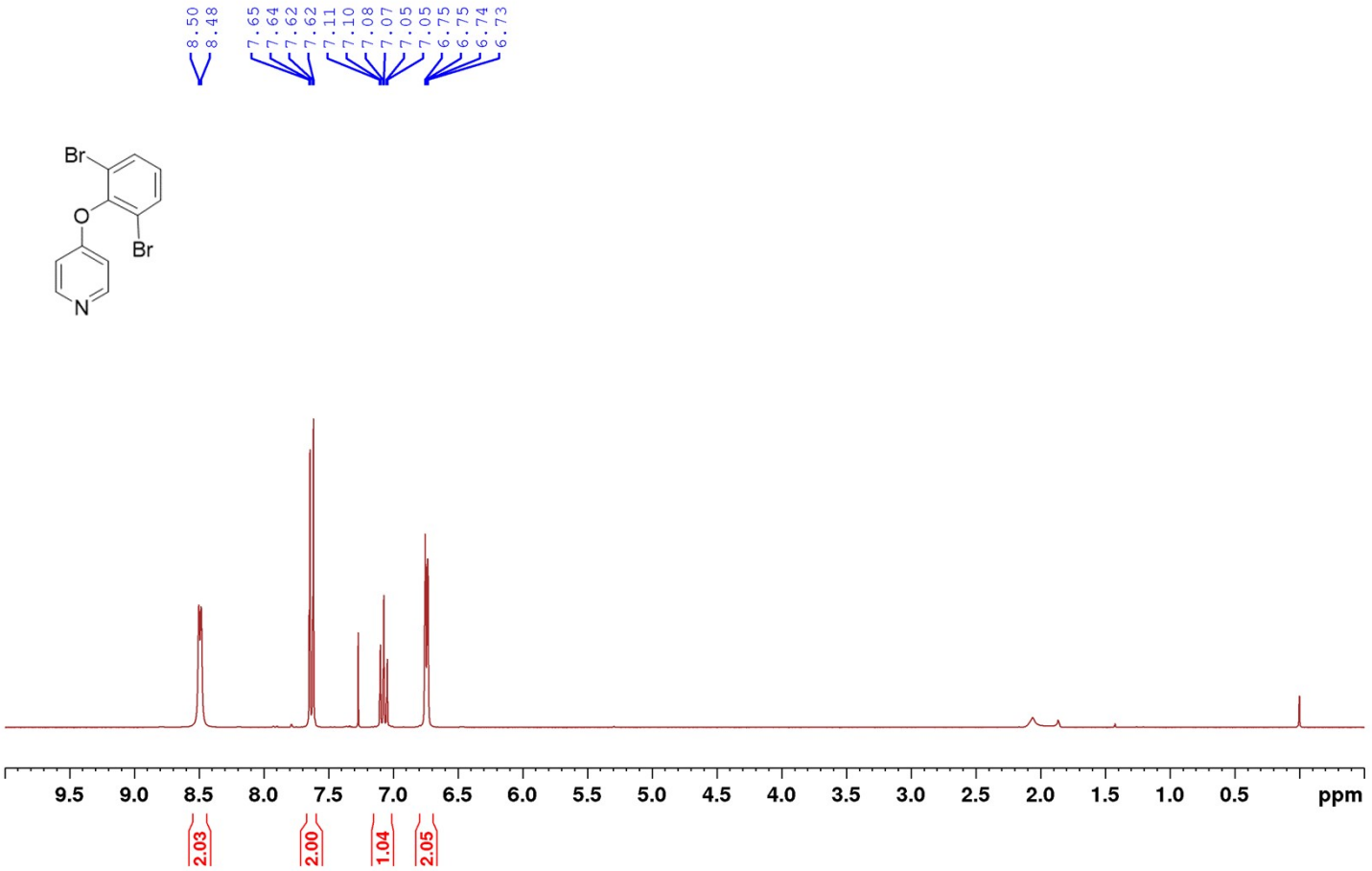

171.9
157.3
156.0
146.0
143.5
140.1
130.7
129.6
127.3
124.1
122.7
120.6
119.3
117.1
116.5
112.1
80.6
36.7
31.2
28.1
O
O
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

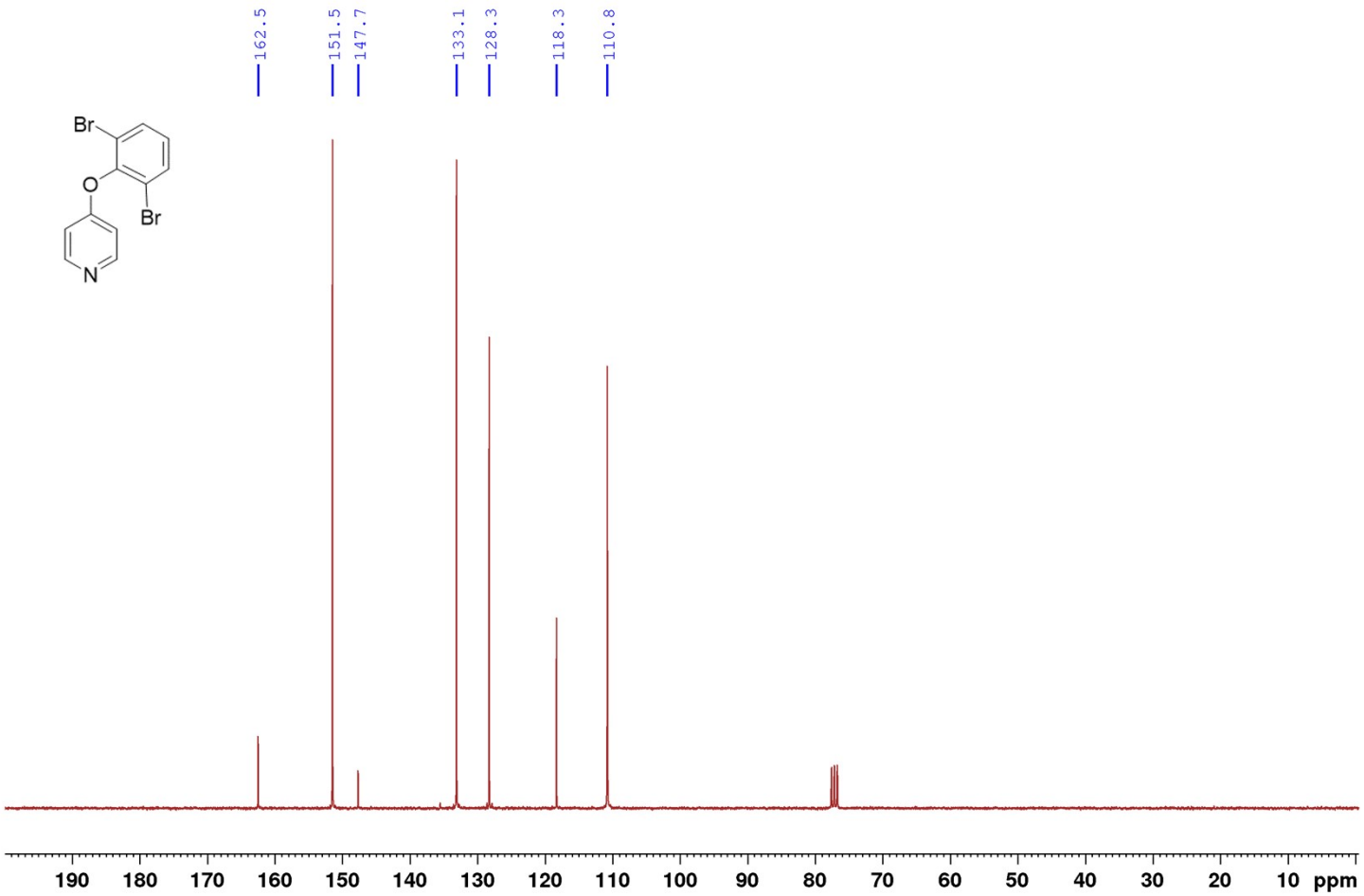
***tert*-Butyl 3-(8-methylbenzofuro[3,2-c]quinolin-2-yl)propanoate 4j**



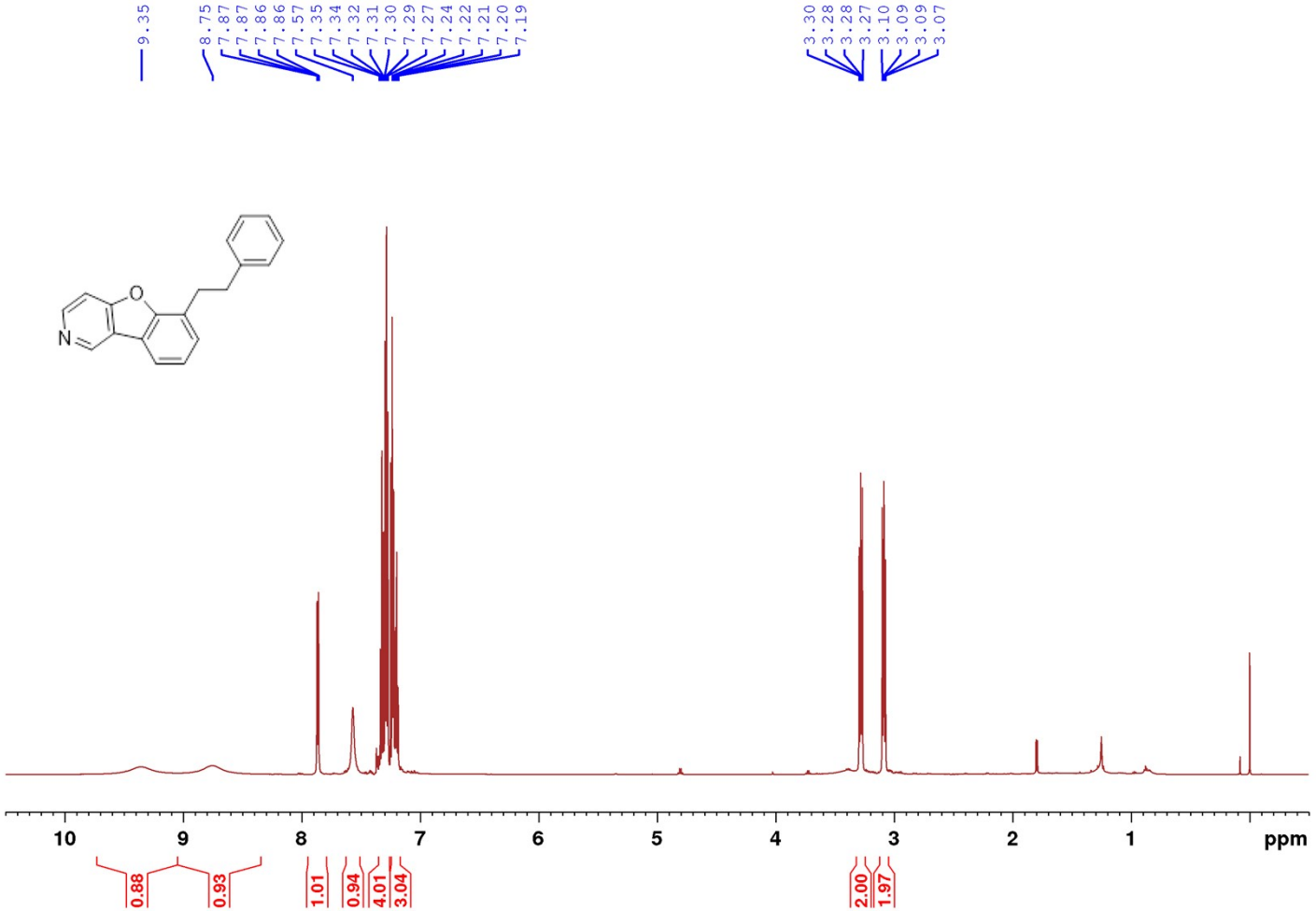

172.0
157.5
154.4
146.1
143.6
139.9
133.8
130.5
129.7
128.4
122.7
120.5
119.3
117.2
116.4
111.6
80.6
36.8
31.2
28.1
21.4
O
O
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

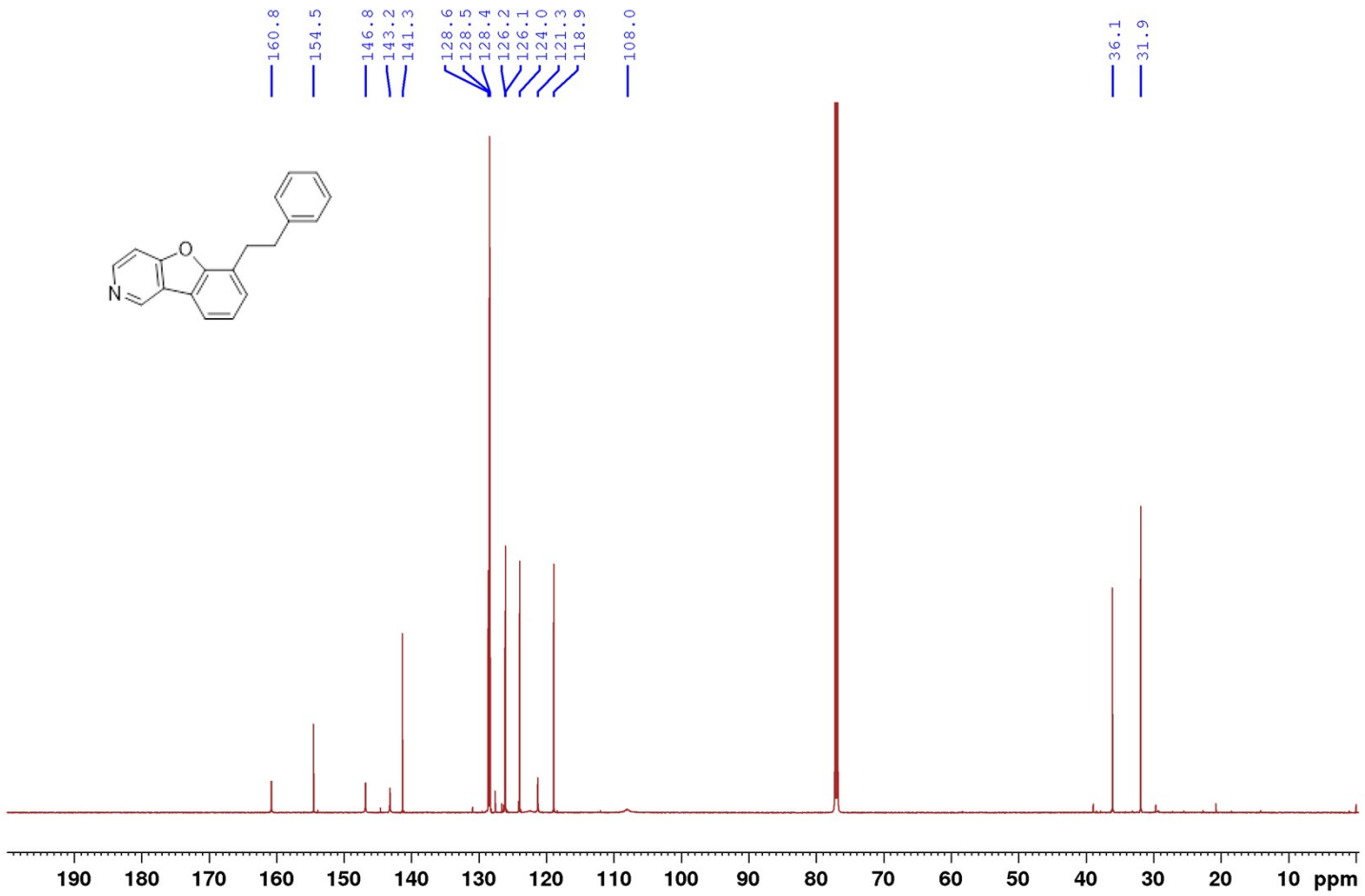
4-(2,6-Dibromophenoxy)pyridine 5



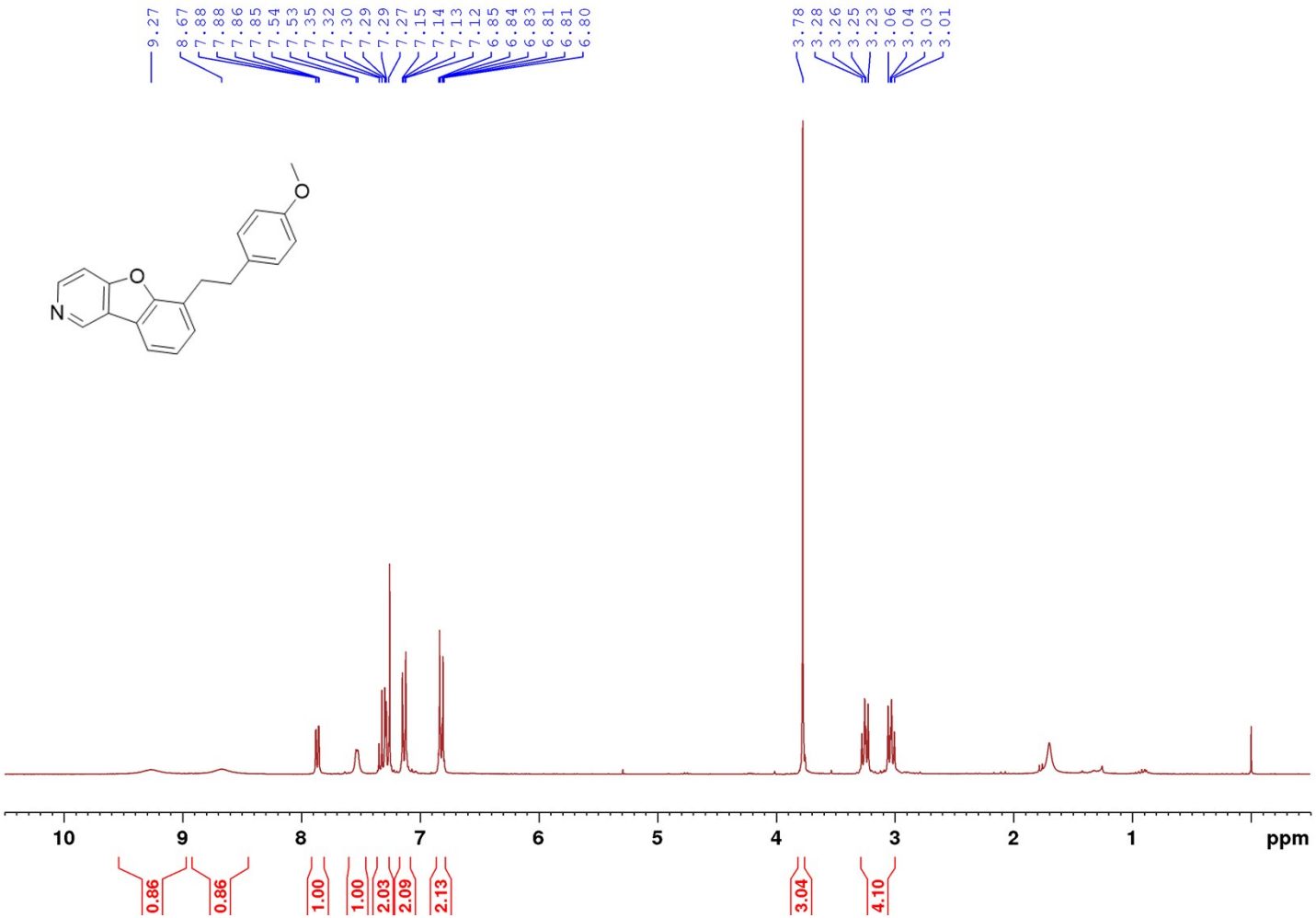

162.5
151.5
147.7
133.1
128.3
118.3
110.8
Br
O
Br
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

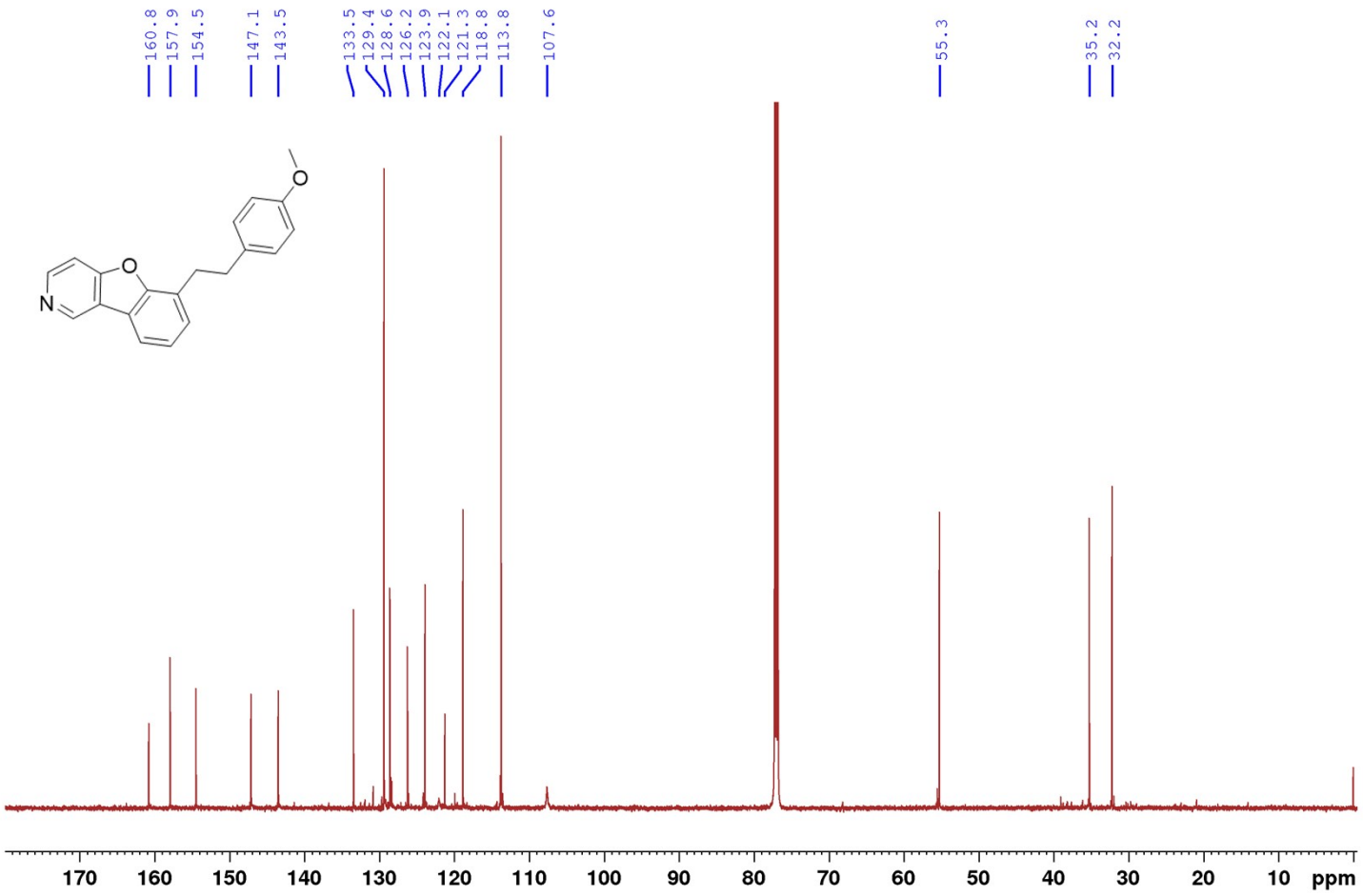
6-phenethylbenzofuro[3,2-c]pyridine 6a



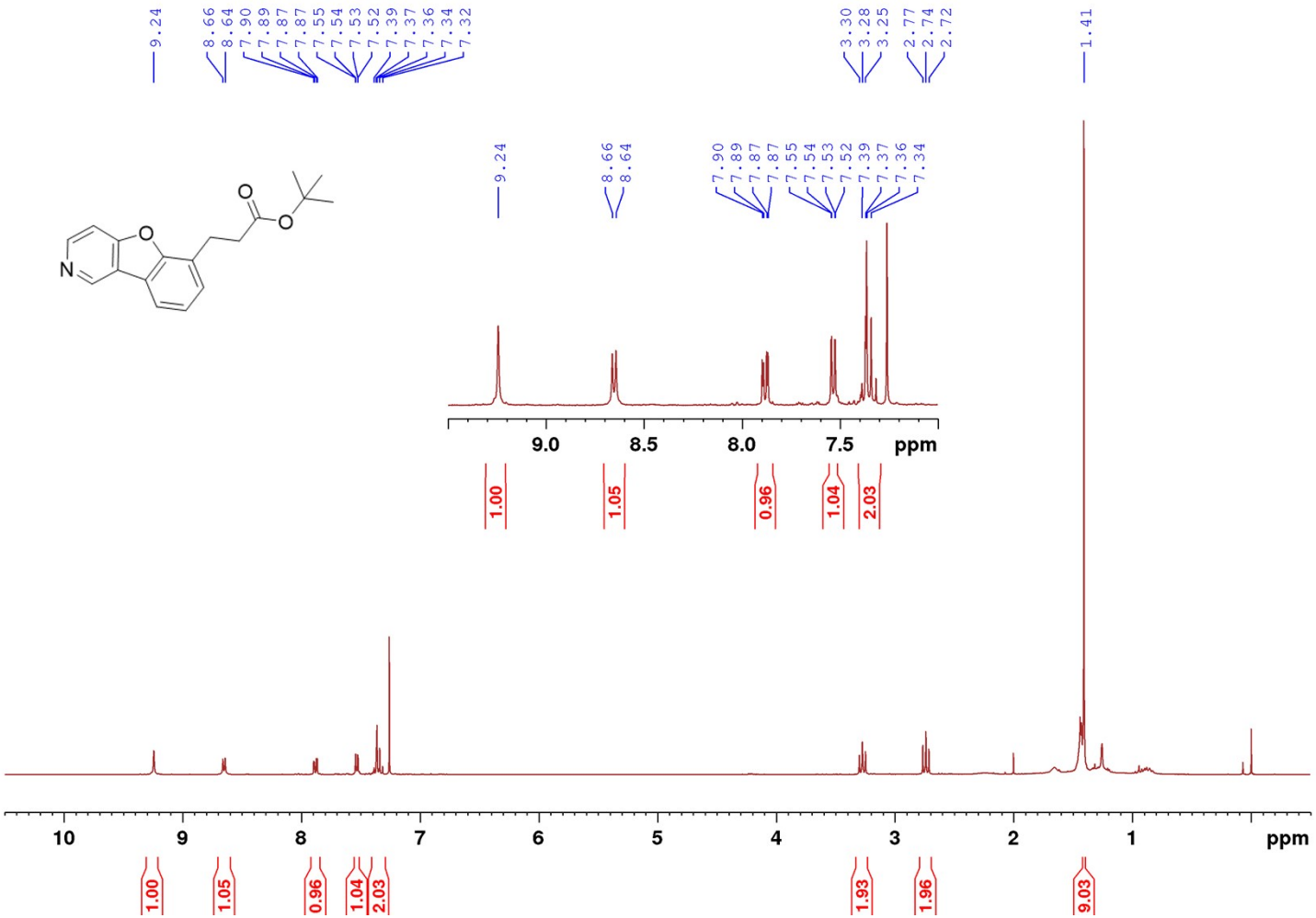

160.8
154.5
146.8
143.2
141.3
128.6
128.5
128.4
126.2
126.1
124.0
121.3
118.9
108.0
36.1
31.9
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

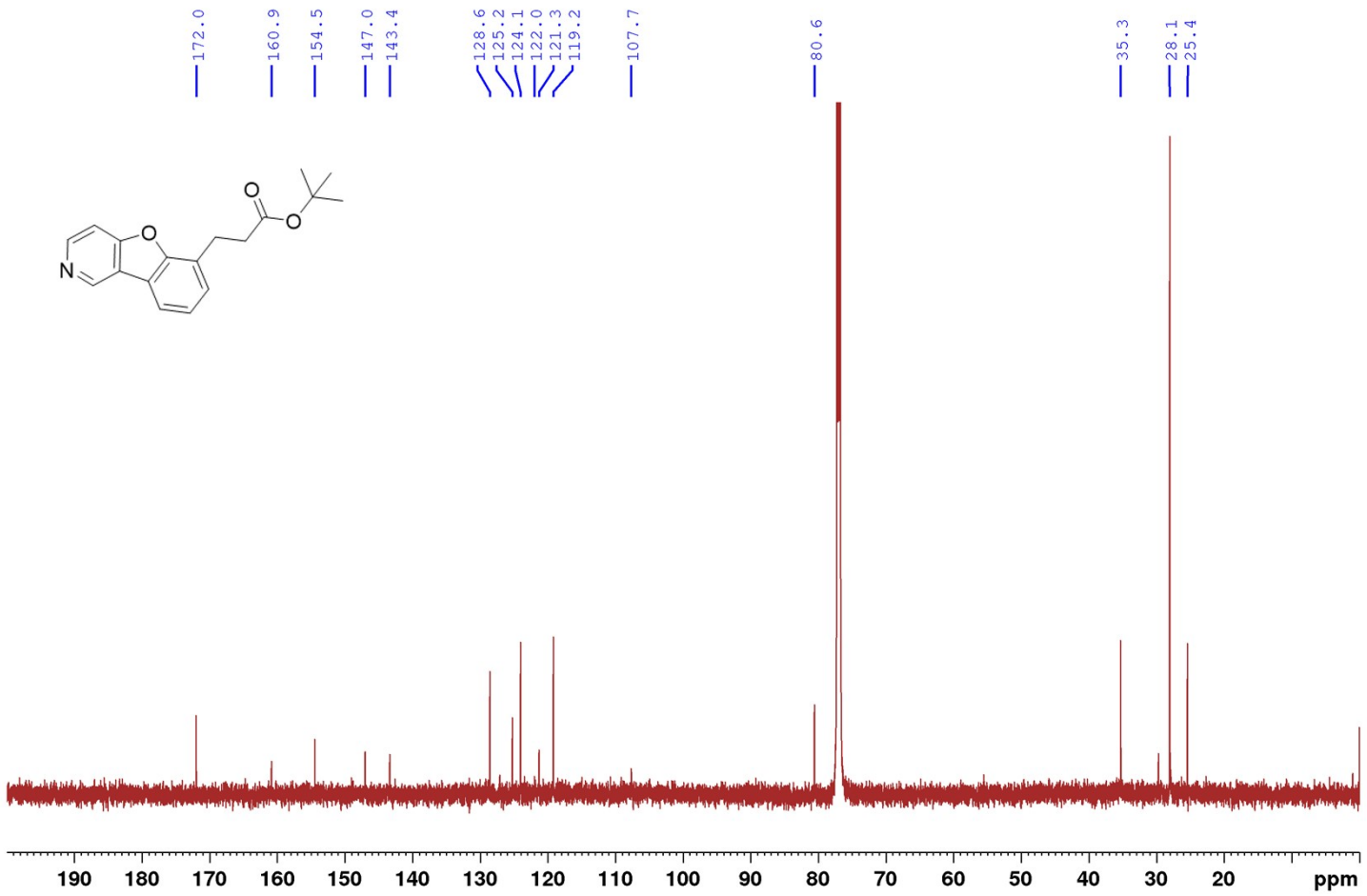
6-(4-Methoxyphenethyl)benzofuro[3,2-c]pyridine 6b



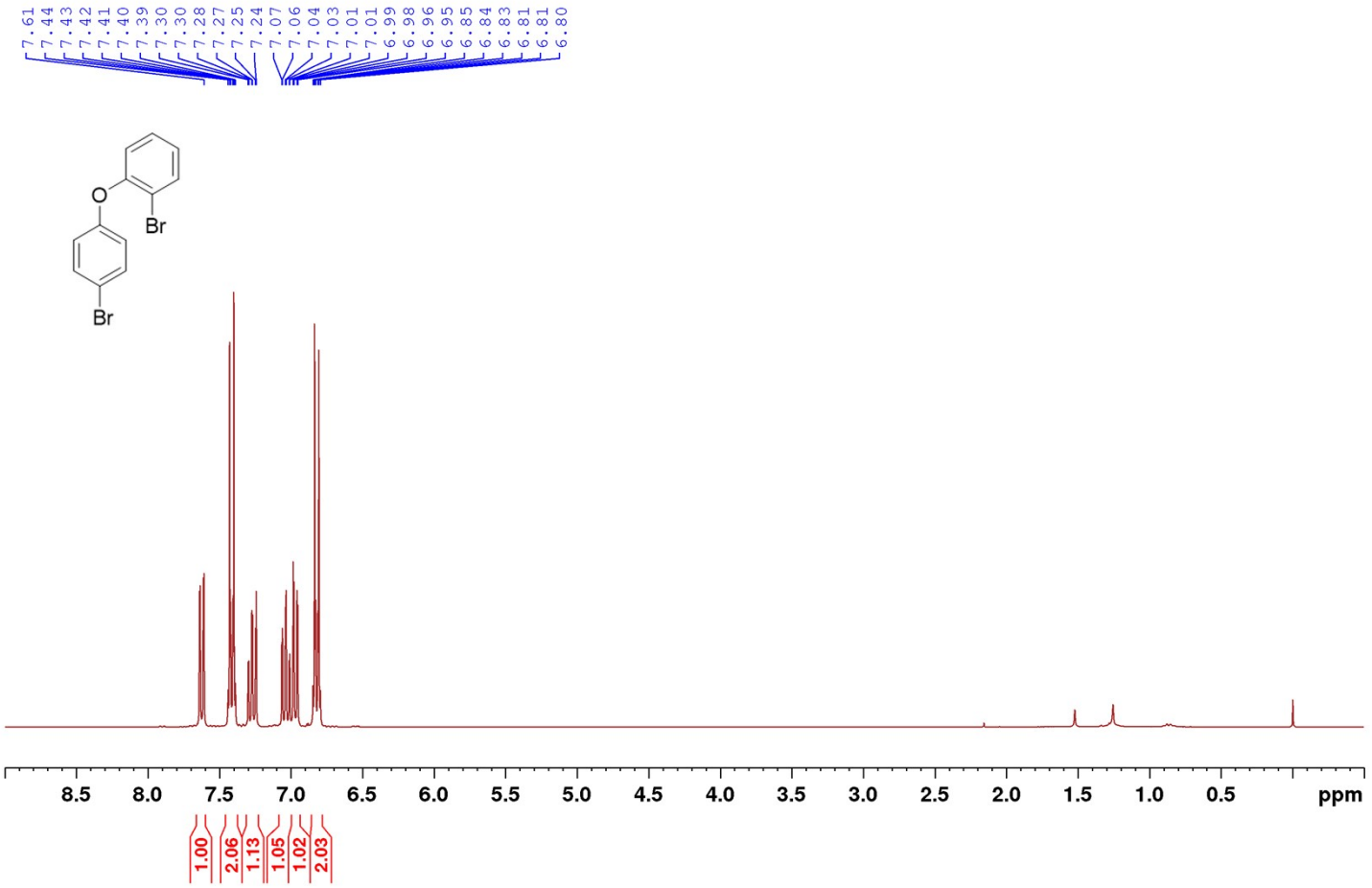

160.8
157.9
154.5
147.1
143.5
133.5
129.4
128.6
126.2
123.9
122.1
121.3
118.8
113.8
107.6
55.3
35.2
32.2
O
N
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

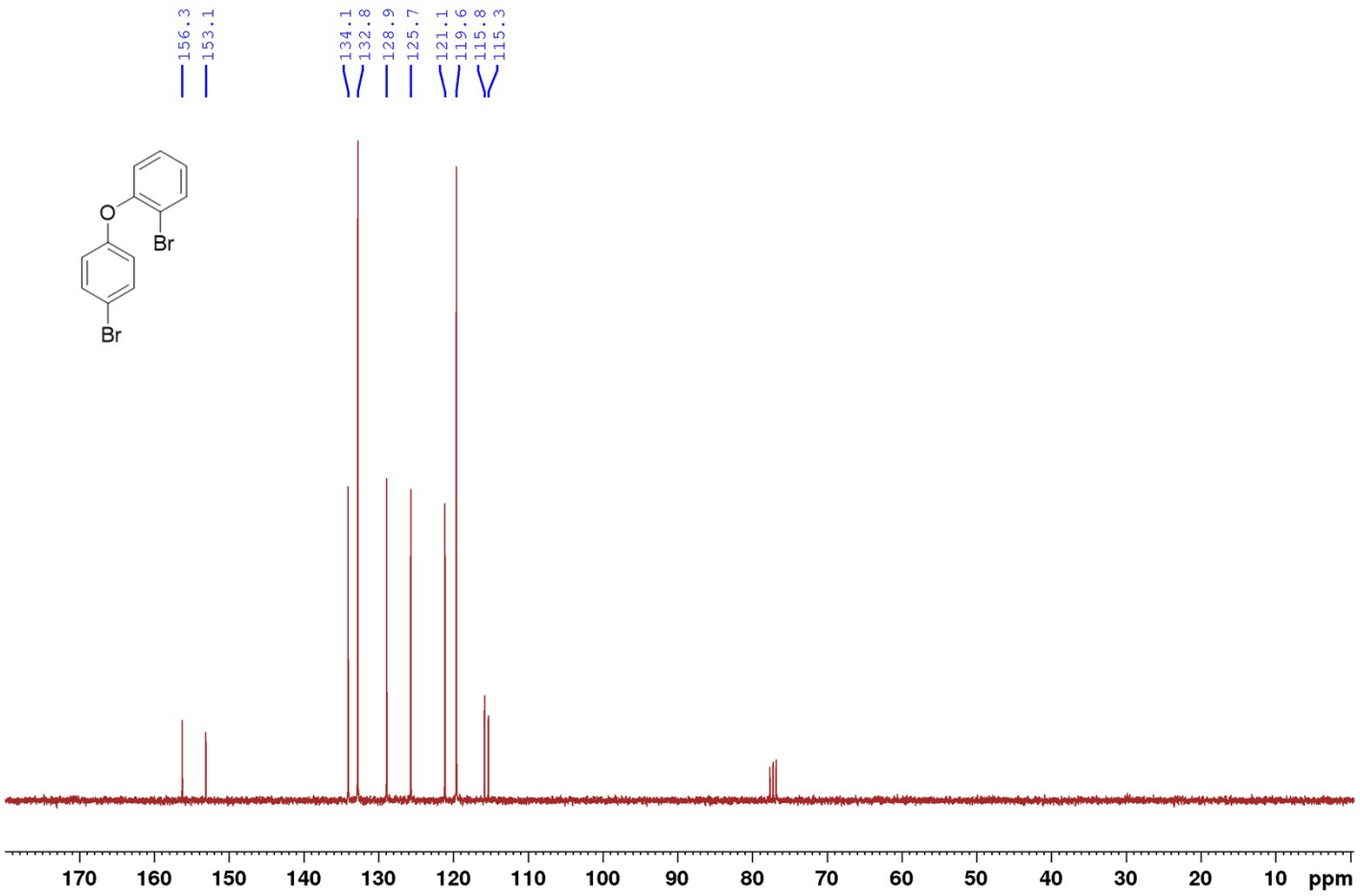
***tert*-Butyl 3-(benzofuro[3,2-c]pyridin-6-yl)propanoate 6c**



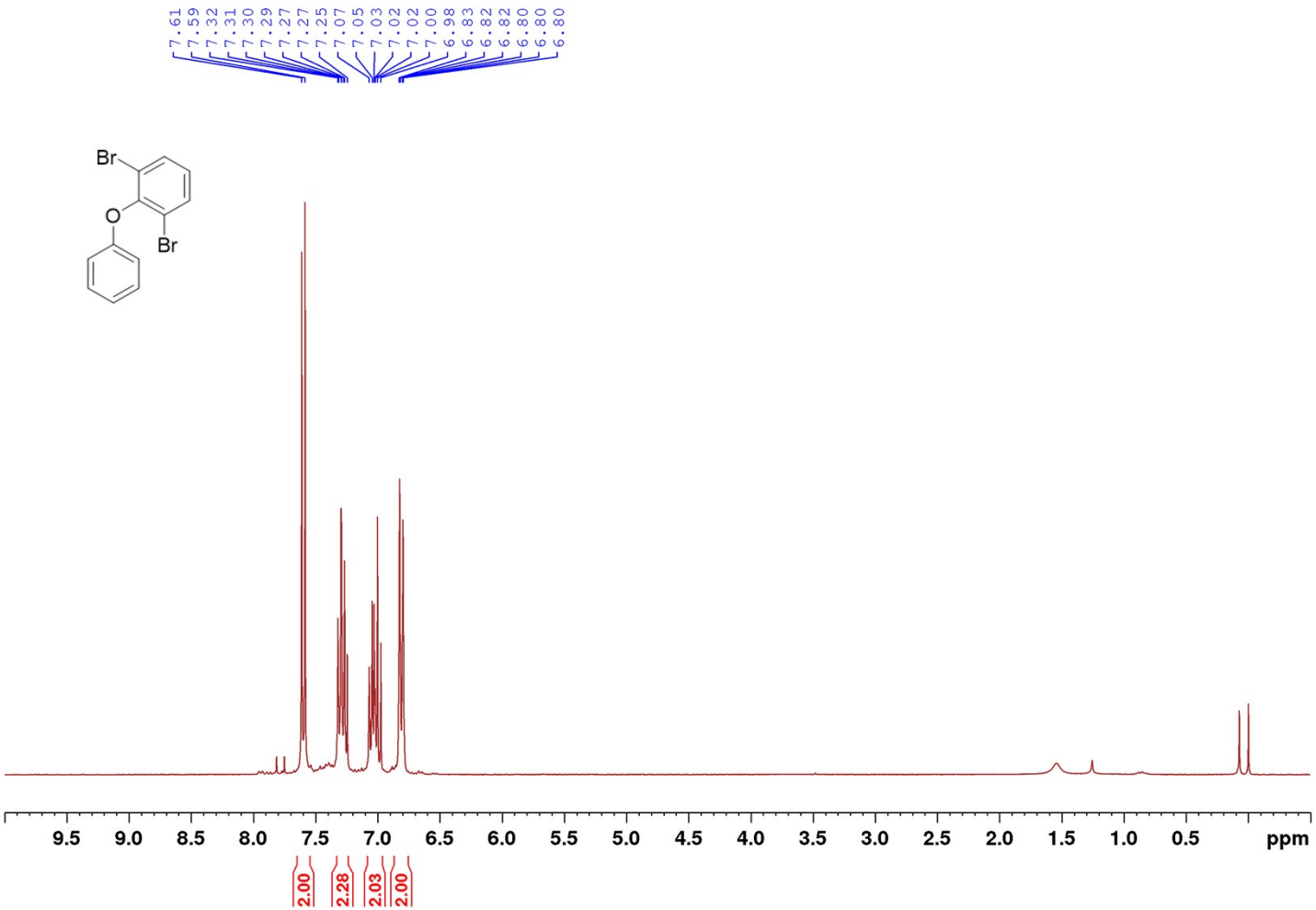

172.0
160.9
154.5
147.0
143.4
128.6
125.2
124.1
122.0
121.3
119.2
107.7
80.6
35.3
28.1
25.4
O
O
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

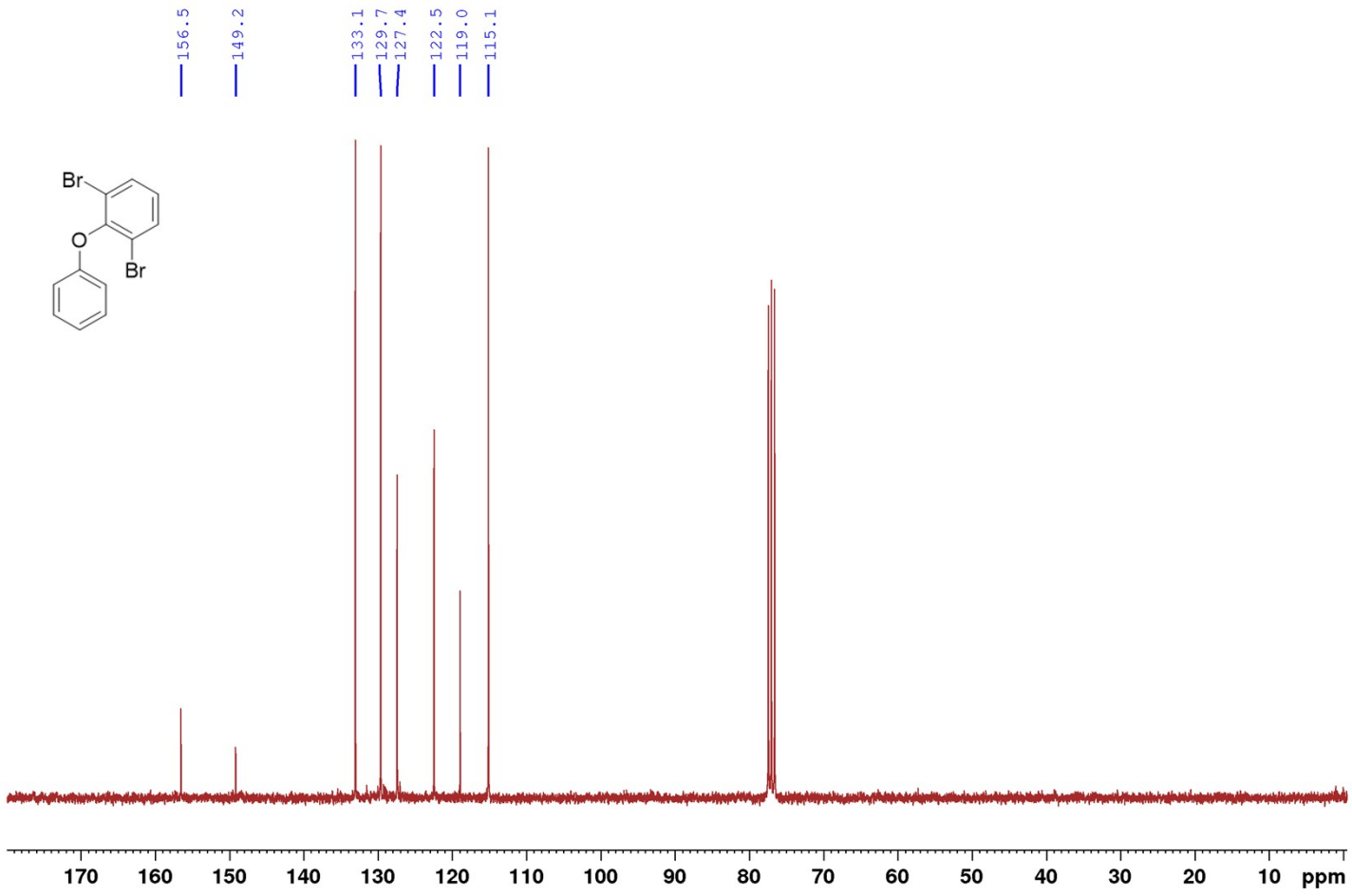
1-Bromo-2-(4-bromophenoxy)benzene 7



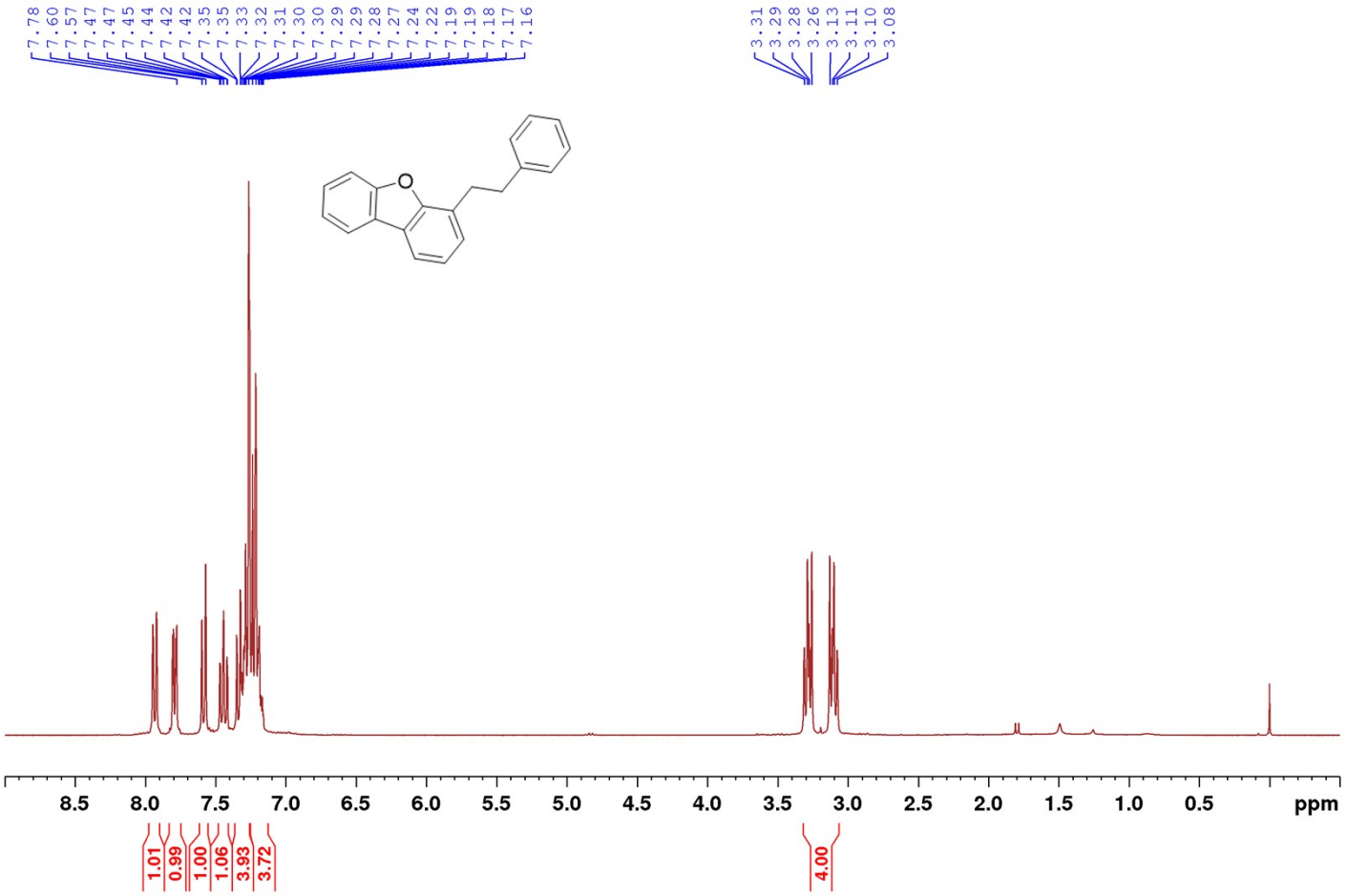

156.3
153.1
134.1
132.8
128.9
125.7
121.1
119.6
115.8
115.3
O
Br
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

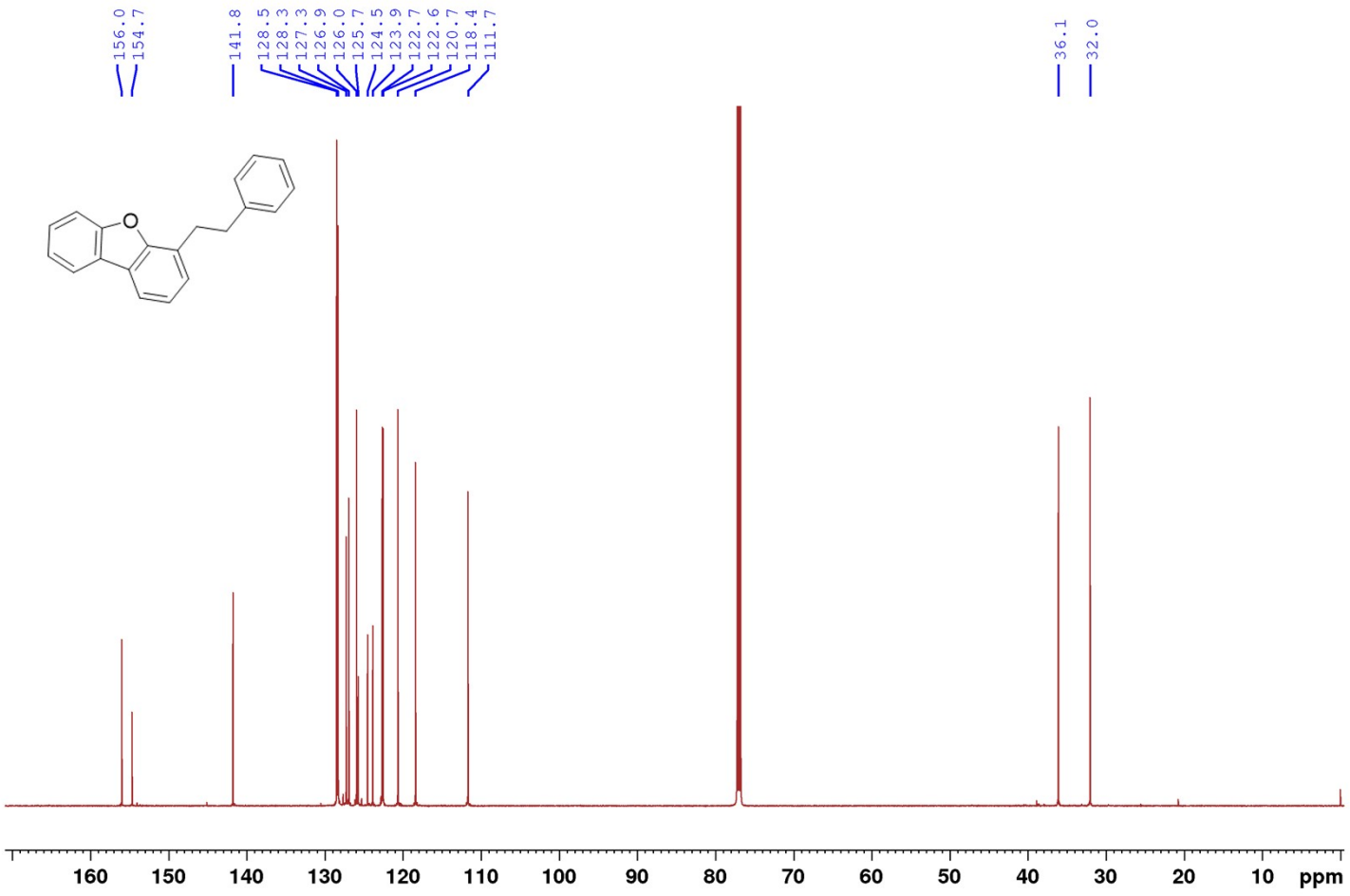
1,3-Dibromo-2-phenoxybenzene 8



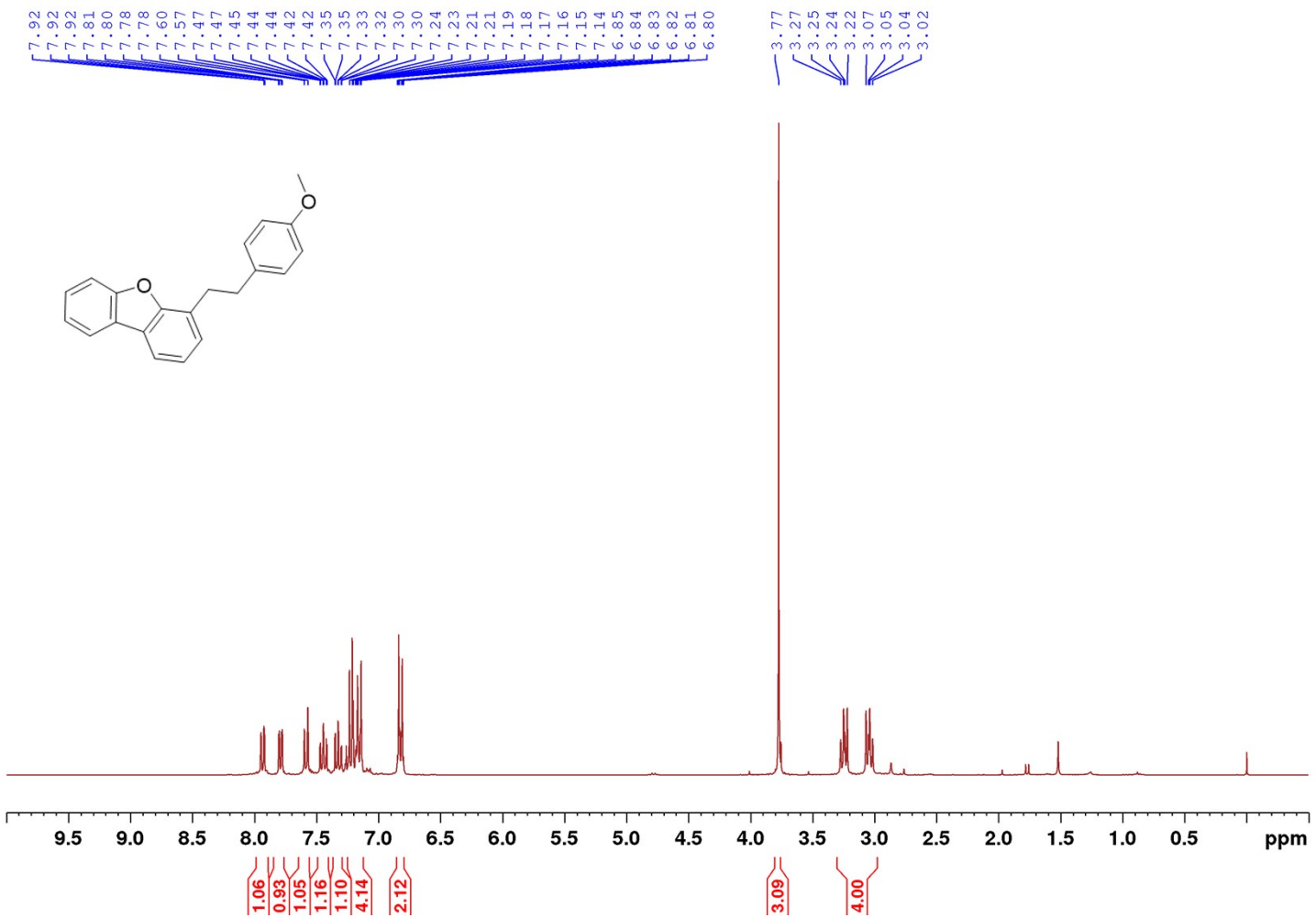

156.5
149.2
133.1
129.7
127.4
122.5
119.0
115.1
Br
O
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

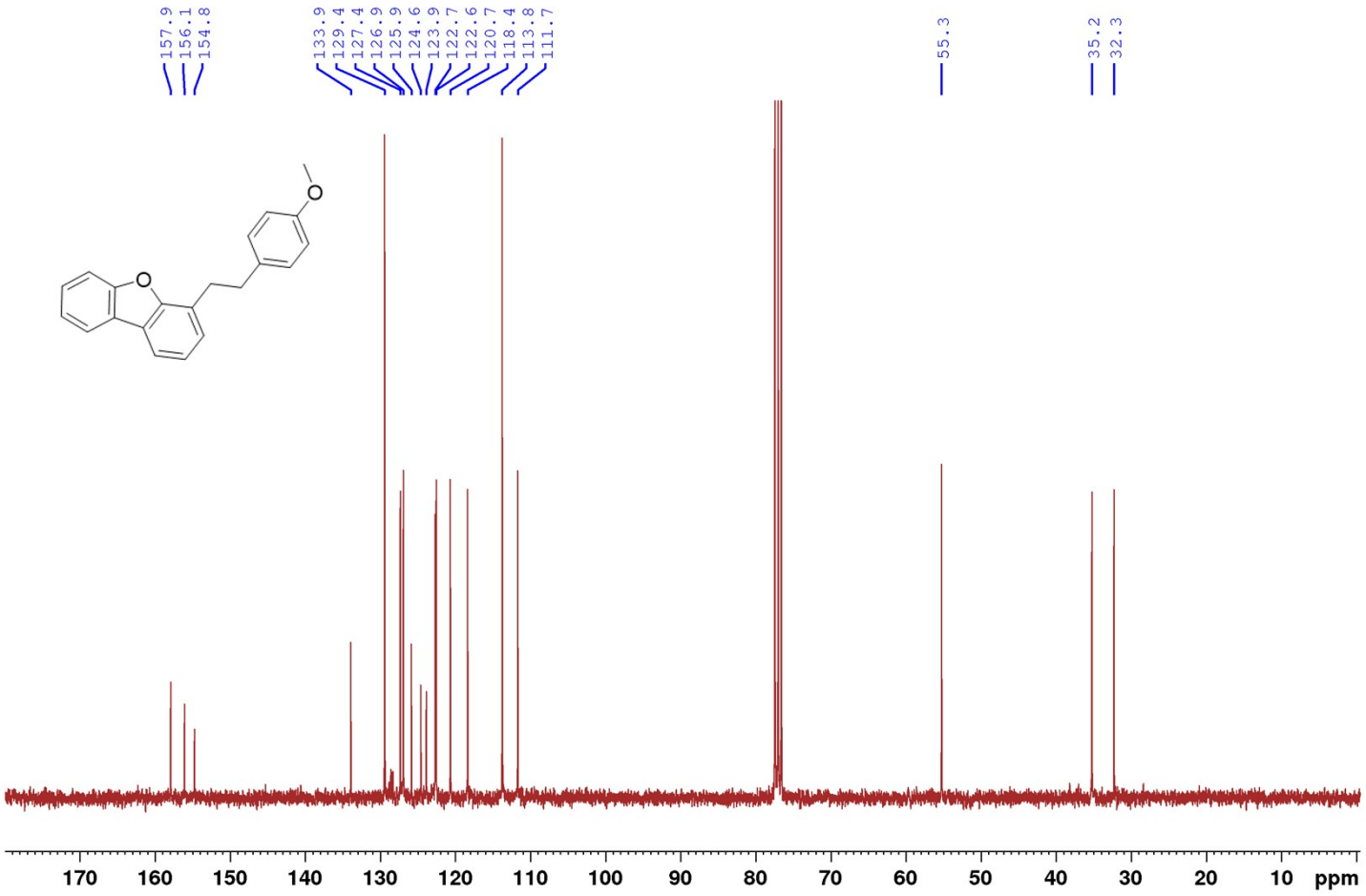
4-phenethyldibenzo[b,d]furan 9a



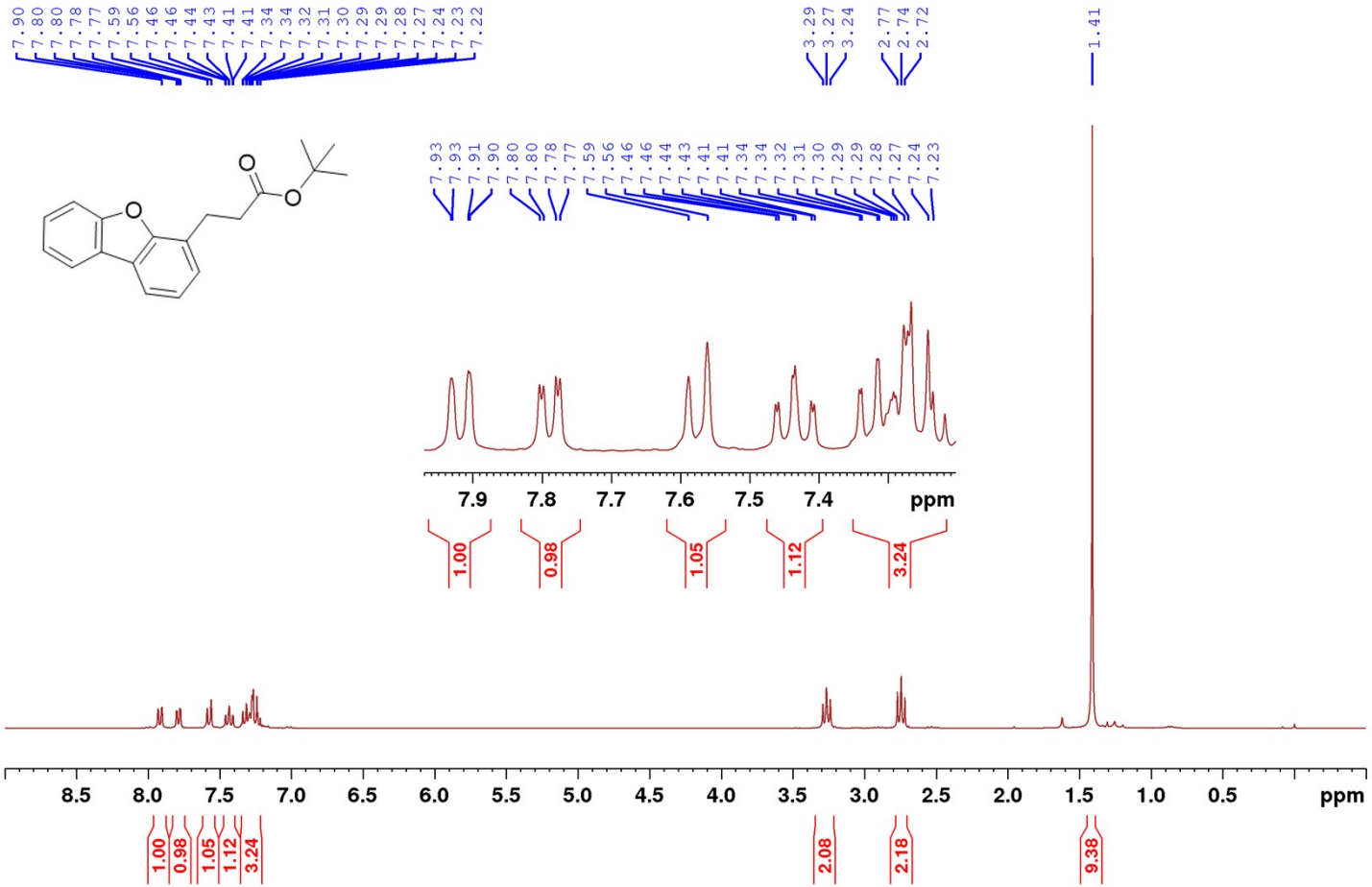

156.0
154.7
141.8
128.5
128.3
127.3
126.9
126.0
125.7
124.5
123.9
122.7
122.6
120.7
118.4
111.7
36.1
32.0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

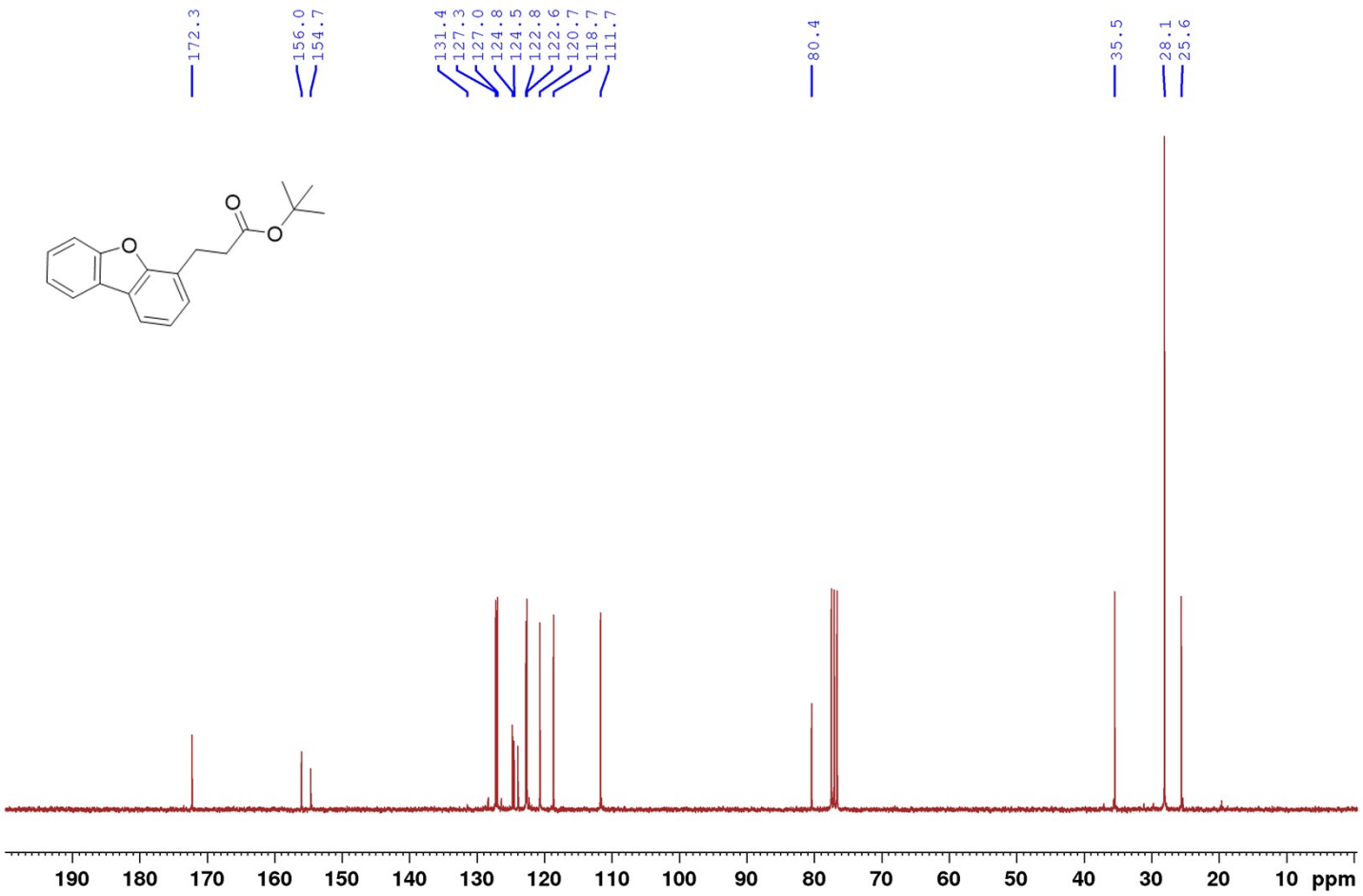
4-(4-Methoxyphenethyl)dibenzo[b,d]furan 9b



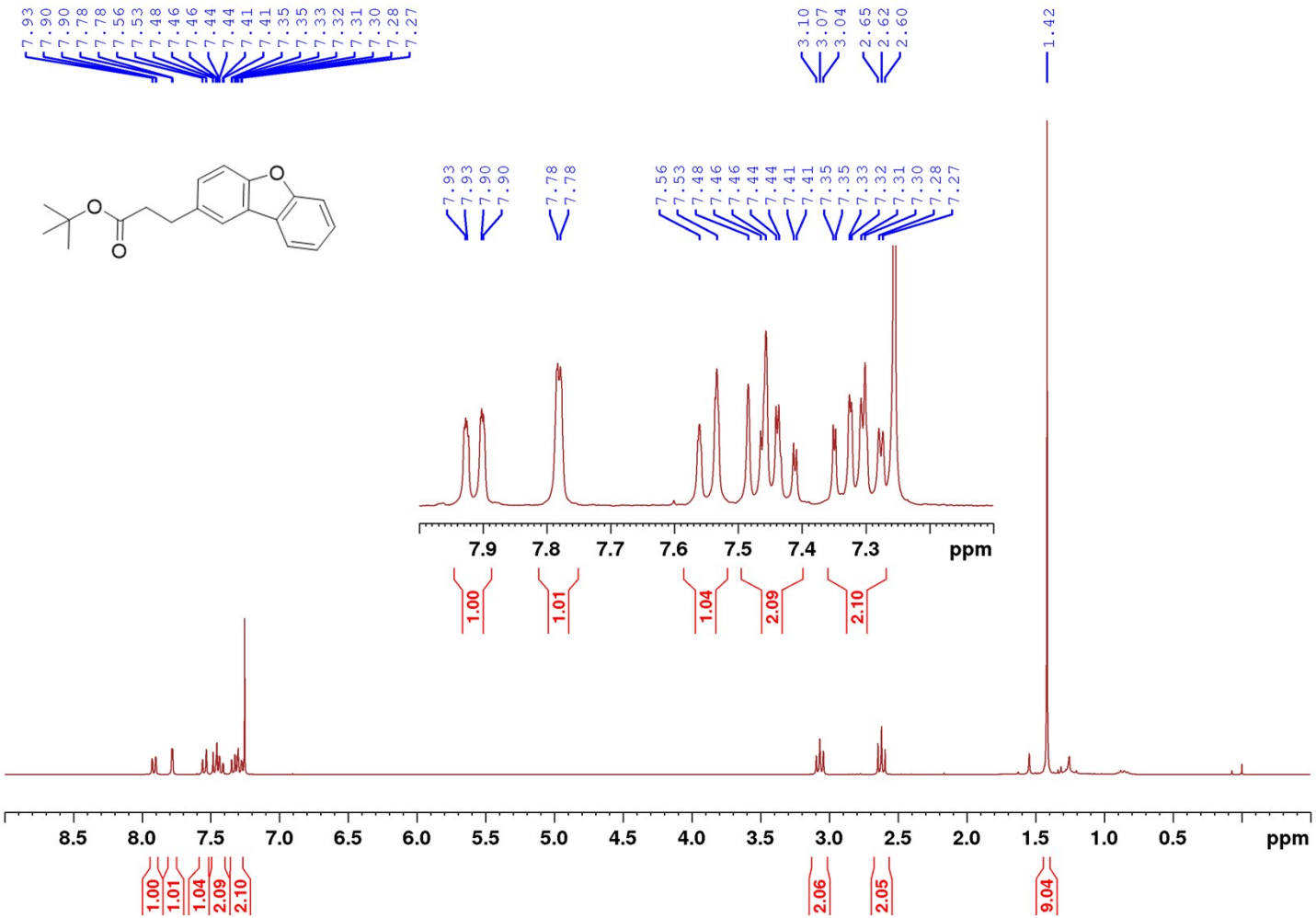

157.9
156.1
154.8
133.9
129.4
127.4
126.9
125.9
124.6
123.9
122.7
122.6
120.7
118.4
113.8
111.7
55.3
35.2
32.3
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

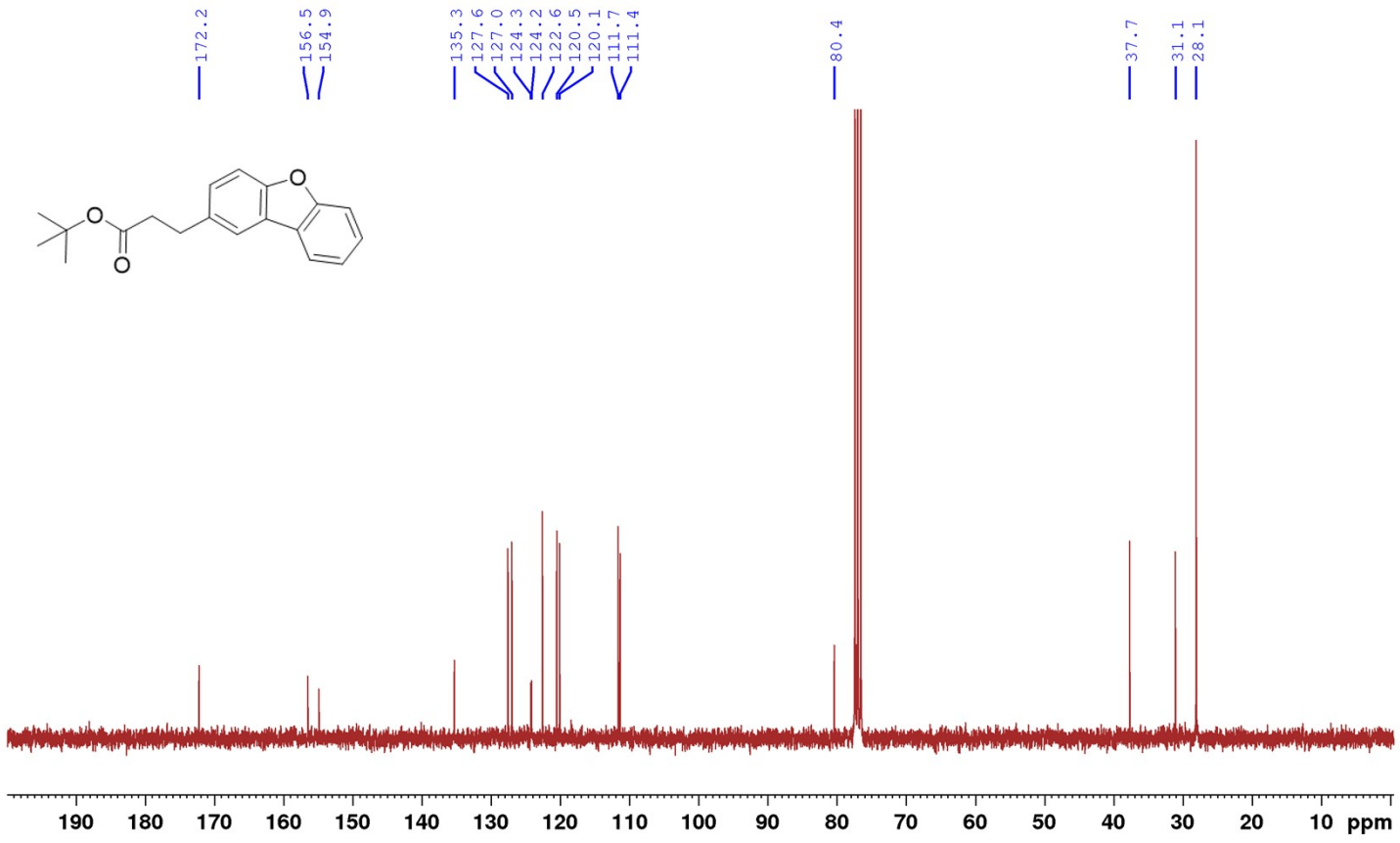
tert-Butyl 3-(dibenzo[b,d]furan-4-yl)propanoate 9c



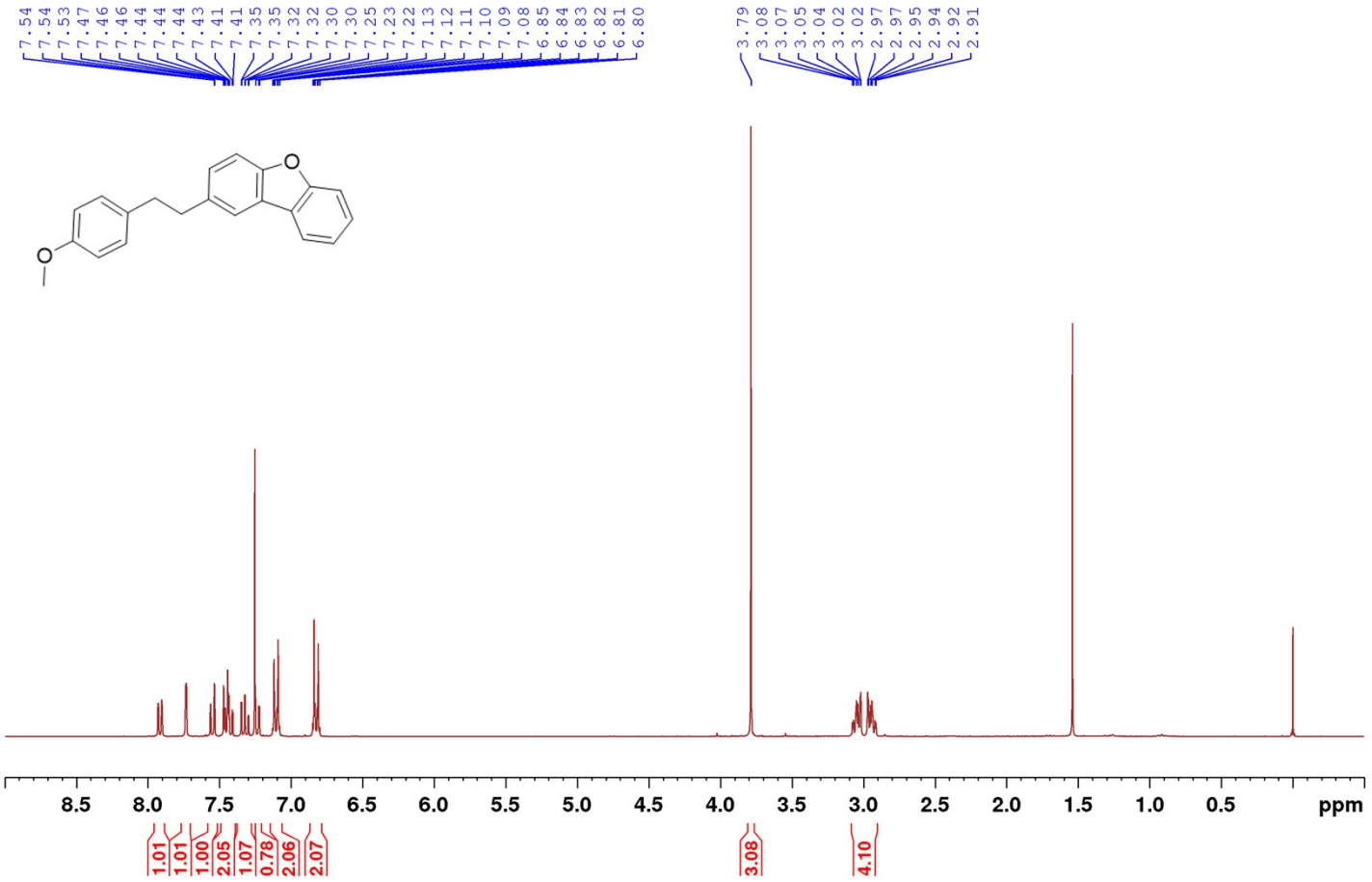

172.3
156.0
154.7
131.4
127.3
127.0
124.8
124.5
122.8
122.6
120.7
118.7
111.7
80.4
35.5
28.1
25.6
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

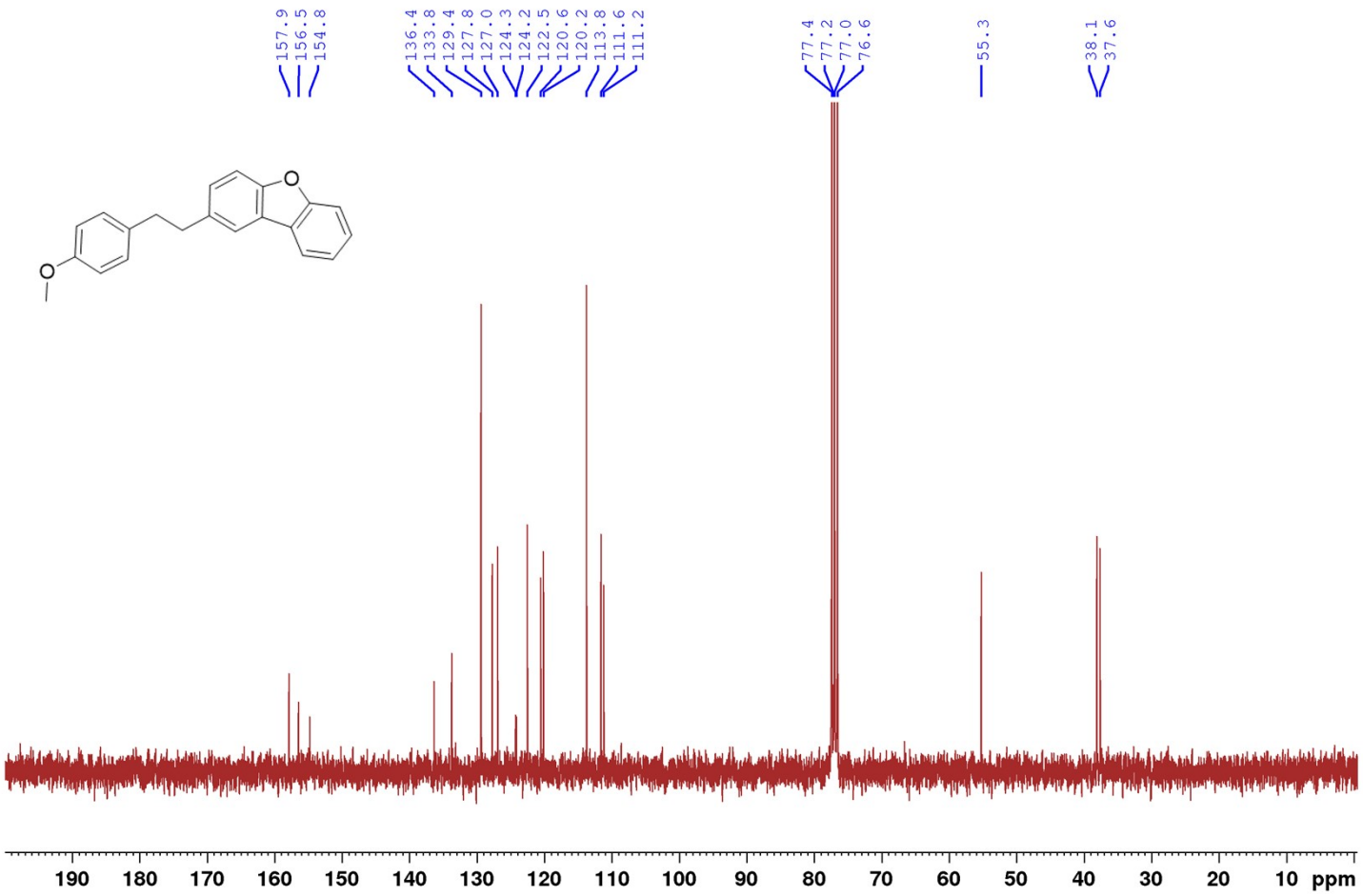
tert-Butyl 3-(dibenzo[b,d]furan-2-yl)propanoate 9d



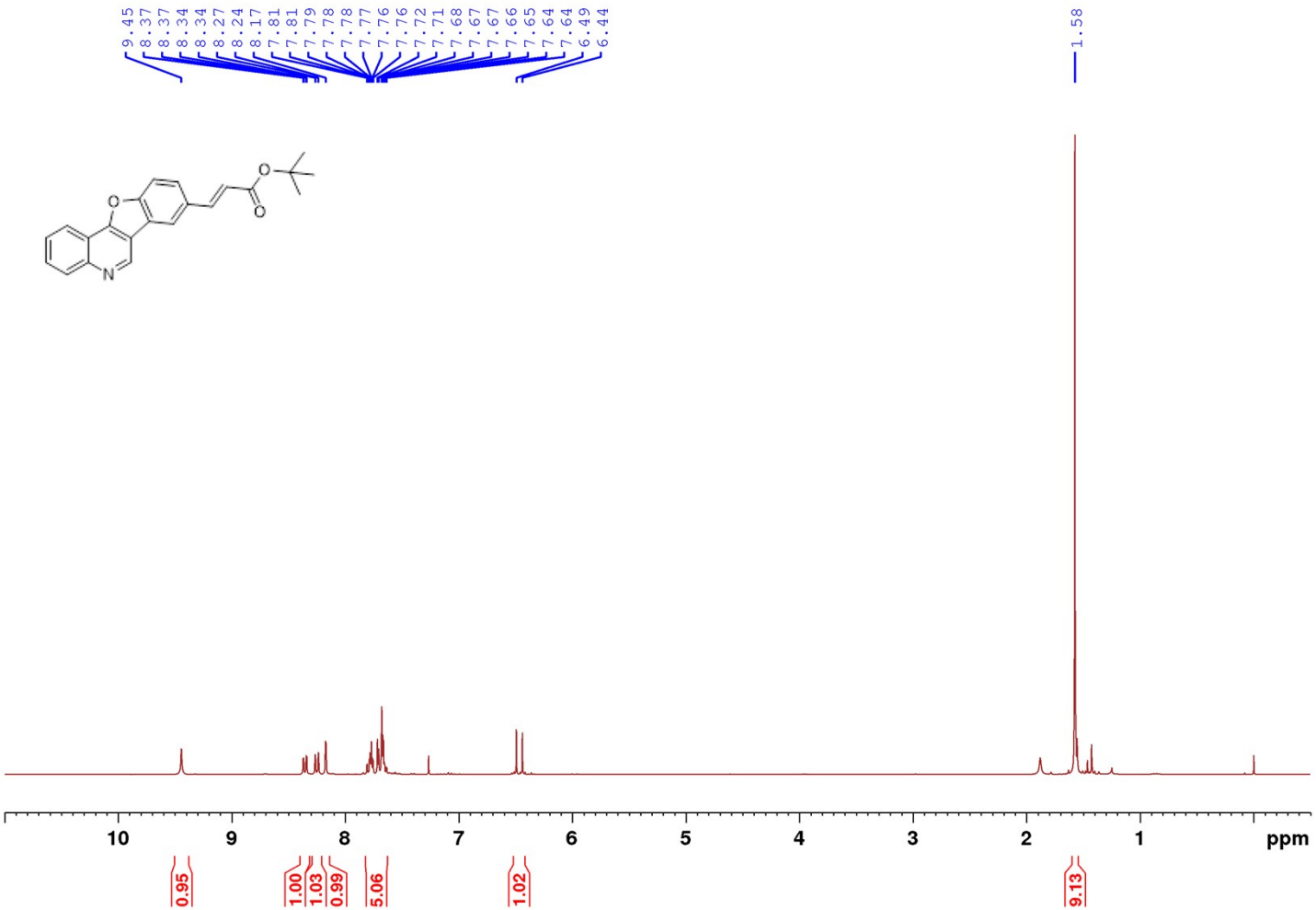

172.2
156.5
154.9
135.3
127.6
127.0
124.3
124.2
122.6
120.5
120.1
111.7
111.4
80.4
37.7
31.1
28.1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

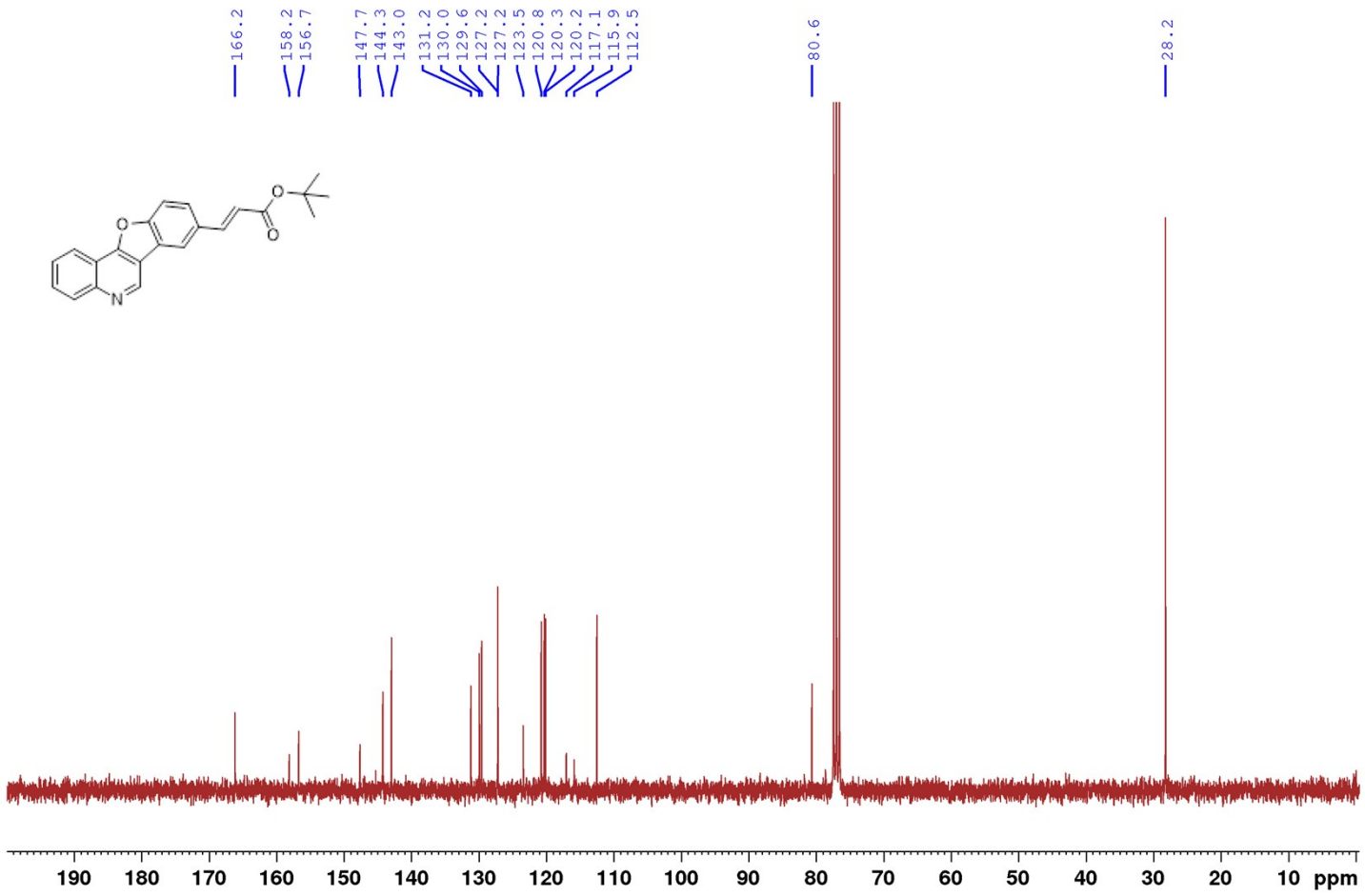
2-(4-Methoxyphenethyl)dibenzo[b,d]furan 9e




157.9
156.5
154.8
136.4
133.8
129.4
127.8
127.0
124.3
124.2
122.5
120.6
120.2
113.8
111.6
111.2
77.4
77.2
77.0
76.6
55.3
38.1
37.6
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

***tert*-Butyl (*E*)-3-(benzofuro[3,2-c]quinolin-8-yl)acrylate S2**




166.2
158.2
156.7
147.7
144.3
143.0
131.2
130.0
129.6
127.2
127.2
123.5
120.8
120.3
120.2
117.1
115.9
112.5
80.6
28.2
O
O
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

2 X-Ray Crystallography Methods

Single crystals were obtained from a saturated solution of methanol by slow evaporation. A suitable crystal was selected on mounted on a **MITIGEN** holder with silicon oil. Data were collected using a ROD, Synergy Custom system, **HyPix** diffractometer equipped with an Oxford Cryosystems low-temperature device operating at a steady temperature of *T* = 100(2) K. Data were measured using *w* scans with Cu K_a radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **CrysAlisPro** 1.171.41.93a (Rigaku OD, 2020). A multi-scan absorption correction was performed using CrysAlisPro 1.171.41.93a[4]. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient of these materials is obtained at λ = 1.54184Å.

The structures were solved, and the space group determined by the **ShelXT**[5] structure solution program using dual methods and by using and by using **Olex2**[6] as the graphical interface. These models were refined by by full matrix least squares minimisation on F^2 version 2016/6 of **ShelXL**[7]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_exptl_absorpt_process_details: CrysAlisPro 1.171.41.93a[4] using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Crystal Data

There is a single molecule in the asymmetric unit for compounds **3a**, **3b**, **3c**, **4d**, **4h**, **4j** and **6a** which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

There is a single molecule in the asymmetric unit for compounds **9a**, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

For compound **9e**, the value of Z' is 2. This means that there are two independent molecules in the asymmetric unit.

Table 1S: X-ray diffraction collection data and refinement details.

Compound	**3a**	**3b**	**3c**	**4d**	**4h**	**4j**	**6a**	**9a**	**9e**
Formula	$C_{23}H_{17}NO$	$C_{23}H_{16}FNO$	$C_{22}H_{21}NO_3$	$C_{24}H_{18}FNO$	$C_{23}H_{23}NO_4$	$C_{23}H_{23}NO_3$	$C_{19}H_{15}NO$	$C_{20}H_{16}O$	$C_{21}H_{18}O_2$
$D_{calc.}$**/ g cm^{-3}**	1.320	1.382	1.326	1.374	1.327	1.296	1.321	1.268	1.291
m**/mm^{-1}**	0.628	0.745	0.707	0.732	0.735	0.086	0.639	0.592	0.645
Formula Weight	323.38	341.37	347.40	355.39	377.42	361.42	273.32	272.33	302.35
Colour	clear colourless	clear colourless	clear colourless	clear colourless	clear colourless	clear colourless	clear colourless	clear colourless	clear colourless
Shape	needle-shaped	irregular-shaped	block-shaped	plate-shaped	block-shaped	prism-shaped	block-shaped	plate-shaped	plate-shaped
Size/mm^3	0.24×0.05×0.02	0.28×0.05×0.03	0.12×0.10×0.06	0.19×0.18×0.03	0.12×0.09×0.05	0.09×0.02×0.01	0.39×0.06×0.04	0.18×0.11×0.02	0.30×0.10×0.06
T**/K**	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal System	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
Flack Parameter	-	-0.10(7)	-	-	-0.16(8)	-	-	-	-
Hooft Parameter	-	-0.10(7)	-	-	-0.11(7)	-	-	-	-
Space Group	$P2_1/c$	$Pna2_1$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	P-1	$P2_1/c$
a**/Å**	4.80750(10)	12.4459(2)	19.3497(7)	5.6809(2)	5.40640(10)	12.0444(9)	13.1980(2)	6.3822(4)	7.6458(2)
b**/Å**	27.2149(4)	27.6090(4)	7.1784(2)	13.8095(5)	9.64370(10)	5.6218(3)	5.61880(10)	10.2110(8)	6.14330(10)
c**/Å**	12.4496(2)	4.77340(10)	12.8947(5)	21.8999(9)	36.2282(5)	27.7622(17)	18.6771(3)	11.3886(12)	66.279(2)
α**/°**	90	90	90	90	90	90	90	84.533(7)	90
β**/°**	92.5230(10)	90	103.665(4)	91.229(3)	90	99.864(7)	97.2680(10)	89.069(7)	91.529(2)
γ**/°**	90	90	90	90	90	90	90	74.931(6)	90
V/Å^3	1627.27(5)	1640.23(5)	1740.37(11)	1717.66(11)	1888.86(5)	1852.0(2)	1373.91(4)	713.37(11)	3112.05(13)
Z	4	4	4	4	4	4	4	2	8
Z'	1	1	1	1	1	1	1	1	2
Wavelength/ Å	1.54184	1.54184	1.54184	1.54184	1.54184	0.71073	1.54184	1.54184	1.54184
Radiation type	Cu K_α	Cu K_α	Cu K_α	Cu K_α	Cu K_α	Mo K_α	Cu K_α	Cu K_α	Cu K_α
θ_{min}**/°**	3.248	3.201	4.704	3.784	4.745	3.919	3.376	3.899	3.335
θ_{max}**/°**	76.365	76.759	76.710	76.633	76.382	30.328	74.889	66.473	66.497
Measured Refl's.	15653	15030	10678	3518	18320	12007	19810	5814	30515
Indep't Refl's	3254	2914	3488	3518	3778	4623	2774	2417	5621
Refl's I≥2 σ(I)	2923	2791	2955	3311	3609	2595	2494	2067	5280
R_{int}	0.0347	0.0310	0.0296	.	0.0385	0.0616	0.1188	0.0579	0.1228
Parameters	226	235	239	245	257	248	190	190	418
Restraints	0	1	0	0	0	0	0	0	372
Largest Peak	0.177	0.154	0.332	0.670	0.135	0.246	0.308	0.566	0.617
Deepest Hole	-0.219	-0.194	-0.225	-0.720	-0.192	-0.292	-0.415	-0.479	-0.585
GooF	1.062	1.065	1.096	1.091	1.029	0.992	1.025	1.171	1.090
wR_2 **(all data)**	0.0957	0.0794	0.1443	0.4329	0.0751	0.1166	0.1564	0.3906	0.3493
wR_2	0.0932	0.0786	0.1391	0.4312	0.0739	0.0972	0.1520	0.3868	0.3480
R_1 **(all data)**	0.0454	0.0313	0.0509	0.1488	0.0311	0.1270	0.0607	0.1453	0.1323
R_1	0.0402	0.0299	0.0446	0.1448	0.0293	0.0530	0.0564	0.1351	0.1298

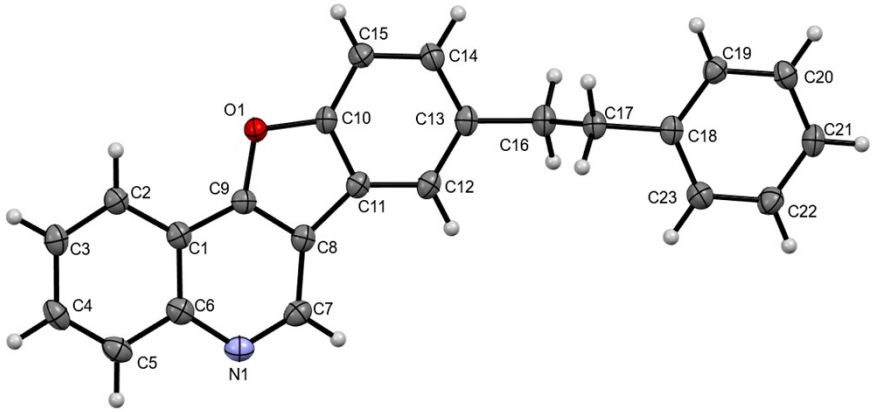


Figure 2S: Thermal ellipsoid of compound **3a** drawn at the 50% probability level

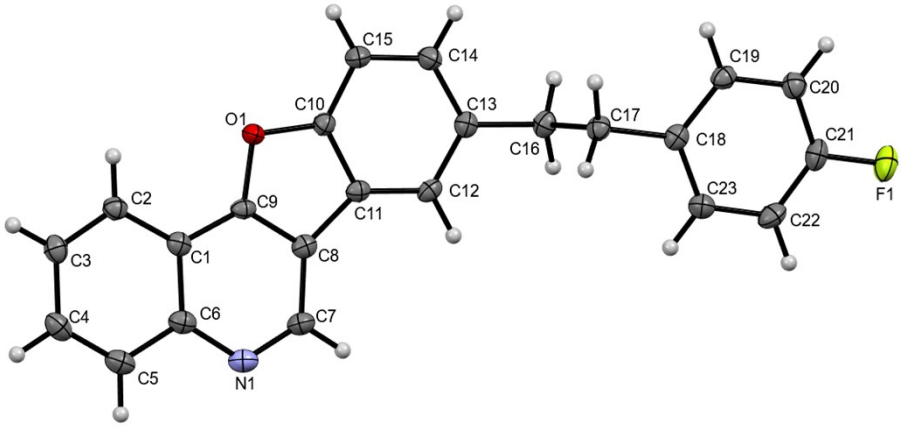


Figure 3S: Thermal ellipsoid of compound **3b** drawn at the 50% probability level

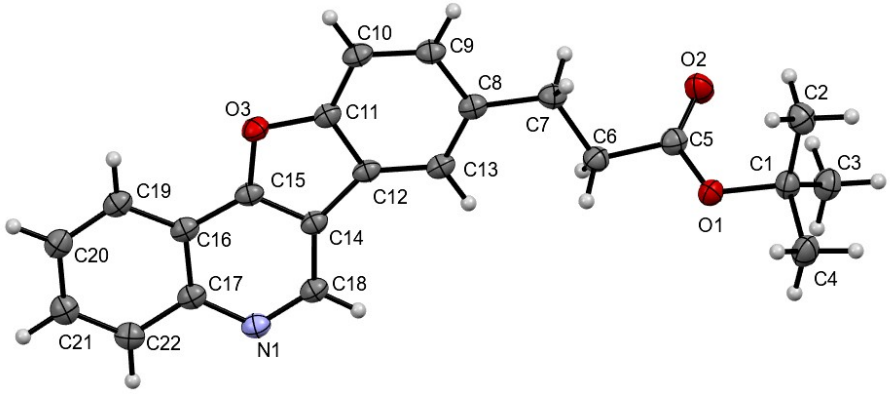


Figure 4S: Thermal ellipsoid of compound **3c** drawn at the 50% probability level

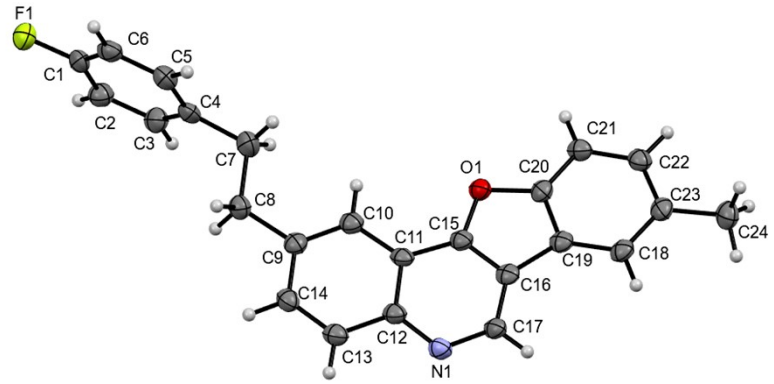


Figure 5S: Thermal ellipsoid of compound **4d** drawn at the 50% probability level

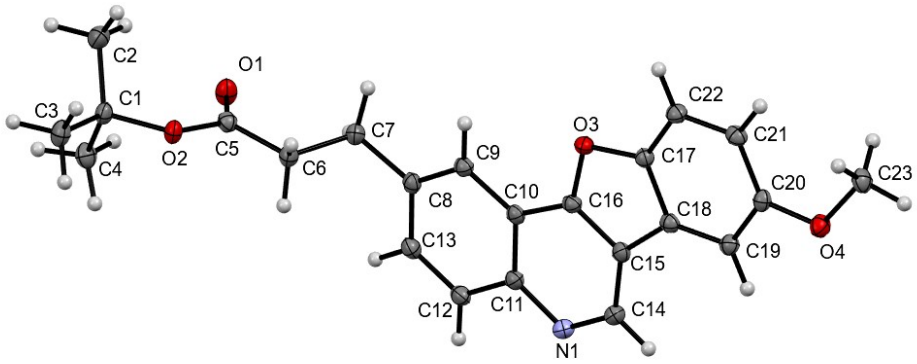


Figure 6S: Thermal ellipsoid of compound **4h** drawn at the 50% probability level

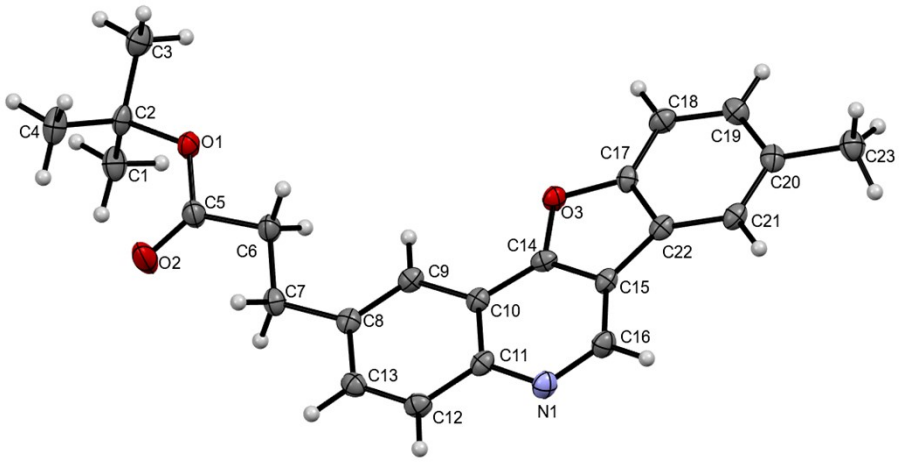


Figure 7S: Thermal ellipsoid of compound **4j** drawn at the 50% probability level

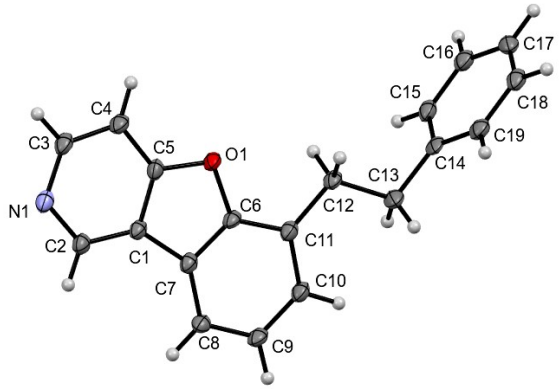


Figure 8S: Thermal ellipsoid of compound **6a** drawn at the 50% probability level

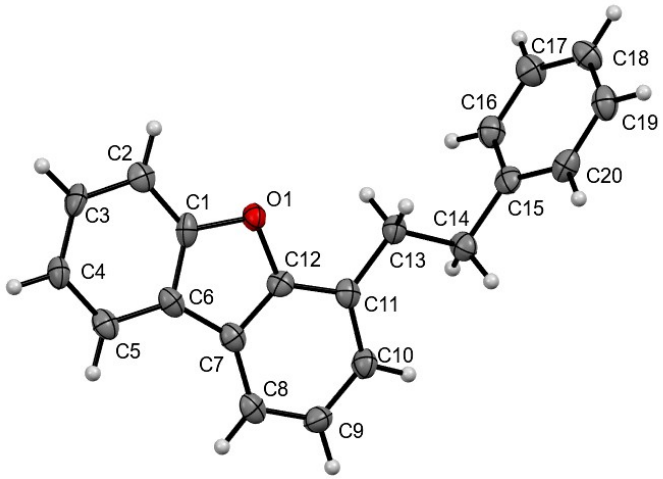


Figure 9S: Thermal ellipsoid of compound **9a** drawn at the 50% probability level

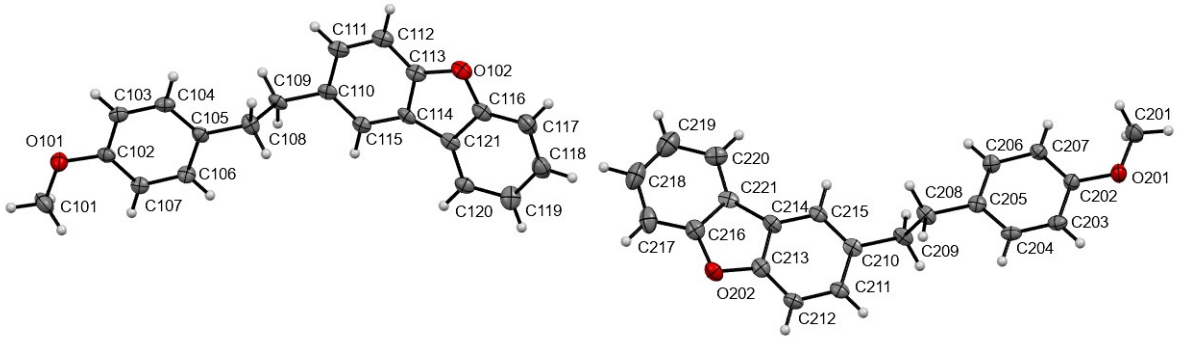


Figure 10S: Thermal ellipsoids of compound **9e** drawn at the 50% probability level

3 Calculation of Green Metrics

The following formulae were used to calculate the following; atom economy (AE), atom efficiency (AEf), Carbon efficiency (CE), reaction mass efficiency (RME), optimum efficiency (OE), process mass intensity (PMI), mass productivity (MP), E-factor, solvent intensity (SI) and water intensity (WI).[8] For RME calculation, neither catalyst nor solvent is included in this calculation. For the calculations including hydrogen gas, it assumed that 1 eq. of H_2 was incorporated into the final product for these calculations. When solving metrics that include solvent, it assumed that all 5 eq. of TBAOAc is used as solvent in these calculations.

$$AE = \frac{molecular\ weight\ of\ product}{total\ molecular\ weight\ of\ reactants} \times 100$$

$$AEf = AE\ \times yield\%$$

$$CE = \frac{amount\ of\ carbon\ in\ the\ product}{total\ carbon\ present\ in\ reactants} \times 100$$

$$RME = \frac{mass\ of\ isolated\ product}{total\ mass\ of\ reactants} \times 100$$

$$OE = \frac{RME}{AE} \times 100$$

$$PMI = \frac{total\ mass\ of\ input\ material\ in\ the\ whole\ process}{mass\ of\ product}$$

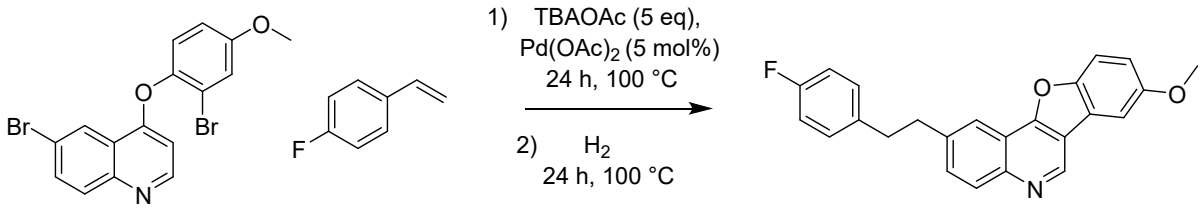
$$MP = \frac{1}{PMI} \times 100$$

$$E\ Factor = PMI - 1$$

$$SI = \frac{total\ mass\ of\ solvents\ exclud.\ water\ in\ whole\ process}{mass\ of\ product}$$

$$WI = \frac{total\ mass\ of\ water\ used\ in\ the\ whole\ process}{mass\ of\ product}$$

<u>Green metrics for 2-(4-fluorophenethyl)-8-methoxybenzofuro[3,2-c]quinoline **4g**</u>



MW 409.08 g/mol MW 122.14 g/mol MW 371.41 g/mol

Materials used for metrics calculations: 6-bromo-4-(2-bromo-4-methoxyphenoxy)quinoline **1b** (100.00 mg, 0.244 mmol), 4-fluorostyrene (33.00 mg, 0.269 mmol), tetrabutylammonium acetate

(369.00 mg, 1.22 mmol), $Pd(OAc)_2$ (2.74 mg, 0.0122 mmol), hydrogen gas (0.40 mg, 0.202 mmol), 2-(4-fluorophenethyl)-8-methoxybenzofuro[3,2-c]quinoline **4g** (75.00 mg, 0.202 mmol, 83% yield).

$$AE\ 4g = \frac{371.41}{409.08 + 122.14 + 2.016} \times 100 = 70$$

$$AEf\ 4g = 70\ \times 83\% = 58$$

$$CE\ 4g = \frac{(24\ \times 0.202)}{(16\ \times 0.244) + (8\ \times 0.269)}\ \times 100 = 80$$

$$RME\ 4g = \frac{75}{100 + 33 + 0.4}\ \times 100 = 56$$

$$OE\ 4g = \frac{56}{70} \times 100 = 80$$

$$PMI\ 4g = \frac{100 + 33 + 0.4 + 2.74 + 369}{75} = 7$$

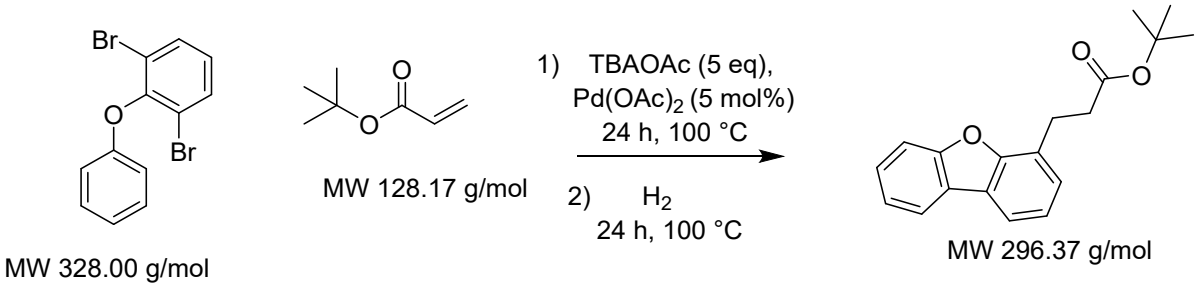
$$MP\ 4g = \frac{1}{7} \times 100 = 14$$

$$E\ Factor\ 4g = 7 - 1 = 6$$

$$SI\ 4g = \frac{369}{75} = 5$$

$$WI\ 4g = \frac{0}{75} = 0$$

Green metrics for *tert*-butyl 3-(dibenzo[b,d]furan-4-yl)propanoate **9c**



Materials used for metrics calculations: 1,3-dibromo-2-phenoxybenzene **8** (100.00 mg, 0.300 mmol), *tert*-butyl acrylate (43.60 mg, 0.340 mmol), tetrabutylammonium acetate (460.00 mg, 1.500 mmol), $Pd(OAc)_2$ (3.40 mg, 0.0150 mmol), hydrogen gas (0.40 mg, 0.213 mmol), *tert*-butyl 3-(dibenzo[b,d]furan-4-yl)propanoate **9c** (67 mg, 0.213 mmol, 74% yield).

$$AE\ 9c = \frac{296.37}{328.00 + 128.17 + 2.016} \times 100 = 65$$

$$AEf\ 9c\ = 65\ \times 74\% = 48$$

$$CE\ 9c = \frac{(19\ \times 0.213)}{(12 \times 0.300) + (7\ \times 0.340)}\ \times 100 = 68$$

$$RME\ 9c = \frac{67}{100 + 43 + 0.4} \times 100 = 47$$

$$OE\ 9c = \frac{47}{65} \times 100 = 72$$

$$PMI\ 9c = \frac{100 + 43 + 0.4 + 3.40 + 460}{67} = 9$$

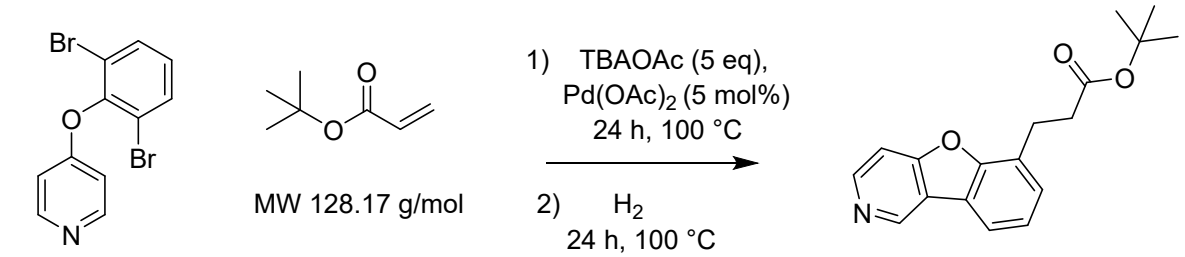
$$MP\ 9c = \frac{1}{9} \times 100 = 11$$

$$E\ Factor\ 9c = 9 - 1 = 8$$

$$SI\ 9c = \frac{460}{67} = 7$$

$$WI\ 9c = \frac{0}{67} = 0$$

Green metrics for *tert*-butyl 3-(benzofuro[3,2-c]pyridin-6-yl)propanoate **6c**



Materials used for metrics calculations: 4-(2,6-dibromophenoxy)pyridine **5** (100.00 mg, 0.304 mmol), *tert*-butyl acrylate (42.90 mg, 0.334 mmol), tetrabutylammonium acetate (458.00 mg, 1.520 mmol), $Pd(OAc)_2$ (3.41 mg, 0.015 mmol), hydrogen gas (0.45 mg, 0.222 mmol), *tert*-butyl 3-(benzofuro[3,2-c]pyridin-6-yl)propanoate **6c** (66 mg, 0.222 mmol, 73% yield).

$$AE\ 6c = \frac{297.35}{328.99 + 128.17 + 2.016} \times 100 = 80$$

$$AEf\ 6c = 80\ \times 73\% = 58$$

$$CE\ 6c = \frac{(18\ \times 0.222)}{(11 \times 0.304) + (7\ \times 0.334)} \times 100 = 70$$

$$RME\ 6c = \frac{66}{100 + 42.9 + 0.45} \times 100 = 46$$

$$OE\ 6c = \frac{46}{80} \times 100 = 58$$

$$PMI\ 6c = \frac{100 + 42.9 + 0.45 + 3.41 + 458}{66} = 9$$

$$MP\ 6c = \frac{1}{9} \times 100 = 11$$

$$E\ Factor\ 6c = 9 - 1 = 8$$

$$SI\ 6c = \frac{458}{66} = 7$$

$$WI\ 6c = \frac{0}{67} = 0$$

Average metrics for our one-pot Mizoroki-Heck/direct arylation/hydrogenation reaction:

$$AE\ = \frac{70 + 65 + 80}{3} = 72$$

$$AEf = \frac{58 + 48 + 58}{3} = 55$$

$$CE\ = \frac{80 + 68 + 70}{3} = 73$$

$$RME = \frac{56 + 47 + 46}{3} = 50$$

$$OE\ = \frac{80 + 72 + 58}{3} = 70$$

$$PMI = \frac{7 + 9 + 9}{3} = 8$$

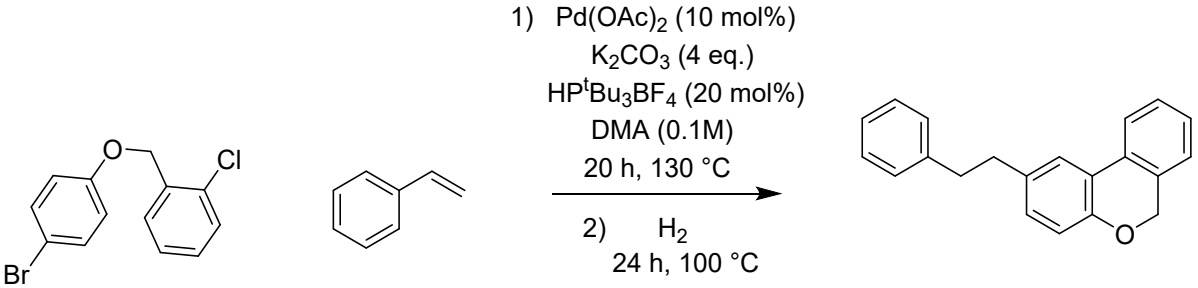
$$MP = \frac{14 + 11 + 11}{3} = 12$$

$$E\ Factor = \frac{6 + 8 + 8}{3} = 7$$

$$SI = \frac{5 + 7 + 7}{3} = 6$$

$$WI = \frac{0 + 0 + 0}{3} = 0$$

Green metrics for Fagnou *et. al.* compound 2-Phenethyl-6*H*-benzo[c]chromene[9]



MW 297.58 g/mol MW 104.15 g/mol MW 286.37 g/mol

Reagents used for metrics calculations: 1-(2-chlorobenzyloxy)-4-bromobenzene (106.0 mg, 0.36 mmol), potassium carbonate (197.0 mg, 1.43 mmol), $Pd(OAc)_2$ (8.0 mg, 0.036 mmol), styrene (36.0 mg, 0.36 mmol), HP(*t*-Bu)$_3BF_4$ (26.0 mg, 0.071 mmol), hydrogen gas (0.5 mg, 0.248 mmol), dimethylacetamide (3384 mg, 3.6 mL) and 2-Phenethyl-6*H*-benzo[c]chromene (71.0 mg, 0.248 mmol, 69%).

$$AE = \frac{286.37}{297.58 + 104.15 + 2.016} \times 100 = 71$$

$$AEf = 71 \times 69\% = 49$$

$$CE = \frac{(21 \times 0.248)}{(13 \times 0.36) + (8 \times 0.36)} \times 100 = 69$$

$$RME = \frac{71}{106.0 + 36.0 + 0.5} \times 100 = 50$$

$$OE = \frac{50}{71} \times 100 = 70$$

$$PMI = \frac{106.0 + 36.0 + 0.5 + 8.0 + 26.0 + 197.0 + 3384.0}{71} = 53$$

$$MP = \frac{1}{53} \times 100 = 2$$

$$E\ Factor = 53 - 1 = 52$$

$$SI = \frac{3384}{71} = 48$$

$$WI = \frac{0}{71} = 0$$

Table 2S: Green metrics (AE, AEf, CE, RME, OE, PMI, MP, EF, SI, WI)

Entry	4g	9c	6c	Average of 4g,9c and 6c	chromene (Fagnou)
Best yield%	83	74	73	77	69
AE (%)	70	65	80	72	71
AEf (%)	58	48	58	55	49
CE (%)	8	68	70	73	69
RME (%)	62	47	46	50	50
OE (%)	89	72	58	70	70
PMI (g g^{-1})	7	9	9	8	53
MP (%)	14	11	11	12	2
EF (g g^{-1})	6	8	8	7	52
SI (g g^{-1})	2	3	3	6	48
WI (g g^{-1})	0	0	0	0	0

Graph 1S: Additional Green Metrics analysis in relation to **Figure 1** in main manuscript for our one-pot average and the current state of the art.[9]

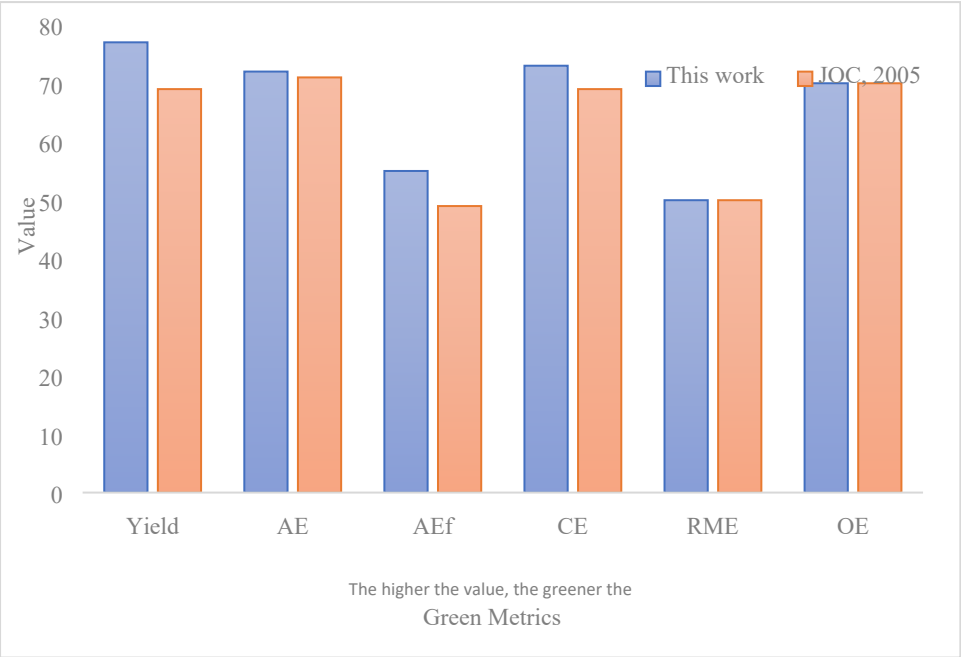
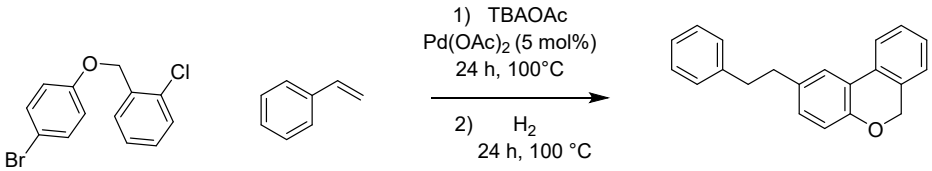


Table 3S: Calculation for inverse of EF, SI and PMI as per **Graph 1** in main manuscript

Green Metric	As calculated		1/calculation		Multiply by 10	
MP	12	2	N/A	N/A	N/A	N/A
EF	7	52	0.1429	0.0192	14.29	1.92
SI	6	48	0.1667	0.0208	16.66	2.08
PMI	8	53	0.1250	0.0189	12.5	1.89

<u>Comparison of Fagnou's Substrate to Our Substrate:</u>

Table 4S: Fagnous Substrate using our conditions



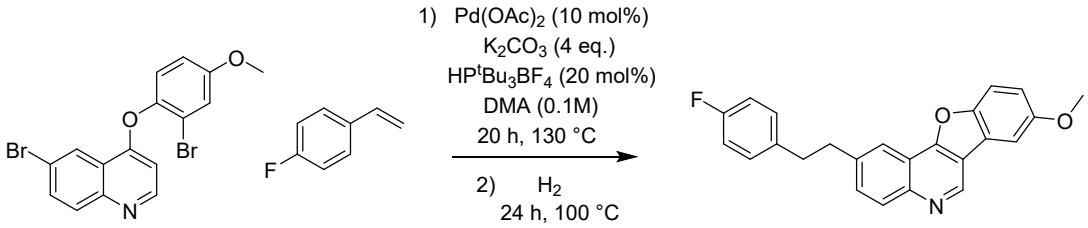
MW 297.58 g/mol MW 104.15 g/mol MW 286.37 g/mol

Material	RMM (g/mol)	mol	Weight (mg)	Yield %	Carbons
1-(2-chlorobenzyloxy) -4-bromobenzene	297.58	0.336	100.00		13
TBAOAc	301.5	1.680	506.59		
4-FluoroStyrene	122.14	0.370	45.15		8
$Pd(OAc)_2$	224.5	0.017	3.77		
2-Phenethyl-6*H*-benzo[c]chromene	286.37	0.279	79.90	83	21

H_2	2.016	0.279	0.56

Green Metric	Value
AE	67.90
Aef	56.36
CE	79.98
RME	54.83
OE	80.75
PMI	8.21
MP	12.18
EF	7.21
SI	6.34
WI	0.00

Table 5S: Our substrate using Fagnou's conditions.



MW 409.08 g/mol MW 122.14 g/mol MW 371.41 g/mol

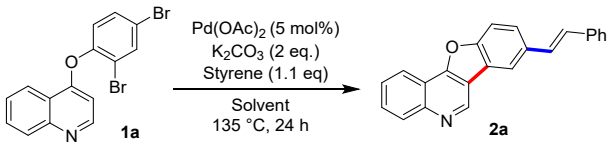
Material	**RMM (g/mol)**	**mol**	**Weight (mg)**	**Yield %**	**Carbons**
SM	409.08	0.36	147.27		16
4-Fluorostyrene	122.14	0.36	43.97		8
$Pd(OAc)_2$	224.5	0.036	8.08		
K_2CO_3	138.2	1.43	197.63		
$HPtBu_3BF_4$	290.13	0.071	26		
DMA	87.12	0.36	3384		
H_2	2.016	0.248	0.50		
Product	371.41	0.248	92.11	69	24

Green Metric	Value
AE	55.32
Aef	38.17
CE	68.89
RME	48.04
OE	86.85
PMI	41.34
MP	2.42
EF	40.34
SI	36.74
WI	0

Green metrics for scale up reaction can be found in Section 5, Table 8S below.

4 Additional Solvents Used in Optimisation Scope

Table 6S: Additional solvents used in optimisation scope



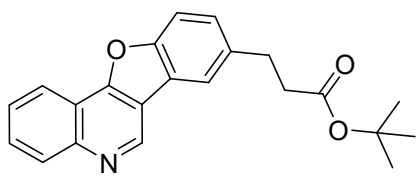
Entry	Solvent	Conversion to 2a[a]
1.	DMA	92%
2.	DMF	87%
3.	Sulfolane	80%
4.	2-Me THF	64%
5.	1,4-Dioxane	65%
6.	Toluene	60%
7.	N-methyl pyridone	90%
8.	N-benzyl pyrrolidone	90%
9.	N-butyl pyrrolidone	93%
10.	Ethylene Carbonate	0%
11.	CPME	56%
12.	Cyrene	60%

[a]Conversion to product **2a** from substrate **1a** determined by ^{1}H NMR analysis

5 Scale up Reaction Experimental Data:

Procedure for Atmospheric Pressure Scale-Up Reaction:

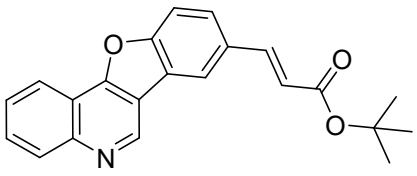
Gram scale reaction for benzofuroquinoline **3c**



To a Schlenk flask was added the quinoline substrate **1a** (1.00 g, 2.64 mmol, 1 eq), *tert*-butylacrylate (0.425 mL, 2.90 mmol, 1.1 eq.), $Pd(OAc)_2$ (0.030 g, 0.132 mmol, 5 mol%) and tetrabutylammonium acetate (3.98 g, 13.19 mmol, 5 eq.) which was stirred at 100 °C for 24 hours. 1-Butanol (4 mL) was then added, and the reaction was purged with hydrogen and let stir under an atmosphere of hydrogen at 100 °C for 30 hours. A second loading of $Pd(OAc)_2$ (5 mol%) was added and the reaction was let stir under a H_2 atmosphere for a further 8 hours at 100 °C. This was followed by a second addition of 1-butanol (30 mL) which was let stir under H_2 for another 8 hours at 100 °C. The reaction solvent was removed under reduced pressure,

dried on a hi-vac line for 24 hours and an NMR yield was taken with trimethoxybenzene as internal standard. (NMR yield: 45%)

Procedure for Elevated Hydrogen Pressure Scale-Up Reaction:



To a Schlenk flask was added the phenoxyquinoline substrate (1.00 g, 2.64 mmol, 1 eq.), *tert*-butylacrylate (0.425 mL, 2.90 mmol, 1.1 eq.), $Pd(OAc)_2$ (0.030 g, 0.132 g, 5 mol%) and tetrabutylammonium acetate (3.97 g, 13.19 mmol, 5 eq.) which was stirred at 100 °C for 24 hours. The reaction mixture was then transferred to a hydrogenation crucible (**Table 7S**, run 2 and 3, 1-butanol [8 mL] was added) and heated to 100 °C. The pressure of hydrogen was adjusted to preference and the reaction was monitored by ^{1}H NMR. The crude reaction mixture was loaded directly onto silica gel for purification by column chromatography. The benzofuroquinoline intermediate **2S** eluted in cyclohexane:EtOAc (100:0 - 70:30).

Results

We undertook a gram scale reaction and were pleased to find that the Heck and C-H activation reactions proceeded very cleanly (99% conversion, 88% isolated yield). However, the hydrogenation step was more sluggish (initially as per General procedure 2). It was necessary to add solvent to the reaction mixture at the hydrogenation step, presumably to aid in the solubility of hydrogen gas. 1-Butanol (4 mL) was added to the mixture at the hydrogenation step, however the hydrogenation did not exceed 42% conversion even after extended reaction time (30 hours). A second addition of $Pd(OAc)_2$ (5 mol%) was added, and stirred for a further 8 hours, however, no increase in product was observed. In a final effort, additional 1-butanol (30 mL) was added, however, a total of 45% NMR yield was obtained of the target compound in addition to some degradation of material. We tried some more forcing conditions to achieve full conversion to the target reduced compound. We subjected our alkene intermediate to hydrogen pressures as high as 4 bar at 100 °C, however no conversion to our reduced product was detected (see **Table 7S** below).

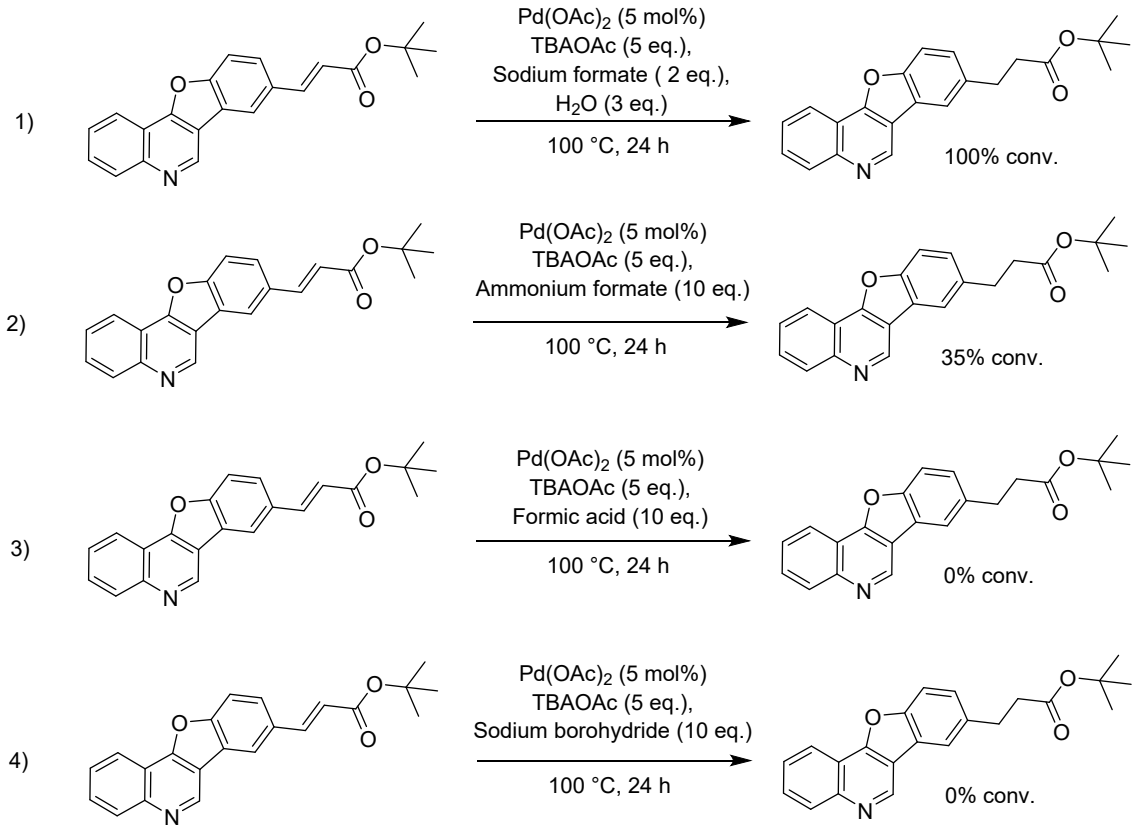
Run	1-Butanol (mL)	Pressure (bar)	Temp (°C)	Time (h)	Conversion
	0	3	100	2	SP + SM
1	0	3	100	+1	SP + SM

	0	4	100	+1	SP + SM
2	8	1.5	50	3	SM
	8	2.5	50	+1	SM
	8	3.5	50	+3	SM
3	8	2.5	100	3	SM
	8	3.5	100	+3	SM

Table 7S: Scale-up pressure Hydrogenation conditions

SP = Side Products, SM = Starting Material, '+' indicates additional run time

6 Transfer Hydrogenation Attempts



General reaction conditions for transfer hydrogenation viability test.

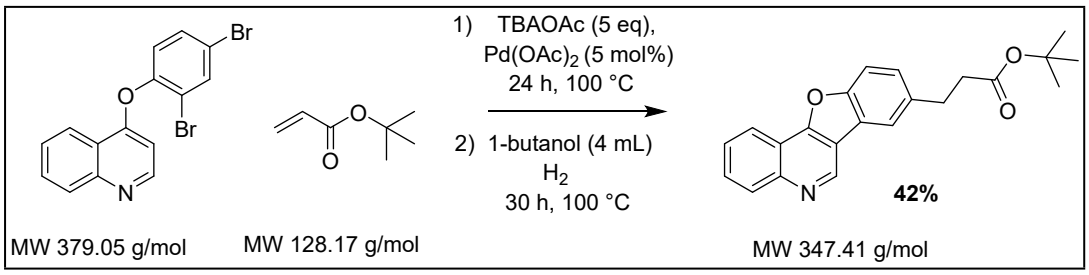
To 4 separate reaction vials was added Heck intermediate 2S (0.26 mmol), $Pd(OAc)_2$ (5 mol%), TBAOAC (5 eq.) and one of; sodium formate (2 eq.) and water (3 eq.), ammonium formate (10 eq.), formic acid (10 eq.) or sodium borohydride (10 eq.). The four reactions were let stir at 100 °C for 24 hours after which time the crude mixtures were filtered and underwent 1H NMR analysis. Sodium formate gave the best result with 100% conversion to the reduced product and therefore was escalated to the scale-up one-pot conditions.

Procedure for the One-Pot Scale up Reaction:

To a schlenk flask was added phenoxyquinoline 1a (1.00 g, 2.64 mmol, 1 eq.), $Pd(OAc)_2$ (0.030 g, 5 mol%, 0.132 eq.), tert-butylacrylate (0.425 mL, 2.90 mmol, 1.1 eq.), and TBAOAc (3.98 g, 13.19 mmol, 5 eq.) which was stirred at 100 °C for 24 h. Sodium formate (0.359 g, 5.28 mmol, 2 eq.) and water (0.078 mL, 7.92 mmol, 3 eq.) was added and let stir at 100 °C for a further 24 h. The crude mixture was filtered and 1H NMR analysis of the crude mixture was obtained. Trace amount of the reduced product 3c was formed.

Green Metric calculations for the scale up reaction performed at atmospheric pressure

Table 8S: Scale up reaction at atmospheric pressure at 42% yield.



Material	RMM	Mol	Weight (g)	Yield %	carbons
SM	379.05	2.64	1.00		15
TBAOAc	301.5	13.19	3.97		
t-butylacrylate	128.17	2.90	0.37		7
$Pd(OAc)_2$	224.5	0.13	0.030		
Product	347.41	1.11	0.38	42	22
H_2	2.016	1.11	2.23		
1-butanol	74.12	43.71	3.24		

Green Metric	Scale-up Value	Fagnou's substrate/Fagnous Conditions Values	Our substrate/Fagnous conditions Values	% Difference 'A'[a]	% Difference 'B'[a]

AE	68	71	55	-4%	21%
Aef	29	49	38	-52%	-28%
CE	41	69	69	-51%	-51%
RME	11	50	48	-130%	-127%
OE	16	70	87	-127%	-139%
PMI	20	53	41	91%	71%
MP	5	2	2	87%	71%
EF	19	52	40	94%	73%
SI	12	48	37	118%	99%
WI	0	0	0	0%	0%

'A' = percent difference of Scale-up vs Fagnou's substrate using Fagnou's state-of-the-art conditions; 'B' = percent difference of Scale-up vs our substrate using Fagnou's state-of the-art conditions; [a] A negative percent difference indicates a less favourable outcome for our scaled-up process vs Fagnou's process

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